Gold Nanoparticle - Modified Zinc Oxide Nanoparticles as Novel Photocatalytic Materials

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GOLD NANOPARTICLE – MODIFIED ZINC OXIDE NANOPARTICLES
AS NOVEL PHOTOCATALYTIC MATERIALS

by

Nayane Udawatte

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GOLD NANOPARTICLE – MODIFIED ZINC OXIDE NANOPARTICLES AS NOVEL PHOTOCATALYTIC MATERIALS

Nayane Udawatte, Ph.D.
Western Michigan University, 2010

The current study entails the construction of a novel nano-composite catalyst based on ZnO and Au nanoparticles and demonstrates its distinctive photocatalytic characteristics. Monodisperse gold nanoparticles (GNPs) passivated with monolayers of tiopronin or glutathione were synthesized via facile methods, and they were assembled on ZnO nanoparticles to form the nano-catalyst.

Steady state and time resolved photoluminescent studies on the nano-composite revealed interesting charge transfer characteristics within the nano-composite. Enhanced photooxidation of rhodamine 6G was observed for the nano-composite over bare ZnO, and modulation of photoactivity with the extent of GNP loading was illustrated. Photoreduction of thionine over the nano-composite was found to have similar characteristics.
Significance of band edge energies of the semiconductor and the ability of GNPs to modulate them, consequently affecting the photocatalytic properties of nano-composite is discussed. Calcination, applied as a post-synthesis treatment method was found to be detrimental for the photocatalytic activity of nano-composites. Preliminary experiments suggested the potential of these nano-composites to be used as effective photocatalysts in treating environmentally significant pollutants such as pesticides.
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Nayane Udawatte
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CHAPTER 1
INTRODUCTION

1.1. Nanoscale Materials

Nanoscale materials are those where at least one of their characteristic dimensions lie between approximately 1 and 100 nanometers (nm). Within this length scale, the characteristics of the matter could become significantly different from individual atoms or molecules and from their bulk counterparts. Thus, their study has recently been recognized as a novel area of science, and is generally termed 'Nanoscience'. However, even more popular is the term 'Nanotechnology', which signifies the construction of functional devices based on the controlled assembly of nanoscale objects for specific technological applications. The significance of this relatively new area of study is exemplified by a number of national and international initiatives promoting its research. Funding agencies are devoting a major part of their funding for nanotechnology, and likewise the amount of research that is performed in this field has dramatically increased during the past couple of decades.

Nanoparticles (NPs), particles with dimensions between 1 to 100nm, are probably the most researched materials within the field of nanotechnology, and they exhibit unique electronic, optical, photonic and catalytic properties\textsuperscript{1,2} due to their intermediate size between quantum and bulk materials and large surface-to-volume ratios. Tremendous scientific progress has been made in the past few
years in the synthesis, characterization and functionalization of such nanoparticles.

The physical and chemical properties of a material are mainly determined by the type and the extent of the motions its electrons are free to perform, and is determined by the space the electrons are confined to. In the bulk material, electrons are unconfined, and their motion is not quantized. Thus, the electrons can absorb any amount of energy, and use it to simply increase their kinetic energy. Once restricted within an atom, molecule or a nanomaterial however, the motion of the electrons becomes highly confined, and quantization begins to appear. For example, within atomic or molecular orbitals, the allowed types of electronic motion have well-defined energies that are different from one another. The smaller the space in which the restricted motion takes place, i.e. stronger the confinement, the larger the energy difference between the allowed energy levels of the various motions will be. The strongest confinements take place within atomic nuclei where the nucleons are restricted to within a few femtometers, and electronic confinement within atoms becomes the next strongest.

Similarly, in the particles with dimensions of few nanometers, the electronic 'quantum' confinement could cause the materials to display significantly different characteristics from the bulk. As an equally important phenomenon, optical and other physical and chemical properties of the nanoparticles become
sensitive to the size and the shape of the particle, allowing the fine tuning of the material by simply changing its dimensions. This research particularly focuses on the characteristics of gold and zinc oxide nanoparticles and the physicochemical aspects of their photocatalytic activity.

1.2. Gold Nanoparticles

The chemistry and physics of gold nanoparticles (GNPs) has emerged as a broad sub discipline within nanomaterial and colloidal science. Their remarkable optical and electrochemical properties and high chemical stability have made them become a model system in the exploration of a wide array of phenomena including self-assembly, bio-labeling, catalysis, cancer therapy, and DNA melting and assays. While such promising characteristics will certainly make them the key materials and building blocks in the 21st century, the discovery of GNPs is far from new to science.

Historically, gold colloids were the first nanosized inorganic particles to be scientifically investigated. While the first ancient inscriptions on gold predates to 2,000 B.C., the extraction of gold is traced back to 5th millennium B.C. It is probable that 'soluble' colloidal gold appeared around 5th or 4th century B.C., where they were used mainly for aesthetic and curative purposes. Colloidal gold was used to make ruby glass and for coloring chemicals, and the soluble gold was considered to possess fabulous curative powers towards various diseases until the middle ages. The earliest scientific investigations on gold colloids were
performed by Faraday, where in 1857 he reported the formation of colloidal gold via the reduction of a chloroaurate (AuCl₄⁻) solution by phosphorous.¹¹ In the 20th century, a large number of methods for the preparation of colloidal gold was reported,¹² especially after the very influential development of synthetic protocols by Schmid¹³ and Brust,¹⁴ where highly stable gold nanoparticles passivated by a monolayer of alkanethiols could be prepared.

Figure 1.1 illustrates the change in the electronic structure of a metal when the particle size is reduced from the colloidal/bulk state down to just a few atoms. The quasi-continuous density of states of the bulk is replaced by a discrete energy level structure in a cluster, where the electronic confinement begins to take effect. The conduction band separates from the valence band causing a ‘band gap’, and the metallic nature of the material is replaced by semiconductor-like properties. This size-induced transition is observed for small enough metal particles of sizes generally below 20nm. In a small molecular cluster with few metal atoms, energetically well-defined bonding and antibonding molecular orbitals could be found.

The intriguing optical properties of gold nanoparticles, as reflected by their intense color, are attributed to their unique interaction with incident light. The motion of the conduction band electrons in a metal nanoparticle is restricted due to the quantum confinement, and in the presence of an oscillating electromagnetic field of light, they undergo a collective coherent oscillation in
resonance with the frequency of radiation, which is termed surface plasmon resonance (SPR).\textsuperscript{15} This oscillation induces a charge separation between the free electrons and the ionic metal core, which in turn exerts a restoring Coulombic force making the electrons oscillate back and forth on the particle surface resulting in a dipole-type oscillation. The SPR oscillation induces a strong absorption of light, the so-called surface plasmon band, near 520 nm for nanoparticles in the 5 to 20 nm range. The nature of the SPR was rationalized by Mie in 1908,\textsuperscript{16} where surface plasmon absorption and resonance was attributed to the dipole oscillations of free electrons in the conduction band occupying the energy states immediately above the Fermi energy level.

Light absorption by gold nanoparticles is strongly enhanced due to SPR excitation, and is about 5 – 6 orders of magnitude larger than that of dye molecules.\textsuperscript{17} A similar trend exists for light scattering, the other process contributing to the total amount of scattered radiation. GNPs have been employed for many uses based on these optical properties including biomedical sensing and detection, therapeutic applications and as contrasting agents in cellular imaging.

Particularly interesting is the fact that there is a sharp drop of surface plasmon absorption with decreasing core size for GNPs below 3 nm in diameter.\textsuperscript{18} It completely disappears when the core diameters are lower than 2 nm. Within this cluster regime, the quantum-size effects set in strongly, and the surface
scattering of conduction electrons causes the damping of surface plasmon resonance. Absorption and electrochemical spectra of very small (less than 2nm in diameter) gold clusters develop distinct step-like structures\textsuperscript{19} indicative of strong molecule-like properties with discrete energy levels in the valence and conduction bands which enable the definition of a HOMO – LUMO (highest occupied and lowest unoccupied molecular orbitals) gap for such small clusters.

\textbf{Figure 1.1} Illustration of the electronic states in a metal particle with bulk properties and its overlapping band structure, a large cluster of cubic close-packed atoms with a small band gap ($E_g$) and a simple tri-atomic cluster with fully separated bonding and antibonding molecular orbitals.
1.3. **Semiconductor Nanoparticles**

At times called 'quantum dots', semiconductor nanoparticles are small crystalline particles with typical dimensions in the range of 1 to 100nm, where the size-dependent optical and electronic properties become evident. Such phenomena were first described in the literature as early as 1967, where changes in optical absorption were observed for small AgI crystals. Rather systematic studies on semiconductor nanoparticles were performed and reproducible synthetic methods for a wide range of colloidal material were developed in early 1980s by Brust and Matijevic.

Due to the attractive characteristics, semiconductor nanoparticles are being explored for a vast number of potential uses in many different fields. In the environmental remediation and renewable energy technologies, they're employed for photocatalytic oxidation, solar cells, fuel cells and bio fuels. They are utilized as chemical and biochemical sensors in the determination of DNA, proteins, small molecules, metal ions, gases and other inorganic substrates. Further they have shown potential to be used in detection and therapy of cancer, as materials with nonlinear optical properties and in fabrication of single-electron transistors.

In bulk semiconductors, electronic excitation involves the formation of an electron and a hole, i.e. the charge carriers, which are separated by distances that encompass a number of molecules or ions that make up the material. This
distance, termed ‘Bohr radius’, is on the nanometer length scale. The energy difference between the top of the valence band and the bottom of the conduction band is the minimum amount of energy required for the generation of charge carriers, and is known as ‘band gap energy’, $E_g$ of the semiconductor. The separated electron–hole pairs bound by weak Coulombic attractions, also called excitons, would transport through the bulk of the semiconductor until they are trapped, annihilated or relaxed by the radiative recombination of the electron and the hole.

If the physical size of the semiconductor material were to be reduced such that it becomes comparable to or smaller than the Bohr radius, it would reduce the space in which the charge carriers mobilize, and thus would confine their motion. Consequently, the kinetic energy and the excitation energy of the charge carriers increase resulting in an increase of the band gap energy, as depicted in Figure 1.2. The important visible effect of this phenomenon is the increase of energy of the band gap absorption and that of the photoluminescent emission, and become dependent upon the dimensions of the particle. This, and the fact that the surface-to-volume ratio increases greatly in this size regime, causes novel properties to emerge, that are not possessed by either the bulk semiconductors or the individual ions or molecules that make up the material.

Practically, semiconductor nanoparticles demonstrate several additional features attributable to their crystal and surface imperfections. Real
semiconductor crystals contain flaws such as interstitial atoms, impurities, dislocations and defects.\textsuperscript{30} Due to the large surface-to-volume ratio of nanoparticles, these imperfections are mainly found on the surfaces of them. A key consequence of the existence of such defects is that they could act as traps for the charge carriers, electrons and holes, which could significantly modulate the photophysical properties of the semiconductor nanoparticles.\textsuperscript{31}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.2}
\caption{Change in the electronic structure of a semiconductor material as the number $N$ of monomeric units increases from unity to clusters of more than 2000.}
\end{figure}

1.4. Photocatalysis by Nanoparticles

With the demonstration of photoelectrolytic splitting of water by Honda and Fujishima\textsuperscript{32} in 1972, modern era of photocatalysis was born. The term
'photocatalysis' could be defined as the acceleration of a photoreaction by the presence of a catalyst. Intensive research efforts have been devoted to the development of novel photocatalytic materials, with the aim of utilizing solar energy to address the increasing global concerns of environmental remediation and clean fuel production. Semiconductor-based photocatalytic materials are found to be the most successful due to their electronic structure, which is characterized by a filled valence band and an empty conduction band resulting in favorable optical properties, and additionally for their durability and the low cost. Nanosized semiconductors are of special interest, as their large surface-to-volume ratio and tunable optical absorption by choice of particle size make them highly versatile.

Activation of the semiconductor for a photocatalytic reaction is achieved through the absorption of a photon (hv) of energy equal to or higher than its band gap energy. An electron (e−) from the valence band can interact with such a photon and will get promoted to the conduction band, with the concomitant generation of a hole (h+) in the valence band. The fate of these charge carriers may take different paths as illustrated in Figure 1.3. Firstly, the excited state conduction band electrons and the valence band holes can recombine either at the surface (reaction b) or within the bulk (reaction c) and dissipate the excess energy as heat, or they might get trapped at metastable surface (reaction d) or internal (reaction e) defect sites. At the surface of the semiconductor, photogenerated
electrons can reduce an electron acceptor, A (reaction \(f\)), and photogeneration
holes can oxidize an electron donor, D (reaction \(g\)). The combination of these
two reactions represents the overall process of semiconductor sensitized
photoreaction, and can be summarized as follows:

\[
A + D \xrightarrow{\text{Semiconductor}} A^- + D^+
\]

If \(\Delta G^0\) for the reaction \(1.1\) is negative in the absence of the semiconductor and
light, the semiconductor-sensitized photoreaction is an example of
photocatalysis.

In addition to free valence band holes and conduction band electrons, the
trapped charges will also ultimately participate in the photoredox chemistry
occurring at the surface.\(^{30}\) However, the charges trapped at a deep trap will have
a lesser photoreactivity due to its low redox potential.\(^ {29}\) In order for a
semiconductor photocatalyst to be efficient, the interfacial charge transfer
processes (reactions \(f\) and \(g\)) must be able to effectively compete with the major
deactivation processes involved in the charge recombination (reactions \(b\) and \(c\)).

In the absence of suitable electron and hole scavengers, the stored energy of the
excitons is dissipated via charge recombination within a few nanoseconds.\(^{33}\) If a
suitable scavenger or a defect site that could trap the charges is available, the
recombination may be prevented and subsequent redox reactions would occur
within a timeframe of microseconds to milliseconds. An increase in either the
The recombination lifetime of charge carriers or the interfacial charge transfer rate constant is expected to result in higher quantum efficiency for the photocatalytic process. In general, it has been found that up to 90% of the charge carriers can undergo recombination.\textsuperscript{34}

\textbf{Figure 1.3} Primary steps occurring on a semiconductor particle following photoexcitation: (a) formation of charge carriers by a photon, (b) electron-hole recombination at the surface, (c) charge recombination occurring within the bulk, (d) charge trapping on the surface states, (e) charge trapping within the bulk, (f) photogenerated electrons reducing the electron acceptor, A at the surface, (g) photogenerated holes oxidizing the electron donor, D at the surface.

The valence band electrons are powerful oxidants with reduction potential between +1.0 and +3.5V vs. NHE (normal hydrogen electrode) depending on the semiconductor and pH, whereas the conduction band electrons are strong...
reductants with reduction potentials varying between +0.5 and -1.5V vs. NHE. Therefore, it is clear that illuminated semiconductors have the potential to drive a wide variety of photocatalytic reactions.

In the bulk semiconductor electrodes used in photocatalysis, only one type of charge carrier, either holes or electrons, is available for reaction due to band bending at the semiconductor-metal interface. On the contrary, nanosized semiconductor particles behave as short-circuited electrodes where both electrons and holes are present on the surface. Thus it is critical that the charge recombination is suppressed, and the interfacial charge transfer is promoted in order to obtain the best possible quantum efficiency in semiconductor nanoparticles.

Nanosized semiconductor particles have become very popular as photocatalysts for a number of reasons. One of the main reasons could be their large surface area compared to the volume, enhancing the number of active sites massively. Additional flexibility arises from the ability to tune the band gap by changes in size, thus enabling the enhancement of redox potential of the valence band holes and the conduction band electrons. However, one disadvantage of nanosized semiconductor particles is the need for light with shorter wavelengths for photocatalytic activation, due to band broadening. Thus only a smaller percentage of a polychromatic light source would be used for photocatalysis.
On the other hand, the solvent reorganization free energy for a charge transfer to a substrate was found to remain unperturbed by the particle size, whereas the driving force for the redox reaction is increased in the nanoparticles. The combined effect could be expected to cause an increase in the rate constant of the charge transfer at the surface of the nanoparticles, leading to an enhancement in photoactivity for systems in which the rate limiting step is the interfacial charge transfer.

Enhanced photocatalytic activity of nanoparticles over their bulk phase has been reported in number of studies. However, some have found the contrary to be true. Zhang et al. demonstrated that while the photoactivities increase as the semiconductor nanoparticle size is reduced, below a certain particle size the activity begins to drop as the particle size is further reduced. The photoactivity is low in large particles due to the strong charge recombination within the bulk, which could be minimized by reduced particle size, as the surface area and the number of active sites are increased. Photonic efficiency will further enhance due to the higher interfacial charge transfer rates. However, when the particle sizes are extremely small, i.e. few nanometers, surface recombination of charges becomes a dominant process as the charges are generated very close to the surface, and thus could rapidly reach the surface and undergo surface recombination, a process that is much faster than the interfacial charge transfer. Therefore, the enhancement of interfacial charge transfer rate would be
outweighed by the increased surface recombination rate in ultra-small semiconductor nanoparticles below a certain size limit.

Since the first account of light driven redox reactions with nanocrystalline semiconductor systems where water decomposition was attained with TiO$_2$ nanoparticles,$^{46}$ a vast amount of research has been performed in this field. Particularly well studied are metal oxides, sulfides and selenides such as TiO$_2$, ZnO, WO$_3$, V$_2$O$_5$, Ag$_2$O, ZnS, CdS, PbS, Cu$_2$S, MoS and CdSe.$^{47}$ Many of these semiconductors possess band gap energies sufficient for promoting or catalyzing a wide range of chemical reactions of interest. Among these semiconductors, titanium dioxide (titania) has proven to be one of the most suitable for various applications as it has an appropriate band gap, is stable and has low biological toxicity. However, Zinc oxide is also a promising alternative with a similar band gap to that of TiO$_2$, and relatively low toxicity.$^{48,49}$ The most appealing characteristic of ZnO however, is that its significantly higher activity towards photocatalytic degradation$^{50,51}$ and sensitization$^{52}$ processes compared to commonly studied titanium dioxide.

Figure 1.4 provides the band gap energies and band edge positions for a number of common semiconductor materials.$^{53}$ Knowledge of the band positions indicate the thermodynamic limitations for the photoreactions that could be carried out with the respective charge carriers. As an example, if reduction of a species is to be executed, the position of semiconductor conduction band has to be above the
relevant redox level. It should be noted, however, that the free energy of the excitons will be smaller than the energy of the band gap. This phenomenon occurs due to the significant configurational entropy of the excitons arising from the large number of translational states in the valence and conduction bands that are accessible to the mobile charge carriers.\textsuperscript{47}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Figure 1.4 Positions of conduction and valence bands of several common semiconductors in an aqueous electrolyte at pH 1. The number within the band gap indicates the band gap energy in electron volts (eV). The standard potential (vs. NHE) of several common redox couples are presented on the right.}
\end{figure}
1.5. **Enhancing Photocatalytic Activity**

Despite the considerable advantages of using semiconductors as photocatalysts for various applications, one significant drawback in semiconductors is electron–hole recombination, which in the absence of proper redox species causes the photocatalytic activity to drop considerably. Thus it represents a major energy wasting step, as well as a barrier in achieving a higher quantum yield. Another drawback of the wide band gap semiconductors is that they can only utilize the radiation in near-UV and UV regions, which is merely a small portion of the solar spectrum. Several approaches have been investigated in order to achieve improved charge separation and enhance the interfacial charge transfer reactions, and also to red-shift the absorption band edge into the visible light region so as to utilize a wider range of the solar radiation:

1. Use of redox species as electron or hole scavengers.
2. Coupling the photocatalyst with photosensitizers.
3. Coupling two types of semiconductors.
4. Doping and surface modification of semiconductor.

**1.5.1. Use of redox species**

One way to inhibit electron–hole recombination is to add another irreversible electron or hole acceptor to the reaction. The enhancement may come in several different ways: the redox species could increase the number of trapped charges and avoid recombination, generate more reactive radical species (for e.g.
hydroxyl radicals, \( \cdot \text{OH} \) or increase the reaction rate of the intermediate compounds.

In many water based applications, dissolved oxygen has been chosen as an electron scavenger. However, with only dissolved \( \text{O}_2 \) as the catalyst, success of this method is limited by the amount of dissolved oxygen. Hydrogen peroxide\(^{54}\) is one of the more successful candidates due to its electron-accepting nature, where it could react with conduction band electrons to generate hydroxyl radicals which can in turn be employed in processes such as photodegradation of organic pollutants. Peroxodisulphate\(^{55}\) (\( \text{S}_2\text{O}_8^{2-} \)) is another powerful oxidizing agent with standard potential of \( E^\circ = 2.01 \text{V} \) that decomposes to \( \text{SO}_4^{2-} \) upon UV irradiation. The sulfate anion radical in turn, is a very strong oxidant (\( E^\circ = 2.6 \text{V} \)) and is capable of oxidizing a variety of organic materials.

1.5.2. Coupling with photosensitizers

Dye sensitization of semiconductors is a process where the photoexcitation of a chromophore (dye) is followed by an interfacial electron transfer from the dye into the conduction band of the semiconductor\(^{56}\) to initiate reactions under the illumination of the visible light. This technique is advantageous since the electron transfer into the conduction band of the semiconductor does not involve generation of a hole, and the possibility of charge recombination becomes minimal. Additionally, a wider range of the solar spectrum may be utilized since the dyes are capable of absorbing visible radiation. Such systems
have found wide use in solar cells and also in the photocatalytic degradation of organic matter. However, in most cases, the dyes are not stable once the photocatalyst is exposed to band gap illumination and may degrade.

1.5.3. Composite semiconductors

Coupling different semiconductors via either a core-shell or surface island structures can result in improved photocatalytic efficiency. When a large band gap semiconductor is coupled with a small band gap semiconductor with a more negative conduction band position, conduction band electrons can be transferred from the small band gap semiconductor to the large band gap semiconductor, generating a strong electron–hole separation. This concept has been applied to various coupled systems including CdS/TiO$_2$, WO$_3$/TiO$_2$ and SnO$_2$/TiO$_2$ and enhanced photocatalytic efficiency was demonstrated.

1.5.4. Doped semiconductors

This approach has focused on modifying the semiconductor such that the band gap matches the solar spectrum better. By doping the semiconductors with ionic species, the absorption can be shifted towards the visible region. Many transition metal ion dopants such as Cr(III), Fe(III), Mo(V), Ru(III), Os(III), Re(V), V(IV) and Rh(III) and combinations thereof have been used to dope semiconductors, and significantly improved photoreactivity for both oxidation and reduction is reported. Additionally, non-metal doping has also been
investigated, where nitrogen has received the most attention. Other non-metals explored include C, F, S and P.

Metal ion dopants incorporated into the semiconductor lattice, mainly at substitutional sites cause the formation of additional energy levels in the band gap of the semiconductor. Consequently, they can function as both hole and electron traps, and mediate interfacial charge transfer. This is only effective if the metal ion is doped near the surface of semiconductor particles, and in case of deep doping, the metal ions will likely behave as recombination centers, detrimentally affecting the redox processes.

Anions incorporated into a semiconductor may occupy either lattice or interstitial sites, and will be decisive on their effect on photocatalysis. Unlike metal ions, anions are less likely to form recombination centers and therefore, are more effective in enhancing the photoactivity of semiconductors. Additionally, band gap narrowing caused by the hybridization of the electronic orbitals can result in an increase in the visible light activity of the semiconductor.

1.5.5. Metal/semiconductor composites

Combination of noble metals such as Au, Ag, Pt, Pd and Ni with semiconductors on a nanometer scale has shown to enhance the photocatalytic activity. The noble metal can act as a reservoir for conduction band electrons, minimizing the charge recombination, as a result of the difference in the Fermi levels
characterized by the work function of the metals and the band structure of the semiconductors.\textsuperscript{67}

As illustrated in Figure 1.5,\textsuperscript{68} under the illumination of radiation with energy higher than the semiconductor band gap, photoelectrons are generated in the conduction band of the semiconductor. The accumulation of electrons raises the Fermi level of the semiconductor to further negative values. The energetic difference at the semiconductor/metal interface will then drive the electrons from the conduction band of the semiconductor into the metal nanoparticle, which in turn causes the Fermi level of the metal to shift negatively. The electron transfer could continue until the Fermi levels of the metal and the semiconductor are equilibrated with each other.

\textbf{Figure 1.5} Fermi level ($E_f$) equilibration and electron transfer at a metal-semiconductor interface under UV light irradiation. (A) energy level equilibration before irradiation; (B) equilibration after irradiation. (CB: conduction band, VB: valence band)
Noble metals such as Au, make Schottky barriers upon contact with a semiconductor. Unlike ohmic contact, a Schottky contact leads to a rectified charge carrier transfer from the semiconductor to the metal, so that the charges on the metal nanoparticle will be retained until a secondary electron transfer can occur to the redox species.

1.6. Gold Nanoparticles as Catalysts

Gold is a metal well known for being chemically inert, and is indeed one of the most inert metals in the group 8 elements. In the 1970s, however, the catalytic activity of nanosized gold particles supported on Al₂O₃ and MgO were reported for oxygen and hydrogen transfer reactions, although these studies did not receive much attention. Later in 1989, Haruta et al. discovered that gold nanoparticles supported on Co₃O₄, Fe₂O₃ or TiO₂ are highly catalytically active towards CO and H₂ oxidation, NO reduction, CO₂ hydrogenation and catalytic combustion of methanol. This work, for the first time illustrated the superiority of the gold as a catalyst and has inspired a vast amount of research focusing on novel catalytic systems based on GNP's in recent decades. It is now known that bare gold nanoparticles are not particularly active, but when nanoparticles with sizes below 5 nm, deposited on a semiconductor support with high dispersity, become extremely effective catalysts for various chemical transformations.
Gold nanoparticles when supported on semiconductor nanoparticles have proven to be highly successful in photocatalytic transformations. As illustrated before, only a small fraction (~5%) of photogenerated charge carriers generated in bare semiconductor particles could be utilized to induce interfacial redox processes. In contrast, gold nanoparticle-deposited semiconductor nanoparticles introduce significant enhancements to photocatalytic processes. Hiesgen et al. reported a 40% enhancement in the hole transfer efficiency in a flash photolysis study of gold-capped TiO₂ nanoparticles.

Despite the extensive studies on such metal and semiconductor nanoparticle composite systems, the photodynamics of their catalytic processes are still largely unknown. Fundamental understanding of the photoinduced interactions between semiconductor and metal, as well as the interfacial charge transfer process in nano-composites is important to elucidate the role of the noble metal nanoparticles in semiconductor-assisted photocatalysis.

1.7. Advanced Oxidation Processes

Pollution of water, arguably the most valuable natural resource, has become a major concern today, as the consequences of water pollution become more and more evident. Hence, treating and recycling polluted waters has become one of the main priorities of modern society, and as a result, social, political and legislative authorities are imposing increasingly severe regulations on water contamination.
Many of the conventional wastewater treatment techniques such as agglomeration, filtration and activated carbon adsorption are only able to concentrate the pollutant or transfer it onto different system, without degrading it. Furthermore, they are not effective enough to produce water with acceptable levels of the most persistent pollutants such as phenols, pesticides, organic solvents, household chemicals and drugs. A secondary treatment stage is often required to fulfill this objective, where advanced oxidation processes (AOP) have recently shown much promise.

AOPs can be broadly defined as aqueous phase oxidation methods based on the involvement of highly reactive species, mainly hydroxyl radicals in the mechanisms, leading to the complete destruction of the target pollutant according to Equation 1.1. A wastewater treatment process based on AOPs can result in the complete mineralization of pollutants to CO₂, water and inorganic compounds, or at least their transformation into more innocuous products. Additionally, the partial decomposition of non-biodegradable organic pollutants may also lead to biodegradable intermediates.

\[
\text{AOPs} \rightarrow \cdot\text{OH} \rightarrow \frac{\text{Pollutant}}{\rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Inorganic ions}}
\]

All advanced oxidation processes are characterized by a common feature: production of extremely reactive \(\cdot\text{OH}\) radicals. With a standard potential of \(-2.8\text{V}\), \((\text{OH}^- \rightarrow \cdot\text{OH} + \text{e}^-)\)²⁹ the hydroxyl radicals are able to attack most of the organic
molecules. They are also benefitted by very little selectivity towards substrates that enable the treatment of various types of pollutants. Added versatility of AOPs also comes from the fact that there are different possible ways for the production of the reactive species (•OH radicals) thus allowing a better compliance with a specific treatment method.

The AOPs can be either homogeneous or heterogeneous. Homogeneous AOPs utilize UV radiation for the degradation of compounds in combination with one or more than one of the reagents such as ozone (O3), hydrogen peroxide (H2O2) and Fe(II). These reagents produce hydroxyl radicals under UV irradiation, which in turn causes the degradation of the pollutant. In addition, utilization of ultrasound in order to assist the generation of radicals is also reported. Homogeneous AOPs have shown the potential of treating various types of pollutants including explosives, drugs, solvents and dyes.

Heterogeneous advance oxidation processes employ a solid phase catalyst, activated by UV or visible light irradiation, to carry out the degradation process. In contrast to homogeneous processes, heterogeneous AOPs processes do not use expensive oxidizing chemicals such as hydrogen peroxide and ozone, as ambient oxygen can become the oxidant. Further, the photocatalyst is not consumed during the process, and can be easily recovered, reused or recycled. If the photocatalytic process can employ solar radiation, the cost of the radiation source can also be cut back.
The most promising candidate for the heterogeneous AOPs is semiconductor nanoparticles due to their high photoactivity, stability, lesser toxicity and lower cost. One important criterion for the semiconductor nanoparticles to be employed as photocatalysts is that the redox potential of the $\text{H}_2\text{O}/\cdot\text{OH}$ couple lies within the semiconductor band gap such that $\cdot\text{OH}$ radicals could be generated under band gap illumination. Several semiconductors have band gap energies sufficient for catalyzing a wide variety of chemical reactions, and the most interesting candidates include $\text{TiO}_2$ and $\text{ZnO}$.

1.8. Summary of Research

The research discussed in the following chapters focuses on a composite system that consists of gold nanoparticles tethered on the surface of zinc oxide nanoparticles. Such a system displays exciting electron and energy dynamics and novel photochemical properties. The goal of the current research was to investigate the essential characteristics of a carefully designed and constructed $\text{ZnO}$ and $\text{Au}$ nanoparticle system, and explore its ability to successfully treat some of the harmful pollutants found in wastewater.

Chapter 2 describes the improved synthesis methods for monolayer-capped water-soluble gold nanoparticles, methods of size isolation to obtain GNPs with narrow size distributions, and their characterization with electron micrography and spectrometry. Further, the assembly of $\text{Au}$ nanoparticles on the surfaces of $\text{ZnO}$ nanoparticles will be discussed along with the characterization of $\text{ZnO}/\text{GNP}$
nano-composites. Successful passivation of nano-composites by uniform silica shells is also illustrated. Finally, the thermal treatment techniques performed upon the composites in order to modulate their photocatalytic activities are illustrated.

The third chapter engages in the discussion of photodynamic characteristics of ZnO/GNP nano-composites. The photoluminescent properties of the composite system are characterized by steady-state fluorescence measurements, and also via time-resolved fluorescence upconversion techniques. The insights that are derived from the above results will be examined.

Chapter 4 and 5 explore the photocatalytic activities of ZnO/GNP nano-composites. Two dyes are applied as model systems in order to probe the photocatalytic efficiency of the nano-composites. The use of Rhodamine 6G for the photocatalysis via an oxidative pathway, and the use of thionine for the reductive photocatalysis are discussed in chapter 4 and 5 respectively. The effects of the extent of gold nanoparticle loading and the thermal treatment of nano-composites on photocatalytic behavior are analyzed. In order to recognize the mechanistic and energetic aspects of oxidative and reductive photocatalysis of nano-composites, photolysis of the dyes in the presence of different electron and hole scavengers are performed. A resultant discussion on the perceptivity of physicochemical and photocatalytic nature of the novel nano-composite catalytic system is presented.
Details of precursory experiments focusing on future expansions of the current study are presented in Chapter 6, in which the potential of the nano-composites to be employed as photocatalysts in the degradation of pesticides is illustrated. Means of optimizing photocatalytic activity of the nano-composites are also discussed.
1.9. References

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CHAPTER 2
SYNTHESIS AND ASSEMBLY OF THE NANO-CATALYST

The design and synthesis of the gold nanoparticles and their assembly on the ZnO nanoparticle surfaces will be described in this chapter. Characterization of thus prepared nano-catalysts will also be illustrated.

2.1. Supported Gold Catalyst Preparations

2.1.1. Conventional methods

The very first supported gold catalysts were prepared by Sermon et al. using an impregnation technique where chloroauric acid (H\textsubscript{3}AuCl\textsubscript{4}) was reduced to metallic gold on silica (SiO\textsubscript{2}) and alumina (Al\textsubscript{2}O\textsubscript{3}) substrates.\textsuperscript{1} Since then, various methods for preparation of supported gold nanoparticle catalysts have been reported.\textsuperscript{2} Generally, the techniques can be classified into two classes:

1. The support and the gold precursor are formed at the same time.
2. The gold precursor is applied to the preformed support.

The first method, termed coprecipitation, incorporates the precipitation of both the supporting material and the gold simultaneously from an aqueous solution of metal salt. The process is single stepped and convenient, but, suffers from several limitations: It has been reported that some of the Au nanoparticles could be embedded in the bulk, instead on the surface of the support.\textsuperscript{3} Further, this technique is not applicable to all metals and metal oxides as the successful
coprecipitation depends on the rate of precipitation and affinity of the species towards each other.

The second method, where the gold nanoparticles are precipitated onto the surface of pre-formed support particles, offers better versatility and provides different alternative procedures in achieving composite materials. One technique that is often employed is deposition-precipitation (DP), whereby the hydroxide or hydrated oxide is deposited on to the support surface as a result of gradual raising of pH of the solution in which the support is suspended. This basic method has numerous variations. For instance, aqueous Au salt is reduced by a reducing agent such as sodium borohydride (NaBH₄) in the presence of colloidal metal oxide nanoparticles, and due to the electrostatic affinity of the gold ions and the semiconductor support surface, stable gold nanoparticles will be formed on the support surface. Most of the deposition-precipitation methods involve HAuCl₄ as a precursor, but the presence of chloride (Cl⁻) could be detrimental in obtaining small Au nanoparticle sizes since the chloride ion promotes mobility and agglomeration of Au species during any thermal treatment. In addition, Cl⁻ ion may poison some catalytic reactions. Therefore special treatment methods may be required to remove excess Cl⁻ ions, as simple washing may not remove the remaining chloride ions.

Another technique is chemical vapor deposition (CVD), where a volatile organogold compound reacts with the surface of the support, on which it
decomposes resulting in zero-valent gold nanoparticles. The gold nanoparticles obtained via CVD, however, are found to be of broader size distributions.9

2.1.2. Deposition of preformed GNPs

In situ generation of gold nanoparticles on semiconductor supports as described in the previous section suffers from several limitations. First of all, there is very little control over the nanoparticle sizes obtained. Additionally, they result in nanoparticles with broader size distribution that is hard to control. Further, factors affecting the charge transfer processes that occur during catalytic reaction are difficult to assess. Conversely, the use of preformed GNPs capped with bifunctional bridging ligands in the preparation of the catalysts offers a number of advantages: Particle size could be controlled independently, and very narrow size distributions can be obtained via well established methods. Additional steps to reduce gold, remove the impurities or thermal post-treatments to stabilize the composites are not necessary.

Several examples are available in the literature where preformed GNPs were assembled on semiconductor nanoparticles in order to be used as catalysts. Gold nanoparticles with stabilizing agents such as polyvinylalcohol (PVA), polyvinylpyrrolidine (PVP) and tetrakis(hydroxymethyl)phosphonium chloride (THPC) have been employed in preparation of such catalyst composites.10 The study that is described in the following chapters utilizes preformed GNPs
stabilized with alkylthiol monolayers in the assembly of nano-composite catalyst.

2.2. Gold Nanoparticle Synthesis

The synthesis of ultrafine monodisperse particles is a major challenge in nanotechnology research, due to the extremely high surface energies of such particles of small dimensions. Nanoparticles undergo fast agglomeration in order to diminish surface energy. Thus, they require a protective coating during synthesis in order to keep them in a dispersed state. The general procedure that is most common and effective in the preparation of metal nanoparticles is in which the metal ions are reduced by a reducing agent in the presence of protective ligands, where nanoparticles with a surface monolayer of the capping ligand are obtained.

Schmid’s gold clusters protected by phosphine ligands [Au$_{55}$PPh$_3$)$_{12}$Cl$_6$] of about 1.4 nm reported in 1981,$^{11}$ long remained unique for the study of metallic nanomaterials. These gold nanoparticles, however, had limited usability due to their delicate synthesis, the difficulty in isolating in pure state and their poor stability. A very influential synthetic protocol was subsequently introduced by Brust et al., now termed ‘Brust – Schiffrin’ method, where Au nanoparticles protected by a monolayer of alkanethiolate ligands were fabricated via a two phase liquid – liquid reaction.$^{12}$
The Brust – Schiffrin method of GNP synthesis has had a considerable impact, because it allowed, for the first time, the facile production of highly stable GNPs of modest dispersity and controlled sizes ranging in diameter from 1.5 to 5.2 nm. The thiol ligands very strongly bind to gold due to the soft character of both Au and S, and the GNPs protected by thiols can easily be handled and functionalized just as any other stable organic or molecular compound. However, a post-synthesis size fractionation is usually required to obtain nanoparticles with optimal dispersity.\textsuperscript{13}

The general Brust – Schiffrin reaction is illustrated in Figure 2.1. The alkanethiol (RSH) polymerizes with the organic-dissolved Au(III) salt, \( \text{AuCl}_4^- \), reducing it to \( \text{Au(I)} \) according to Equation 2.1. Subsequent addition of \( \text{BH}_4^- \) leads to alkanethiol protected gold clusters (Equation 2.2).\textsuperscript{14}

\[
\text{AuCl}_4^- + \text{RSH} \rightarrow (-\text{Au}^\text{(I)}\text{SR}-)_n \\
(-\text{Au}^\text{(I)}\text{SR}-)_n + \text{BH}_4^- \rightarrow \text{Au}_x(\text{SR})_y
\]

The reaction’s behavior is consistent with the general nucleation – growth – passivation process: Smaller GNP core sizes are obtained with larger thiol molar ratios, fast reductant addition and low temperatures produce smaller, more monodisperse GNPs, immediate quenching of the reaction or use of sterically bulky ligands result in a high abundance of smaller nanoparticles.\textsuperscript{15}
Figure 2.1 Schematic diagram of general Brust – Schiffrin synthesis of thiolate capped gold nanoparticles depicting polymerization, nucleation and growth.

This primary two-phase method generates very stable gold nanoparticles that are soluble in non-polar organic solvents, but not soluble in polar or aqueous solvents. However, solubility of GNPs in polar solvents is required for applications such as sensors, molecular recognition, drug delivery as well as catalysis. Brust et al. later extended the synthesis to $p$-mercaptophenol capped GNPs in a single phase system,$^{16}$ which opened up avenues to the synthesis of GNPs stabilized by a variety of functional thiol ligands,$^{17,18}$ including ligands that offered water solubility to gold nanoparticles.$^{19,20}$
2.2.1. Size dispersity and separation

As the dimensions of nanoparticles are a controlling factor of their chemical and physical properties, the synthesis and isolation of monodisperse nanoparticles are required for tuning and elucidating their catalytic and other characteristics. However, kinetically controlled reactions such as Brust's synthesis always results in a distribution of GNP core sizes instead of well-defined molecular compositions. Monodisperse particles could be expected to possess exact chemical and physical characters in every particle. Hence, isolation of monodisperse gold nanoparticles is necessary before they are applied in catalytic studies.

Brust's method allows some coarse control of nanoparticle size and dispersity by varying the initial reactant thiol-to-metal ratio, strength of the reducing agent and the temperature of the reaction. Several post synthesis methods such as heating, etching, annealing and vapor treating have been able to yield specific sizes of monodisperse samples but have not demonstrated a wider range of size control of GNPs. Various size isolation methods have also been demonstrated to separate polydisperse as-prepared GNPs into smaller size distributions. Such isolation methods include gel electrophoresis (GE), capillary electrophoresis (CE), size exclusion chromatography (SEC), ion exchange chromatography (IEC), high performance liquid chromatography (HPLC), ultracentrifugation and molecular imprinting.
While some of these methods provide high fractionation into monodisperse sizes, their sample yields are extremely low. HPLC results in the separation of micrograms of GNP s per run\textsuperscript{32} whereas CE affords fractionation of only nanogram amounts of nanoparticles per run\textsuperscript{29}. Chromatographic techniques also suffer from weaknesses such as irreversible adsorption of nanoparticles to the packing materials. In comparison, solvent fractionation methods\textsuperscript{24,35} offer decent separation resolution while providing the highest yields on the milligram scale. The technique is simple and affordable and there are a number of solvents and solvent mixtures that can lead to a variety of solvent polarities, which are capable of separating many types of gold nanoparticles.

Generally, solvent fractionation is performed by dissolving the nanoparticles in a solvent at a high concentration followed by the slow addition of a miscible non-solvent until crystallization occurs. The solid phase is collected and further nanoparticle fractions can be obtained from the liquid phase repeating the same procedure.

However, the use of solvent fractionation has not shown success in size isolation of water soluble gold nanoparticles. The only techniques that have been reported to be used for the separation of water soluble GNPs are gel and capillary electrophoreses\textsuperscript{28,36}, which can only provide minute amounts of samples that are insufficient for subsequent investigations. In the current work,
we illustrate the successful application of the solvent fractionation method to isolate water soluble gold nanoparticles.

The water-soluble nanoparticles remain stable in polar solvents due to the solvation of polar functional groups such as carboxyls and amines. The electrostatic repulsion also introduces a barrier to aggregation. Gradual addition of a non-solvent (non-polar solvent) can produce size-dependent flocculation of the nanoparticles.37

The addition of a non-polar solvent decreases the average polarity of the solution and reduces the solvation of the functional groups, thereby lowering the energetic barrier to flocculation. The largest particles in the solution experience the greatest effect due to the larger number of functional groups on their surface that increases their overall polarity. These large particles have a higher probability of overcoming the reduced energy barrier, and thus become enriched in the precipitate. The removal of a specific subset of particles from the as-prepared nanoparticles narrows the size distribution in both supernatant and the precipitate. This phenomenon was successfully utilized in size isolation and narrowing the dispersity of the water soluble gold nanoparticles that were prepared in this study.

### 2.2.2. Tiopronin and glutathione capped gold nanoparticles

The current research utilized water soluble gold nanoparticles passivated with ligand monolayers of tiopronin and glutathione. Tiopronin (N-2-
mercaptopropionylglycine) is a pharmaceutically important drug with the trade name ‘Thiola’ (Figure 2.2) that is used primarily for the treatment of the rare disease cystinuria. It may also be used to treat Wilson’s disease and rheumatoid arthritis.\textsuperscript{38-40} Notably, it possesses a free terminal carboxyl group that renders it water soluble and provides a handle for further reactivity. Tiopronin monolayer-protected gold clusters were first synthesized by Templeton et al., in which they utilized modified single-phase Brust’s reactions in a polar methanol/acetic acid solution and made GNPs of $1.5 - 1.9$ nm in diameter.\textsuperscript{36}

Glutathione (GSH) is a bulky tripeptide ($L-\gamma$-glutamyl-$L$-cysteinyl-glycine) with a thiol group and a highly abundant component, present at ca. $5\text{mM}$ level, in plant and animal cells (Figure 2.2).\textsuperscript{41} Among other functions, it mainly serves to maintain the cellular potential at a reducing state, thereby protecting biomolecules against oxidative damage from free radicals.\textsuperscript{42} Its reductive activity is generally outlined in Equation 2.3.

\begin{equation}
2 \text{GSH} \rightleftharpoons \text{GSSG} + 2 \text{H}^+ + 2 \text{e}^-
\end{equation}

Equation 2.3

Very small glutathione-capped gold clusters, identified to be Au$_{28}$(SG)$_{16}$ with a diameter of only 0.9nm, were the first report on such nanoparticles, in which size isolation of the particles was achieved by electrophoretic methods.\textsuperscript{43} Tiopronin and glutathione are used as bifunctional bridging ligands for passivating gold nanoparticles, where the carboxylic acid groups present in
tiopronin and glutathione molecules could be used to anchor the gold nanoparticles on a semiconductor surface.\textsuperscript{44,45}

![Figure 2.2](image.png)

**Figure 2.2** Structures of tiopronin and glutathione. The commercial tiopronin is a racemic mixture while glutathione is in L form.

### 2.3. Tiopronin Capped Gold Nanoparticle Synthesis

#### 2.3.1. Chemicals

All reagents were of ACS grade or higher purity. Tetrachloroauric acid trihydrate, \textit{N}-2-mercaptopropionylglycine (tiporonin), sodium borohydride, methanol and acetonitrile were purchased from Sigma-Aldrich. Glacial acetic acid was purchased from J.T. Baker. Ultra pure water with a resistivity of 18 M\(\Omega\) cm was obtained by purifying distilled water through a PureLab Plus UV/UF water purification system.

#### 2.3.2. Synthetic details

Gold nanoparticles were synthesized utilizing a modified procedure from literature.\textsuperscript{36} In a typical reaction, 1 g of tetrachloroauric acid and 0.083 g of tiopronin were co-dissolved in a mixture of 64 ml methanol and 16 ml of acetic acid, which resulted in a maroon colored solution. The solution was stirred
rapidly for ca. 1 hour, during which the solution color faded and resulted in a colorless solution. Under vigorous stirring, 0.16 g of NaBH₄ freshly dissolved in 48 ml of water was added slowly to this solution. The solution immediately turned into a black-brown color, and the stirring was continued for 45 mins.

Excess solvent from the resulting solution was removed under reduced pressure and at ca. 30 °C using a rotary evaporator until a thick slurry was left. The product was washed with 3 portions of acetonitrile with the last portion left overnight.

2.3.3. Size separation of GNPs

Size separation of the as-prepared gold nanoparticles was done by dissolving the cleaned product in a 1:1 mixture of methanol and acetonitrile. A few drops of water were needed to trigger the initial solvation of the GNPs. A portion of the as-prepared gold nanoparticles that are of smaller dimensions dissolved in the solution, and was discarded. The precipitate was collected and re-dissolved in a 1:3 mixture of water and methanol. The desired tiopronin monolayer protected gold nanoparticles were extracted into the solution. The solution was separated from the precipitate and the solvent was removed using a rotary evaporator. The solid gold nanoparticles, obtained as a black powder were stored at -4 °C.
2.3.4. Characterization

Dilute GNP solutions in water were freshly prepared for each characterization. UV/Vis optical absorbance spectra were recorded using a Perkin Elmer Lambda 40 spectrophotometer.

Standard carbon coated formvar films on 400 mesh copper grids purchased from Electron Microscopy Sciences were treated in concentrated nitric acid fumes for ca. 5 seconds in order to reduce the hydrophobicity of the formvar film, and was washed in water. The GNP solutions were drop cast on the treated grids and were dried under vacuum for at least 2 hours for transmission electron micrographic (TEM) measurements. The TEM images were obtained using a Jeol JEM 1230 transmission electron microscope operating at 80kV. Images were recorded at 500,000 X magnification using a Gatan BioScan 792 wide-angle CCD camera. Gold nanoparticle core diameters were measured manually using Scion Image (Release: 4.0.3.2 Alpha) software.

2.3.5. Results and discussion

Water-soluble tiopronin-passivated GNP synthesis is different from the classical Brust’s method in several ways. The reaction is performed in methanol/acetic acid mixture rather than in toluene. The decolorization that occurs after the addition of tiopronin indicates the reduction of Au(III) species into Au(I)-SR polymer, that was reported to be of a different structure than that was suggested for Brust’s reaction. The presence of acetic acid is critical to maintain the pH of
the solution during the synthesis. In the absence of acetic acid, the nanoparticles will not be stable in methanol and will aggregate irreversibly.\textsuperscript{36}

All previously reported water soluble GNP syntheses have utilized dialysis via a cellulose ester membrane as the purification method, which is cumbersome and time consuming that usually takes around 3 – 5 days of processing.\textsuperscript{46,47} We describe a simpler purification method by non solvent acetonitrile, which removes most of the impurities, and further cleansing takes place during the solvent fractionation steps that ultimately lead to GNPs pure enough for the purposes of the current study.

Size extraction was achieved by a simple solvent fractionation method using water as the solvent and methanol as the non-solvent. Satisfactorily monodisperse gold nanoparticles with good yields were obtained without the use of electrophoretic techniques.

Figure 2.4 illustrates the UV/Vis absorbance spectrum of isolated tiopronin-protected GNPs. The surface plasmon absorption is clearly visible for these relatively larger nanoparticles, and it occurs at 510nm, at a blue-shifted wavelength, conforming to the fact that the SPR maximum is dependent upon the particle dimensions. For GNPs with diameters of 9, 15, 22, 48 and 99, the absorption maxima ($\lambda_{\text{max}}$) were reported to be at 517, 520, 521, 533 and 575 nm respectively.\textsuperscript{15}
One of the most common characterization techniques of nanoparticles, TEM provides a photograph of gold cores of the nanoparticles. In this study, TEM was used to assess the dispersity of the GNP core sizes and shapes, and also the purity of the samples. A TEM image that is illustrative of the nanoparticles is shown in Figure 2.4. The average size of the nanoparticles were calculated to be 3.7 nm with a standard deviation of 0.6 nm. The inset of Figure 2.4 is a histogram of core size distribution of tiopronin capped GNPs.

![Absorbance vs. Wavelength](image.png)

**Figure 2.3** Optical absorption spectrum of 3.7nm tiopronin capped gold nanoparticles.
2.4. Glutathione Capped Gold Nanoparticle Synthesis

2.4.1. Chemicals

Tetrachloroauric acid trihydrate, L-γ-glutamyl-L-cysteinyl-glycine (glutathione), sodium borohydride, methanol and acetonitrile of at least ACS grade were purchased from Sigma-Aldrich and were used as received. Ultra pure water with a resistivity of 18 MΩ cm was obtained by purifying distilled water through a PureLab Plus UV/UF water purification system.

2.4.2. Synthetic details

A modified literature procedure was utilized to synthesize glutathione passivated gold nanoparticles.\(^{36}\) 1 m mol (0.39 g) of HAuCl\(_4\) was dissolved in a stirred solution of 30 ml of methanol and 20 ml of water, which resulted in a...
bright yellow solution. 1 m mol (0.31 g) of glutathione is added to the rapidly stirred Au(III) solution. The solution turned light brown and slowly turned colorless within 40 minutes, indicating the reduction of Au(III) into Au(I) and polymerization with glutathione. A NaBH₄ solution, freshly made by dissolving 5 m mol (0.19 g) of NaBH₄ in 40 ml of water was slowly added to the vigorously stirred Au(I) polymer solution, which caused the solution to immediately turn dark brown due to the formation of gold nanoparticles. The solution was quickly transferred into a water bath kept at 50 °C, and stirring was continued for 1 hour. The resulting solution was evaporated to near dryness on a rotary evaporator at 30 °C.

2.4.3. Size separation of GNPs

In order to size isolate gold nanoparticles, the as-prepared product was dissolved in 10 ml of water. Selective recrystallization was performed by adding about 0.5 ml of methanol to the nanoparticle solution. The solution was centrifuged at 3000 rpm for 5 minutes and the precipitation was separated. The process was repeated for the supernatant until four recrystallization products, labeled R1, R2, R3 and R4 respectively, were obtained. The remaining solution was clear light brown indicating almost all GNPs were precipitated off during the process.

The four GNP samples were purified by washing with 3 portions of methanol followed by 3 portions of water methanol mixture. The water content of the
washing solutions was gradually increased until the gold nanoparticles almost dissolved. This technique ensured that all polar impurities had been removed. The GNPs were recovered by centrifugation after each wash. The resultant products were kept under methanol at 4 °C until they were ready to be used.

2.4.4. Results and discussion

In order to achieve larger average core size, a few variables were changed. Higher glutathione : Au(III) salt ratio results in smaller GNPs. therefore, a lower glutathione : AuCl₄⁻ ratio of 1 : 1 was applied for current synthesis. Too low an amount of glutathione leads to rather polydisperse GNPs. Initial reports suggested that the water : methanol solvent ratio also plays a critical role in determining the GNP core sizes. Higher methanol content (water : methanol = 3:4) produced nanoparticles with core diameters of ca. 1nm.⁴³ A water : methanol ratio of 2 : 1 was able to provide nanoparticles with larger cores. The dispersity of the GNPs was found to be dependent upon the reduction temperature, where higher temperatures providing better monodispersity. As a result, a reduction temperature of 50 °C was chosen as the best condition.

The literature only describes electrophoretic⁴⁸ and chromatographic⁴⁹ methods as suitable methods for size separation of glutathione protected GNPs which are both complex and lack the capability of yielding GNPs in adequate quantities for further applications. However, we successfully applied the recrystallization method using water and methanol as solvent and non-solvent respectively, to
isolate GNPs with four different average sizes from a single synthesis at high yield.

Figure 2.5 Optical absorption spectra of the glutathione GNPs obtained via selective recrystallization from the as-prepared nanoparticle solution. The spectra have been normalized at 250 nm for comparison.

Optical absorption spectra of the four residues obtained, illustrated in Figure 2.5, clearly indicate the different average sizes of the gold nanoparticles obtained through the recrystallization procedure. Spectra of the residue R1 and R2 show surface plasmon bands at 550 nm and 500 nm respectively indicating their average sizes are above 2.5 nm. Relatively weak and blue shifted SP band of R2
points to smaller core sizes compared to those of R1. The residues R3 and R4 resulted in nearly featureless absorbance spectra with no SP band absorption indicative of their smaller sizes.\textsuperscript{51}

\textbf{Figure 2.6} Representative TEM images of glutathione gold nanoparticle residues R1, R2, R3 and R4 obtained via selective recrystallization of as-prepared nanoparticle solution. Insets illustrate the size distribution of GNPs in respective samples. The length of scale bars is 50 nm.
TEM images of the fractionated gold nanoparticle residues are provided in Figure 2.6. Average sizes of the nanoparticles were calculated by manually counting ca. 100 particles in the given images. The inset in each image shows histograms for the particle size distribution of corresponding fraction. The first residue R1 contained aggregations to a large extent and lacked any useful dispersity. The average sizes and the standard deviation of the GNPs in the residue R2, R3 and R4 were $3.9 \pm 0.9$ nm, $3.1 \pm 0.6$ nm and $2.1 \pm 0.3$ nm respectively. It is evident from the TEM image analysis that the utilization of the explained synthesis procedure and size-selective precipitation was able to produce three different sizes of glutathione passivated gold nanoparticles with narrow size distribution.

2.5. Assembly of GNPs on ZnO Nanoparticle Surfaces

As briefed in section 1.4, ZnO is a wide band gap semiconductor with a band gap energy ($E_g$) of 3.2 eV, which is comparable to that of TiO$_2$ and is one of the few oxides that shows quantum confinement effects in an experimentally accessible size range (<7 nm). It has become one of the most important semiconductor materials in fundamental research and for applications in fields such as optoelectronics, sensors and actuators. Another advantage of ZnO is that it is biocompatible and biosafe due to its low toxicity. However, its photocatalytic behavior is not thoroughly studied. Thus, we have selected ZnO nanoparticles in this work, to study their catalytic activity in combination with Au nanoparticles.
2.5.1. Chemicals

ZnO nanopowder with average size <100 nm, and BET surface area of 15 - 25 m²g⁻¹ was purchased from Sigma-Aldrich and was used as received. Ultra-pure water with a resistivity of 18 MΩ cm was obtained by purifying distilled water through a PureLab Plus UV/UF water purification system.

2.5.2. Assembly of the nano-composite

The ZnO/Au nano-composites were prepared using a facile procedure. A dispersion of ZnO nanoparticles was prepared by adding 0.25 g of ZnO nanoparticles in 300 ml of water and sonicating the solution in a Branson 2510 ultrasonic water bath for about 10 minutes until the nanoparticles are fully dispersed.

A sample of the desired type of gold nanoparticles, prepared as described in sections 2.3 and 2.4, was dissolved in ca. 5 ml of water to make a concentrated GNP solution. In order to calculate the gold nanoparticle concentration, a known volume (200 µl) of this solution was placed in a vacuum dessicator overnight to completely remove the solvent, and weight of the residue was recorded.

A calculated volume of the GNP solution, depending on GNP loading required, was added dropwise into the rapidly stirred ZnO dispersion over 1 minute. The solution was then stirred slowly for 5 hours so that all the GNPs are bound to ZnO nanoparticles. The solution was occasionally sonicated in order to minimize agglomeration during stirring. The product was recovered by centrifugation at
3500 rpm for 10 minutes, and the supernatant was discarded. The residue was dried under vacuum and was stored under inert atmosphere until used.

2.5.3. Characterization

In order to characterize the products, 4 mg of ZnO nanoparticles or the composite were dispersed in 40 ml of water by sonicating for 10 minutes. Each sample was placed in a quartz cuvette for optical measurements. The optical absorbance and photoluminescence (PL) of these samples were measured. Steady state photoluminescence was determined using Edinburgh Instruments FLS920 spectrofluorimeter. Transmission electron microscopic images were also obtained for every sample prepared.

2.5.4. Results and discussion

Figure 2.7(A) shows a UV/Vis absorbance spectrum of the ZnO nanoparticles dispersed in water. An absorption maximum is observed at 376 nm, that is comparable to the onset of absorption of macrocrystalline ZnO. The TEM image of ZnO nanoparticles shown in Figure 2.7(B) illustrates the highly dispersed nanoparticles of various sizes and shapes. The wavelength of the absorption maxima is thus well correlated with this observation considering the larger average size of ZnO nanoparticles.
Figure 2.7 (A) Optical absorption spectrum of a water solution of ZnO nanoparticles, (B) TEM image of ZnO nanoparticles showing particles of various sizes and shapes. The scale bar length is 50 nm.
Binding of gold nanoparticles on the ZnO nanoparticle surface can be understood from the surface properties of ZnO. Zinc oxide is an amphoteric oxide and therefore, the nature of charges on ZnO surface becomes a function of the pH of the surrounding medium. In an acidic pH, the particle surface becomes positively charged. The surface polarization can be described by Equation 2.4, where Zn-OH represents a surface adsorption site. In a basic medium, the reverse will be true, where the particle surface is negatively charged and the surface polarization is indicated by Equation 2.5.

\[
\begin{align*}
\text{Zn-OH} + \text{H}^+ & \rightleftharpoons \text{Zn-OH}_2^+ \\ 
\text{Zn-OH} + \text{OH}^- & \rightleftharpoons \text{Zn-O}^- + \text{H}_2\text{O}
\end{align*}
\]

It can be easily conceived that therefore, a specific value of pH exists at which the overall charge on the particle surface becomes neutral. This value, which is characteristic of specific material, corresponds to its point of zero charge (pH$_{pzC}$). pH$_{pzC}$ of zinc oxide is reported to be between 9.0 – 10.3, and therefore in neutral aqueous solutions where pH is around 7, the surface of ZnO will carry a net positive charge that would lead to strong adsorption of anionic species on ZnO nanoparticles.

The free tiopronin molecule has a single carboxyl group with a $pK_a$ of 3.5, and the glutathione molecule carries two carboxyl groups where $pK_1$ is 2.1 and $pK_2$ is 3.5. However, once attached to the gold nanoparticles, the acidity of these
ligands may decrease significantly due to the close packing of the ligands, which is caused by the charge repulsion between the ionized carboxyl groups lying at close proximity. Therefore, $pK_a$ values measured for ligands bound to GNPs could be as much as 2 units higher than those of the free form. Nevertheless, the acid dissociation constants of tiopronin and glutathione are sufficiently higher that at neutral solutions, the carboxyl groups of those ligands bound to gold nanoparticles will stay ionized. As a result of this overall negative charge on gold nanoparticles passivated with tiopronin and glutathione, the GNPs will readily bind to positively charged ZnO nanoparticle surfaces through electrostatic interactions as shown in Figure 2.8.

**Figure 2.8** Schematic illustration of the process of GNP capped with tiopronin or glutathione binding on ZnO nanoparticles via electrostatic interactions.

Various levels of gold nanoparticle loadings were attempted. It was concluded that weight percent of 0–8% tiopronin GNP loading with respect to ZnO was most suitable for the photocatalytic studies. Figure 2.9 illustrates the TEM images of nano-composites made by loading upto 8% (w/w) of 3.7 nm tiopronin GNPs that was described in section 2.3, and the increase in surface coverage by
gold nanoparticles with the initial amount of GNP addition is clearly visible. It was also observed that there were no free gold nanoparticles on the TEM grid except for 8% loading, confirming that all the gold nanoparticles were indeed attached to ZnO surfaces. At 8% loading, it is clear that all the surface active sites of ZnO have been occupied and thus a small amount of unbound gold nanoparticles could be found on the TEM grid.

Similar experiments were carried out to synthesize nano-composites with glutathione-capped GNPs. Figure 2.10 and Figure 2.11 depict TEM images of nano-composites made with 3.9 nm glutathione GNPs (R2) and ZnO nanoparticles. According to Figure 2.10, up to 4% weight loading of GNPs, all gold nanoparticles are found to be attached to ZnO surfaces and no unbound nanoparticles could be seen on TEM images. However, beyond 4% weight loading, an abundance of free GNPs are found on the TEM grids of as-prepared composites (Figure 2.11). The washed and dried products did not contain any unbound GNPs at any sample, indicating that the excess GNPs could be washed away by centrifugation-separation.

It is also worth noting that despite the similar size of tiopronin capped and glutathione capped gold nanoparticles, the TEM images indicate that ZnO surface saturation by gold nanoparticles is reached at a lower loading level for glutathione GNPs. This could be an indication of lower strength of interaction between glutathione GNP and ZnO.
Figure 2.9 TEM images of ZnO nanoparticles loaded with different weight ratios of 3.7 nm tiopronin capped GNPs. Length of the scale bars is 50 nm.
Figure 2.10 TEM images of dried nano-composites made by depositing 3.9 nm glutathione GNPs on ZnO. Up to 3% (w/w) GNP loading does not indicate unbound GNPs on TEM grid.

Optical absorption spectra of the nano-composites made with tiopronin and glutathione capped GNPs on ZnO are shown in Figure 2.12. For the comparison purposes, all the spectra were normalized at band edge absorption maxima around 376 nm. Apart from a slight shoulder around 500 nm, all the composites show similar absorption, indicating the addition of GNPs at this loading level does not significantly affect the light absorption profile of ZnO nanoparticles.
Figure 2.11 TEM images of the nano-composite made with 3.9 nm glutathione GNP and ZnO nanoparticles, indicating the unbound gold nanoparticles at higher loading levels beyond 4% (w/w).
2.6. ZnO Surface Modification with Ligands

As the bridge between gold nanoparticles and ZnO surface, the passivating ligand of gold nanoparticles plays an important role in charge and/or energy transfer between the nanoparticles. Therefore, recognizing the effects of these capping agents on ZnO surface was found to be of importance, especially during calcination of the nano-composites (See section 2.7).

In addition to glutathione, cysteine was selected as a ligand to be used as a surface modifier. Cysteine, an amino acid, is similar to glutathione and tiopronin in that it possesses a thiol group and a carboxyl group in its structure (Figure 2.13). Therefore it could mimic the characteristics of those ligands. However, L-
cysteine has a much lower decomposition temperature of about 176 °C, and it could be expected that during a calcination process (vide infra) above this temperature, cysteine will completely decompose and will be removed from the solid phase.

![Chemical structure of L-cysteine](image)

**Figure 2.13** Chemical structure of L-cysteine.

### 2.6.1. Experimental details

L-cysteine was purchased from Sigma-Aldrich and was used as received. A stock solution of glutathione was prepared by dissolving 7.4 mg of glutathione in 10.0 ml of ultra-pure water. A cysteine stock solution was made by dissolving 6.4 mg of cysteine in 10.0 ml of water.

250 mg of ZnO nanopowder was dispersed in 150 ml of ultra-pure water and was sonicated for 10 minutes until the entire amount of solid is fully dispersed. In order to prepare glutathione modified ZnO, 1.0 ml of the glutathione stock solution was slowly added to the stirred ZnO solution. For cysteine modification, 500 µl of the cysteine stock solution was added. The solutions were stirred for 5 hours, and were centrifuged at 3500 rpm for 10 minutes to obtain the solid
product. The solid was dried in a vacuum dessicator for 24 hours and was stored under inert atmosphere until used.

2.6.2. Discussion

Carboxyl acid groups on glutathione and cysteine are fully dissociated at neutral pH, and also possess a higher affinity towards metal oxides. Therefore, the ligands are supposed to be assembled on ZnO surface via carboxylate groups rather than through thiols, which mimics GNP binding process.

Structure of the gold nanoparticles with a diameter of 3.9 nm was assumed to be \( \text{Au}_{2406}\text{SR}_{268} \). Amount of ligand that was used to modify ZnO surface was estimated based on this data. The calculations were made so that the number of ligands added corresponded to 2% GNP loading on ZnO surface.

2.7. Calcination of Nano-Composites

The key to produce highly active heterogeneous photocatalysts is to enhance the capability of photogenerated charge carriers to undergo surface chemical reactions and minimize recombination of the charge carriers. Application of an appropriate post-treatment method can improve the photocatalytic performance of the catalyst. One such post-treatment option that was utilized in this investigation is calcination of the nano-composite at a higher temperature. Calcination has shown to have prominent influence on the prepared photocatalysts depending on the method of preparation and the end usage.\(^{62-64}\) Calcination can increase the crystallinity of the material which generally
enhances the activity by reducing the density of defects that act as recombination centers. Another goal of calcining the nano-composites is to eliminate the organic matter, especially the ligand layer on the GNP so that the gold nanoparticles become in direct contact with the semiconductor surface thereby enhancing the charge transfer efficiency.

2.7.1. Experimental details

The dried nano-composites were ground into a fine powder and a small amount, ca. 10 mg, was placed in a covered porcelain crucible, and was calcined at a predetermined temperature, usually at 300 or 500 °C. Calcinations were performed in a Fisher Scientific programmable muffle furnace. The muffle furnace was preheated to the required temperature and the samples were then placed in the furnace for 1 hour. The calcinated samples were kept under inert atmosphere until they were ready to be used.

Aqueous solutions of the calcined samples were prepared the same way as described in Section 2.5.3. Briefly, 4 mg of the composite was dispersed in 40 ml of water by sonicating for about 10 minutes, and were drop-casted on TEM grids that were treated with acid previously (See Section 2.3.4). The TEM grids were dried under vacuum for 2 hours and TEM imaging was performed.

2.7.2. Results and discussion

Three gold nanoparticle loadings, 0.5%, 2% and 6% of the 3.9 nm glutathione-capped GNP/ZnO were selected to be tested for the effect of calcination on
photocatalytic efficiency of the nano-composites. They were subjected to calcination at different temperatures ranging from 200 to 450 °C. The time duration of calcination was kept constant at 1 hour.

Figure 2.14 illustrates TEM images of the nano-composites made with different loadings of 3.9 nm glutathione gold nanoparticles on ZnO, before and after calcining at 300 °C for 1 hour. The images indicate that the integrity of the composites was not compromised during calcination, and calcined composites did not have any unbound GNPs resulting from thermal treatment.

The gold nanoparticles on composites at low GNP loading levels (0.5%), do not show significant visible changes due to calcination. However, at higher loadings, i.e. 6%, some larger gold nanoparticles up to 9 nm in diameter can be found on ZnO surfaces. The melting point of Au is much lower at 1064 °C compared to that of other noble metals. Furthermore, due to the quantum size effects, the melting point of gold nanoparticles rapidly decreases as a function of reducing particle size when the diameters are lower than about 5 nm, and it is reported that for gold nanoparticles with a diameter of 2 nm, the melting point could be as low as 300 °C. Therefore, the GNPs may coagulate much more readily during the calcination at 300 °C. This phenomenon could be explained as follows.
Figure 2.14 TEM images of composites that were dried (left) and calcined (right) at 300 °C for 1 hour. Three different glutathione GNP loadings are shown.
During composite assembly, the gold nanoparticles are preferentially deposited on the atomic scale defect sites on the ZnO surface. When the nano-composites are subjected to calcination temperatures, GNPs may reach their melting point that enhances their mobility on the ZnO surface. Then, the nanoparticles can diffuse limited distances through the ZnO particle surface and undergo Ostwald ripening by agglomerating with adjacent GNPs.\(^ {68}\) Ostwald ripening is a growth-loss process by which large particles grow at the expense of smaller particles, usually resulting in bimodal distribution. As a result, an enlargement of gold nanoparticles is seen at higher loading levels of the nano-composite. However, at low levels of nanoparticle loading, the GNPs are far enough from each other that any agglomeration and Ostwald ripening is minimized.

2.8. Application of Silica Shells

In order to understand the photocatalytic mechanism of the prepared nano-catalysts, it is imperative to study their excited state energetics within very short time scales. It was found that the nano-composites are not stable under powerful laser beams that are used in the ultra-fast spectroscopic instruments used in such experiments. Therefore, a way of passivating the nano-composite so that the material is stable in the solution under laser irradiation was required. One option is to encapsulate the nano-composites in a polymer matrix such as polyethylene glycol\(^ {69}\) and polyacrylic acid\(^ {70}\) derivatives. These passivators can afford extended stability. However, they are unable to provide protection against
photoelectron scavenging by oxygen and photoanodic dissolution of chalcogenide semiconductor particles in aqueous solutions.

An alternative process is to deposite a layer that is capable of impeding electron, proton and oxygen diffusion to the nanoparticle surface. A suitable candidate for this purpose is amorphous silica. Silica (SiO$_2$) is chemically inert and optically transparent, therefore will not affect the solid state properties of the nanoparticles. Furthermore, a silica shell would enhance the photostability by preventing surface adsorbates and redox species reaching the nanoparticle surface and the hydrophilicity of silica would make the nanoparticles readily soluble in water. Therefore, silica was selected as the passivation agent for the nano-composites in their optical characterization techniques. Application of silica shells on various types of nanoparticles in order to achieve different objectives including, enhancing photo and chemical stability, imparting inertness and biocompatibility and incorporation of chromophores to be used as contrast agents have been reported.

### 2.8.1. Chemicals

(3-aminopropyl)trimethoxysilane (APS), tetraethoxysilane (TEOS), 28% ammonium hydroxide in water solution, ethanol and methanol, all at or above ACS grade purity, were purchased from Sigma-Aldrich, and were used as received. Ultra pure water with a resistivity of 18 MΩ cm was obtained by
purifying distilled water through a PureLab Plus UV/UF water purification system.

2.8.2. Experimental details

Silica shells were grown using a modified Stöber process from literature.\(^{71,75}\) 10 mg of ZnO or the nano-composite were suspended in 50 ml of ethanol by sonicating the solution for about 10 minutes. 20 \(\mu\)l of APS was slowly added to the stirred suspension and stirring was continued for 1 hour. At the end of 1 hour, the suspension was sonicated again to ensure that the composite is fully dispersed, and 25 \(\mu\)l of ammonium hydroxide, 500 \(\mu\)l of water and 110 \(\mu\)l of TEOS were slowly added to the stirred suspension. The speed of stirring was lowered to gentle stirring and was left for 24 hours for the shell growth. The product was recovered by centrifuging at 3500 rpm for 10 minutes. In order to remove any impurities and unreacted species, the silica coated product was washed thrice with ethanol and once with methanol, centrifuging after each wash to isolate the product.

2.8.3. Results and discussion

In order to obtain uniform coverage of silica in the nano-composites, it is required that the nanoparticle surface provides enough nucleation sites so that a controlled growth of the shell could be achieved. The ZnO surfaces do not possess significant affinity for silica, and attempting to grow silica may cause silica to self-nucleate and form independent silica particles. In order achieve
enhanced affinity of silica towards the nano-composite surface and generate
nucleation sites for silica growth, a silane coupling agent must be used. The
coupling agent that was utilized for this purpose is APS, and the amine (NH₂)
group on APS will have a strong affinity towards the ZnO surfaces that are
generally positively charged.⁷⁶

The first step was to anchor the APS molecules on ZnO surface as illustrated on
Figure 2.15, Reaction 1. Selection of the appropriate amount of APS is critical as
a lower amount will trigger self nucleation of silica, and excess APS can cause
cross-linking of the nanoparticles.⁷¹ A molar ratio of 1:1 between APS and
overall Zn(II) was found to work well for this purpose. Addition of water and
ammonia triggers the hydrolysis of APS into silicates according to Reaction 2 in
Figure 2.15, on which TEOS hydrolysis continues until a uniform shell of SiO₂ is
obtained. The Reaction 3 in Figure 2.15 is detailed in Equation 2.6.

\[
\text{Si(OEt)}_4 + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{EtOH} \quad 2.6
\]

\[
\text{Si} - \text{OH}_{\text{Surface}} \rightleftharpoons \text{SiO}^-_{\text{Surface}} + \text{H}^+ \quad 2.7
\]

Hydrolysis of the silanes in to silica catalyzed by water and NH₃ according to
Equations 2.6 and 2.7, is a complex process. Water catalyzes the hydrolysis and
increases the nucleation rate and therefore, a lower water content will favor the
growth of nanoparticle seeds over fresh nucleations. However, a sufficient
amount of water is needed to stabilize the silica coated particles via ionization of
silanol groups according to Equation 2.7. Presence of ammonia also catalyzes the hydrolysis by enhancing the forward reaction in Equation 2.7, and minimizes self nucleation of silica.\textsuperscript{71} A molar ratio of 1:4 for TEOS:Zn(II) was chosen so that cross-linking is minimized and a sufficient shell thickness is achieved.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure215.png}
\caption{Schematic illustration of the surface reactions involved in the formation of thin silica shells on the nano-composites.\textsuperscript{73,77}}
\end{figure}
TEM images of silica shelled ZnO and 3.9nm glutathione capped GNP loaded composites are shown in Figure 2.16. It can be seen that there are no self-nucleated silica particles. All nanoparticles are found to be evenly covered with 6 to 9 nm thick SiO₂ shells. Clusters of nanoparticles are seen to be passivated with a single silica layer. This is possibly due to the natural tendency of ZnO nanoparticles to form clusters, and not a result of the silica shell passivation.

**Figure 2.16** TEM images of ZnO and glutathione GNP/ZnO composite nanoparticles with SiO₂ shells. Length of the scale bar is 50 nm.
Optical absorption spectra of ZnO, 1% and 5% GNP loaded composites with SiO₂ shells are depicted in Figure 2.17. All silica shelled nanoparticles show very similar absorption profiles with a broader absorbance at longer wavelengths. This could be attributed to the higher scattering of light introduced by the silica shells. Additionally, a slight red shift of the band edge from 374 to 377 nm is seen when the SiO₂ shell is applied. As observed in Figure 2.16, silica shells are formed over entire clusters of ZnO nanoparticles, which could result in slight energy level merging, resulting in a bathochromic shift of the band edge.\textsuperscript{52}

![Normalized optical absorption spectra of silica shelled nanocomposites](image)

**Figure 2.17** Normalized optical absorption spectra of silica shelled nanocomposites. Absorption of bare ZnO is also shown for comparison.

### 2.9. Conclusions

This chapter described the facile syntheses of tiopronin and glutathione passivated water soluble gold nanoparticles. Despite literature reports in which
size isolation of water soluble nanoparticles needed electrophoretic methods, solvent fractionation and selective precipitation methods were applied successfully that resulted in GNPs with dispersities as low as 14%.

Photocatalytic nano-composites were made by the assembly of the GNPs on ZnO nanoparticles. The 3.7 nm tiopronin capped and 3.9 nm glutathione capped gold nanoparticles were assembled on ZnO nanoparticles utilizing the strong electrostatic attractions between the positively charged ZnO surface and the carboxylate groups on tiopronin and glutathione. Various amounts of GNPs were loaded on ZnO nanoparticles, up to 8% by weight, in order to investigate the possible effect on gold loading on photocatalytic efficiency of the nano-composites.

The catalysts were calcined at 300 °C in an attempt to remove the ligand shell of the GNPs and study the resultant effect on photocatalysis. The gold nanoparticles were found to coagulate at this calcination temperature due to Ostwald ripening, when the GNP loading on ZnO was higher.

Silica shells were grown on the nano-composites to prevent their degradation during photoluminescent studies. It was found that SiO₂ shells of about 6 – 9 nm developed evenly for all types of nano-composites.
2.10. References

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CHAPTER 3
PHOTOLUMINESCENT PROPERTIES OF NANO-CATALYSTS

3.1. Introduction

One of the interesting physical properties of semiconductor nanoparticles is their optical characteristics, which is distinguished by features such as broad absorption spectrum, narrow and tunable photoluminescence spectra, high fluorescent quantum yields, large Stoke's shifts and stability against photobleaching.\textsuperscript{1-4} Therefore, semiconductor nanoparticles have motivated intense research in recent years for the realization of numerous applications related to their optical properties. Notable areas include light-emitting devices,\textsuperscript{5,6} lasers,\textsuperscript{7,8} photovoltaics,\textsuperscript{9,10} detectors\textsuperscript{11,12} and biolabels.\textsuperscript{13-15} One of the crucial functionalities of semiconductor nanoparticles that is probed in many of these applications is the ability to act as very effective donor fluorophores.\textsuperscript{16}

Conversely, when placed in close proximity of radiation emitters, gold nanoparticles are able to effectively quench fluorophore emissions. Both charge transfer (CT) or energy transfer (ET) processes are considered to be major deactivation pathways for such systems.\textsuperscript{17,18} The dominant route for a specific system will depend on various factors, but most importantly it is influenced by the distance between the donor and the acceptor ($d_{DA}$).\textsuperscript{19}
3.1.1. Energy transfer

Energy transfer to GNPs resulting in PL quenching can occur over a broad range of wavelengths due to several reasons. First, since the spherical GNPs have no specific dipole moment as molecular quenchers do, energy transfer to gold nanoparticles takes place for any orientation of the donor relative to the surface of the GNP. Secondly, due to the larger size of GNP compared to a dye molecule, the ET efficiency decays slower with distance from the donor, as compared to the case of a molecular acceptor. Additionally, the large absorption cross-section of GNPs especially near their surface plasmon resonance, enhances their performance as energy acceptors. Finally, in contrast to molecular acceptors, the gold nanoparticles are able to quench photoluminescence via suppression of the radiative rate.

Several analytical treatments have been put forth to describe the fluorescence quenching by proximal acceptors. The initial analyses were based on Forster resonance energy transfer (FRET) model that describes ET as a radiationless process due to dipole-dipole electromagnetic coupling of donor and acceptor. The energy transfer rate of FRET process exhibits a $1/d^{6}$ dependence, and therefore is only influential within distances less than 100 Å.

Fluorescence quenching by metallic nanoparticles has often been found to occur over much larger distances than those associated with molecular quenchers dictated by the Forster mechanism. Hence, a second theory, nanosurface
energy transfer (NSET)\textsuperscript{25,26} was introduced, which is based on approximating a donor-metal nanoparticle pair to a point dipole with an infinite surface. The physical origin for NSET has been attributed to the interaction of the electromagnetic field of the donor dipole interacting with nearly free conduction electrons of the accepting metal.\textsuperscript{26} Fluorescence quenching based on NSET exhibits a much weaker distance dependence of $1/d_{DA}^4$, and therefore, extends over a larger distance compared to FRET, normally up to 220 Å. NSET also treats ET as an additional non-radiative pathway and both theories assume that there is no interference to the donor radiative rates.

### 3.1.2. Charge transfer

In contrast to the ET process, an electron is physically transferred from the excited donor to an acceptor in the vicinity. Depending on the nature, magnitude and energetics of the electronic interaction of the separated donor (D) and acceptor (A), the electron transfer process can proceed via (a) a coherent tunneling process, superexchange, or (b) a process involving a redox mechanism of the bridge (B).\textsuperscript{27} Superexchange, which is quantum mechanical tunneling through electronic orbitals, is mediated by a virtual D$^+B^-A$ state for electron transfer, where these states are not in fact populated. The exponential dependence of superexchange rate constant on separation distance, $d_{DA}$ can be expressed by Equation 3.1, where $k_0$ is maximum rate constant at $d_{DA} = 0$ and $\beta$ is
the attenuation factor that depends on coupling of the donor acceptor pair and
the energy of mediating state.\textsuperscript{27}

\[ k_{CT} = k_0 e^{(-\beta_d d_{DA})} \]  \quad 3.1

In the second, so called 'chemical' mechanism, the electron actually resides on
the bridge and may be delocalized over the entire bridge or diffuse by hopping
between bridging sites. Thus, the state $D^+B^-A$ becomes real rather than virtual.
When diffusive hopping becomes rate limiting, the distance dependence of
electron transfer is Ohmic, where the rate is inversely proportional to the $D - A$
separation. If the energy difference of the mediating state from ground state
$\Delta E_{DB}$ is positive, the rate will depend on this energy gap and can be expressed by
Equation 3.2, where $N$ is the number of repeated bridging units.

\[ k_{CT} \propto \frac{1}{N} e^{\left( -\frac{\Delta E_{DB}}{RT} \right)} \]  \quad 3.2

In general, the dominant mechanism of the charge transfer is determined by the
bridge length. Shorter bridges produce large amounts of wavefunction overlap
between the donor and the acceptor electronic orbitals, making the
superexchange mechanism dominate for spacers in the range of 5 – 10 Å. For
sufficiently longer bridges, CT will be governed by the hopping mechanism.\textsuperscript{28}

Exponential distance dependence of charge transfer rates have been
demonstrated for organic thiols and alkanes, suggesting electron transfer via
tunneling. In a mercaptopropionic acid passivated CdSe nanoparticle and citrate passivated gold nanoparticle system, PL quenching was found to occur through charge transfer rather than energy transfer via relatively short mercaptopropioninc and citrate ligands. Conduction band electron transfer from TiO$_2$ nanoparticles to gold nanoparticles through hexanethioli ligands has also been reported. The nano-composites under current study have glutathione molecules as the spacer between ZnO nanoparticles and gold nanoparticles, which has dimensions of less than 1 nm. Therefore, it is possible that electron transfer would be favored over energy transfer when these nano-composites are photoexcited.

This chapter discusses the steady state and time resolved photoluminescence of ZnO nanoparticles and the effects of surface modifications by 3.9 nm glutathione gold nanoparticles. ET/CT processes that occur between ZnO and gold nanoparticles will be analyzed.

3.2. Experimental Details

3.2.1. Steady state photoluminescence

A water solution of the catalyst, ZnO, nano-composite or silica capped nano-composite, was made by adding 4.0 mg of the solid in 40 ml of water and sonicating for 10 minutes. The solutions were placed in a fluorimetric cuvette for steady state analyses. Steady state photoluminescence was measured using an
Edinburgh Instruments FL900 spectrofluorimeter with photoexcitation wavelength set at 330 nm.

3.2.2. *Time-resolved photoluminescence*

Concentrated solutions of silica capped or uncapped catalysts were prepared by dispersing 40.0 mg of the catalyst in 40 ml of water. The time-resolved fluorescence measurements of the nanoparticles were made using the femtosecond fluorescence upconversion technique\textsuperscript{31} using an upconversion system from CDP Instruments. The system used the third harmonic at 267nm generated from a mode-locked broad band Ti-sapphire laser (Tsunami, Spectra Physics) with the fundamental set at 800 nm as the excitation radiation. The samples were placed in a 1 mm thick quartz cell and rotated continuously during measurements. Decay traces of the parallel polarized band edge emissions were obtained using a photo multiplier tube integrated with a double monochromator that provided spectral resolution. Stability of the samples was verified by repetition.

3.3. **Results and Discussion**

3.3.1. *Steady state photoluminescence*

Photoluminescence (PL) of a water solution of ZnO was recorded with the excitation wavelength set to 330 nm, before and after purging the solution with Ar. The resultant spectra shown in Figure 3.1, illustrates two emissions, one at 374 nm and the other broad emission at 497nm. The stronger emission at 374
nm that corresponds precisely to the band edge absorption of ZnO (See section 2.5.4) is attributed to the direct radiative recombination of excitons.\textsuperscript{32,33} This wavelength corresponds to a transition energy of 3.32 eV, a slight blue shift of 0.06 eV with respect to the band edge emission energy, 3.26 eV of bulk ZnO crystals,\textsuperscript{34} indicating a small quantum confinement effect. The green emission near 497 nm is reportedly due to charge carrier relaxations via trap states.\textsuperscript{32,35-37} These trap states could be mostly Zn\textsuperscript{2+} or O\textsuperscript{2-} vacancies.\textsuperscript{36}

Purging the solution with Ar caused the nanoparticles to aggregate and precipitate from the solution, which is confirmed by the absorption profiles in the inset of Figure 3.1. PL emission intensity of the purged sample was adjusted for the loss of absorption with respect to the band edge absorbance. It could be seen that the intensity of exciton emission has increased by about 5.6 times after purging the sample, while the trap state emission diminished. Therefore it could be understood that the radiative pathway via trap states and some other non-radiative pathways were deterred in the absence of dissolved gases, most probably oxygen, which strongly enhanced excitonic emission. Dissolved oxygen is known to be a non-specific fluorescence quencher.\textsuperscript{38} However, the current observations indicate that in the absence of O\textsubscript{2}, the visible emission intensity reduced, which indicates that O\textsubscript{2} molecules bound to ZnO surface, possibly at oxide vacancies, are responsible for behaving as trap states for charge carriers. It
is known that excited conduction band electrons could react with surface bound oxygen according to Equation 3.3, and form a superoxide radical anion.\textsuperscript{39}

\[ e_{CB}^- + \text{ZnO} \cdots \text{O}_2 \rightarrow \text{ZnO} \cdots \text{O}_2^- \] \hspace{1cm} 3.3

\[ \text{ZnO} \cdots \text{O}_2^- + h\nu_B \rightarrow \text{ZnO} \cdots \text{O}_2 + h\nu_{\text{vis}} \] \hspace{1cm} 3.4

\[ \text{ZnO} \cdots \text{O}_2^- + \text{H}^+ \rightarrow \text{ZnO} + \text{HO}_2^* \] \hspace{1cm} 3.5a

\[ 2 \text{HO}_2^* + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \] \hspace{1cm} 3.5b

**Figure 3.1** Photoluminescence spectra of ZnO nanoparticles in water before and after purging the solution with Ar. The emission intensity of the purged solution was adjusted based on the loss of absorption at 374 nm, as shown in the inset.

The radical species bound to ZnO surface behave as a trap of conduction band electrons. The fate of such surface bound trap states could be twofold.\textsuperscript{40} First, they could recombine with valence band holes according to Equation 3.4,
resulting in an emission of visible photons. Secondly, they can undergo solution reactions as shown in Equation 3.5 that result in hydrogen peroxide while regenerating $O_2$. In the absence of oxygen, both radiative and non-radiative pathways described by Equations, 3.4 and 3.5 would be blocked, leading to a significant enhancement of direct exciton recombinations accompanied by strong UV emission.

The effect of surface bound gold nanoparticles on the photoluminescent properties of ZnO were investigated by recording the emission of 0.1 g l$^{-1}$ solutions of the composites and the resultant spectra are provided in Figure 3.2. In comparison to the emission of ZnO, the nano-composites show significantly weaker, featureless emission that shows a maximum around 383 nm. Further, except for the 0.5% GNP loading that shows slightly more intense emission, all nano-composites yielded emission profiles with similar intensities regardless of GNP loading.

Influence of gold nanoparticles on charge carrier dynamics is clearly evident in this result, in which on average, visible emission drops by 84% and UV emission reduces by 71% due to the assembly of GNPs on ZnO nanoparticle surface. Drastic reduction of visible emission indicates that trapping of conduction band electrons and the consequent processes described by Equations 3.3 – 3.5 are no longer active. Decline in exciton emission suggests that radiative recombination of charge carriers were also minimized.
Due to the characteristic nature of gold nanoparticles to readily accept electrons,\textsuperscript{41} most of the electrons photoexcited into the conduction band of ZnO will migrate to the attached gold nanoparticles, thereby lessening exciton recombinations. Quenching of trap emission indicates that the electron transfer into GNPs is favored over trapping process, and the fact that gold nanoparticles are more likely to be bound to surface defect sites that could act as trap points, may also contribute to the reduction of emission related to surface traps.

Additionally, considering the wavelength range from 360 - 625 nm, on average there is a 78\% loss of overall PL emission when GNPs were assembled on ZnO, which implies that the rest of the lost energy was utilized in non-radiative processes. Since the rate of thermal recombinations that mostly occur via lattice
relaxations cannot be expected to be altered by surface assembly of GNPs, it could be presumed that majority of excess energy was utilized for the surface redox reactions, which are responsible for photocatalytic processes.

Further insights into the exciton dynamics can be obtained by analyzing the luminescence of silica capped ZnO and nano-composites. However, as it was not possible to quantify the amount of SiO₂ present in the samples, the relative PL intensity of these materials becomes meaningless. Therefore, only the intensity normalized emission spectra are shown in Figure 3.3.

The trap state related visible emission of ZnO is seen to be significantly quenched with the application of the silica shell, which signifies that charge trapping indeed occurs at surface sites and silica shell passivation restricts such processes by preventing oxygen molecules from reaching the semiconductor surface.

In comparison with Figure 3.2, it could be immediately seen that the exciton emission that was lost when GNPs were assembled on ZnO surface is mostly recovered when the nano-composites were passivated with silica. It is therefore evident that the gold nanoparticles enhanced the non-radiative surface charge transfer reactions with the solvent species, which are averted by the presence of the SiO₂ shell, in turn enhancing radiative relaxation of the excitons giving rise to strong UV emission.
Figure 3.3 PL emission spectra of SiO$_2$ shelled ZnO and nano-composites with different glutathione GNP loadings in water. PL spectrum of bare ZnO is also included, and the spectra were normalized at the maximum intensity for comparison. Excitation wavelength was set at 330 nm.

### 3.3.2. Time-resolved photoluminescence

Determination of time-resolved photoluminescence was first attempted with ZnO and GNP loaded ZnO with no silica passivation. However, it was found that detailed characterization by time-resolved PL was difficult due to the material degradation under the strong laser illumination, which resulted in non-reproducible PL decay profiles. Silica shell passivation of the nanoparticles as described in Section 2.8 was performed to improve the stability during the time-resolved luminescence measurements. SiO$_2$-passivated nanoparticles were found to be very stable under laser irradiation and additional measurements were performed with those systems.
Figure 3.4 (A) Normalized PL decays of ZnO and 2% GNP composites. (B) PL decays with corresponding bi-exponential fits for ZnO and 2% GNP composite.
ZnO and 2% glutathione GNP loaded nanocomposites were used to acquire time-resolved PL. The data was fitted with a bi-exponential decay using Origin (Version 8 SR4) software, and lifetimes of the decay processes were derived. Amplitude average lifetimes\textsuperscript{42,43} were computed using Equation 3.6 for the comparison of the PL decays.

\[
\langle \tau \rangle_{\text{ave}} = \frac{\sum a_i \tau_i}{\sum a_i}
\]

3.6

Here, \(\langle \tau \rangle_{\text{ave}}\) is the amplitude average lifetime, \(\tau_i\) are the photoluminescence lifetimes and \(a_i\) are the corresponding amplitudes. Figure 3.4 shows the decay curves for band edge luminescence with the respective exponential fits, and Table 3.2 provides the parameters derived from bi-exponential fitting.

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<td>(2.61 \times 10^3)</td>
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<td>(\tau_1) (fs)</td>
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<td>(2.15 \times 10^5)</td>
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<td>(a_2)</td>
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<tr>
<td>(\tau_2) (fs)</td>
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<td>(2.23 \times 10^4)</td>
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<td>(\chi^2)</td>
<td>0.99757</td>
<td>0.99493</td>
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<td>(\langle \tau \rangle_{\text{ave}}) (ps)</td>
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Table 3.1 Parameters derived from bi-exponential fits to the PL decay profiles of ZnO and 2% GNP composites in water. Average lifetime of each decay is also included.
Figure 3.5 PL intensity decay and exponential decay fits for SiO$_2$ shelled ZnO nanoparticles and nano-composites.
Figure 3.4(A) depicts normalized PL decay curves for ZnO and 2% GNP composite, which plainly shows that photoluminescence decay becomes faster in the presence of gold nanoparticles. Fitted curves from bi-exponential decay model are shown in Figure 3.4(B). Satisfactory fitting is indicated by the values obtained for goodness of fit ($\chi^2$) shown in Table 3.2.

<table>
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<th>Parameters</th>
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<th>(5% Comp)SiO$_2$</th>
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<td>0.99797</td>
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<td><strong>154.7</strong></td>
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**Table 3.2** Parameters derived from 3-component exponential fits to the PL decay profiles of silica shelled ZnO and 1%, 5% GNP loaded nano-composites. Computed average lifetimes are also shown.

Time-resolved photoluminence of silica shell passivated ZnO, 1% and 5% GNP loaded nano-composites was measured, and the curves fitted in to 3-component exponential decays as illustrated in Figure 3.5. Parameters of the fits are presented in Table 3.2. The goodness of fit values indicate successful fitting. The computed average lifetimes of PL decays are consistent with those obtained
from nanoparticles without silica shell passivation. A shortening of the average lifetime is also seen for GNP composites.

Photoluminescence lifetime of materials such as ZnO, related to the average time the excitons spend before they are annihilated, is dependent upon light - matter interactions, i.e., the radiative decay of the exciton and various non-radiative processes such as charge trapping at deep-level traps and surface states, surface chemical reactions and multi-phonon scattering. Unlike in the case of bulk material, luminescent properties of ZnO nanoparticles largely depend upon synthetic methods, particle size and structure, and importantly the defects in bulk and surface of the nanoparticle. Therefore, various PL decay lifetimes based on single and bi-exponential models have been reported for ZnO nanostructures, with shortest UV emission lifetime from 30 ps up to 1.0 ns for the longest lifetime. The lifetime associated with green emission due to trap states are reportedly longer, in the microsecond range. The current study only focused on the emission due to exciton relaxation.

The PL decay of ZnO fitted into a bi-exponential model, which is consistent with most of the literature. The short time constant at 23 ps and the long time constant at 293 ps also are in good agreement with many reports. The existence of two decay rates signifies that there are two radiative pathways involved in the 374 nm emission. However, the exact nature of such routes is still not fully understood. Time constants in the range of 200 – 350 ps have been
measured even for highly crystalline ZnO nanostructures and thin films.\textsuperscript{48,52} Therefore, decay with a time constant of 224 ps at 75\% amplitude could be attributed to a very shallow trap state emission, while the fast component with the time constant 23 ps is possibly due to free exciton decay. While it is difficult to resolve the nature of aforementioned trap states, the fact that majority of the charge relaxations occur via such trap states imply their high abundance within ZnO crystals.

Shortening of the PL decay time constant in the presence of gold nanoparticles indicates the generation of additional non-radiative decay processes, which could be attributed to energy or charge transfer from ZnO to Au nanoparticles. The efficiency of such a competitive radiationless process ($\Phi_{NR}$) could be estimated according to Equation 3.6.\textsuperscript{53}

$$\Phi_{NR} = 1 - \frac{\tau_{DA}}{\tau_D}$$

Here, $\tau_{DA}$ is the average PL lifetime of ZnO in the presence of GNP and $\tau_A$ is the average lifetime of ZnO luminescence in the absence of gold nanoparticles. This treatment results in an efficiency of 31.7\% for the energy transfer from ZnO nanoparticles to GNPs of the nano-composites. However, considering the extent of PL quenching, which was about 78\% on average, the energy transfer efficiency based on lifetime reduction is a significant underestimation.
The silica shell passivated ZnO nanoparticles showed a PL decay constant that is similar to that of bare ZnO, even though the steady state PL profiles are considerably different. Enhancement of PL emission in silica passivated ZnO does not seem to affect the luminescence decay lifetime.

Efficiencies of ET/CT to GNPs in SiO2 passivated nano-composites as calculated by Equation 3.6, are 21.8% and 24.2% for 1% and 5% GNP loaded nano-composites respectively. The efficiencies are seen to be slightly lower than that obtained for 2% GNP nano-composite without silica shells, and could indicate the involvement of solvent in the non-radiative transfer process that is minimized by the application of silica shell. Additionally, the trivial increase in the average decay constants with nano-composites with higher GNP loading suggests that the PL decay kinetics are only minimally affected by the amount of GNP present on ZnO surface.

As discussed in Section 3.1, distance between the donor and the acceptor dictates whether the nano-radiative process between ZnO and Au nanoparticles is a charge transfer or energy transfer. Length of glutathione molecule, specifically the distance between the thiol and two carboxyl groups will govern the space between ZnO and gold nanoparticles. The atomic distances from S to C of the first carboxyl group was determined to be about 6.5 Å, and to the second, about 7.1 Å. Thus, it is evident that the ZnO and gold nanoparticles are separated from a distance that is in sub nanometer range. Such small spacers can be
expected to favor charge (electron) transfer over Forster type energy transfer processes, and information from steady state PL of the nano-composites and the results from photocatalytic measurements that are described in the following chapters suggest that the excited state of the nano-composites indeed undergo charge transfer rather than an energy transfer process.

3.4. Conclusions

The photoluminescence of ZnO nanoparticles was found to consist of two emissions, one in the UV region related to the exciton recombination and the other visible emission resulting from conduction band electrons that are bound in surface trap states. It was suggested that these trap states are related to surface bound O\textsubscript{2} molecules.

Severe quenching of luminescence of ZnO nanoparticles were observed when gold nanoparticles were assembled on ZnO indicating the strong charge transfer between ZnO and Au nanoparticles. Relatively higher quenching of visible emission was attributed to the blocking of surface bound trap states by the presence of GNPs.

The application of SiO\textsubscript{2} shells had a strong influence on PL properties by passivating the ZnO surface, consequently enhancing the exciton emission while suppressing trap state related luminescence. The inability of GNPs to quench PL of the silica-passivated nano-composites indicated the involvement of surface species in the charge mediation process by gold nanoparticles.
Time-resolved PL studies of ZnO nanoparticles implied two decay pathways of excitonic relaxations. While the faster process could be attributed to direct exciton recombinations, the dominant, slower process pointed to the existence of a shallow trap state in ZnO nanoparticle. The PL decay in the presence of GNPs was found to be faster resulting in a charge transfer efficiency of about 32%.

Silica-shell passivation did not influence the time dependent luminescent properties as it did for steady state emission of nanoparticles. Decay time constants for ZnO and nano-composites were comparable, and the drop in the decay time constants when GNPs were assembled were slightly lower leading to lessened charge transfer efficiencies, possibly due to prevention of solvent participation by silica shells.

While further investigation may provide better insights in to the excited state processes of these nano-composites, the short bridging distance of ZnO and Au nanoparticles suggest the illuminated composites undergo electron transfer rather than energy transfer, which is further confirmed in the following chapters and is also supported by previous literature.
3.5. References


CHAPTER 4

CATALYSIS IN AQUEOUS MEDIA

4.1. Introduction

Heterogeneous photocatalysis by semiconductors, classified as an advanced oxidation process (See Section 1.7), is one of the widely studied systems in the field of catalysis. The first recognition and implementation of semiconductor sensitization for mineralization of organic matter came in 1983 with the work of Ollis, et al.\textsuperscript{1,2} Since then, semiconductor nanoparticles have been successfully applied in the complete mineralization of a wide variety of substances including pesticides,\textsuperscript{3} pharmaceuticals,\textsuperscript{4} dyes\textsuperscript{5} and biomaterials.\textsuperscript{6}

All of these investigations have been performed using water as a medium because the focus of the majority of such studies has been in applications involving treatment of polluted water, and semiconductor nanoparticle catalysis has proven to work successfully in the instances where pollutants are found to resist conventional treatment methods.\textsuperscript{7} Despite such advantages, the effective application of semiconductor nanoparticles is hampered by limitations caused by high charge carrier recombination rates as discussed in section 1.5, and assembly of noble metals on semiconductor surfaces has been shown to enhance photocatalytic efficiency via charge rectification.\textsuperscript{8} The ZnO/Au nano-composites that have been synthesized in the current study were employed in order to probe the charge transfer mechanisms that are responsible for the enhanced
photocatalytic efficiencies in such systems. This chapter is devoted to the investigations performed in aqueous media.

A suitable substrate was required to make the study of photocatalytic behavior of the novel nano-catalyst systems possible. The dye, Rhodamine 6G (R6G) was selected for this purpose, based upon several factors. Rhodamine 6G has a strong optical absorbance and photoluminescence in the visible region, thus its degradation could be studied rather effortlessly by following the absorption or photoluminescence profile. It is photostable, under UV or Visible irradiation. Additionally R6G is one of the widely utilized dyes that has significant environmental impact since it can survive conventional water remediation technologies such as adsorption and biological treatment. Thus, studying facile degradation routes of R6G is deemed important, and several studies have documented its degradation characteristics.

Rhodamine 6G, (chemical structure is given in Figure 4.1) is a cationic xanthene dye that is used commonly in lasers, as forensic labels and in fabric dyeing. It is highly colored with a molar extinction coefficient of 116000 M\(^{-1}\) cm\(^{-1}\) and has strong fluorescence with quantum yield (\(\Phi_f\)) of 0.94. Combined with its good water solubility, R6G proved to be an appropriate substrate for the current investigation. The dye is produced with chloride, perchlorate or tetrafluoroborate as the counterion. R6G chloride salt (Molar weight: 479.01 g mol\(^{-1}\)) was employed in this study.
Figure 4.1 Chemical structure of rhodamine 6G ($C_{28}H_{31}N_2O_3^+$)

4.2. Kinetics of Photocatalytic Degradation

Many of the reports on solution phase photocatalytic degradation of organic substrates over illuminated semiconductor particles, indicate that the degradation follows the Langmuir-Hinshelwood kinetic model.\textsuperscript{13-15} This treatment is subject to the assumptions that sorption and desorption of the redox couple is in rapid equilibrium and that the rate determining step of the reaction involves both species present in the monolayer at the solid-liquid interface.\textsuperscript{16}

When the concentration of the substrate ($C_0$) is low, in millimolar range, the Langmuir-Hinshellwood relationship can be simplified to an apparent first-order equation, as given in Equation 4.1, where $C$ is the substrate concentration at time $t$ (illumination time), $k$ the reaction rate constant and $K$ the adsorption coefficient of the reactant.\textsuperscript{17}
\[ \ln\left(\frac{C_0}{C}\right) = kKt = k_{app}t \]

4.1

A plot of \( \ln \frac{C_0}{C} \) versus time follows a straight line, the slope of which equals the apparent first order rate constant \( k_{app} \). A number of studies have shown that their results could be reasonably explained through first order kinetics.\(^{18-21}\)

There is a general agreement that photocatalytic mineralization of an organic substrate with irradiated semiconductor particle would follow Langmuir-Hinshelwood model for four possible scenarios:\(^{22}\)

1. Reaction takes place between two adsorbed substances,

2. Reaction occurs between a reactive species in the solution and the adsorbed substrate molecule,

3. Reaction takes place between a reactive species linked to the surface and a substrate molecule in solution,

4. Reaction occurs when both species are in the solution.

In all the cases, the rate expression would be similar to that derived from the Langmuir–Hinshelwood model, but it is not possible to distinguish whether the process is taking place on the surface, at the interface or in the solution.

However, for the situations where only the relative efficiency of photocatalytic degradation is needed to be evaluated, fitting data to any particular model is not required. Instead, most of the current discussion will only involve determination
of the relative change in absorbance at the maximum absorption of the dye, $\Delta A/A_0$ at time $t$, where $\Delta A$ is the change in absorbance and $A_0$ is the initial absorbance at $t = 0$.

4.3. Experimental Details

4.3.1. Photocatalysis setup

A schematic of the experimental setup that was utilized in the photocatalytic degradation studies during this research is provided in Figure 4.2. The setup consisted of the following equipment:

1. Xenon lamp:

   A xenon arc lamp from Perkin Elmer (PE 300 BUV) with a nominal power of 300 W was used as the radiation source. This lamp provided a broad range of light that covered both UV and visible regions (200 nm to 1100 nm).

2. Real-time spectrometer:

   A UV/Vis spectrometer was used to obtain real-time measurements of optical absorption of the substrates during photodegradation. The Ocean Optics HR2000 CG spectrometer that was used is equipped with 2048 pixel CCD array detector that is capable of acquiring a full spectrum between 200 and 1100 nm. The integration time for each spectrum was set to 11 ms.
3. UV/Vis radiation source

The radiation source provides the light required for the spectrometric measurements. Ocean Optics DH-2000-BAL was the light source, and it emits a continuous and stable output from 215 nm to 2000 nm through a deuterium lamp and a tungsten halogen lamp.

4. Filters

Two optical filters were used between the Xe lamp and the reaction mixture in order to eliminate the unwanted radiation. An IR (infra red) short pass filter was used to remove IR radiation that would cause the samples to heat up. A 320 nm long pass filter was used to cut off radiation of very short wavelengths that could lead to the degradation of the reaction components.
The optical path between the radiation source, reaction mixture and spectrometer was facilitated by optical fibers. The spectrometer was interfaced with a computer that was used for data acquisition and storage.

### 4.3.2. Procedures and methods

R6G stock solution with a concentration of 278 µM was prepared by dissolving 4.0 mg of R6G chloride salt in 30 ml of ultra-pure water, and was stored at 4 °C until it was ready to be used. The stock solution was left at room temperature for at least 30 minutes before being used for an experiment, so that it reaches room temperature. 4.0 mg of ZnO nanoparticles or the nano-composite was added in to 40 ml of ultra-pure water and sonicated for about 10 minutes, and it served as the catalyst stock solution (1.23 mM). This solution was made fresh for each experiment.

**Photolysis under air**

For photocatalytic experiments performed under atmospheric conditions, a quartz fluorimetric cuvette with 10 mm path length was cleaned in aqua regia, and 150 µl of the R6G dye solution (13.9 µM), 1.0 ml of the catalyst or ZnO solution (409 µM) and 2.0 ml of ultra-pure water were added and stoppered. The solution was mixed by flicking the cuvette and placed in the photolysis setup. The degradation of the dye was evaluated by recording its UV/Vis absorbance in-situ. Full absorbance spectra were recorded at 1 minute intervals, for 30
minutes. Each experiment was repeated at least thrice in order to verify the reproducibility.

*Photolysis under controlled atmosphere*

300 µl of R6G dye solution, 2.0 ml of the catalyst solution and 4.0 ml of ultra-pure water were added to a 20 ml shell vial and the vial was sealed with a rubber septum. The vial was wrapped with aluminum foil to prevent light from entering into the solution and was purged with high purity gas of choice (oxygen or argon) for 30 minutes to remove dissolved atmospheric gases, and then sonicated for a minute in order to fully disperse the catalyst that might have coagulated during purging. A fluorimetric quartz cuvette sealed with a rubber septum was flushed with the gas, and a 3.0 ml portion of the purged solution was transferred into the cuvette using a syringe that had also been flushed with the selected gas previously. This method ensured that the purged solution does not come in contact with the atmosphere until it is photolyzed. The cuvette was placed in the photolysis setup, and the degradation of the R6G was determined as explained before. The UV/Vis absorption spectra were recorded at 1 minute intervals for 30 minutes. Each experiment was repeated at least 3 times.

*Photolysis with additives*

Several experiments were performed where an additional component such as a hole or an electron scavenger was used in rhodamine 6G photolysis (See section 4.5). The stock solutions of the additives, iron (III) chloride, potassium iodate,
potassium thiocyanate and methyl viologen dichloride (MV) were prepared in ultra-pure water, and their concentrations in the reaction mixtures were as follows:

\[
\begin{align*}
[\text{FeCl}_3] &= 1.54 \times 10^{-3} \text{ mol l}^{-1} \\
[\text{KIO}_3] &= 1.56 \times 10^{-3} \text{ mol l}^{-1} \\
[\text{MV}] &= 1.19 \times 10^{-3} \text{ mol l}^{-1} \\
[\text{KSCN}] &= 1.37 \times 10^{-4} \text{ mol l}^{-1}
\end{align*}
\]

When methanol was used as an additive in the aqueous phase, a 1.0 ml portion of methanol was added.

When additives were used under atmospheric conditions, 150 µl of R6G dye solution and 1.0 ml of the catalyst were added to a fluorimetric quartz cuvette. The required amount of the additive was placed in the solution, and ultra pure water was added such that the final volume became 3.0 ml. The solution was mixed and then placed in the photocatalytic setup. UV/Vis spectra were recorded as explained before.

For the experiments where an additive was used under inert atmosphere, 300 µl of R6G stock solution and 2.0 ml of catalyst were placed in a 20 ml shell vial. The required amount of the additive and ultra pure water was added such that the total volume became 6.0 ml. The vial was sealed with a rubber septum, covered
with aluminum foil and purged with Ar for 30 minutes. A 3.0 ml portion of the
solution was then transferred into a purged cuvette as explained before, and was
photolyzed.

4.4. Aspects of R6G Photolysis by Nano-Composites

4.4.1. Rhodamine 6G degradation

Figure 4.3A-C illustrates the in situ optical absorption spectra of an experiment
where R6G degradation was studied with different additives. Strong absorption
of Rhodamine 6G is observed at 525 nm, while band edge absorbance of ZnO
occurs at 375 nm. The plot in Figure 4.3D shows the relative change in
absorption maximum of dye for the experiments. The photostability of R6G was
tested by irradiating the dye in the absence of the photocatalyst. According to
Figure 4.3A, the dye is extremely stable under UV/Vis radiation on this time
scale, where only 2.5% loss of peak absorbance is seen during 30 minutes of
irradiation. Significant enhancement of photocatalytic efficiency could be seen
when the GNP loaded composite was used as the catalyst. The nano-composite
causes complete bleaching of the dye within 30 minutes, while only partial
decomposition is realized with ZnO. Furthermore, there is no evidence of the
appearance of new absorption peaks as degradation continues, which indicates
that no intermediate organic species were generated. The decomposition is
found to be permanent where the dye gets irreversibly decolorized, indicating
complete mineralization of the substrate has occurred.24
Figure 4.3 Degradation of aqueous rhodamine 6G solution under UV/Vis irradiation. In the presence of (A) no additives, (B) ZnO nanoparticles and (C) nanocomposite with 3% glutathione GNP loading. Relative rates of degradation are compared in (D).

4.4.2 Effect of GNP loading

The concentration of gold nanoparticles deposited on the semiconductor surface is crucial to the photocatalytic behavior of the nano-composite. Previous reports
suggest the existence of an optimal level of metal nanoparticle loading on the surface of semiconductor nanoparticles, which provides the best catalytic activity.\textsuperscript{25-27} Therefore, it was found to be crucial to study the effect of the amount of GNP bound to the surfaces of ZnO nanoparticles on their photocatalytic degradation activity of dyes.

\textit{Tiopronin GNP photocatalyst}

Photocatalytic efficiency of the nano-composite made with 3.7 nm tiopronin GNPs (See Section 2.5) were tested by following the degradation of R6G as described in section 4.3.2. Figure 4.4(A) depicts the dependence of photocatalytic efficiency of the nano-composites on GNP loading. It could be seen that efficiency of R6G decomposition is higher for all nano-composites compared with bare ZnO nanoparticles, and complete degradation takes place during the monitored time duration. The first 5 minutes of the photolysis is plotted in Figure 4.4(B), to which linear regression was applied in order to obtain relative photocatalytic efficiencies of the nano-composites. The slope of the linear fits was plotted against percentage weight of gold in each composite, as shown in the inset. The data could be fitted by a 2nd order polynomial curve, which provided the maximum at 5.2%. Thus, it could be concluded that the optimum level of 3.7 nm tiopronin GNP loading to be 5.2% Au by weight relative to ZnO.

The reported optimum loading level of metal nanoparticles deposited on semiconductors varies widely over literature. While for Pt nanoparticles
deposited on TiO₂, the optimal weight loading was found to be around 0.5%,²⁸,²⁹ for Ag nanoparticles, maximum efficiency was reported to be at 0.24%.²⁷ For a system with Au on TiO₂, the best catalytic efficiency was found to be as high as 17% by weight.²⁶ Such differences could arise for multiple causes such as the type and the size of metal nanoparticles, type of semiconductor, method of deposition and the reaction monitored.

However, all of the systems described above, despite being very different from each other, show a level of metal loading where the catalytic activity is highest. There could be several reasons for the photocatalytic activity to decrease at higher metal loadings. Metal nanoparticles absorb and scatter light very efficiently.³⁰ Therefore, when the semiconductor surface is overly crowded with such metal nanoparticles, the amount of radiation that reaches the semiconductor could be diminished causing the photoexcitation process to lessen. Further, the metal nanoparticles could block most of the active sites on the semiconductor surface that would prevent surface redox reactions. Additional adverse effect could come from steric hindrance caused by the metal nanoparticles such that the substrates are obstructed from reaching the semiconductor surface for the photoreaction.
Figure 4.4 (A) Dependence of R6G degradation efficiency on 3.7 nm tiopronin GNP loading. (B) Linear fits for the first 5 minutes of decomposition. The inset shows the change of slope of the linear fits with weight percentage of GNP loading.
Glutathione GNP photocatalyst

Photocatalytic efficiency of nano-composites made with 3.9 nm glutathione-passivated GNPs was tested by following the decomposition of R6G as explained in section 4.3.2. The results of such an experiment are provided in Figure 4.5, along with data of R6G degradation by bare ZnO. Relative change of maximum absorption of the dye is plotted for different GNP loadings of the catalyst in Figure 4.5(A). In order to compare photocatalytic efficiency of each nano-composite, dye decomposition data for the first 5 minutes were plotted as provided in Figure 4.5(B), and linear regression was applied. The inset is a plot of slope of the fits versus weight percentage of Au relative to ZnO. A second order polynomial fit was applied to the data except for the results from 0.5% and 1% GNP loading.

As in the case of tiopronin capped GNP catalyst, these nano-composites show enhanced photocatalytic efficiency in R6G degradation regardless of the extent of GNP loading. However, the overall enhancement is found to be lower compared to that of tiopronin GNP catalyst. While tiopronin GNPs provided a minimum of 81% enhancement of photocatalysis compared to ZnO, for glutathione GNPs, the minimum photocatalytic enhancement was only 32%.

Glutathione GNP catalyst showed unusually high catalytic activity with 0.5 and 1% GNP loadings, and these data were masked to obtain the fitted curve. While this result is not readily explained, rest of the data indicated a gradual
enhancement of photocatalytic activity with the increase of GNP loading, unlike the observations with tiopronin GNP catalyst. However at 6%, a maximum amount of GNPs were bound to ZnO surface where free GNPs were detected in solution (See section 2.5.4). Therefore, maximum possible enhancement of photocatalytic activity of glutathione GNP catalyst is dictated by the extent of gold nanoparticle loading on ZnO surface.
Figure 4.5 (A) Dependence of R6G degradation efficiency on 3.9 nm glutathione GNP loading. (B) Linear fits for the first 5 minutes of decomposition. The inset shows the change of slope of the linear fits with weight percentage of GNP loading. The data points shown in red were excluded during curve fitting.
4.4.3. Effect of calcination of the composites

Various post-treatment methods are applied and tested in order to improve the activity of photocatalytic materials.Calcination of photocatalysts is one of the widely used techniques that have shown promise in enhancing the activity of semiconductor photocatalysts. Therefore it was of interest to test the photocatalytic behavior of calcined nano-composites.

Figure 4.6 Effect of calcination of ZnO nanoparticles as measured by the photodegradation of R6G. RT: ZnO not calcinated.

ZnO nanoparticles were first calcined at several different temperatures in order to identify how calcination affects the base catalyst. Figure 4.6 depicts the degradation of R6G by ZnO nanoparticles annealed at 250, 300 and 400 °C for 1 hour. It is clear that calcination at these temperatures does not have a significant effect on the photoactivity of ZnO nanoparticles. However, a slight drop in
catalytic efficiency could be observed for all the calcined nanoparticles. The
difference of activity between nanoparticles calcined at various temperatures is
negligible. Accordingly, an annealing temperature of 300 °C was selected for the
calcination study of nano-composites.

Three different gold loadings, 0.5%, 2% and 6% were picked in order to analyze
the photocatalytic behavior of nano-composites once they were calcined. These
composites were calcinated at 300 °C for 1 hour and their catalytic activity was
assessed via rhodamine 6G degradation.

Figure 4.7 illustrates the results from such an experiment. It could be seen that,
lower (0.5%) and higher (6%) GNP loaded catalysts' photocatalytic efficiency
drops slightly once they are calcined. However, the activity of 2% GNP
deposited nano-composite is enhanced once annealed.

This result implies the existence of two factors, one detrimental and the other
beneficial, that affect the photocatalytic efficiency of the calcined nano-
composites. It could be understood that the factor that enhances the catalysis is
the existence of gold deposits on ZnO surface. Therefore, an investigation was
needed to determine the second element that affects unfavorably at either low or
higher amounts of GNP deposition.
Figure 4.7 Effect of calcination of glutathione GNP catalysts as measured by the degradation of R6G dye.
4.4.4. Effect of the ligands in calcination

It is assumed that the organic ligand shell of gold nanoparticles decomposes during calcination, resulting in direct attachment of GNPs on ZnO nanoparticle surface. However, this hypothesis could be questioned when the detrimental effects of calcination upon photocatalytic activity, as discussed in section 4.4.3, are taken into consideration. Therefore, ZnO nanoparticles modified with ligands, glutathione and cysteine (See section 2.6), were annealed using an equivalent procedure, and their photocatalytic activity towards the degradation of R6G was assessed. The results are illustrated in Figure 4.8, along with the degradation rates of ZnO and calcined ZnO for comparison purposes.

![Figure 4.8](image)

Figure 4.8 R6G photolysis by (A) glutathione (Glu) and (B) cysteine (Cys) modified ZnO nanoparticles (RT) and by the nanoparticles calcined at 300 °C. Results of photolysis by bare ZnO are also provided for comparison.
Surface modified ZnO nanoparticles that are not calcined show photocatalytic activities which are similar to those of bare nanoparticles. However, once calcinated, catalytic activity of ligand modified ZnO drops drastically compared to that of calcined ZnO nanoparticles. The decline of catalytic activity is seen to be independent of the type of the ligand, where both glutathione and cystein modified nanoparticles showed similar reduction in photolysis rate.

The result indicates that both ligands have a catalyst poisoning effect when they are calcinated, despite the low decomposition temperature of cysteine. Although the decomposition temperature of ligands is lower that the calcination temperature applied in this study, it is clear that in the presence of ZnO, the normal decomposition does not take place, but instead, species that act as catalyst poisons are formed.

It is known that, sulfur species bound to surfaces of metal oxides such as CeO$_2$, Al$_2$O$_3$, Cu$_2$O and ZnO can lead to poisoning of the metal oxide’s catalytic activity. Sulfur-containing species like H$_2$S and SO$_2$ are found to react with metal oxide surfaces at temperatures above 150 °C and based on X-ray photoelectron spectroscopic (XPS) studies, it has been reported that sulfur converts to highly oxidized states such as sulfites or sulfates on these metal oxides. Therefore, it is highly probable that sulfur from the thiol groups on glutathione and cysteine react with the ZnO surface when the catalyst is calcined and form a layer that consists of ZnSO$_3$ or ZnSO$_4$. Such salt deposits would be
responsible for the catalyst deactivation observed in the current study. The presence of noble metals have been reported to not affect this type of catalyst poisoning,\textsuperscript{36,39} and therefore, the reduction of photocatalytic efficiency of calcinated GNP-bound nanocomposites could also be explained via the same phenomenon.

4.5. Mechanistic Studies of Photocatalysis in Aqueous Media

4.5.1. Effect of oxygen

According to the literature, oxygen is deemed to be necessary for complete mineralization of an organic substrate over semiconductor photocatalysts in an aqueous medium.\textsuperscript{40} Oxygen may act as an electron acceptor, but could be involved in the formation of other reactive species such as superoxides, hydrogen peroxide and hydroxyl redicals, and also play a role in stabilization of reactive intermediates and direct photocatalytic reactions.\textsuperscript{41} The effect of oxygen for the degradation of R6G over the nano-composites was assessed by performing the photocatalytic reaction under oxygen-enriched and oxygen-purged argon atmospheres.

The photocatalytic degradation of R6G was assessed in oxygen-enriched and oxygen-depleted aqueous solutions using ZnO and 2\% glutathione GNP nano-composite catalysts, and the results are given in Figure 4.9. Results from experiments performed under regular atmospheric conditions are also included for comparison purposes. In an oxygen purged solution, R6G degradation ceases
completely, regardless of the type of the catalyst used. Additionally, when the solution was saturated with O$_2$, the decomposition rate is significantly enhanced. The ZnO catalyst becomes as efficient as the 2% GNP nano-composite, and efficiency of the 2% GNP nano-composite is seen to become even higher. Therefore, it could be concluded that the presence of oxygen is essential for the photocatalytic degradation of substrates in aqueous media.

![Figure 4.9](image.png)

**Figure 4.9** R6G degradation by ZnO and 2% glutathione GNP loaded composite (Comp) in O$_2$ enriched and O$_2$ depleted Ar environment. Results for experiments performed under atmospheric conditions are also included for comparison.

**4.5.2. Effect of electron scavengers**

In order to ascertain the mechanism of photocatalytic activity of the nanocatalysts, it is important to identify the fate of photogenerated charge carriers, electrons and holes. The conduction band electrons could reduce the organic
substrate, or react with other electron acceptors such as O₂ either adsorbed on the catalyst surface or dissolved in solution.²² It was shown in the previous section that the presence of oxygen is required for the photocatalytic reaction to occur. Whether the role of O₂ in this reaction is scavenging photogenerated electrons could be verified by performing the reaction in the presence of a different electron acceptor in an oxygen purged solution. Several electron scavengers exist that suit the purpose, and Fe(III),⁴²,⁴³, IO₃⁻⁴⁴,⁴⁵ and methyl viologen (MV)⁴⁶,⁴⁷ were selected for this study. The electron accepting processes of these species are shown in the following equations.

\[
\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \\
\text{IO}_3^- + e^- + 2\text{H}_2\text{O} \rightarrow \text{IO}^- + \text{H}_2\text{O}_2 + \text{OH}^- + \text{OH}'
\]

The electron acceptors were applied in R6G degradation reactions performed under oxygen depleted Ar atmosphere, as detailed in Section 4.3.2. The results are depicted in Figure 4.10. When Fe(III) was used as the electron scavenger, the degradation of R6G occurs at a significant rate, but is lower than the rate with atmospheric conditions. Additionally, the positive effect of gold nanoparticles is also evident, where enhancement of degradation is even stronger than that of under air.
Iodate was also able to trigger the degradation, but the reaction rate was lower. ZnO outperformed the nanocomposite slightly, but the difference could be within the experimental error. However, it is clear that GNP was not able to provide an enhancement of photocatalysis in this situation.

In contrast to Fe(III) and IO₃⁻, Methyl viologen was not able to act as an electron scavenger for R6G decomposition. The maximum absorbance measured around 525 nm is found to increase slightly with time, as indicated by the small negative slope of the graph. This is due to methyl viologen (MV²⁺) reduction in to MV cation radical (MV⁺⁺) under UV irradiation,⁴⁸ which has an absorption in the visible region with a maximum around 610 nm.⁴⁹

Several conclusions can be drawn from these experimental results. It was shown that despite the absence of oxygen, the photocatalytic degradation was possible if an appropriate electron scavenger was present. Therefore, it could be concluded that oxygen was indeed functioning as an electron scavenger in the decomposition process. Further, it was seen that the effect of electron scavengers could vary widely. The difference in the effectiveness may be a result of the different reduction potentials of these additives compared to the band gap of ZnO. For an example, the redox potential of MV²⁺/MV⁺⁺ couple lies above the conduction band position of ZnO, thus MV²⁺ reduction by ZnO becomes thermodynamically unfavorable.
Figure 4.10 Effect of electron scavengers Fe$^{3+}$, IO$_3^-$ and MV on R6G decomposition over ZnO and 2% glutathione GNP composite (Comp). The reactions were carried out in Ar atmosphere. R6G degradation in the absence of additives is also shown.
4.5.3. Effect of hole scavengers

Studying the role of photogenerated holes will also facilitate realizing the mechanisms of photocatalytic degradation. The valence band holes reportedly could oxidize the organic substrate or react with hydroxyl ions or water to produce hydroxyl radicals.\(^{22}\) Involvement of photogenerated holes on photocatalytic decomposition of the substrate could be tested by using hole scavengers during the degradation process. If the holes are participating in the reaction, the decomposition rates will be reduced in the presence of a hole scavenger. Many types of hole scavengers have been used, including aliphatic alcohols,\(^{50,51}\) carboxylic acids\(^{52}\) and thiocyanates,\(^{53}\) among others. Methanol and thiocyanate were chosen as hole scavenging additives for this study. The reaction thiocyanate undergoes with photoformed holes are given in Equation 4.5a and 4.5b,\(^{54}\) whereas the action of methanol on holes is given by Equation 4.6.

\[
\text{SCN}^- + h^+ \rightarrow \text{SCN}^* \\
\text{SCN}^* + \text{SCN}^- \rightarrow (\text{SCN})_2^{-*} \\
\text{CH}_3\text{OH} + h^+ \rightarrow \cdot\text{CH}_2\text{O} + \text{H}^+
\]

Rhodamine 6G degradation by ZnO and 2% glutathione GNP catalyst was monitored in the presence of methanol or thiocyanate, under atmospheric conditions. The results, shown in Figure 4.11, indicate that both the hole
scavengers were able to hinder the photocatalytic reaction. Methanol was able to fully prevent the degradation possibly due to the higher concentration of it compared to that of thiocyanate. Additionally, 2% GNP composite showed significantly better degradation rate than that of ZnO, indicating the composite was able to suppress the effect of thiocyanate better. During the first 5 minutes, the drop in the slope was only 74% for 2% GNP composite compared to that of 87% reduction with ZnO.

![Graph](image)

**Figure 4.11** Effect of hole scavengers methanol and SCN⁻ on R6G degradation over ZnO and 2% glutathione GNP loaded (Comp) catalyst. Degradation results without additives are also shown.

### 4.5.4. Dye sensitization

Sensitization of ZnO by rhodamine 6G dye (See section 1.5.2) under visible light irradiation, where photoexcited dye injecting electrons into the conduction band
of ZnO is an important phenomenon that needs investigation. Since the radiation source that was used in the current study provided a broad band of light covering both UV and visible regions and the visible light could excite the dye molecules that may result in sensitization of the semiconductor.

The existence of dye sensitization was examined by the use of two filters in addition to the existing UV and IR filters so that only a narrow band of radiation of specific wavelengths could be used to irradiate the reaction mixture. One filter was a band pass filter that passes light between 310 and 430 nm through, and the other, a high pass filter which cuts off radiation below 455 nm. The absorption spectra of the filters are shown in Figure 4.12, along with absorption spectra for ZnO and R6G dye. Use of band pass filter will eliminate visible radiation that is responsible in exciting R6G dye, but will let UV radiation through enabling the excitation of ZnO. The visible radiation that is needed to excite the dye, while avoiding UV radiation that could excite ZnO, can be obtained by applying the high pass filter.
Figure 4.12  Normalized optical absorption spectra of 310-430 nm band pass (BP), and 455 nm high pass (HP) filters, along with the absorption spectra of ZnO and R6G in water.

Degradation of R6G by ZnO and 2% GNP catalyst with either the high pass or the band pass filter was monitored, and the results are illustrated in Figure 4.13. When the band pass filter was used to selectively irradiate the catalyst, slightly lesser degradation rate was obtained, for both ZnO and 2% GNP catalyst. The reduction could be partially due to the absorption and scattering of light from the additional filter. When the high pass filter was used to cut off catalyst excitation and irradiate the dye, a slow but very similar decomposition rate was seen for both ZnO and GNP catalyst, and shows that dye sensitization of the catalyst partially contributes to the degradation process. Degradation through dye sensitization follows a straight line instead of the typical curve, and could
suggest a different mechanistic pathway. Further, the degradation rates being very similar for both catalysts indicate that GNP are not involved in the degradation process, and supports fact that the degradation mechanism is different.

Figure 4.13 R6G degradation by ZnO and 2% GNP composite via selective irradiation using 310 – 430 nm band pass (BP) and 455 nm high pass (HP) filters. Degradation profiles of photolysis performed without filters are also plotted for comparison.

4.5.5. Mechanism of rhodamine 6G degradation

Temporal evolution of rhodamine 6G optical absorption spectrum was shown in Figure 4.3, and the region of the dye’s peak absorption is illustrated in Figure 4.14. These spectra show two types of changes. Firstly, there is an overall decrease in absorbance. Secondly, as illustrated in the inset of Figure 4.14, there is a significant hypsochromic shift in the absorbance maximum, where the
original peak at 525 nm changes down to about 500 nm. Therefore, it is apparent that R6G degradation occurs via two competitive pathways. As mentioned in Section 4.4.1, the loss of absorbance is attributed to the destruction of the dye chromogen.\textsuperscript{24} The fact that there was no growth of spectra, even in the UV region indicates that no intermediate organic matter was produced in the process. The hypsochromic shift of the absorption maximum has been attributed to the $N$-de-ethylation of the dye, leading to the production of rhodamine-like species.\textsuperscript{5,11} Absorbance maximum of rhodamine is reported to occur at 498 nm,\textsuperscript{24} which agrees well with the current observations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.14.png}
\caption{Optical absorption spectra of R6G during its degradation with 3\% GNP catalyst showing the hypsochromic shift of absorption maximum during a 30 minute photolysis. The inset illustrates the change in absorption maxima from 525 nm to 500 nm.}
\end{figure}
The current observations match well with a degradation process via an oxidative pathway. Further, it was found that the photogenerated electrons are scavenged by oxygen, and hole scavengers were able to hinder the reaction. Therefore, it is evident that photogenerated holes are directly responsible in decomposing R6G through oxidation. Accordingly, the reactions that are responsible for the degradation of R6G by ZnO catalyst can be expressed as follows:

\[
\begin{align*}
\text{ZnO} + h\nu_{(UV)} &\rightarrow \text{ZnO} \left( e_{\text{CB}}^- + h_{\text{VB}}^+ \right) \quad 4.7 \\
\text{H}_2\text{O} &\rightarrow \text{H}^+ + \text{OH}^- \quad 4.8 \\
\text{ZnO}(h_{\text{VB}}^+) + \text{H}_2\text{O} &\rightarrow \text{ZnO} + \text{H}^+ + \text{OH}^* \quad 4.9 \\
\text{ZnO}(h_{\text{VB}}^+) + \text{OH}^- &\rightarrow \text{ZnO} + \text{OH}^* \quad 4.10 \\
\text{ZnO}(e_{\text{CB}}^-) + \text{O}_2 &\rightarrow \text{ZnO} + \text{O}_2^* \quad 4.11 \\
\text{O}_2^* + \text{H}^+ &\rightarrow \text{HO}_2^* \quad 4.12 \\
\text{Dye} + \text{OH}^* &\rightarrow \text{Degradation} \quad 4.13 \\
\text{Dye} + h_{\text{VB}}^+ &\rightarrow \text{Oxidative degradation} \quad 4.14 
\end{align*}
\]

Under UV irradiation, conduction band electrons and valence band holes are produced (Equation 4.7), and water autoionization (Equation 4.8) results in small amounts of H\\(^+\) and OH\\(^-\) ions. Photogenerated holes may directly oxidize the substrate (Equation 4.14), but more likely will react with surface bound
hydroxyl groups (Equation 4.10) or water molecules (Equation 4.9) to form a 'trapped' hole ($0^*$) on the surface, which is usually described as an adsorbed $OH^*$ radical.\textsuperscript{50} The conduction band electrons will react with electron acceptors such as $O_2$ adsorbed on semiconductor surface or dissolved in solution, reducing it to superoxide anion radical $O_2^{*-}$ (Equation 4.11). Protonation of superoxide radical (Equation 4.12) produces a hydroperoxyl radical that also has electron scavenging ability as $O_2$, which helps prolong the lifetime of the photogenerated holes. These highly reactive surface bound ($0^*$) or solvated ($OH^*$) radical species are reported to be mainly responsible for the photodecomposition of organic substrates by semiconductors.

It is of importance to recognize the influence of gold nanoparticles for the dye degradation. The transfer of photogenerated electrons from the semiconductor to the metal nanoparticles, where the metal nanoparticle acts as a sink for electrons, has been studied widely.\textsuperscript{56,57} Additionally, gold nanoparticles have shown the ability to store electrons in a quantized fashion.\textsuperscript{58,59} Therefore it is evident that the ability of gold nanoparticles to abstract photoformed electrons, thereby decreasing the recombination rate of the excitons and lengthening the lifetime of photogenerated holes, is directly responsible for the enhancement of photocatalytic activity of the nano-composites. However, it was also discussed in section 4.5.1 that in the absence of an electron acceptor such as $O_2$ that is able to withdraw the stored electrons from the nanoparticles, the photocatalytic
degradation would not proceed. It is possible that back electron transfer from the gold nanoparticles to ZnO is also a very fast process. Therefore, unless an electron scavenger receives the electrons stored in GNPs, they return back to the semiconductor and undergo recombination, consequently stopping any surface redox reactions.

Decomposition of the substrate through photosensitization by visible radiation takes place through a different pathway than the mechanism involved under UV irradiation, and can be explained using following reactions:\(^6\)

\[
\text{Dye} + h\nu_{(\text{Vis})} \rightarrow ^1\text{Dye}^* \text{ or } ^3\text{Dye}^* \\
^1\text{Dye}^* \text{ or } ^3\text{Dye}^* + \text{ZnO} \rightarrow \text{Dye}^{**} + \text{ZnO}(e_{\text{CB}}^-) \\
\text{ZnO}(e_{\text{CB}}^-) + \text{O}_2 \rightarrow \text{O}_2^{**} + \text{ZnO} \\
\text{Dye}^{**} + \text{OH}^- \rightarrow \text{Dye} + \text{HO}^* \\
\text{Dye} + 2\text{HO}^* \rightarrow \text{H}_2\text{O} + \text{Oxidation products} \\
\text{HO}_2^* + \text{H}^* + \text{ZnO}(e_{\text{CB}}^-) \rightarrow \text{H}_2\text{O}_2 + \text{ZnO} \\
\text{H}_2\text{O}_2 + \text{ZnO}(e_{\text{CB}}^-) \rightarrow \text{OH}^* + \text{OH}^- + \text{ZnO} \\
\text{Dye}^{**} + \text{O}_2^{**} \rightarrow \text{DO}_2 \rightarrow \text{Degradation products} \\
\text{Dye}^+ + \text{HO}_2^* (\text{or } \cdot\text{OH}) \rightarrow \text{Degradation products}
\]
Dyes are excited to the appropriate singlet or triplet states by visible radiation (Equation 4.15) followed by electron injection from the excited dye molecule into the conduction band of ZnO nanoparticles (Equation 4.16), where the dye is converted to a cationic dye radical that leads to the degradation of the dye. The cationic dye radical can readily react with hydroxyl ions and undergo oxidation (Equations 4.18, 4.19) or react with $O_2^-$ (Equation 4.11), $HO_2^*$ or $HO^*$ species to generate intermediates that ultimately lead to mineralization (Equation 4.20 – 4.23).

The experiments described in section 4.5.4 shows that photooxidation is the major pathway for the photodecomposition of rhodamine 6G dye, whereas the contribution from photosensitization is minimal. It has been reported that efficiency of photosensitization is strongly affected by adsorption of the dye on semiconductor surface.\textsuperscript{61} In the current study, the extent of dye adsorption would be minimal, due to electrostatic repulsion between the positively charged ZnO surface and cationic R6G dye molecules. Additionally, the solutions were subjected to photolysis immediately after the addition of components. It could thus be inferred that this lack of adsorption of R6G on ZnO is the cause for the low efficiency of decomposition via photosensitization. A graphical representation of major photooxidation processes involved is provided in Figure 4.15.
4.6. Conclusions

This chapter involved the investigation of photocatalytic properties of ZnO - GNP nano-composites in aqueous solutions. Rhodamine 6G dye was selected as the substrate. It was shown that R6G undergoes complete and irreversible degradation with these catalysts, and loading of gold nanoparticles resulted in a prominent enhancement in photocatalytic activity of ZnO. While all gold loaded nano-composites performed better than bare ZnO, significant change in efficiency could be seen with different levels of gold loading.
Calcination was attempted as a post-treatment method to improve photocatalytic efficiency of the nano-composites, however, it was seen that photocatalytic performance of calcined composites were generally lower than that of the original nano-composites. Although the decomposition temperatures of glutathione and cysteine are lower than the calcination temperature, the sulfur oxide species that are formed when calcinated in the presence of ZnO, these ligands were believed to form sulfur oxidizes on semiconductor surface, poisoning the photocatalyst.

It was concluded that R6G undergoes complete degradation via photooxidation that is caused by photogenerated holes and resultant OH• and other radical species. However, the photooxidation was found to be prevented unless the reaction mixture contains oxygen or other species that are able to scavenge photoformed electrons. It was also realized that dye sensitization does not have a significant contribution towards the R6G decomposition. Minimal adsorption of the dye was suggested as the reason for this observation.
4.7. References

(22) Konstantinou, I. K.; Albanis, T. A. Applied Catalysis B: Environmental 2004, 49, 1.


CHAPTER 5
PHOTOCATALYSIS IN NON-AQUEOUS MEDIA

5.1. Introduction

Oxidative characteristics of valence band holes in irradiated semiconductor systems and their applications in degradation of substrates were discussed in the previous chapter. Similarly, the electrons transferred to the conduction band of a semiconductor possess a strong reductive power that is related to the conduction band position of the semiconductor. If the potential of conduction band edge is more negative than the reduction potential of the redox couple, an electron transfer from the conduction band of the semiconductor to the substrate is possible, consequently reducing it. Simultaneous scavenging of photogenerated holes must also be carried out for such a process to be successful.

Photocatalytic reduction via conduction band electrons of a photoexcited semiconductor has been of great interest in conversion of CO₂ into useful fuels such as methanol or methane and also has been applied in the removal of toxic pollutants such as Cr(VI) and Hg(II), and in other significant chemical conversions. However, relatively much less attention has been paid to the reductive photochemistry of semiconductors compared to photooxidation processes. Especially, the suitability of ZnO as a photocatalyst in photoreduction is not well investigated. This chapter therefore engages in discussing the
photoreduction characteristics of ZnO nanoparticles and the effects of gold nanoparticle assembly on photocatalytic efficiency.

Thionine (TH) was selected as the substrate in studying photoreduction attributes of the nano-composites. Thionine is a dye from thiazine family, which is strongly metachromic and is widely used in biological staining.\textsuperscript{12} Its structure is shown in Figure 5.1.

\begin{center}
Figure 5.1 Chemical structure of thionine.
\end{center}

5.2. Experimental Details

Experimental procedures that were used in this section are similar to those explained in Section 4.3.2. Thionine acetate and methanol were purchased from Sigma-Aldrich, and a stock solution of thionine in methanol was prepared by dissolving 5.0 mg of thionine acetate in 30.0 ml of methanol. The stock solution concentration is 0.580 mM. A catalyst stock solution was prepared by adding 4.0 mg of ZnO or nano-composite in to 40.0 ml of methanol and sonicating it for 10 minutes.

5.2.1. Photolysis under controlled atmosphere

2.0 ml of the catalyst, 200 \(\mu\)l of thionine and 4.0 ml of methanol were added to a 20 ml shell vial and the vial was sealed with a rubber septum. The solution was
purged with Ar for 30 minutes, and then sonicated for a minute to redisperse any coagulated catalyst. A fluorimetric quartz cell was also sealed with a rubber septum and flushed with Ar. Using a syringe flushed with Ar, a 3.0 ml portion of the solution was transferred into the cuvette, such that no atmospheric contact was made during the process. The cuvette was placed in the photolysis setup and was photolyzed for 5 minutes. The photolysis setup was the same as that was described in Section 4.3.1. The optical absorption spectra of the solution were acquired at every 10 seconds with an integration time of 11 ms, for 5 minutes. Each experiment was repeated thrice in order to verify the reproducibility.

A few experiments were carried out replacing the solvent methanol with water. In such situations, exact same procedure, explained previously was followed, only switching to water as the solvent in all preparations.

5.2.2. Photolysis under air

Some control experiments were performed without purging atmospheric gases from the solution. For such experiments, 1.0 ml of the catalyst, 100 µl of thionine and 2.0 ml of methanol were added to a cleaned fluorimetric cuvette. The cell was flicked several times until the solution is well mixed and was stoppered with a rubber septum. The cuvette was placed in the photocatalysis set up, and the degradation was determined as explained in Section 5.2.1.
5.2.3. Photolysis with additives

During mechanistic studies, electron scavengers, Fe(III) and methyl viologen were used as additives. Fe(III) chloride and methyl viologen dichloride stock solutions were prepared in methanol, and their concentrations were as follows:

\[
[\text{FeCl}_3] = 1.54 \times 10^{-3} \text{ mol l}^{-1}
\]

\[
[\text{MV}] = 1.19 \times 10^{-3} \text{ mol l}^{-1}
\]

Experimental procedure was similar to that described in Section 5.2.1. In a 20 ml shell vial, 2.0 ml of the catalyst, 300 µl of thionine, 2.0 ml of the additive and 2.0 ml of methanol was mixed, purged with Ar and a 3.0 ml portion of this solution was photolyzed in a fluorimetric cuvette.

5.3. Aspects of Thionine Photolysis by Nano-Composites

5.3.1. Thionine photolysis

Degradation of thionine in deaerated methanol solutions are illustrated by the evolution of its optical absorption spectra in Figure 5.2. Thionine dye is found to be very stable under UV irradiation according to Figure 5.2(A). Only about 7% degradation was seen during 30 minutes of irradiation, a time length about 20 times longer than the typical experimental time employed. Degradation of the dye was monitored by following the absorption maximum at 600 nm, and it is seen from Figure 5.2(D) that, in the presence of the catalyst, an extremely fast degradation takes place, and the blue color of the solution disappears and a
colorless solution results. Further, a strong, 71% enhancement of catalytic activity could be seen when 2% glutathione-capped 3.9 nm GNP loaded catalyst was used instead of ZnO.

Careful observation of the absorption spectra reveals the appearance of new bands in the UV region. Two isobestic points are seen around 266 and 318 nm, indicating that thionine converts into a different organic species during photolysis.

Reversibility of the thionine photolysis was tested by photolyzing the dye in the presence of catalyst for 200 s, and then aerating the solution by bubbling air into it. The effect, observed by absorption, is shown in Figure 5.3. It could be clearly seen that the dye, fully degraded after 200 s of photolysis, is completely regenerated once aerated. Therefore, it could be concluded that photolysis of thionine only results in a reversible redox reaction and no mineralization takes place, in contrast to the photocatalytic processes described for aqueous solutions.
Figure 5.2 Degradation of thionine in deaerated methanol solution under UV/Vis irradiation. (A) with no catalyst, (B) with ZnO and (C) with 2% GNP loaded ZnO. Relative change in maximum absorbance is plotted in (D).
**Figure 5.3** Optical absorption spectra of thionine illustrating regeneration of the dye when aerated.

### 5.3.2. Effect of GNP loading

Assembly of gold nanoparticles was able to provide significant enhancement of photocatalytic oxidation through charge rectification. However, the mechanistic aspects of that process may not be directly applicable to photocatalysis in non-aqueous systems as the thermodynamic and kinetic aspects would be different. There are a few reports on photoreduction of substrates using metal-modified semiconductor systems,\textsuperscript{13,14} and it was recognized that a thorough photocatalytic study on the effects of well-defined gold nanoparticles assembled on ZnO nanoparticles is necessary.

Photolysis of thionine in deaerated methanol solutions were carried out with bare and 3.9 nm glutathione GNP (see Section 2.5) loaded ZnO catalysts as
described in Section 5.2. In order to estimate the photocatalytic efficiency of each catalyst, the relative change in maximum absorbance of the dye was plotted against time, and the results are illustrated in Figure 5.4. Gold nanoparticles were able to cause significant enhancement in photocatalytic activity compared to ZnO, regardless of the extent of GNP loading. A minimum of 27% enhancement of photocatalytic rate was obtained by GNP deposition.

The first 30 seconds of photolysis data were used to perform linear regression, as seen in Figure 5.4(B), and the inset shows slopes of the linear fits plotted against the weight percentage of GNP loading compared to ZnO. The data point in red that corresponds to 1% GNP loading had an unusually low catalytic activity. This data was masked in obtaining the polynomial fit, and it suggests a maximum efficiency at 1.1% GNP loading. This result was found to be in contrast with that obtained from photooxidation experiments where the photocatalytic efficiency kept increasing beyond 6% GNP loading. The fact that the maximum efficiency was reached at very low gold loading levels compared to photooxidative reactions are possibly indicative of different energetics of the photocatalytic system in non-aqueous media. The literature suggests maximum efficiencies of 0.24%, and 2% for Ag nanoparticle deposits, which are not very different from the currently obtained results.
Figure 5.4 (A) Degradation profiles of thionine in deaerated methanol solutions by ZnO and nano-catalysts loaded with different amount of 3.9 nm glutathione GNPs. (B) Linear regression applied to the first 30 seconds of the degradation. The inset shows the slopes of linear fits against weight percentage of GNP loading.
5.3.3. Effect of calcination

The influence of calcination on photoreductive characteristics of semiconductor photocatalysts has not been reported. This section discusses the photocatalytic efficiency of calcined ZnO and nano-composite photocatalysts on degradation of thionine.

The effect of calcination on ZnO was initially determined as illustrated in Figure 5.5. It is evident that despite the difference in calcination temperatures, the thionine decomposition rate is very similar, and the slight differences would be within the experimental error. Therefore, 300 °C was selected as the calcination temperature for GNP loaded nano-composites.

![Figure 5.5](image)

**Figure 5.5** Thionine degradation efficiency of calcined ZnO at different temperatures as measured by relative change in maximum absorption of thionine. RT: un-calcined ZnO.
As described before, in order to test the effect of calcination on nano-composites, three nano-composites with GNP loadings 0.5%, 2% and 6% that were calcined at 300 °C for 1 hour were used to photolyze thionine in anaerobic conditions in methanol. The results are shown in Figure 5.6. The plots also include the photocatalytic rates from composites prior to calcination.

It could be seen that the effect of calcination is dependent upon the level of GNP loading. While 2% GNP loaded composite shows only minor loss in activity due to calcination, 0.5% and 6% GNP loaded catalysts indicate a significant amount of catalyst poisoning, which caused a notable reduction of photocatalytic activity in calcined product.

This observation is very similar to the calcination effect seen for photooxidation reactions that were tested with rhodamine 6G dye, and could be understood in the same context. It could be perceived that there are beneficial and detrimental effects that counteract each other in these gold nanoparticle loaded nano-composites. The detrimental effects outweigh the benefits at lower and higher loadings, but they could offset each other at average loading levels such as 2% GNP loading.
Figure 5.6 Effect of calcination on the photocatalytic activity of glutathione GNP nano-composites, as measured by thionine photolysis.
5.3.4. Effect of ligands in calcination

The detrimental effects could be caused by the degradation of ligand shell of gold nanoparticles. In order to determine how ligands affect photocatalytic efficiency in non-aqueous media, glutathione and cysteine passivated ZnO nanoparticles that were calcined as described in section 2.7, were employed to determine the efficiency of thionine photolysis.

The results of these experiments are shown in Figure 5.7, along with those from ZnO and calcined ZnO for comparison. Interestingly, the glutathione-modified ZnO showed a slight enhancement of photocatalytic activity over ZnO. Also, calcination of this product had only a negligible lowering effect on photocatalytic efficiency. On the other hand, cysteine modified ZnO behaved very similar to unmodified ZnO nanoparticles, where photolysis rate of uncalcined product was equal to that of ZnO, and once calcined the degradation rate lowered slightly, and was comparable to the profile of calcined ZnO.

It should be noted that the trends observed here are different from those obtained with GNP nano-composites, where calcination had an unfavorable effect on all three nano-composites. Therefore, it is difficult to specifically rationalize the current findings. However, according to the observations made during studies on oxidative photocatalysis in Section 4.4.3, the current results could also be attributed to the decomposition products of the passivating
ligands, even though it was not possible to confirm it via experiments on ligand modified ZnO nanoparticles.

**Figure 5.7** Thionine photolysis by glutathione (Glu) and cysteine (Cys) modified ZnO nanoparticles before and after calcination. For comparison, degradation results from bare ZnO before and after calcination are also provided.

5.4. **Mechanistic Studies of Photolysis in Non-Aqueous Media**

5.4.1. **Effect of oxygen**

Dissolved oxygen was determined to be a conduction band electron scavenger during the studies on oxidative catalysis described in Section 4.5.1, where the presence of O2 was found to be a prerequisite for the photocatalysis to continue. Therefore, it was of importance to investigate the role of oxygen in the present non-aqueous reaction conditions.
Thionine photolysis was carried out in unpurged solutions as described in Section 5.2.2, with ZnO and 2% glutathione GNP loaded catalyst. An additional photolysis was carried out with ZnO in an O₂ saturated solution. The degradation profiles of these experiments are shown in Figure 5.8(A). Decomposition of TH under Ar is also included for comparison. The reversibility of degradation was verified by leaving the photolyzed reaction mixture in air for 1 hour and recording its absorption, which is given in Figure 5.8(B).

Substantial reduction in photocatalytic efficiency can be seen for unpurged solutions. Also, there is very little difference in activity when different catalysts are used. Therefore, it is evident that dissolved oxygen has a significant interference for the photodegradation of thionine. It could be perceived that thionine uses conduction band electrons in its degradation, and in the presence of O₂, an electron scavenger, the competition for electrons causes thionine decomposition to become slower.

The decomposition rate of thionine in O₂ saturated solution was seen to be similar to those under atmospheric conditions. Two conclusions can be drawn from this observation. Firstly, it could be determined that the species responsible for the reduction of catalysis is indeed, dissolved oxygen. Secondly, since the rate of decomposition is comparable with atmospheric conditions, the electron scavenging efficiency of O₂ should be independent of the oxygen concentration in the solution. Oxygen is known to strongly bind on ZnO surfaces,
and it could be presumed that most of the O$_2$ is bound on ZnO surface rather than dissolved in methanol\textsuperscript{16-18}. Photocatalytic rate would not therefore depend on the diffusion of O$_2$ through the solution, as surface-bound oxygen molecules would be responsible for most of the electron scavenging that takes place.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.8.png}
\caption{Effect of O$_2$ on photolysis of thionine. (A) Degradation profiles of TH with ZnO under air and O$_2$ enriched solution, and with 2\% GNP loaded catalyst under air. Decompositions under Ar are also shown for comparison. (B) Optical absorption spectra of TH, showing the reversibility of the degradation under air.}
\end{figure}
5.4.2. Effect of electron scavengers

The reactions in the presence of oxygen provided information on the functionality of conduction band electrons. In order to further recognize the role of these charge carriers in thionine photolysis, two electron scavengers, Fe(III) and methyl viologen (MV) were employed.

Effect of Fe(III)

Temporal evolution of the absorption spectra of a reaction mixture where thionine was photolyzed by ZnO in the presence of Fe(III), is illustrated in Figure 5.9(A). The strong absorption peak near 370 nm in the beginning of the photolysis is due to Fe(III), and its intensity decreases with time. The absorption at 600 nm, from thionine also reduces indicating its degradation. As time progresses, a weak absorption band appears at around 800 nm, which could be attributed to the production of Fe(II).

The change of the absorption intensities at 370 nm, 600 nm and 780 nm with photolysis time is plotted in Figure 5.9(B). It should be noted that the spectrometer was not able to record absorbance values beyond 2. Thus, extensive noise was recorded below 400 nm due to the strong absorption of Fe(III). However, Fe(III) concentration gradually decreases with the photolysis time indicating the reduction of Fe(III) to Fe(II). Due to its low extinction coefficient, formation of Fe(II) is difficult to observe from the absorption at 780 nm.
Figure 5.9 Effect of Fe(III) in photodegradation of thionine by ZnO. (A) Evolution of optical absorption spectra during photolysis. (B) Variation of absorbance at specific wavelengths indicating the change in concentration of different species in the reaction mixture.
The concentration of thionine does not change until about 110 s, as seen from the absorption at 600 nm, and then a gradual degradation is seen. This shows that thionine decomposition was prevented in the beginning due to the competition from the large concentration of Fe(III) for conduction band electrons. Thionine degradation could proceed only after the Fe(III) concentration was significantly lower, and illustrates the necessity of electrons for this process.

![Graph showing degradation profile](image)

**Figure 5.10** Degradation profile of thionine by ZnO and 2% GNP loaded nano-composite in the presence of Fe(III) as an electron scavenger. Decomposition in the absence of additives is also shown for comparison.

Thionine degradation in the presence of Fe(III) is shown in Figure 5.10, where ZnO and 2% glutathione GNP loaded composite were used as the catalyst. When the electron scavenger Fe(III) is present in large quantity, thionine degradation
is almost completely prevented, and only when Fe(III) concentration becomes significantly less, does the thionine decomposition appears to begin. It can thus be understood that, the conduction band electrons are directly involved in thionine photodegradation, and Fe(III) reduction was favored over thionine reduction. The positive effects of gold nanoparticles could also be observed, where GNP nano-composite showed higher photocatalytic rate even in the presence of Fe(III).

Effect of MV

Figure 5.11(A) depicts the development of optical absorption spectra for a thionine reduction with 2% glutathione GNP catalyst in the presence of methyl viologen. Apart from the steady loss of thionine absorption at 600 nm, appearance of two new absorptions could be seen at 395 nm and at 605 nm, which confirms the formation of methyl viologen cation radical, MV$^{+}$ by the reduction of MV$^{2+}$. Methyl viologen (MV$^{2+}$) does not have any optical absorbance beyond 300 nm.

The evolution of absorption at 395 nm that is due to MV$^{+}$ and at 600 nm from thionine was plotted against time as shown in Figure 5.11(B). It can be seen that absorption intensity at 600 nm is rapidly lost, indicating an immediate and quick degradation of thionine. But the development of the absorption peak at 395 nm is negligible until thionine photolysis is almost complete at around 75 s, beyond
which there is a significant growth of MV absorption. These observations further illustrate the role of conduction band electrons in thionine photolysis.

Figure 5.11 Effect of MV in photolysis of thionine with 2% GNP catalyst. (A) Temporal evolution of absorption spectra of the reaction mixture. (B) Variation in absorption at specific wavelengths indicating the change in concentration of thionine and MV with time.
Comparison of the effect of MV in thionine photolysis is shown in Figure 5.12(A). Degradation profiles of thionine in absence of MV have also been added for comparison purposes. A rather interesting phenomenon could be observed in this outcome: the presence of MV shows opposite effects with different catalysts, where MV enhances the catalytic efficiency when ZnO was employed as the catalyst, and it lessens the photocatalytic activity of 2% GNP catalyst.

When ZnO catalyst was used, MV was able to induce a strong, 48% enhancement to thionine degradation. It is thus evident that MV acts as an electron mediator such that the conduction band electrons are efficiently transferred in to thionine molecules. Initially, the concentration of methyl viologen only shows slight changes since the MV$^{2+}$ molecules that reduce into MV$^*$, transfer an electron to thionine and oxidize back to MV$^{2+}$. Fast reduction of MV begins as TH is fully degraded as seen in Figure 5.11(B).

With 2% GNP catalyst, apparently the energetics of the catalytic system becomes unfavorable and the catalytic efficiency of thionine drastically drops by 43%. This could be attributed to the efficient electron transfer from the conduction band of the irradiated semiconductor to the gold nanoparticles. Because of the very high Helmholtz capacitance of the metal-solution interface compared to the space-charge capacity of semiconductors, most of the excited electrons will accumulate on GNPs rather than on the semiconductor.$^{22}$ This will cause the Fermi level of GNPs to shift negatively towards the conduction band of ZnO as
discussed in Section 1.5.5. However, it would not reach the conduction band potential, as thionine continues to abstract electrons directly for its reduction. Therefore, the Fermi level of GNPs can be expected to lie at a significantly lower potential than the conduction band, which could prevent energy transfer to MV that has a reduction potential of -0.45 V (for MV$^{2+}$/MV$^{••}$, vs. NHE), consequently hindering the electron-mediating process that was observed with ZnO catalyst.

However, the preceding explanation only suggests that thionine degradation could occur at the original rate, as MV could not participate in the process, but will not clarify the strong reduction of its photodegradation. But the reason could be rather straightforward. It should be noted that the concentration of thionine in the reaction mixture is 19.3 μM, while the concentration of MV is more than 60 times higher at 1.19 mM. Since the current reactions are diffusion-limited, the ability of thionine to reach the ZnO surface for redox process would be limited in the presence of MV, lowering the photodegradation rate.

Once the degradation of thionine completes, a slow methyl viologen reduction begins. MV reduction that did not occur with the nano-composite initially becomes possible now, once all thionine molecules are depleted. Then, further electron accumulation will continue to take place on the GNPs increasing their Fermi level. Once the Fermi level reaches redox potential of MV, reduction of methyl viologen also becomes possible.
Figure 5.12 Thionine degradation profiles with ZnO and 2% GNP composite (Comp) catalysts in the presence of MV. Degradations without additives are also included for comparison.

5.4.3. Effect of hole scavengers

In Section 4.5.3, it was found that methanol was an excellent scavenger of valence band holes. Therefore, the current experiments were performed in methanol solution, so that the catalytic behavior of conduction band electrons can be specifically investigated. It was of interest however, to study the significance of methanol in thionine degradation. Therefore, thionine decomposition was performed using water as a solvent instead of methanol, as described in Section 5.2.1. At the end of the photolysis, the solutions were aerated and the absorbance was recorded to ensure the recovery of thionine absorption, which confirms the reversibility of the reaction.
Profiles of thionine decomposition in water and methanol are depicted in Figure 5.13, and show a 43% reduction in photodegradation of thionine when water was used as the solvent. Water reportedly could also act as an electron scavenger\textsuperscript{25} according to Equation 5.1, but the current observations suggest that water is a weak hole scavenger compared to methanol.

\[ \text{ZnO}(h\nu_{\text{VB}}) + \text{H}_2\text{O} \rightarrow \text{ZnO} + \text{H}^+ + \text{OH}^- \]  \hspace{1cm} 5.1

**Figure 5.13** Thionine decomposition profiles for reactions performed in methanol and water, with ZnO as photocatalyst.

### 5.4.4. Dye sensitization

In order to realize the complete picture of substrate degradation process in methanol solutions, whether there is an involvement of dye sensitization has to be investigated. As explained in Section 4.5.4, a 310 – 430 nm band pass filter
that could exclusively excite ZnO band edge, and a 455 nm high pass filter that only illuminates thionine absorption band were used. The optical absorption spectra of the filters along with those of ZnO and thionine are illustrated in Figure 5.14, which shows that the filters could effectively illuminate specific species.

![Optical absorption spectra](image)

**Figure 5.14** Optical absorption spectra of the band pass (BP) and the high pass (HP) filters. Spectra of ZnO and thionine are also shown.

The decomposition of the dye in presence of each of the filters is shown in Figure 5.15. It could be seen that when thionine was selectively excited, degradation is extremely low unlike the observations made in rhodamine degradation, with a 88% reduction in activity with ZnO and a 93% drop when 2% GNP composite was used. It could therefore be concluded that there is no significant effect from
dye sensitization, and the slight decomposition may be attributed to the scattered radiation reaching the photolysis cell.

Figure 5.15 Thionine photolysis profiles with band pass and high pass filters in place for ZnO and 2% GNP composite as catalysts. Degradation profiles without the filters are also included.

When the ZnO band edge was excited using the band pass filter, the photolysis efficiency does not change significantly with ZnO as the catalyst. However, with 2% GNP composite was used, a 40% reduction in photocatalytic activity could be seen, and the degradation profile becomes very similar to that of the ZnO catalyst. The behavior is in contrast to the results of oxidative degradation, where both catalysts performed similarly. These data indicates that the photocatalytic enhancement provided by gold nanoparticles was lost when only the band edge was irradiated. This implies that the gold nanoparticle system has
to be in some excited state for GNPs to mediate conduction band electrons from ZnO to the substrate. While it was not possible to distinctly identify the type of photoexcitation the gold nanoparticles underwent, it should be noted that radiation that is related to the surface plasmon absorption of these nanoparticles that occur near 520 nm (See Figure 2.5) was blocked with this filter. Further, any involvement of the excitation of glutathione molecules can be excluded since the radiation related to their absorption that takes place below 220 nm, is removed by the UV filter used in the photolysis setup. Therefore, lack of excitation of gold core is suggested as the reason for the drop in photolytic efficiency under band edge illumination.

5.4.5. Mechanism of thionine degradation

The observations described so far clearly indicate the thionine accepts conduction band electrons on ZnO and undergoes a reductive degradation. Reduction of thionine is reported to be a two-step process, and the reaction with the conduction band electrons of ZnO can be illustrated by Equations 5.2, 5.3 and the structural change is given in Figure 5.16.

\[
\text{ZnO(e}_{\text{CB}}) + \text{TH}^+ \rightarrow \text{ZnO} + \text{TH}^* \\
2 \text{TH}^* \rightarrow \text{TH}^+ + \text{TH}^- 
\]

Thionine (\(\text{TH}^+\)) is first converted into a semireduced radical form, \(\text{TH}^*\). This semireduced form is unstable, and undergoes disproportionation to generate the
leuco form of the dye TH\textsuperscript{+}. The leuco form is stable in inert atmospheres, and does not absorb in visible region, resulting in a colorless solution. The appearance of absorption peaks in the UV region of the spectrum can be attributed to leuco thionine.\textsuperscript{27}

\[
\text{ZnO}(h\nu_B) + \text{CH}_3\text{OH} \rightarrow \text{ZnO} + \cdot\text{CH}_2\text{OH}
\]

\[
\cdot\text{CH}_2\text{OH} + \text{TH}^+ \rightarrow \text{TH}^- + \text{CH}_3\text{OH}
\]

Figure 5.16 Structural changes in thionine that occur during its reduction. Methanol scavenges the valence band holes according to Equation 5.4 and oxidizes into a methoxy or hydroxyl radical.\textsuperscript{28} There is a possibility for the reduction of the dye by secondary reductants such as these as in Equation 5.5. However, this has been reported to be a rather negligible pathway.\textsuperscript{27}

Figure 5.17 schematically illustrates the processes that take place during photocatalytic reduction of thionine with GNP composite catalysts in an inert atmosphere. Irradiation of the catalyst generates conduction band electrons and valence band holes. Holes get scavenged by the solvent methanol, while most of the conduction band electrons transfer to the gold nanoparticles. Thionine
molecules abstract electrons mostly from GNPs and from the ZnO surface and undergo reversible reduction.

**Figure 5.17** Major processes involved in photocatalytic reduction of thionine by GNP modified ZnO nanoparticles.

### 5.5. Conclusions

This chapter focused on photocatalytic processes of ZnO and 3.9 nm glutathione-capped gold nanoparticle modified ZnO composites. The substrate selected was thionine, and it was found that thionine degraded reversibly into a colorless species when catalytically photolyzed. While close to 1% GNP loading provided best activity, any amount of GNP present could enhance the photocatalytic efficiency compared to bare ZnO nanoparticles.
Calcination of the composites affected the thionine decomposition differently based on the GNP loading. While 0.5% and 6% gold nanoparticle loadings showed detrimental effects, 2% loading had no significant consequence by calcination. It is possible that the residual species of glutathione are responsible for these observations.

Electron accepting species such as \( \text{O}_2, \text{Fe(III)} \) and MV were found to significantly modify thionine photolysis, and confirmed the importance of conduction band electrons in thionine degradation. It was found that the reduction potential of the substrate with respect to the energy level of the conduction band of ZnO was crucial in the photoreduction process, where it determined the ability of the catalyst to reduce a particular substrate. In the presence of more than one substrate, their redox potential determined the order of reduction, and as was seen in Section 5.4.2, could mediate the reduction of a second substrate.

Gold nanoparticles were found to enhance photocatalytic activity by acting as sinks for conduction band electrons. Additionally, presence of gold nanoparticles could significantly modulate the energetics of the catalyst, since the position of the Fermi level is dependent upon the extent of the electrons that have accumulated in the GNPs. As a result, photocatalytic behavior that is considerably different from bare ZnO was seen for GNP modified composites.

A remarkable observation was made when the reaction solution were irradiated with specific wavelengths of light. It was observed that the photocatalytic
enhancement resulting from gold nanoparticles disappear when only the ZnO band edge was excited. It was suggested that some form of excitation of the gold core is also required for the electron mediation of GNPs to occur.
5.6. References


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CHAPTER 6
FUTURE DIRECTIONS

6.1. Improving the Catalyst and Process

During the current study, various fundamental aspects and applicability related to the photocatalytic activity of ZnO nanoparticles and the prominent enhancements achieved by the careful assembly of Au nanoparticles were investigated. However, there are a number of attributes in this photocatalytic system that deems optimization.

Gold nanoparticles of only a limited size range, around 4 nm, were employed in this investigation. However, substantial dependence of catalytic properties of gold nanoparticles has been reported, and significant variations of the results could also be seen. Thus, it is imperative to study the catalytic activities resulting from gold nanoparticles of different sizes in order to obtain the optimal catalytic activity.

It was found that the catalytic efficiency of annealed nano-composites was lower due to the decomposition products of the passivating ligands. This shows that the ligand shell of GNPs may act as a barrier for the catalytic activity. Catalysts with better performance may be obtained by the use of direct deposition methods to assemble GNPs on ZnO surface. However, the methods such as deposition precipitation suffer from drawbacks such as poor control of GNP size,
lack of monodispersity and limited loading levels.\textsuperscript{4-6} Thus, it would be advantageous if such direct deposition methods could be improved to overcome these shortcomings and ZnO – Au nano-composites could be synthesized with assemblies of monodisperse and size controllable GNPs.

Photocatalytic reactions by semiconductor nanoparticles performed in aqueous media are significantly influenced by the solution pH, since surface charge, band edge positions and stability of the generated reactive species are strongly depend upon solution pH.\textsuperscript{7-9}

Preliminary experiments were conducted to study the effect of pH on R6G degradation over ZnO and GNP modified nano-composites. Tiopronin-passivated 2 nm Au nanoparticles assembled on ZnO at 0.8 and 4\% by weight, were used as the nano-catalyst. pH was adjusted to 9 by dropwise addition of 1 M ammonium hydroxide solution into the reaction mixture. Catalyst solutions with and without the adjusted pH were used to photolyze rhodamine 6G.

Another interesting result, as illustrated in Figure 6.1, was obtained from this experiment. Basifying the solution had a minimal effect on the catalytic activity of ZnO nanoparticles, which shows similar decomposition rate at both neutral and basic pH. On the contrary, pH was found to strongly influence the catalytic behavior of GNP-loaded nano-composites, where extremely fast decomposition of R6G could be observed when the pH was raised to 9. Further investigation is required to decipher this notable observation.
Figure 6.1 Effect of pH on R6G degradation by ZnO and nano-composite.

6.2. Applicability toward Pollutant Decomposition

Rhodamine 6G and thionine were used in this study as model substrates in investigating the photocatalytic behavior of nano-composites. However, it is of importance to investigate the applicability of these novel photocatalysts on actual environmental pollutants. Precursory investigations were carried out to realize the capability of the nano-composites to photodegrade several pesticides that have been reported to be causing extensive water pollution.

6.2.1. Water pollution by pesticides

Pesticides are one of the few types of chemicals that are intentionally released to the environment in order to control the populations of harmful organisms in agriculture. While pesticides can in many instances improve the quality and
quantity of crops by effectively controlling the adverse effects of pests, they can also impose serious consequences, where they cause disruptions to major ecosystems and loss of biodiversity. Further, pesticides are found to cause significant effects on human health. One major route the general population comes in contact with pesticides is via ground water contamination.\(^\text{10}\)

The extent of ground water contamination by pesticides was illustrated in a study by US geological survey (USGS) published in the 2006 report ‘Pesticides in the Nation’s Streams and Ground Water, 1992 – 2001’, where it was found that at least one pesticide was detected in water from all streams studied, and about one third of the deeper wells, which are fed by major aquifers used for water supply, contained one or more pesticides or degradates.

Although the number of pesticides in use is extremely high, the largest usage tends to be associated with only a small number of pesticide products. Such most abundantly applied chemicals have the highest potential to be leached in to ground waters. For instance, atrazine, the most commonly used herbicide in US (30,000 tons/year)\(^\text{11}\) is one of the most frequently detected and present at the highest concentrations in water streams.

6.2.2. Pesticide degradation

Along with atrazine, other two herbicides, metolachlor and diuron, all among the most frequent water contaminants in US, were selected for initiatory studies on applicability of the nano-composites towards pesticide degradation. Chemical
structures of the compounds are given in Figure 6.2, and the UV/Vis absorption spectra are shown in Figure 6.3.

(a) 
(b) 
(c)

Figure 6.2 Chemical structures of (a) atrazine, (b) metolachlor and (c) diuron.

Figure 6.3 Normalized optical absorption spectra of the pesticides.

Many degradation products of pesticides possess toxicities the same as or higher than those of the parent compounds. Therefore, it is crucial that degradates are specifically identified during a decomposition process. UV/Vis absorption, the
technique used in this study to monitor degradation of the substrate therefore becomes insufficient. Liquid chromatography coupled with mass spectrometry (LC/MS) was identified as a suitable technique for this purpose.

Optimized conditions for LC/MS technique were obtained for a Shimadzu LCMS-2010A fitted with a 3 cm C18 column and an electrospray ionization (ESI) probe. Aqueous stock solutions of the pesticide standards obtained from Sigma-Aldrich were prepared with concentrations of 74.2 μM, 77.2 μM and 631 μM for atrazine, diuron and metolachlor respectively. 10 μl of each solution was injected to the column set at 40 °C. The mobile phase was optimized to 60% methanol, and 40% water with added 0.1% formic acid as the ionization agent. The flow rate was set to 0.2 ml/min.

Mass chromatograms of the pesticides, obtained using the above conditions are illustrated in Figure 6.4, which resulted in retention times of 5.6 min, 10.3 min and 20.0 min for atrazine, diuron and metolachlor respectively. The insets in the corresponding plots provide the mass spectra of the chromatographic peak region deducted from the background. It is therefore possible to confirm that LC/MS can successfully be applied in separation, quantification and identification of the selected pesticides during a degradation process.
**Figure 6.4** Mass chromatograms of the pesticides analyzed by LC/MS. Mass spectra of the respective chromatographic peaks are given in the insets after baseline deduction.
Preliminary investigations were performed in order to verify the capability of the nanoparticles to photocatalytically degrade the pesticides under study. All solutions were prepared in aqueous media. 1.0 ml of 1.23 mM ZnO, 1.0 ml of water and 1.0 ml of the pesticide stock solution was mixed in a fluorimetric cuvette and placed in the photocatalytic setup.

Temporal evolution of the optical absorption spectra for each of the pesticides by ZnO nanoparticles during 30 minutes of irradiation is illustrated in Figure 6.5. It could be seen that absorbance profile of the atrazine solution did not change significantly, indicating that it was not decomposed by ZnO during this time frame. However, an overall reduction in absorption was seen for diuron, signifying the possibility of complete degradation of the pesticide. Some evolution of UV/Vis absorption could also be seen for metolachlor, where a slight increase of absorption was detected around 300 nm. This observation could be attributed to a partial decomposition or a conversion of the pesticide into a species that has an absorption in 300 nm region.
Figure 6.5 Temporal evolution of UV/Vis absorption spectra of pesticides during their photocatalytic degradation for 30 minutes by ZnO nanoparticles.
Results discussed so far suggest that the nano-composite systems that were developed in the current study could effectively be used for the photocatalytic degradation of different pesticides, and could possibly be extended to other types of water contaminants. With additional investigation, this nano-composite system may have the potential to be applied as an efficient photocatalyst for water decontamination.
6.3. References


