Synthesis and Characterization of Monolayer Protected Gold Nanoparticles and a Gold-Titanium Dioxide Nanocomposite intended for Photocatalytic Degradation of Environmental Pollutants

Piyadarsha Amaratunga
Western Michigan University

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SYNTHESIS AND CHARACTERIZATION OF MONOLAYER PROTECTED GOLD NANOPARTICLES AND A GOLD-TITANIUM DIOXIDE NANOCOMPOSITE INTENDED FOR PHOTOCATALYTIC DEGRADATION OF ENVIRONMENTAL POLLUTANTS

by

Piyadarsha Amaratunga

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Faculty of The Graduate Collage
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requirements for the
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Department of Chemistry
Advisor: Ekkehard Sinn Ph.D.

Western Michigan University
Kalamazoo Michigan
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SYNTHESIS AND CHARACTERIZATION OF MONOLAYER PROTECTED GOLD NANOPARTICLES AND A GOLD-TITANIUM DIOXIDE NANOCOMPOSITE INTENDED FOR PHOTOCATALYTIC DEGRADATION OF ENVIRONMENTAL POLLUTANTS

Piyadarsha Amaratunga, Ph.D.
Western Michigan University, 2010

Semiconductor and metal clusters in the nanometer size regime display interesting optical, electronic and chemical properties that are size dependant. Highly monodisperse gold nanoparticles of different sizes have been synthesized and isolated by newly developed methodologies, using tiopronin as the capping ligand. Titanium dioxide nanoparticles (TiO₂) have been used as the photocatalytic center and gold nanoparticles have been attached on TiO₂ to make a nanocomposite. According to the findings, gold nanoparticles play a vital role in enhancing the photocatalytic activity of TiO₂, by facilitating the charge separation. Further, the photocatalytic activity also can be tuned by changing the gold loading on TiO₂. The applicability of the nanocomposite has been evaluated towards the degradation of environmental pollutants.
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Piyadarsha Amaratunga
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CHAPTER 1

INTRODUCTION

Nanotechnology is a rapidly evolving field owing to its numerous potential benefits towards mankind. Unique chemical and physical properties of nanosized materials have inspired research in recent decades and the fascinating findings have revolutionized the field of science.\(^1\) Diverse applications in healthcare, home and garden, electronics, energy conversion, automotive science, catalysis and sensors have emerged and existing applications are countless.\(^2\) The annual global investment in nanotechnology research and development is US $9 billion.

Fundamental knowledge of the nanotechnology is essential to utilize nanotechnology towards applications. Nanoparticles are describes as particles in the size range of 1 to 100 nanometers. This lies between the dimensions of bulk materials (>micrometers) and the dimensions of the atomic and molecular scale (Angstroms(Å)). Quantum chemical expressions are used to explain the materials in atomic or the molecular state. The solid state physics of condensed matter, is used to explain the nature of the bulk materials. Since nanosized materials exhibit unique properties,\(^3\) simple quantum chemistry or classical laws cannot be extrapolated in order to explain their characteristics. The most important feature of nanoparticles is that their properties are dependent on their dimensions. The size dependence
of chemical and physical properties is extremely significant in the size range of 1 to 10 nanometers. In the smaller size regime, particles have high surface area per unit volume. Moreover, the smaller sizes also exhibit quantum confinement effects. Both of these phenomena drive the higher activities and unique physico-chemical properties at the nanoscale. Energy level spacing, capacitance and melting temperature are some of the properties that change with the size of nanoparticles. Metal nanoparticles are the most popular category due to their stability towards various applications.

Many metal species, including Au, Ag, Al, Co, Cu and Pt, have close-packed lattice structure with a Face Centered Cubic (FCC) conformation. In the simplest version of the FCC conformation, a single atom is surrounded by 12 similar atoms. This can produce a nanoparticle with 13 atoms. If one more layer of 42 atoms is attached on top of this core, it forms a nanoparticle with 55 atoms. Larger nanoparticles also can be obtained by adding more layers.

![FCC lattice structure and nanoparticle](image)

Figure 1-1 (a) FCC lattice structure and (b) a nanoparticle with 13 atoms
The possible numbers of atoms in the resulting particle called “Magic Numbers”. For n complete layers, the atoms of (N) FCC crystal arrangement is given by the following formula.\(^6\)

\[
N = \frac{1}{3} [10n^3 - 15n^2 + 11n - 3]
\]

The number of atoms on the surface is \((N_{\text{surf}})\)

\[
N_{\text{surf}} = 10n^2 - 20n + 12
\]

Theoretically, magic number nanoparticle (N= 1, 13, 55, 147……) can be highly stable.\(^7\) However, nanoparticles obtained after synthesis do not always follow this magic number rule.\(^8\) Protecting groups are added on the nanoparticles surface during the synthesis process to ensure the stability. Interactions among the core atoms and the interactions between core atoms and the surface ligands determine the properties of the final structure.\(^9\) Therefore, nanoparticles with above magic numbers may or may not be the most stable species in the applications.

1.2. Energy Picture in the Nanoscale

Solid materials have energy bands. The core electrons, in the inner orbitals of the atoms, are less significant in determining the properties of the material.\(^6\) In contrast, the outer electrons in the valence shells significantly contribute to the formation of the crystal or lattice structure and the nature of these
electrons defines the energy states of the material. These energy levels that are occupied with electrons are called "Valance Band". In an insulating material, electrons are localized in the bonds. The energy region which contains free and mobile electrons are called the ‘Conduction Band”.

Figure 1-2 displays the schematic energy level diagrams of a semiconductor and a metal. The close lines show the availability of charge carriers in each energy level. Semiconductor has a filled valance band and an unoccupied conduction band and the gap between two bands are smaller than that of an insulator. Therefore, there is a greater possibility that some of the valance band electrons can be promoted to the conduction band. Metals have a filled valance band and a partially filled conduction band. Due to the availability of the delocalized electrons in the conduction band, metals are capable of carrying current.

Figure 1-2 Energy bands of a semiconductor and a metal
The energy picture in Figure 1.2 is for a bulk semiconductor material. Electrons and holes experience an attractive coulomb force and they are separated by Bohr radius. When the particle size is reduced, the movement of the electron pair is confined to a limiting space. The energy structure for this situation is described by quantum mechanical laws. These particles that have electrons in the well-defined energy states are called Quantum Dots (QD). QD display a band structure with discrete energy levels.

Figure 1.3 shows the schematic energy structure of a semiconductor quantum dot and of the bulk material. The bulk material has a large number of
closely-spaced energy levels and has a broad absorption spectrum. In contrast, the quantum dot has a small number of discrete energy levels like in an atom and it shows a discrete absorption spectrum. The expression for the size-dependent energy gap between the lowest unoccupied and the highest occupied energy levels are given as following equation

\[ E_g(QD) = E_g(Bulk) + \frac{k}{R^2} \]

where \( E_g(QD) \) is the energy gap in QD, \( E_g(Bulk) \) is the energy gap in the bulk material, \( k \) is a constant that depends on the effective masses of electrons and holes and \( R \) is the radius of the QD. According to the equation, the energy gap of the QD depends on its radius and the energy gap increases with decreasing core size.

1.3. Gold Monolayer-Protected Clusters

Nanoparticles are prepared aiming at various applications. Stability is an important factor that determines the significance and the value of nanoparticle. Nanoparticles are passivated with ligands in order to attain expected stability. These capping agents have greater affinity towards the metal and are able to self-assemble on the metal surface (Figure 1-4). The resulting nanoparticles are called monolayer-protected clusters (MPC). Even though the primary function of the capping layer is to ensure the stability of
MPC, it has been found that the manipulation of the capping ligands yields diverse chemical and physical characteristics.

Figure 1-4 A gold core passivated with hexanethiol monolayer

When gold MPC are stabilized with thiol ligands, they demonstrate promising constancy towards aggregation. These MPC also can be isolated and re-dissolved in different solvents. It was believed that the gold contributes to build the core and thiol ligands are bonded to the core with sulfide bonds (Figure 1-4). X-ray crystallographic investigations of Au_{25} and Au_{102} structures have revealed that small gold MPC having unexpected configurations. Gold is not only a part of the core but also a part of capping monolayer. Most of the gold atoms participate in the formation of MPC as semiring or “Staple” structure. Instead of direct binding, thiol ligands (R) binds to the core via bridging coordination.
1.3.1. Optical properties and applications

In the optical and electronic point of view, gold MPC can be divided into two categories of sizes. One is small-sized MPC (<2.2 nm), that exhibit molecular like properties in the optical and electronic investigations and the bigger-sized MPC (>3 nm), that show metal like characteristics. The bigger-sized MPC have bright colors due to surface plasmon resonance absorption (SPR). The color of the larger MPC changes from red to purple-red depending on their size. Until now, vast majority of the optical applications have focused on the SPR absorbance. SPR absorbance of metal particles occurs due to collective oscillation of conductive band electrons in the presence of electromagnetic radiation. The resulting energy decay is non-radiative and
the energy is converted to heat. In the case of gold MPC, SPR exists from 500 nm to 600 nm of the absorbance spectrum and the position depends on the dielectric environment of the metal core, i.e. the nature of the ligand and the solvent.\textsuperscript{16} Most importantly, the SPR absorbance depends on the size of MPC. Equivalent dimensions of nanoparticles to intracellular matter have made it possible to use nanoparticles in biological applications.\textsuperscript{4} SPR absorbance is highly beneficial in imaging and sensing purposes. MPC can be functionalized with a probe that is compatible with the biomolecular target and can be incorporated to the cell interior. Previously, dye molecules have been used to image the intracellular structure of the cell. MPC are replacing dyes, because the absorbance cross section of metal MPC is 5 orders of magnitude or more larger than those of molecules.\textsuperscript{1} Moreover, MPC are highly photostable, compared to dye molecules.

In 1997, Mirkin et al. demonstrated the possibility of using the size dependant colorimetric properties of gold nanoparticles in the detection of single stranded target oligonucliotides.\textsuperscript{17} Gold nanoparticles have been modified with mcaptoalkyl oligonucliotide via sulfur gold bonding. The hybridization between complimentary single stranded oligonucleotides created aggregations of nanoparticles (Figure 1-6). The color of the initial solution is red and it changes to purple upon aggregation. As mentioned previously, the SPR absorbance depends on the size of the gold cluster. After
the aggregation, the bigger-sized clusters behave as larger nanoparticles. This finding opened a broad research area related to biological applications of gold and other metal nanoparticles.

![Diagram of nanoparticle aggregation](image)

**Figure 1-6 Aggregation of nanoparticles upon addition of polynucleotide target**

El-Sayed has utilized the SPR of colloidal gold to diagnose cancerous cells. Cancerous cells contain higher amount of epidermal growth factor receptor (EGFR). They modified the gold nanoparticles surface with anti-EGFR antibodies and targeted them to cancer cells. Gold nanoparticles were also observed inside the non-cancerous cells but the uptake of cancerous cells was found to be 600% greater than that of non-cancerous cells. The difference in the cell types was analyzed by optical microscope and absorption spectroscopy. The SPR absorbance band is relatively narrower for cancerous cells due to lesser aggregations. These results suggest the possibility of using nanoparticles in biological imaging.
1.3.2. Electrochemical properties and applications

Size-dependant electrochemical properties drastically change in the size scale of 1 to 4 nm. It has been demonstrated that the metal core can act as an electron storage center.\textsuperscript{19-21} Therefore, detailed investigation of the mechanism of electron transfer into the metal core is essential. "Quantization of double layer capacitance charging" is one of the fundamental and fascinating electrochemical phenomenon that occurs in MPC. Interestingly, this depends on the core size of MPC. When MPC are subjected to an electric field, the particles behave as tiny capacitors and are charged by definite potential intervals.

![Diagram](image)

Figure 1-7 Schematic representation of the capacitance of MPC (C) and the resistance at the interface (R)
The relationship between the charging voltage ($\Delta V$) for each electron transfer step and the capacitance ($C$) of the MPC is given by the following equation, where $e$ is the charge of the electron.

$$\Delta V = \left[ \frac{e}{C} \right]$$

The capacitance of MPC depends on its size and it should increase with increasing size. This size-tunable capacitance has been demonstrated using MPC of different sizes. The charging energy required to inject electrons into the gold core also depends on the size. While Chaki et. al.\textsuperscript{22} reported a 100 mV difference in each charging steps ($\Delta V$) for 3.7 MPC, Wolfe et al.\textsuperscript{23} had observed a 185 mV differences for 2.0 nm MPC in voltammetric results. These results illustrate that higher energy is required to charge small sized MPC. This behavior is dominant in smaller gold clusters. According to Lee et al.,\textsuperscript{24} 1.1 nm MPC exhibit wide gaps between charging steps in cyclic voltammetry and differential pulse voltammetry. This behavior is attributed to the molecule-like behavior of smaller MPC. Lee at. al. assigned the peak positions to HOMO and LUMO energy levels of the nanocluster. Therefore, electrons are being injected to HOMO and LUMO energy levels during the voltametry experiment. Figure 1-7 represents a generic diagram of the changes in the voltametry during the core size change.
Murray et al.\textsuperscript{12} has explained that the charged MPC can be isolated from the solution and can be used for further reactions. In addition, molecule-like $[\text{Au}_{25}(\text{SC}_2\text{Ph})_{18}]^{1-}$ has been employed as a metal ion sensor.\textsuperscript{25} The spectroscopic and voltammetric (Fig 1-9) response of MPC to addition of Cu$^+$, Ag$^{2+}$ and Pb$^{2+}$ have been monitored. An adduct formation with Ag$^+$ ions has been probed with mass spectrometry. This new finding has proven the possibility of using the molecule-like MPC for detection purposes.
1.3.3. Catalytic properties and applications

Initially gold nanoparticles were believed to be catalytically inert. Haruta\textsuperscript{26} discovered that the gold nanoparticles can be used as catalytic conversion centers for carbon monoxide (CO) oxidation. They used supported gold on manganese oxide surface. According to the findings, the adsorption of CO takes place at the metal-oxide interface but the catalytic reaction take place on the gold cluster. It was found that the nanoparticles are active when supported on metal oxide surface. This pioneering discovery stimulated substantial studies on heterogeneous gold catalysis using metal oxide support. Different methods of fabrication of gold clusters on metal surfaces\textsuperscript{27}
have been discovered and broad range of catalytic applications have been studied over the last decade.

Goodman et al. demonstrated the size-dependent catalytic properties of supported gold clusters towards oxidation of CO. They deposited nanoclusters from 1 to 6 nm on single crystal titania surface. It was found that the conversion efficiency of CO primarily depends on the size of the nanosized gold deposits and 3 nm size displayed the highest activity (Fig 1-7). Smaller and larger clusters have lower activities. A combination of scanning tunneling microscopy and kinetic studies has revealed that the quantum size effect plays a major role towards the CO oxidation efficiency.

![Graph showing size-dependent catalytic activity of gold titania towards oxidation of CO](image)

Figure 1-10 Representative schematic of size dependant catalytic activity of gold titania towards oxidation of CO
Supported gold catalysis became popular after this exploration. There are many research efforts that describes fundamental studies of the catalytic processes and applications.\textsuperscript{34-38} Gold nanoparticles also can be combined with photocatalytically active metal oxides such as titanium dioxide (TiO\textsubscript{2}) and this has become exciting and rapidly evolving area of heterogeneous catalysis research. According to current knowledge, gold nanoclusters dramatically improve the photocatalytic efficiency of a semiconductor. Further details will be discussed in the following sections.

### 1.4. Fundamentals of Gold Nanoparticle Synthesis

As has been repeatedly described previously, it is highly desirable to synthesize nanoparticles of various sizes while keeping uniform cluster sizes throughout the sample. Most synthetic routes suffer from the creation of a mixture of cluster sizes. Various reaction parameters have to be changed and manipulated in order to avoid the above obstacles. Therefore, a fundamental understanding of the cluster formation principles is extremely important.

There are two major approaches that can yield gold nanoclusters; physical methods and chemical methods. Physical methods fabricate nanoparticles by direct size reduction of bulk gold. Chemical routes generate nanoparticles by atomic gold precursors.

Metal vapor synthesis, laser ablation and digestive ripening methods are common physical routes.\textsuperscript{10} A major disadvantage of the physical preparations
is their inability to produce uniformly sized nanoparticles. This has become predominant, especially in the preparation of smaller sizes. In contrast, wet chemical procedures are much more versatile.

1.4.1. Fundamentals of chemical synthesis

In 1950 LaMer described a theory about cluster formation in solutions. His theory was based on the formation of sulfur sols, starting from the decomposition of sodium thiosulfate in hydrochloric acid. The results have been generalized elsewhere to describe the reaction kinetics of nanoparticle formation. The basic steps in the reaction are precursor formation, nucleation, growth and aging. Figure 1.10 illustrates the elemental steps during the solution phase method.

Figure 1.11 Precursor concentration during the nanoparticle synthesis
Precursor species are being formed until the nucleation threshold is reached. Intermediate precursors have been identified during thiol passivated gold nanoparticle synthesis. According to Jin et al., the precursors are bigger-sized aggregations of 100-400 nm. They speculate that these bigger clusters disintegrate after the addition of the reducing agent. In the gold nanoparticle synthesis reactions, the nucleation starts immediately after addition of the reducing agent, and the precursor concentration drops rapidly. Clusters undergo further growth by accumulation of the precursor and increase in nanoparticle size. Finally, the prepared clusters can be subjected to aging, coarsening or aggregation, depending on the nature of the reaction environment. In order to obtain monodispersed nanoparticles, the rate of the nucleation should be relatively higher than that of growth. If the nucleation rate is slow, the growth can be started at different times resulting in a broad range of sizes. Therefore, the fast addition of the reducing agent is important. Alivisatos et al. have shown the lower monomer concentration favors larger core sizes. In the case of gold nanoparticle synthesis, this phenomenon has been observed under low thiol ratio, i.e with low polymer precursor formation.
1.5. Photocatalytic Degradation of Environmental Pollutants

Inadequate access to clean water and sanitization is one of the most pervasive global challenges. Enormous amounts of pollutants are accumulated in inland and marine water bodies due to civilian and industrial activities. These chemicals include textile dyes, herbicides, pesticides and pharmaceutical compounds. These undesirable substances are toxic to aquatic life, microorganisms and human beings. Some of these species, such as dyes are released to water on a large scale. They reduce the visibility in aquatic environments and can be poisonous to aquatic organisms. The other category consists of the material occurring in trace levels but which have enormous toxic effects to humans. With the increase of the global population and its needs, these environmental concerns intensified every day. Therefore, there is a global demand for developing efficient methodologies to remove these pollutants.

Chemical, physical and biological environmental remediation methods have been introduced to address water purification and sanitization. Some of the physical methods are ultrafiltration, reverse osmosis, coagulation and ion exchange on synthetic resins. The major drawback of the physical method is that they just transfer material to another phase.
Chemical and biological methods aimed at complete destruction of the pollutants. Microbial or enzymatic degradation is carried out during the biological treatments.\textsuperscript{45} Ozonation is one of the chemical methods.\textsuperscript{46}

However, the traditional methods are chemically, energetically, and operationally intensive, involve large capital cost and require engineering expertise and infrastructure.\textsuperscript{47} Therefore the development of economically and environmentally favorable, non-sophisticated, inexpensive and robust methods is at high demand.

Advanced oxidation processes such as heterogeneous photocatalysis have been introduced to address the limitations and drawbacks of the conventional methods.\textsuperscript{48} These new methods involve formation of highly active species such as hydroxyl radicals, electrons or holes to perform effective detoxification of polluted water. Heterogeneous photocatalytic applications are popular because the complete mineralization of the materials takes place in mild conditions. Identification of current environmental pollutants and characterization of their chemical and biophysical nature is essential to the design of efficient photocatalytic materials. Depending of the nature of the pollutant material, the physiochemical properties of the photocatalyst can be tailored to achieve complete mineralization.

The photocatalytic activity of the photocatalyst towards a wide variety of pollutants has been analyzed and their chemical transformation routes have
been identified during the last several decades. The most fascinating feature of photocatalysis is its lower cost owing to the use of solar energy as the primary energy source for the degradation process. Usually, semiconductor materials with near ultraviolet band gap energies are used as the energy conversion centers. According to Beenackers et al.\textsuperscript{49} an efficient photocatalyst should be photoactive, able to utilize visible or near ultraviolet radiation, biologically and chemically inert, photostable, inexpensive and non toxic.

\subsection*{1.6. Semiconductor Photocatalysis}

Si, TiO\textsubscript{2}, AnO, WO\textsubscript{3}, CdS, ZnS, SnO\textsubscript{2}, WSe\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3} are some of the common photocatalytic materials.\textsuperscript{50} Even though each of these is technically viable for photocatalytic applications, some of them have some practical limitations. For instance, CdS and ZnO do not exhibit long term stability.\textsuperscript{50} Among the above mentioned semiconductor materials, TiO\textsubscript{2} has become the most widely used and most intensively studied material.\textsuperscript{43}

During photocatalytic reactions, the near ultraviolet region of the solar spectrum is utilized to trigger the electron-hole separation in semiconductor materials(Figure1-12). The resulting electrons and holes can be utilized to initiate further reactions. Most importantly, the reaction conditions can be manipulated in order to harvest electrons or holes depending on the requirement. These reactions are becoming popular because they can be carried out at ambient temperature. Most importantly, the process can
completely mineralize organic compounds producing carbon dioxide and other inorganic species as byproducts.

![Figure 1-12 Electron hole separation in a semiconductor](image)

1.6.1. TiO₂ as a photocatalyst

As mentioned previously, TiO₂ has been demonstrated to be the most technically viable photocatalyst. Choi⁵¹ has summarized the important features of TiO₂ that determines its versatility. TiO₂ can be used in water, air and solid phases to initiate reactions. TiO₂ is especially suitable for environment-related applications because it is an extremely stable, non-toxic, safe to handle and an inexpensive substance. Scientists have studied various research aspects of TiO₂ from its fundamental reaction kinetics and mechanisms to its various commercial applications.

The elemental steps of the photocatalytic processes take place in TiO₂ are summarized below. First, electrons are excited to the conduction band leaving
behind holes in the valance band (eq1). Electrons and holes can be recombined and the energy is released as heat (eq2). Holes are reacted with the hydroxyl ions or water molecules on the surface, creating hydroxyl radicals (eq3). Electrons are scavenged by the oxygen or any other reducing species in the solution medium (eq4).

\[
\begin{align*}
\text{TiO}_2 + \nuv &\rightarrow e_{cb}^- + h_{vb}^+ \quad \text{(1)} \\
e_{cb}^- + h_{vb}^+ &\rightarrow \text{TiO}_2 + \text{heat} \quad \text{(2)} \\
h_{vb}^+ + \text{OH}^- &\rightarrow \text{OH}^- \quad \text{(3)} \\
e_{cb}^- + \text{O}_2 &\rightarrow \text{O}_2^- \quad \text{(4)}
\end{align*}
\]

One of the fascinating features of TiO\textsubscript{2} is that its reactivity can be manipulated by changing the reaction environment. If oxygen is present in the reaction medium, it scavenges the electrons those are being generated during the reaction. As a consequence, holes/hydroxyl radicals are available for further reactions. This is called the 'oxidation path' because both holes\textsuperscript{52} and hydroxyl radicals\textsuperscript{53} are capable of oxidizing redox couples in the solution.

If the electrons are utilized to initiate further reactions, it is called the 'reduction path'. To harvest electrons, oxygen should be removed from the reaction environment and a hole scavenger, such as ethanol, should be added to the reaction mixture.
1.6.2. Improved photocatalysis with TiO$_2$ nanocomposites

Unfortunately, the photogenerated holes and electrons can undergo fast recombination. $^{54}$ This is a major limiting factor when using TiO$_2$ as a photocatalyst. It has been reported that the charge recombination can be minimized by combining TiO$_2$ with noble metals.$^{51,55}$ The role of gold,$^{56-58}$ silver,$^{59}$ platinum$^{51,60,61}$ and palladium$^{62}$ metal deposits have been investigated toward the enhancement of the photocatalytic activity of semiconductor materials. Figure 1-13 shows a schematic diagram of a semiconductor that in contact with gold nanoparticle.

![Figure 1-13](image_url)

**Figure 1-13** Enhanced photocatalytic reactivity of TiO$_2$ using MPC

When metals are closely associated with TiO$_2$, the excited electrons on TiO$_2$ can transfer to the metal due to the difference in the Fermi levels of metal and the semiconductor. The Schottky barrier between the semiconductor and metal nanoparticle can promote the electron transfer out of the TiO$_2$. Metal nanoparticles can act as a sink that accepts and accumulates electrons.
Due to the electron equilibration between metal and the semiconductor, the Fermi level of the composite system will move towards more negative potentials when the system is irradiated. These processes enhance the charge separation efficiency in TiO$_2$.

**Using gold-TiO$_2$ composites in oxidative pathway**

Kamat and workers have demonstrated the beneficial role of gold nanoparticles on TiO$_2$ for oxidative photocatalytic reactions. In that work, the photooxidation of a dye was carried out in the presence of a metal nanoparticle-modified TiO$_2$ electrode. The reactions are carried out in aqueous media in the presence of dissolved oxygen. In this case, oxygen behaves as an electron acceptor that facilitates the electron-hole separation by scavenging electrons. Therefore holes are being utilized to initiate further reactions by formation of hydroxyl radicals. The effective hole formation in TiO$_2$ in the presence of gold nanoparticles has been probed using a laser-induced charge-separation process.
Figure 1.14 Activity of Au-TiO₂ photooxidation in the presence of oxygen

Using metal gold-TiO₂ composites in reductive pathway

Metal deposits also can be used to enhance the reductive photocatalytic reactions. Agostino et al. have reported that the photodegradation efficiency of TiO₂ towards Uniblue A dye, can be increased by combining gold nanoparticles with TiO₂. Gold modified TiO₂ shows more efficient accumulation of conduction band electrons than regular TiO₂. Such reactions have to be carried out in the absence of oxygen, in order to use the excited electrons efficiently. Further, a known hole scavenger (ethanol) is introduced to the reaction mixture in order to facilitate the electron hole separation.
Figure 1.15 Activity of Au-TiO$_2$ photocatalysis in the absence of oxygen

1.7. Preparation of Metal Semiconductor Nanocomposites

The size, monodispersity, surface coverage and the aggregation resistivity of gold nanoparticles on the TiO$_2$ surface determine the overall photocatalytic activity of the composite system. Therefore, the design of well-defined nanocomposites, with control over the above parameters, is important. Chemical, electrochemical, photodeposition and deposition-precipitation methods are commonly used for the preparation of nano-sized metal clusters on metal oxide surfaces. A major drawback of using these techniques is that they do not exert control over the nature of the metal clusters formed on the semiconductor surface.
In recent years, there have been efforts to fabricate semiconductor-metal nanocomposites by immobilizing pre-synthesized nanoparticles on semiconductor films or nanoparticles. This approach can alleviate the drawbacks that occur during the in-situ reduction of metal on the semiconductor. Additionally, this method is convenient to achieve monodispersity, controlled size and tailored loading. Electrophoretic deposition methods can be used to deposit metal nanoparticles on TiO$_2$ films. In this approach, a film of TiO$_2$ is charged electrically, in order to attach metal nanoparticles dissolved in an organic medium. However, aggregations of metal nanoparticles and multi layer deposition have been encountered during these experiments.

Kamat et al. have utilized a simple adsorption method to functionalize TiO$_2$ films with gold nanoparticles. The TiO$_2$ electrode is functionalized by immersing it overnight in a nanoparticle suspension. Considerable aggregation and growth of gold nanoparticles was observed.

Gold MPC can be attached on TiO$_2$ by self-assembly, by utilizing two approaches. In the first approach, TiO$_2$ is modified with a bi-functional linker and then MPC are attached to it. In the second approach, MPC are modified with a bi-functional linker and attached to TiO$_2$. Zeng et al. have anchored MPC on TiO$_2$ surfaces utilizing the first method (Figure 1.16), by functionalizing TiO$_2$ surface with HSCH$_2$CH$_2$COOH. COOH strongly binds
with TiO₂. When MPC are mixed with TiO₂ solution, they are immobilized on the surface of TiO₂. The final composites have shown a uniform dispersity of MPC on the TiO₂ surface.

![Diagram of MPC self-assembling on TiO₂](image)

Figure 1-16 Self-assembling of MPC on TiO₂

Since capping ligands behave as a barrier toward electronic communication between two materials, the surface ligands may be thermally removed in order to optimize the activity. It was found that, during the removal of tiopronin ligand by thermal treatment, the resulting decomposed sulfur can act negatively on the catalytic activity of TiO₂ by poisoning the active sites. Usually, the percentage of the metal on TiO₂ is less than 5%. Therefore, in this method the TiO₂ has a large excess of ligands on the surface. Therefore, the best possible method of attaching MPC on TiO₂ is by passivation of MPC with a bi-functional ligand during the first step and then attaching them to TiO₂. Fig 1-17 is a schematic representation of this method. X is the
functional group that has affinity towards TiO$_2$. A minimum number of ligands are involved in following this protocol. Even if the ligands are removed by thermal treatment, a minimum amount accumulates on the surface.

Figure 1-17 Attaching MPC on TiO$_2$

In brief, metal nanocomposite materials have great importance. The synthesis of structurally well-defined metal-semiconductor nanocomposites by immobilizing pre-synthesized metal nanoparticles on the semiconductor colloids still remains a great challenge.

1.8. Overview of the Following Chapters

Developments of methodologies that can control the composition and the dimensions of the nanosystems, has enormous interest. The primary goal of the research is to design well-defined nanoscale materials towards environmental applications.
Second chapter describes the synthesis of uniform gold MPC of 1.7 to 4.9 nm. Their characterization with fundamental physical and chemical properties will be discussed.

Chapter 3 aims at designing a gold semiconductor composite material for photocatalytic applications. Gold-semiconductor material can be utilized to perform oxidative and reductive catalytic reactions by changing the reaction environment. Chapter 3 also focuses on testing composites to initiate oxidative degradation of a textile dye called Uniblue A.

Chapter 4 outlines the applicability of the nanocomposite towards oxidative reactions. The photocatalytic activity is probed by utilizing a laser dye called Rhodamine 590 (Rd 590).

Chapter 5 focuses on an application of the composite material. The degradation of a pharmaceutical material called naproxen are discussed and the photocatalytic byproducts of the reaction are analyzed by chromatographic techniques.
1.9. References

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CHAPTER 2

SYNTHESIS OF GOLD MPC

2.1. Introduction

Since the optical, chemical, physical and catalytic properties of MPC vary according to their size,\(^1\) it is important to synthesize different sizes of MPC. Larger gold nanoparticles have properties similar to those of the bulk metal. Smaller nanoparticles exhibit molecule-like properties. It has been demonstrated previously that the metal to molecular transition of the nanoparticles takes place in the size region of 1 nm to 5 nm. Therefore the synthesis of gold monolayer clusters having above dimensions is important. Despite the existence of various protocols toward the synthesis of metal nanoparticles, the one-phase and two-phase Brust \(^2\) method has gained the most favor owing to its ability to give synthetic control over particles size, dispersity and surface functionality. \(^3\) Most importantly, this method gives highly stable MPC that have dense monolayers of surface ligands. These MPC can be dried and re-dissolved in solvents without aggregation. The original Brust reaction yields MPC that are passivated with linear alkanethiols. Therefore, these MPC only can be dissolved in non polar organic solvents. This is one of the limitations of these nanoclusters. Water solubility is a major requirement of any kind of nanomaterial when it comes to biological applications.\(^4\) Researchers have tried to modify the solubility of
MPC by performing place exchange reactions with some ω-functional molecules. But, these efforts were unsuccessful due to the low solubility of the resulting clusters. Therefore, there is a great demand for synthesizing water-soluble MPC using the fundamental concepts of the Brust synthesis. In 1998, Whetten et al. reported water-soluble MPC passivated with the tripeptide glutathione (N-γ-glutamyl-cysteinyl-glycine). They demonstrated that the reduction reaction can be performed in one phase in a water/methanol mixture. Au$_{25}$(SG)$_{16}$ (SG=glutathione) MPC were isolated by gel electrophoresis, and characterized by NMR, UV visible spectroscopy and mass spectroscopy. Importantly, the resulting MPC can be solubilized in water due to the highly hydrophilic nature of the ligand. In 1999, Murray et al. also synthesized water-soluble MPC with tiopronin and Coenzyme A ligands. With this approach, they obtained gold MPC that have core diameters from 1.8 to 3.9 nm with moderate monodispersity. The size of the MPC was controlled by manipulating the gold:ligand ratio and the reaction temperature. They adapted two different methods during the synthesis protocol. Coenzyme A and tiopronin used as the capping ligands. Murray et al. summarized the capability of using numerous protecting ligands, during the Brust method. Kornberg et al. have further proven this possibility by making water-soluble MPC by using 36 organothiolate ligands. These ligands include alcohols, carboxylic acids and proteins. They obtained MPC from 1.4 to 4.0 nm by changing the passivating agent.
Although the average size distribution can be controlled by changing the gold:ligand ratio and the reaction temperature, the above protocols do not yield monodisperse nanoparticles. Previously, near-monodisperse MPC were obtained by utilizing gel electrophoresis\(^6\) and size-exclusion chromatography.\(^9\) These experiments involve sophisticated instrumentation and they are time consuming. Also, these procedures cannot be used in large scale synthesis. Therefore, the development of new strategies to fractionalize different sizes of MPC using straightforward methods is at great demand.

Purification is another important reaction step during the synthesis of MPC. In the initial efforts at a water-soluble gold nanoparticle synthesis, dialysis has been used as the purification method.\(^7\) This is a time consuming process and it also cannot be extended to large scale synthesis. It has been found that the solubility of MPC depends on their size. Therefore, fractionation and the purification of the final product can be achieved through a careful selection of the solvents.\(^6,10,11\) Recrystallization\(^11\) and extraction\(^12\) methods have been used to separate fractions of MPC. During the recrystalization, MPC are dissolved in a solvent that completely solubilize them. Secondly a non-solvent is added slowly, until a cloudy suspension is obtained. When it allows settling down for some time, a fraction of MPC can be obtained as a precipitate. Usually the precipitate consists of bigger sizes. The precipitate is separated by decantation of the supernatant solvent and further addition of non-solvent
gives more fractions of MPC with different sizes. The extraction process also make use of the solubility of MPC in different solvents. Here, the MPC are dried until it solidifies and a solvent is added that is capable of dissolving a particular size.

During this research effort, one-phase Brust method was used in order to synthesize gold-MPC-passivated by tiopronin molecules. Tiopronin is a pharmaceutically important molecule due to its usage in the treatment of cystinuria and rheumatoid arthritis.\textsuperscript{5}

It has a carboxylic end group and an amine group that facilitate solubility in water and in other biological fluids. Synthesis of tiopronin-stabilized MPC of different sizes is important because they can be used in pharmaceutical applications. Different sizes of MPC from 1.7 nm to 4.9 nm have been obtained by altering the reaction parameters. Most importantly, highly monodisperse MPC have been synthesized by the careful selection of solvents.

\begin{center}
\includegraphics[width=0.5\textwidth]{tiopronin.png}
\end{center}

\textbf{Figure 2-1 Tiopronin}
2.1.1. Brust synthesis: Mechanistic aspects

Two major steps are involved in the Brust reaction. Elementary steps of the reaction are described in Figure 2-2 and equations 1 and 2.

\[
\text{Au}^{II} \rightarrow \text{Au}^{I} \quad 1 \\
\text{Au}^{I} \rightarrow \text{Au}^{0} \quad 2
\]

Figure 2-2 Reaction steps involved in the synthesis of MPC

In the first step, gold salt (AuCl₄⁻) is mixed with the capping molecule (RSH). The stirring reaction will form a polymer. Sodium borohydride is introduced to the reaction mixture in the second step which in turn produces MPC by reducing Au¹ to Au⁰.

\[
\text{AuCl}_4^- + \text{RSH} \rightarrow (-\text{Au}^+\text{SR}^-)_n \ldots \ldots (1)
\]

\[
(-\text{Au}^+\text{SR}^-)_n + \text{BH}_4 \rightarrow \text{Au}_x(\text{SR})_y \ldots \ldots (2)
\]

Murray et al.⁸ showed which the reaction is taking place in the nucleation-growth-passivation process. The reaction also follows some fundamental
mechanistic aspects that are useful in manipulating the reaction conditions to generate different sized MPC with various molecular capping moieties. These reaction behaviors are (i) larger thiol:gold mole ratios give smaller core sizes (ii) fast reductant addition and cooled solutions produce smaller, more monodispersed MPC (iii) quenching the reaction immediately following reduction produces a higher abundance of very small core sizes.

When the sodium borohydride is introduced to the reaction mixture, it triggers growth followed by the passivation process. If the reaction mixture contains large amount of thiols, that promotes the passivation process and hinders the growth process. This reaction condition will yield smaller MPC. Following the same phenomenon, smaller thiol concentrations will produces larger MPC.

Temperature also plays a vital role during the synthesis. While low temperatures yield smaller MPC, higher temperatures produce larger sizes. The other important parameter is the speed of the addition of the reducing agent. When the reducing agent is added faster, the reduction of the entire mixture takes place simultaneously, yielding monodispersed particles. The reaction temperature was controlled to harvest MPC of different sizes.
2.1.2. Characterization of MPC

Numerous techniques have been used for the characterization of the metal core and the self-assembled organic monolayer on MPC. Atomic force microscopy, scanning tunneling microscopy, transmission electron microscopy (TEM), X-ray diffraction and mass spectrometry have been used to elucidate the characteristics of the metal core. Among them, TEM is the most extensively used technique, where a beam of electrons are passed through a thin layer of MPC which are immobilized on a metal grid. This method gives the diameter and the shape of the metal core but no information about the ligands can be obtained.

X-ray photoelectron spectroscopy, nuclear magnetic resonance spectroscopy (NMR), thermogravimetric analysis and infrared spectroscopy have been implemented to determine the nature of the organic monolayer. Particularly, $^1$H and $^{13}$C NMR are important for determining the interactions of the individual ligands with the metal core and to recognize the ligand-ligand interactions. Finally, UV visible spectroscopy is utilized to get a fundamental understanding of the overall metal-ligand assembly. Even though it is a simple technique, it is very useful in the characterization of larger nanoparticles that have SPR absorption and to characterize molecule-like smaller nanoparticles. In the present study, tiopronin-protected MPC
have been characterized by employing NMR, UV visible spectroscopy and TEM techniques.

2.2. Experimental

2.2.1. Materials

Gold(III) chloride trihydrate (ACS reagent), tiopronin, acetonitrile, Sodium borohydride and methanol were purchased from Sigma Aldrich.

2.2.2. Synthesis methods

Synthesis of 1.7 nm MPC

0.3 g of HAuCl₄·3H₂O was dissolved in 35 ml of methanol/acetic acid mixture in an Erlenmeyer flask. The resulting solution was cooled to 0 °C in an ice bath for 30 min with continuous stirring. 0.6 g of tiopronin was added to the flask and stirring was continued for another 3 hours in the ice bath. When tiopronin was introduced, the color of the solution changed from yellow to ruby red. During the course of 3 hours the color intensity gradually decreased and finally a colorless solution was observed, confirming the formation of the polymer. The stirring speed was increased and 0.3 g of NaBH₄ (dissolved in 30 ml of ice cold water) was added to the reaction mixture rapidly. A black colored suspension was formed and reaction continued for another one hour at 0 °C. The flask was removed from the ice bath to allow it to come to the room temperature. Stirring was carried out overnight in an oil bath and the temperature was maintained at 40 °C. The solution was dried with rotary
evaporation and the resulting precipitate was dissolved in a small amount of water. 1.7 nm gold MPC was separated by recrystallization in a water :acetonitrile mixture.(pure acetonitrile behaves as a non-solvent for MPC). The first residue was discarded since it contains aggregated and bigger sized MPC formed during the reaction. The second residue was collected, dried and purified by washing several times with acetonitrile. The resulting MPC ware dried in vacuum and stored in the freezer.

Synthesis of 2.2 nm MPC

In a typical reaction, 1.85 g (4.69 mmol) of tetrachloroauric acid and 4.85 g (29.7 mmol) of tiopronin were co-dissolved in 211 ml of 6:1 methanol:acetic acid mixture giving a ruby red solution. This was stirred for 1 hour. The color gradually faded and the solution turned to colorless. Sodium borohydride 3.59 g (94.8 mmol) dissolved in 190 ml of H₂O was added with rapid stirring. Further stirring was carried out for another 45 min. The solvent was then removed under vacuum at 38 °C. The black precipitate was dissolved in methanol and the supernatant was removed. It was further washed with acetonitrile 3 times. The MPC ware extracted with methanol several times. The purity of the final product was tested with NMR spectroscopy. The average size of the MPC was 2.2 nm according to TEM images.
Synthesis of 3.0 nm MPC

0.3 g of HAuCl₄·3H₂O was dissolved in 35 ml of methanol/acetic acid mixture in an Erlenmeyer flask. While continuously stirring, 0.3 g of tiopronin was added to the flask and the stirring was continued for another 5 hours at room temperature. After the addition of tiopronin, the solution color changed from yellow to ruby red. During the course of 5 hours, the color gradually decreased. The stirring speed was increased and 0.133 g of NaBH₄ (dissolved in 16 ml of water) was added to the reaction mixture rapidly. A black colored suspension was formed and reaction carried out for another 20 hours at room temperature. The solution was evaporated under the vacuum and resulting precipitate was dissolved in 5 ml of water. MPC were separated by recrystallization in water:acetonitrile mixture. The initial two residues were discarded since they were black precipitates. The third residue was collected, dried and purified by washing several times with acetonitrile. The resulting MPC were dried in vacuum and stored in the freezer.

Synthesis of 4.9 nm MPC

0.3 g of HAuCl₄·3H₂O was dissolved in 35 ml of methanol/acetic acid mixture in an Erlenmeyer flask. While stirring, 0.128 g of tiopronin was added to the flask and the stirring was continued for another 5 hours at room temperature. After the addition of tiopronin, the solution color changed from yellow to ruby red. During the course of 5 hours, the intensity of the color
decreased. The stirring speed was increased and 0.025 g of NaBH₄ (dissolved in 30 ml of water) was added to the reaction mixture rapidly. A black colored suspension was formed and the reaction carried out for another 20 hours at room temperature. The solution was evaporated under the vacuum and resulting precipitate was dissolved in 5 ml of water. This MPC showed different solubility compared to above synthesis procedures; i.e. the resulting MPC were soluble in acetonitrile and it could not be used as a non-solvent for the recrystallization process. 1,4-dioxane was used instead of acetonitrile in this method. The MPC was separated by recrystallization in water:1,4-dioxane mixture. The initial residue was discarded since it was a black precipitate. The second residue was collected, dried and purified by washing several times with 1,4-dioxane. The resulting MPC dried in vacuum and stored in the freezer.

**Transmission Electron Microscopy**

TEM samples were prepared by placing a drop of diluted aqueous nanoparticle solution onto a carbon-coated Formvar copper grid (Electron Microscopy Sciences, Hatfield, PA). The sample was dried in vacuum for several hours to remove excess water. TEM images were obtained via a GEOL 1230 Electron Microscope operating at 80 KeV.
Spectroscopic measurements

UV visible spectra of a diluted aqueous solution in 1 cm quartz cuvette were recorded with a Perkin Elmer Lambda 40 Spectrometer. Proton NMR spectra were recorded at 400 MHz on a GEOL Eclips 400 FT NMR Spectrometer at room temperature. D₂O was used to dissolve the MPC for NMR measurements.

2.3. Results and Discussion

2.3.1. Synthesis of tiopronin MPC

<table>
<thead>
<tr>
<th>Size of MPC</th>
<th>1.7 nm</th>
<th>2.2 nm</th>
<th>3.0 nm</th>
<th>4.9 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiol:Au Ratio</td>
<td>5:1</td>
<td>5:1</td>
<td>2.3:1</td>
<td>1:1</td>
</tr>
<tr>
<td>NaBH₄:Au Ratio</td>
<td>9:1</td>
<td>10:1</td>
<td>4:1</td>
<td>0.8:1</td>
</tr>
<tr>
<td>Reaction Temperature</td>
<td>0 °C</td>
<td>RT</td>
<td>RT</td>
<td>RT</td>
</tr>
</tbody>
</table>

Table 2-1 Summary of the reaction conditions

(RT: room temperature 25 °C)

Table 2-1 summarizes the results and the reaction conditions of the nanoparticle synthesis procedure. It is well-known that the average size and
the size dispersity of the MPC are mainly controlled by the relative rates of nucleation and growth. In the current synthesis, the formation of smaller-sized particles is facilitated by higher thiol ratios. In the presence of high thiol concentration, the passivation reaction dominates and it does not allow nanoparticles to grow to bigger sizes. The NaBH$_4$ ratio and the reaction temperature at which the reduction is carried out, also plays a major role. A higher concentration of NaBH$_4$ enhances the nucleation and a large numbers of smaller particles are formed before they are subjected to passivation. The opposite phenomenon happens for the lower concentrations of NaBH$_4$. Rate of nucleation is a factor of temperature. Lower temperatures hinder the nucleation process, resulting in smaller colloids. Higher temperatures facilitate the nucleation process that leads to the formation of bigger sized clusters.

Figure 2-3 to Figure 2-6 show the TEM images of different sized MPC with their standard deviations of the size distributions. During the synthesis process of MPC of 1.8 nm, 2.2 nm and 3.0, Murray et al. observed standard deviations of ±0.7, ±1.0 and ± 1.2 nm respectively. The present method gives promisingly monodispersed MPC compared to the previous work. Variation of the standard deviations in the different sizes shows that the monodispersity decreases when the cluster size increases. According to Table 2-1, tiopronin concentration was reduced to obtain larger core sizes.
Figure 2-3 TEM image of 1.7 nm gold nanoparticles (magnification: 600K)

Figure 2-4 TEM image of 2.2 nm gold nanoparticles (magnification: 500K)
Figure 2-5 TEM image of 3 nm gold nanoparticles (magnification: 600K)

Figure 2-6 TEM image of 4.9 nm gold nanoparticles (magnification: 500K)
2.3.2. UV visible spectroscopic results of MPC

Figure 2-7 UV visible spectral comparison of MPC indicates a drastic decrease in the SPR band with the decreasing cluster size. Al-sayed et al.\textsuperscript{15} described the existence of the SPR band of the metal particles and its variations with the size. They mentioned that the position of the SPR band is not a function of the size of the nanoclusters according to the fundamental discussion by Mia theory. But the nanoclusters below 20 nm falls within a special category that the dielectric function is changed with the size, which in turn changes the nature of the SPR band. In the present case, 4.9 nm MPC show more metal like characteristics. Its conduction band
is rich with electrons that can be polarized with incoming light. The 3.0 nm particles have less intense SPR bands owing to their lack of delocalized electrons in the conduction band. The 1.7 nm and 2.2 nm particles do not posses enough polarizable electrons to exhibit surface plasmon resonance. According to the previous discussion, the small MPC are considered to be molecular clusters with localized electrons. This drastic change of the absorption spectra of MPC of the 1.0 to 5.0 nm region have been also noticed previously by Hassain et al. They also have observed the disappearance of the SPR band upon decreasing of the cluster size.

Since the four samples are spectroscopically distinctive, this also strongly supports the proposal of a narrower size distribution in each case. For example, the 2.2 nm sample dos not have any SPR band indicating the absence of the larger core sizes. Even though the TEM results show the size distributions of the small fractions of the sample, bulk measurements like UV visible spectroscopy play a vital role to draw the overall picture of the size distribution.

2.3.3. Characterization of organic monolayer

Multiple techniques have been employed to study the composition and the nature of the organic monolayer. During the initial stages of the characterization of MPC, TEM is carried out in order to obtain a general picture about the core size and this will help to predict the possible number of
ligands on the surface. The number of ligands per core is calculated by using thrmogravimetric analysis. This technique gives quantitative information about the number of organic chains present on the metal surface by calculating weight loss during the thermal treatment. Currently, mass spectrometry has been extensively used to calculate both the organic and metal portions of the clusters. This method gives precise information about weight and the composition of the MPC.

In the typical arrangement, thiols are expected to bind to the Au core by a covalent bond formation. Several modes of bond formation have been postulated. Bardia et al. have investigated the bond formation between gold and sulfur in gold nanoparticles. Utilizing $^{13}$C NMR spectroscopic measurements, they concluded that it is a "thiolate" type bond (Figure 2-8) and not a disulfide.

![Figure 2-8 Thiolate bond formation between gold and linear thiol molecules](image)

MPC with linear alkanethiols have been used in investigations of the nature of the capping monolayer. When a monolayer of thiols is immobilized on a
nanoparticle, their chemical characteristic are expected to be different from those of the solution phase, and of the free molecule. This is attributed to the interactions among alkane chains and the interaction between alkane chains and the metal surface. In particular, the bond formation between gold and sulfur is a vital factor in the determination of the chemical environment of the alkane chains. The NMR chemical shift positions of the alkanethiol monolayers are different from that of the free molecules. An intermediate situation can be expected in the case of MPC. The NMR spectra of the MPC exhibit considerable downfield shifts and peak broadening. The downfield chemical shift has been assigned to the Au-S interactions.  

When the ligand arrangement on the gold surface is considered, the carbon and hydrogen atoms closer to the metal core are more affected by the metal core and Au-S bonding. In the case of octanethiol passivated gold nanoparticles (Figure2-9), the chemical shift peaks due to 1 and 2 carbon atoms has vanished due to strong interaction between the metal core and the organic monolayer. Also, the broadening effect and the changes in the chemical shifts become significant towards the sulfur end. These changes of the NMR spectra have been assigned to a discontinuous change in the magnetic susceptibility at the metal-hydrocarbon interface.
NMR peak identification

In the present study, tiopronin-stabilized gold MPC were analyzed using $^1$H NMR spectroscopy. MPC was dissolved in D$_2$O and the NMR spectra were recorded at room temperature. $^1$H NMR spectra of unbound tiopronin and 1.7 nm MPC are shown in Figure 2-10 and the peaks can be assigned as follows.

Figure 2-10 $^1$H NMR spectra of tiopronin and 1.7 nm MPC dissolved in D$_2$O

Figure 2-9 Au core passivated with octanethiol ligand
In the free molecule, the doublet at 1.4 ppm arises due to the terminal CH$_3$ group (C5), the quartet at 3.6 ppm is due to CH group (C4) and the singlet at 3.94 ppm is due to CH$_2$ group (C2).

The chemical shift information of pure tiopronin and the literature studies were used to assign the peaks for the 1.7 nm MPC. $^1$H NMR of the 1.7 MPC consist of two broad peaks. The broadness of the peaks are mainly attributed to the discontinuity of the magnetic susceptibility at the gold thiol interface.$^{16}$ There are several factors that can be considered to rationalize peak broadening: (a) the tiopronin molecules attached to the metal core exhibit closely packed monolayer structure and are anticipated to behave like a solid structure. Therefore they experience a fast spin-spin relaxation due to dipole interactions.$^{17}$ This behavior is expected to be more intense for the atoms closer to the core. (b) The broadness of the peaks also arises due to chemical shift differences of the binding sites that occur due to the nonspherical nature of the nanoparticles. $^{17}$ According to the high resolution electron microscopic investigations, smaller gold nanoclusters have compact, faceted crystalline gold cores rather than a spherical shape.$^{23}$ Au-thiol binding may occur at the terraces, edges, or vertices of the non-spherical MPC core. Atoms at various sites have different interactions. This effect also falls off rapidly with the distance of the metal core.
The broad chemical shift signal at 1.6 ppm is attributed to terminal CH$_3$ group. The sharp peak at 2.0 ppm is probably due to a minute amount of water in the sample. There are two signals at 3.7 ppm and 3.9 ppm respectively due to CH and CH$_2$ protons.

A small doublet appears on the top of a broad CH$_3$ peak at 1.7 ppm which is similar to the peak position for terminal methyl group of free tiopronin. This may be attributed to the loosely bound monomer or dimer of the tiopronin molecules attached to MPC during the synthesis process. One of the noticeable spectral features is that the CH proton peak is not broadened as expected. This suggests that the CH proton site is sterically blocked (Figure 2-11). Its behavior is inconstant with that expected for a close packed structure. As shown in Figure 2-11, the position of the ligand attachment to the gold core created this situation. In fact, the same phenomenon has been observed previously with CH group of tiopronin-capped Au MPC.

![Figure 2-11 Sterically blocked methylene proton](image)

Figure 2-11 Sterically blocked methylene proton
NMR comparison of MPC

Figure 2-13 shows the $^1$H NMR spectra of MPC from 1.7 nm to 4.9 nm. The sharp peak at 1.9, 2.06 and 2.67 ppm in NMR spectra might be due to the solvent contamination of acetic acid, acetonitrile and dimethyl sulfoxide, respectively. The 4.9 nm MPC exhibit broader peaks compared to 1.7 nm MPC. The bigger clusters are expected to have densely packed thiol layer which is similar to the self-assembled thiol layer on a gold surface. Therefore, the broad peaks arise due to spin-spin relaxation. The close-packed thiol arrangement does not exist in the smaller clusters due to its curvature. Less broadened peaks occur as a result. The difference in the tumbling dynamics also contribute to the difference between the NMR spectra of the two species.

Figure 2-12 Thiol ligand arrangement on 1.7 and 4.9 nm MPC
Figure 2-13 Comparison of the $^1$H NMR spectra of different sized MPC
2.3.4. Luminescence properties of MPC

Optical measurements of the nanomaterials are vital for the determination of their chemical and physical characteristics. The optical properties of the nanoparticles occur primarily due to the core characteristic of the system. But the core structure, ligand structure and core ligand interactions have to be considered in order to rationalize the overall optical phenomenon. Small sized semiconductor and metal clusters exhibit discrete energy levels, due to the quantum confinement effect, and show fluorescence in the presence of electromagnetic radiation. Two fluorescence emission bands can be observed in certain nanocrystals, one from the band edge and the other one from the recombination at the interband gap defect sites at the surface.

Figure 2-14 Typical energy diagram of small sized nanoparticle
The second phenomenon is called the trap emission and it occurs at higher wavelengths of the spectrum. Trap states are surface energy states that can be occupied by charge carriers. Since the trap states are uneven and have dissimilar range of energy levels, usually the trap emission appears as a broad peak.

Luminescence from gold nanoclusters has gained considerable attention. The quantum efficiency of the gold metal films is very small, according to Mooradian\textsuperscript{27} who investigated the photoluminescence of the metals several decades ago. In contrast, the luminescence of the metals of nanometer dimensions have been reported as several orders of magnitudes higher than that of the bulk metals.\textsuperscript{28,29} Whetten et al.\textsuperscript{29} observed the emission of thiol protected MPC and he assign this near IR region fluorescence to an inter-band transition from sp to d orbitals. Link et al.\textsuperscript{30} encountered two emission peaks and he assigned one to a sp to d band recombination emission and the other one at lower wavelengths to intra-sp band transition. Recently, Murray et al. have further probed low energy region emission and found that the emission does not change with the nanoparticle size, but varies with the capping ligand and the core composition of the monolayer-protected cluster.\textsuperscript{31,32} Therefore, this luminescence has been conclusively identified as a trap state emission.
In the current study, a preliminary investigation of the luminescence was carried out with MPC dissolved in Mili-Q water. The solution concentration was adjusted to give a 0.2 absorbance around 500 nm. Therefore, all the MPC absorb the same amount of radiation (photons).

Figure 2-15 Emission from tiopronin MPC

Figure 2-15 shows that the emission intensity decreases with the increasing core sizes. While 1.7 nm MPC show an intense signal, no fluorescence signal from 4.9 nm MPC was observed. Although the absorbance spectral characteristics of these MPC differ widely, the emission spectra of all 3 MPC
lie in the same energy range. Reports on studies of the MPC of similar sizes to the MPC of current synthesis\textsuperscript{33} have revealed that they have different optical band gaps. According to the fundamental quantum confinement viewpoint, the band gap increases with decreasing size. If the above emission is due to the band gap emission, there should be a correlation between the emission energy and the size of MPC. The core size independent emission reflects the participation of surface trap states in this optical phenomenon. Further, the core-size-independent fluorescence also has been observed previously with Au\textsuperscript{32} and Ag\textsuperscript{31} MPC. In addition, the broadness of the emission peak also confirms the involvement of surface trap states.

Excitation spectra of MPC also were recorded in the above aqueous solution.

![Figure 2.16 Excitation spectra of MPC](image-url)
According to Figure 2-15, excitation is taking place in an abroad range and it shows no resemblance to the absorbance profile of MPC. They are relatively flat and the two peaks appear at 385 nm. This indicates that the excitation is not associated with surface plasmon phenomenon. The polarity of the capping ligand is important for the trap state emission. It has been found that the emission linearly increases with the amount of polar ligands on the gold surface.\(^{32}\)

The decrease of fluorescence intensity with the core size is due to the available trap states of the particle. The surface to volume ratio increases with the decreasing core size. Therefore the 1.7 nm particles have higher surface states compared to the 2.2 nm and the 3.0 nm. The 4.9 nm MPC have metal like properties and very low emission can be expected,\(^{27}\) compared to smaller sizes. The sensitivity of the instrument of the current setup is insufficient to see the emission.

2.4. Conclusions

Synthetic strategies have developed to obtain 4 different sizes of gold MPC by manipulating reaction conditions such as gold:thiol ratio, reduction temperature and gold:NaBH\(_4\) ratio. Synthesized gold MPC have higher monodispersity compared to previous approaches. Cluster sizes have been measured by TEM and the fundamental chemical and physical properties have been measured by UV-Visible spectroscopy, NMR and
spectrofluorometry. According to the findings, the characteristics of the metal particles depend on their size. This MPC could be useful to various applications such as catalysis.
2.5. References


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CHAPTER 3

SYNTHESIS OF NANOCOMPOSITE AND REDUCTIVE PATHWAY

3.1. Introduction

TiO$_2$ is the most popular semiconductor material, because it is non-toxic, safe to handle and low in cost.$^{1,2}$ TiO$_2$ films and TiO$_2$ nanoparticles have been used as a photocatalysts for degradation of various organic compounds and heavy metal ions $^{3-5}$. As described previously, metal nanoparticles can enhance the photocatalytic activity of TiO$_2$.$^6$ While acting as a sink for the photogenerated electrons, the metal deposit on the semiconductor surface also can behave as a redox center for catalytic reactions, facilitating the photoelectron transfer to a solution-phase redox couple. Conventional metal deposition methods do not yield well-defined metals deposits or metal nanoparticles on TiO$_2$ surface. The other important factor is the controllability of the number of metal clusters per TiO$_2$ particle, which in turn determines the activity of the final system.

The initial phase of this chapter is focused on designing well-defined TiO$_2$-gold nanocomposites with different loadings of gold nanoparticles on TiO$_2$. The second phase of the chapter describes the measurements of the reductive photocatalytic degradation activity of the composites towards a textile dye called Uniblue A. Further activation of the composites by thermal treatment also will be discussed.
3.1.1. Thermal activation of TiO$_2$-metal nanocomposites

It has been demonstrated that the capping ligand or the shell structure around the metal nanoparticle also play a vital role in interparticle and interfacial surface access properties. There are number of research approaches focused on further activation of metal-semiconductor nanocomposites by removing the capping ligand in a controlled manner. Electrochemical and thermal activation processes have been reported.

In the case of thermal activation, it has been found that the heating of nanoparticles in the temperature range of 200-300 °C can effectively remove the capping organic materials. Zhong et.al. have reported the thermal activation of molecularly wired, supported, gold nanoparticles towards electrooxidation of methanol. Decanethiol capped gold nanoparticles were immobilized on a substrate and the molecular passivation layer was monitored by atomic force microscopic (AFM) imaging. A combination of thermogravimetric analysis and AFM imaging revealed that controlled removal of the ligand monolayer can be achieved by thermal treatment.
3.1.2. Importance of Uniblue A and its degradation

Textile dyes and other industrial dyestuff constituents have been identified as the major organic compounds that pollute the aquatic ecosystems.\textsuperscript{12} About 1-20% of the total dye production is discharged as industrial effluents. These dyes cause serious environmental problems.

Uniblue A (UBA) is a predominant constituent in wastewater-polluted with textile dyes. UBA has been found in textile wastewater systems where C.I Reactive Blue 19 has been used during the dying process.\textsuperscript{13} C.I Reactive Blue 19 is used to dye cellulosic substrates and it is one of the largely used textile dyes in the market. In fact, UBA is the vinyl sulfone form of C.I Reactive Blue 19. UBA has a complicated molecular structure consist of amine, sulfone and quinoid moieties.

![Molecular structure of Uniblue A](image)

Figure 3-1 Molecular structure of Uniblue A
Oxidative and reductive \textsuperscript{14,15} degradation of UBA has been reported. Detailed analysis has been carried out during the photocatalytic degradation through an oxidative pathway.\textsuperscript{13} Three possible pathways have been identified. According to NMR and LC-MS analysis, these pathways are initiated by one electron oxidation of the 1,4-diamino moiety. Radical coupling mechanisms and further oxidation of the byproducts of the initial oxidation products lead to complete degradation under the aerobic conditions.

Even though detailed mechanistic studies have not been done, UBA is expected to be degraded during the reductive pathway, by consecutive reduction of the carbonyl groups in the antraquinoic moiety.\textsuperscript{15} The reduction process will sequentially yields semiantraquinoic and hydroantraquinoic derivatives. Unmodified TiO\textsubscript{2} and modified TiO\textsubscript{2} with silver clusters have been employed during the reductive degradation studies. Dye degradation studies were carried out in a homogeneous organic media.

\textbf{3.2. Experimental}\n
\textbf{3.2.1. Materials}\n
Gold(III) chloride trihydrate (ACS reagent), tiopronin, acetonitrile, Sodium borohydride and methanol were purchased from Sigma Aldrich. TiO\textsubscript{2} nanoparticles (Degussa P25) was purchased from Acros Organics. Acetic acid (A.C.S grade) was purchased from J.T.Baker. Uniblue A sodium salt was purchased from Sigma Aldrich.
3.2.2. Experimental Methods

Preparation of monolayer-protected gold clusters

2.2 nm gold MPC were prepared according to the synthetic procedure mentioned in section 2.2.2.2. In a typical reaction, 1.85 g (4.69 mmol) of tetrachloroaauric acid and 4.85 g (29.7 mmol) of tiopronin were co-dissolved in 211 ml of 6:1 methanol: acetic acid mixture giving a ruby red solution. This was rapidly stirred for 1 hour. The color gradually fades and the solution turned to colorless. Sodium borohydride 3.59 g (94.8 mmol) dissolved in 190 ml of H2O was added with rapid stirring. Further stirring was carried out for another 45 min. The solvent was then removed under vacuum at 38 °C. The black precipitate was dissolved in methanol and the supernatant was removed. It was further washed with acetonitrile 3 times. MPC were extracted with methanol several times until the final extraction contains no MPC.

Preparation of the photocatalyst and characterization

TiO2 nanoparticles were dispersed in a 1:1 Milli-Q water: methanol mixture by simultaneous shaking and sonicating for 30 seconds prior to the anchoring reaction. TEM was carried out by applying a drop of TiO2 suspension onto a carbon coated copper grid. The primary size of the TiO2 nanoparticles is ca. 20 nm and they are cubic in shape, according to TEM measurements (Figure
3-2). Individual nanoparticles were clearly distinguished but several nanoparticles were attached to form aggregates in solution.

Figure 3-2 TEM image of TiO$_2$ Titanium Dioxide

MPC also dissolved in 1:1 Mili-Q water:methanol mixture and various amounts of MPC were added to the above TiO$_2$ suspension to make nanocomposites (1wt%AuMPC-TiO$_2$, 3wt%AuMPC-TiO$_2$, 6wt%AuMPC-TiO$_2$, 9wt%AuMPC-TiO$_2$) with different weight percent of gold loadings (1%, 3%, 6% and 9%). The anchoring reaction was carried out by magnetically stirring for 3 hours. Attachment of MPC on TiO$_2$ was monitored by sampling at different time intervals during the anchoring reaction. In the initial stages of
the reaction, un-bound MPC were found on the grid (Figure 3-3(A)) and after 3 hours of stirring, all MPC were found attached to TiO₂ (Figure 3-3(B)), indicating the completion of the anchoring reaction. The prepared nanocomposites were separated by centrifugation and dried in vacuum overnight. The nanocomposites were stored in the freezer and re-dissolved in water prior to photocatalytic reactions.

Figure 3-3 TEM of the composite during the anchoring reaction

**Thermal treatment**

Thermogravimetric analysis of the prepared 2.2 nm MPC was carried out (Figure 3-4). According to thermogravimetric analysis of the MPC, 62% of the surface ligands can be removed by heating it to 260 °C. Because it is crucial to have some ligands that bind MPC onto TiO₂, the goal was to enhance the activity of the nanocomposites by partially removing the ligands on the MPC. Substantial ligands play a vital role by binding the MPC to TiO₂.
Figure 3-4 Thermogravimetric analysis of 2.2 nm gold MPC

Thermal treatment of the composite systems and TiO₂ was performed using a muffle furnace under air. The temperature rose to 260 °C during 30 min and the sample temperature was maintained at that temperature for another 30 min to obtain thermally treated nanocomposites (1wt%Au-TiO₂, 3wt%Au-TiO₂, 6wt%Au-TiO₂, 9wt%Au-TiO₂). Gradual increase of the temperature helps to maintain the particles size during the thermal process. It is also important to ensure the attachment of the MPC to TiO₂. The stability of the nanocomposites during the thermal treatment was determined by measuring the size change of the MPC and by analyzing whether any unbound MPC remained on the TEM grid.
Photolysis reaction and setup

All bare and gold-attached TiO$_2$ was adjusted to a concentration of 0.0062 g/L, prior to photolysis experiment. Nanocomposite solution was purged with Ar for 30 minutes to remove dissolved oxygen, that behaves as a quencher for exited electrons. Uniblue A is dissolved in methanol and also purged with Ar for 20 min.

The photocatalytic reaction was carried out in a quartz glass cuvette sealed with a rubber septum. Uniblue A was injected to the cuvette that contained TiO$_2$ in an inert atmosphere. The final concentration of Uniblue A was 5.14e$^{-5}$M. The reaction mixture was stirred magnetically during the reaction.

A schematic of the photolysis reaction is shown in Figure 3-5. Briefly, the photolysis reactions were performed with 70 W xenon lamp. Light passes through a UV cutoff filter ($\lambda > 320$ nm, UV-32, HOYA) and an IR filter (HA-30, HOYA) before it focuses on the cuvette that contains the reaction mixture.

Absorbance spectra of the reaction mixture were recorded during the photolysis experiments at 1 min intervals. A portable spectrometer (DH2000-BAL/HR2000, Ocean Optics) was employed to monitor the photolysis efficiency of TiO$_2$ and nanocomposite.
3.3. Results and Discussion

3.3.1. Controlled surface coverage of MPC on TiO$_2$

As described in previous publications, carboxylic acid groups of organic molecules have great affinity towards TiO$_2$.$^{16}$ The pKa for tioprnin protected MPC is 5.5$^{17}$ and the isoelectric point for TiO$_2$ is 7.0.$^{18}$ The Milli-Q water that used for the experiment has a pH of 6.5. MPC are negatively charged and TiO$_2$ particles are positively charged at this pH range. MPC have attached on TiO$_2$ by utilizing this interaction. The interconnectivity between gold MPC and TiO$_2$ has been demonstrated previously.$^{19-21}$ It has been shown that while carboxylic acid group binds to the semiconductor surface, the thiol tail stay on the metal surface. The same phenomenon is expected in the current study (Figure 3-6).
Figure 3-6 Gold MPC bind to TiO₂ via carboxylic acid group

TiO₂ is partially soluble in aqueous solution. It was observed that the solubility of TiO₂ enhanced during the stirring reaction. This should be due to the higher solubility of the tiopronin molecule in polar solvents.

It was anticipated that the size and the amount of the metal clusters can be precisely controlled by this method. Figure 3-7 shows the difference between 1wt%AuMPC-TiO₂ and 6wt%AuMPC-TiO₂. It is apparent that 6wt%AuMPC-TiO₂ has higher density of MPC on TiO₂ than that of 1wt%AuMPC-TiO₂. One of the major achievements of this synthetic strategy is that the MPC loading on TiO₂ can be maintained while maintaining the size of MPC unaffected.

One of the major drawbacks of the previous methods is that metal clusters aggregated on TiO₂ surface. Since the dimensions of the metal clusters determine the overall activity of the composite, it is essential to avoid aggregation. Figure 3-7 shows that there is no aggregation of MPC on the TiO₂ surface. The average particle size of MPC of the 1% and 6% composites are 2.2 nm.
3.3.2. Thermal treatment of MPC

Figure 3-7 TEM images of 1wt%AuMPC-TiO₂ (A) and 6wt%AuMPC-TiO₂ (B)

Figure 3-8 TEM 3wt%Au-TiO₂
3.3.3. Photocatalytic reaction of UBA with TiO$_2$

Uniblue A is an excellent substrate to probe TiO$_2$-initiated photoreduction. It shows a different color in its reduced form.$^{14}$ The blue color of the Uniblue A disappears upon exposure to light, in the presence of TiO$_2$ or TiO$_2$-MPC. The solution becomes yellow in color upon long time exposure. The prominent peaks of Uniblue A at 580 nm and 620 nm are decrease intensity and new peaks appear at 250-450 nm due to the formation of products (Figure 3-9).

![Absorbance](image)

Figure 3-9 Temporal evolution of absorbance spectra obtained during the photocatalytic reaction

The previous experiments, carried out for the oxidative reactions, showed a wavelength shift of the visible band of the dye. This is generally caused by the addition or the removal of the functional groups on the conjugated ring
structure. The byproducts that are formed during this reaction have different molar extinction coefficients and absorbance spectra compared to the original structure.

The spectral changes of the current experiment do not resemble a peak shift during the experiment. The temporal spectral evolution peaks of our experiments are more related to the literature reported spectra of reductive degradation of UBA. Considering this phenomenon and the electronic excitation processes in TiO₂, it can be concluded that electrons are transferred from TiO₂ to UBA. The peak intensity (absorbance) at 580 nm was determined to order to probe the destruction of Uniblue A due to reduction.

The band gap excitation of TiO₂ generates valence band holes and conduction band electrons. These charge carriers may get recombined, get trapped in surface sites of TiO₂ or may participate in further reactions. When a hole scavenger is used in the reaction mixture, more electrons will be available to participate in further reactions. The hole scavenging process will accelerate the formation of electrons. Methanol has been used as the hole scavenger in these experiments. The reactions of TiO₂ in the presence of methanol as the solvent can be summarized as follows. These two processes (eq: 1 and 2), leads to electron accumulation on the condition band and these electrons rapidly react with UBA.
TiO₂ + hν → TiO₂(ecb⁻ + hv)                        (1)
CH₃OH + hv → CH₂•OH + H⁺                          (2)
TiO₂(e⁻) + UBA(ax) → UBA(Red) + TiO₂          (3)

The absence of the oxygen and the presence of methanol are essential factors that facilitate the reduction of UBA under the current reaction conditions. In order to confirm the above explanation, further experiments were carried out in water and water-methanol mixtures under aerobic and anaerobic conditions.

According to Figure 3-10 A, the reaction is negligible in pure water. Reaction also does not take place in pure water, even if the oxygen is removed (Figure 3-10(B)). This indicates that, a hole scavenger is essential for the degradation of UBA. The photogenerated charges will recombine in such a situation.

The reaction also does not take place in water methanol mixture in the presence of oxygen (Figure 3-10(C)). The reaction only occurs, in argon-purged solution of water-methanol mixture (Figure 3-10(D)). This clearly demonstrates the essentiality of methanol and of the anaerobic conditions for the reduction of UBA.
Figure 3-10 Photocatalysis under different conditions

Figure 3-11 Schematic representation of the reactions taking place upon band gap illumination of TiO$_2$

Figure 3-11 represents the elemental reaction steps during the photocatalytic reaction of UBA. The conduction band edge of TiO$_2$ semiconductor is around
The Fermi level of an open circuit TiO$_2$ nanoparticle will be in the mid gap region and its position is defined by the most facile redox species in the solution. When TiO$_2$ is exposed to light, electron-hole pairs are generated and the holes are greatly scavenged by the solvent. When the electrons accumulate in the conduction band, the Fermi level will shift towards the conduction band edge which in turn makes TiO$_2$ thermodynamically more active towards reductive species. Electrons in the conduction band of TiO$_2$ will be transferred to UBA and its reduction takes place upon electron transfer. The reduction of Uniblue A is in two steps. According to cyclic voltametry studies, E$^{1/2}_{1/2}$ were measured at -0.0372 V and -0.591 V vs NHE in CHCl$_3$:EtOH= 90:10 v/v mixture. These peaks of cyclic voltametry were attributed to the sequential reduction of the carbonyl and anthroquinoic moieties of UBA.

The dye also can be degraded due to photosensitization. In such conditions, dye is excited upon irradiation and the excited electrons are transferred to the TiO$_2$ conduction band that in turn initiates the destruction of the conjugated molecular structure of the dye. In order to exclude the occurrence of such a phenomenon, a 455 nm high pass filter placed between the xenon lamp and the photolysis cuvette. The band edge of TiO$_2$ is around 320 nm. Under such a situation, the dye is irradiated without exciting the TiO$_2$. According to Figure 3-12, no photolysis of UBA is observed under such
circumstances. This confirms the fact that the photolysis is primarily due to the electron transfer from TiO$_2$.

![Figure 3-12 Possibility of the dye sensitization](image)

**3.3.4. Enhanced activity with AuMPC-TiO$_2$**

Experiments were carried out with TiO$_2$ samples with different amount of MPC loadings. The change in the absorbance of the UBA was plotted to determine the activity of the catalysts. Figure 3-13 shows that there is no considerable enhancement of the activity of MPC-TiO$_2$ compared to bare TiO$_2$.
Figure 3-14 illustrates a possible explanation for the above behavior. The electronic communication between TiO$_2$ and MPC is obstructed by the surface ligand of the gold nanocluster. Therefore, the expected enhancement does not exhibit in the composite materials. Nano-sized gold clusters also are known to participate as a heterogeneous catalyst by providing a surface to the solution phase reactants. In this particular case, the gold surface is covered and it cannot provide a platform to the reaction.

![Graph showing normalized absorbance change during the reaction](Image)

Figure 3-13 Normalized absorbance change during the reaction
3.3.5. Photocatalytic reaction with thermally treated composite

The photocatalytic reduction of UBA was carried out with thermally-treated samples. According to Figure 3-15, thermal treatment has drastically enhanced the catalytic activity of the nanocomposites. In the case of thermally treated composites, 3wt%Au-TiO$_2$ demonstrates the highest activity. According to the slopes of the above graphs 3wt%Au-TiO$_2$ exhibit 41% enhancement of the photocatalytic activity compared to naked TiO$_2$. Further increase of gold loading reduces the efficiency due to blocking of the active sites.

As a control experiment, same type of experiment with bare TiO$_2$ after the thermal treatment at 260 °C was carried out. A great decrease in the photocatalytic activity was observed. This further confirms the positive effect of the gold clusters on the catalytic activity of TiO$_2$. 
Figure 3-15 Normalized absorbance change of UBA upon reduction with TiO₂ and TiO₂-Au

Figure 3-16 Schematic representation of the function of gold clusters on the photocatalytic reactions
3.3.6. Mechanism of the photocatalytic activity enhancement

Band-gap illumination of TiO$_2$ in deaerated CH$_3$OH-H$_2$O, excites electrons to the conduction band while holes are scavenged by CH$_3$OH (Figure 3-16). These photoelectrons are stable for a relatively long period of time so that they can transfer to adsorbed electron acceptor or solution phase redox couple. When the capping monolayer of MPC is removed, there is a good electronic contact between MPC and TiO$_2$. Therefore photo-generated electrons can additionally transfer to the MPC core, significantly increasing the charge separation.

The Fermi level energy of MPC is 0 V vs NHE. It has been demonstrated that when metals such as Au and Ag are in particles in contact with charged semiconductors, the Fermi levels of the two species equilibrate and metal accepts charge from the semiconductor. The Fermi level of MPC is more positive than that of TiO$_2$ which makes the electron transfer from charged TiO$_2$ to MPC thermodynamically possible.

As a result of above phenomenon, the Fermi level of the system is expected to be between -0.5 and 0.0 V vs NHE and closer to the conduction band edge. This energetic of the Au-TiO$_2$ nanoassemblies will enhances the UBA reduction.

When the exited electrons are scavenged by the metal particles, it leads to the creation of more vacant sites on TiO$_2$, which can accept more exited...
electrons. This makes the photoexitation process kinetically more efficient. In the present Au-TiO₂ assemblies, the surface monolayer of ligands has been removed, so that the gold core is further accessible to UBA in the solution. The naked gold core also promotes the electrons to transfer from TiO₂ to gold.

3.4. Conclusion

This study demonstrates an efficient synthesis protocol to attach nano-sized gold clusters on TiO₂. TEM results have revealed the capability of the current method to immobilize gold MPC on TiO₂ while keeping the particle size intact. The thermal activation procedure has been developed and the activated composites exhibit promising activity towards reductive degradation of UBA. Most importantly, it has been shown that catalytic activity can be changed by manipulation of the surface coverage of MPC on TiO₂.
3.5. References

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CHAPTER 4

OXIDATION OF RD590 WITH THE NANOCOMPOSITE

4.1. Introduction

TiO₂ has proven to be an outstanding photo-active semiconductor material because of its ability to destroy many organic pollutants in the oxidative pathway. The ultimate goal of the semiconductor photocatalysts is its usage in the purification of polluted waste water bodies. Analysis of photocatalytic reactions in water under anaerobic conditions is important since this reaction condition is similar to practical applications. When TiO₂ is illuminated without an added hole scavenger, it is capable of degrading pollutants via an oxidative pathway. Under these experimental conditions, the generated holes react with surface hydroxyl ions to form hydroxyl radicals. Holes and hydroxyl radicals can oxidize organic material in an aqueous environment.

Rhodamine B and Rd 590 belong to a class of dyes called xanthane dyes. These dyes are a major component in laser materials. They also have been extensively used to probe the photocatalytic efficiency of semiconductor materials. The degradation pattern and the products of the dye materials provide valuable information regarding the photochemical and photophysical processes during the photocatalytic reactions.
Figure 4-1 Molecular structure of Rd 590

The oxidative degradation of Rd 590 has been studied during photo-induced reactions. Ryota et. al\(^1\) demonstrated two possible mechanism in the degradation of Rd 590 through oxidative pathways. In the monomeric form, the dye exhibits an intense absorption band at 527 nm. During the degradation in aerobic conditions, the absorption peak at 525 nm gradually decreased with a blue shift from 527 nm to 516 nm. This behavior is attributed to the decomposition of the dye structure by two major pathways. They are N-de-ethylation and destruction of the conjugated structure. Ryota et al. claim that the N-de-ethylated products have similar molar absorption coefficient as that of the original dye. Therefore, this process does not contribute to the reduction of the absorbance band. But the peak shift is mainly ascribed to the N-de-ethylation. The reducing absorbance in the
presence of a photocatalytic reaction is due to the destruction of the ring structure. This photochemical behavior can be utilized to probe the reaction mechanism of the degradation.

This chapter mainly focuses on the possibility of using the TiO$_2$-Au nanocomposite to initiate oxidation reactions. The experiments are carried out in water. The occurrence of the oxidative path is monitored by degradation of Rd 590. The present chapter also aims at exploring the effect of the thermal treatment and the role of the thiol ligand on the photocatalytic activity of the composite system.

4.2. Experimental

4.2.1. Materials

Gold(III) chloride trihydrate (ACS reagent), tiopronin, acetonitrile, sodium borohydride and methanol were purchased from Sigma Aldrich. TiO$_2$ was purchased from Acros Organics. Acetic acid (A.C.S grade) was purchased from J.T.Baker. Rd 590 was purchased from Exiton.

4.2.2. Photocatalyst preparation

The synthesis of gold MPC, synthesis of Au-TiO$_2$ nanocomposite and the thermal treatment experiments were carried out as described in 3.2.2.
4.2.3. Thermal treatment

During these experiments the nanocomposites were thermally treated at 260 °C and 400 °C. In each case, the temperature of the sample was increased up to the desired temperature within 30 min and kept at that temperature for another 30 min.

4.2.4. Photocatalytic experiment

TiO$_2$, gold-attached TiO$_2$ (MPC-TiO$_2$) and gold-attached and thermally treated TiO$_2$ (AuMPC-TiO$_2$) solutions were prepared in a concentration of 23 mg/L in water. An aliquot of Rd 590 stock solution was subsequently added to the solution to give the desired concentration (10 μM). The photocatalytic reaction was carried out in a glass cuvette while stirring the solution magnetically. Photoirradiation employed a 300W Xe lamp as the light source. Light passed through a UV cutoff filter (λ= 320 nm), an IR filter and then was focused on the glass cuvette. The absorption spectrum of the reaction mixture was recorded with an Ocean Optics spectrophotometer (Lamp: HQ-2000-BAL and Detector HR-2000-CG-UV-NIR) in one minute intervals for 30 min. A set of triplicate measurements was carried out for each photocatalytic experiment.
4.3. Results and Discussion

4.3.1. Photocatalysis of Rd 590: Mechanistic aspects

Figure 4-2 Change in Rd 590 absorbance during photocatalysis

In the present study, the photocatalytic activities of the AuMPC·TiO₂ nanoparticle assemblies were examined by monitoring the decrease in absorbance of Rd 590 at its peak maximum (Figure 4-2). Before illuminating with xenon lamp, Rd 590 exhibits an intense absorption band at 525 nm. The orange color of Rd 590 disappears during the reaction and a colorless solution observed upon complete degradation.

The Rd 590 degradation can occur via a reductive or oxidative pathway. Takahashi et.al² carried out the photocatalytic reduction and oxidation of a similar analog of Rd 590, Rhodamine B, in the presence of TiO₂ sols. A new
absorption band at 420 nm observed during the reduction. Steven et.al. 3 assigned this to the semi-reduced radical of Rhodamine B. This behavior is not observed in the oxidation pathway. Further, the dye discoloration was reversible in the reductive experiments.

Since Rhodamine B and Rd 590 have similar molecular structures, the degradation pattern can be compared in order to evaluate the photo-transformation mechanism. This photochemical decomposition phenomenon in aqueous aerobic environment is due to two pathways: N-de-ethylation and the destruction of the conjugate structure of the dye molecules. 1

Electrons and holes generated in the semiconductor are recombined in few tens of picoseconds4-6 after the excitation process. Some charge carriers can transfer into traps. These localized species are comparatively inert. 6 Freely available charges can rapidly and effectively react with the molecular species adsorbed onto the TiO₂ surface.7 It has been found that holes react with hydroxyl groups on the surface and the resulting hydroxyl radicals are capable of oxidizing molecular species in the solution. Interestingly, Geo et.al 8,9 have demonstrated that the generated hydroxyl radicals are more capable of oxidizing the molecular species attached to the semiconductor surface than are the holes. They used the oxidation process of monohydroxy alcohols to prove the hypothesis. Therefore, it can be assumed that the holes participate in the photocatalytic process of the current reaction.
Dye sensitization

When the dye is irradiated in the presence of TiO₂, it also can be degrade due to self-sensitization. In order to rule out the possibility of such a mechanism, photocatalytic experiments were carried out using a 455 nm high pass filter in between the sample and the xenon lamp. According to the absorption spectra of TiO₂, Rd 590 and the 455 nm high pass filter, the high energy component of the lamp does not reach the reaction mixture under the current experimental setup. In other words, semiconductor band gap excitation can be excluded by performing this experiment.

![Figure 4-3 Effect of dye sensitization on the photocatalytic efficiency](image-url)
Figure 4-3 shows that there was insignificant degradation of the dye, when the experiment was carried out in the presence of a 455 nm high pass filter. It can be concluded that the photoinduced self sensitized photolysis has no effect on the photocatalytic reactions. The dye was not stirred with TiO₂ prior to the photocatalytic reaction. This could be the possible mechanism that diminishes the dye sensitization.

**Participation of holes in the reaction**

Under the current experimental conditions, it is anticipated that holes participate in the reaction by producing hydroxyl radicals. Hydroxyl radicals can trigger further reactions, such as oxidation of organics.¹⁰,¹¹ At the same time, electrons are being scavenged by oxygen.¹² The involvement of the holes in the reaction is demonstrated by using a known hole scavenger during the reaction. A regular irradiation experiment was carried out in the presence of SCN⁻, a known hole scavenger. The photogenerated holes are capable of oxidizing SCN⁻ at the semiconductor interface¹³, producing (SCN)₂⁻ as follows.

\[
h^+ + SCN^- \rightarrow SCN^- \quad \text{...............} \quad (1)
\]

\[
SCN^- + SCN^- \rightarrow (SCN)_2^- \quad \text{...............} \quad (2)
\]
Figure 4-4 Effect of SCN⁻ on the photocatalytic efficiency

Different amounts of SCN⁻ were introduced to the reaction mixture prior to photolysis. Experiments were carried out with bare TiO₂. Figure 4-4 shows that there is a good correlation between the SCN⁻ concentration and the rate of the oxidation of Rd 590. When the SCN⁻ concentration is increased, the rate of the oxidation of Rd 590 decreased accordingly, suggesting that SCN⁻ is competing with hydroxyl ions to react with the holes created in the valence band. As a consequence, a lesser amount of hydroxyl radicals is generated on the surface of TiO₂, which in turn reduces the rate of the reduction of Rd 590. This confirms that the holes drive the oxidation of Rd 590 in TiO₂.
Participation of oxygen in the reaction

In order to demonstrate the importance of the participation of oxygen in the reaction, same experiments were carried out in anoxic conditions. The reaction mixture was purged with argon for 30 min to remove dissolved oxygen, prior to photolysis. According to Figure 4-5, the photocatalytic reaction was completely quenched, when oxygen is removed. This shows that oxygen plays a vital role in the photocatalytic degradation of Rd 590.

Figure 4-5 Effect of oxygen on the photocatalytic efficiency

The role of oxygen in photocatalytic reactions can be different. In this particular case, oxygen is expected to be an electron scavenger that facilitates efficient electron-hole separation. In order to confirm the participation of oxygen as an electron scavenger, oxygen was substituted with IO₃⁻, a known
electron scavenger\textsuperscript{14}. Argon-purged IO$_3^-$ solution was introduced to the argon-purged reaction mixture, prior to the photolysis. The degradation of the dye was restored in the presence of IO$_3^-$. Figure 4-5 confirms that oxygen is participating in this reaction as an electron scavenger.

4.3.2. Effect of thermal treatment temperature

According to the catalytic activity studies of the chapter 3, 3wt\%Au-TiO$_2$ exhibits the highest catalytic activity. Therefore that sample was selected to study the temperature effect of the composite system toward the degradation of Rd 590. Figure 4-6 shows the fractional change during the photocatalytic activity of different systems. There is no enhancement of the photocatalytic activity after anchoring 3wt\% of gold MPC on TiO$_2$ (TiO$_2$ and MPC-TiO$_2$ in Fig 4-6).

Figure 4-6 Effect of thermal treatment on the photocatalytic activity
It has been demonstrated that the capping ligand or the shell structure around the metal nanoparticle also plays a vital role in the interparticle and interfacial surface access properties. Even though the ligands are important for linking MPC with TiO$_2$, they also can act as a barrier that hinders the electronic contact. Therefore, the above behavior is ascribed to the effect of the tiopronin ligand that covers the gold surface. Metal nanoparticles are usually combined with semiconductor materials to enhance their photocatalytic activity. In order to achieve this goal, the metal should be closely associated with the semiconductor. In other words, there should be a proper electronic communication between gold MPC and TiO$_2$.

According to the results (Figure 4-6), the thermally treated sample at 260 °C exhibits a drastic enhancement of the activity against the degradation of Rd 590, compared to bare TiO$_2$.

XPS studies of 3wt%AuMPC-TiO$_2$ and 3wt%Au-TiO$_2$ were carried out and compared to gain a better insight into the problem (Figure 4-7). $S_{2p3}$ Binding energy (BE) peak at of 162 eV is due to the existence of bounded sulfur on the sample. Figure 4-7 (a) confirms the presence sulfur bound to the gold core through sulfide bond formation. As described previously, sulfur has strong affinity towards gold atoms. This further proves the existence of ligands bound to the gold core via sulfide bond formation.
Figure 4.7 XPS at room temperature (a) 260 °C (b) and 400 °C (c)
In contrast, the composite heated at 260 °C does not contain any bound sulfur (Figure 4·7 (b)). BE peaks of S$_{2p3}$ at 168 eV show the existence of oxidized sulfur species on the composite.$^{19}$ Combination of TGA and XPS results of the thermally treated sample at 260 °C shows that, at 260 °C, the surface sulfur ligands have been completely degraded. This should be the reason for the enhanced photocatalytic activity with the thermally treated samples. Even though oxidized sulfur species occur at the surface of the composite, they are minute in quantity. Therefore, they do not have a negative contribution towards photocatalytic activity.

According to the previous investigation by Kegeyama et.al.,$^{20}$ heat treatment at elevated temperature has a positive effect on the activity of TiO$_2$-supported gold nanoparticles towards the oxidation of carbon monoxide. They raised the temperature from 200 to 600 °C to achieve higher turnover frequencies of the oxidation reactions. Therefore the temperature was increased up to 400 °C during the heat treatment. Figure 4·6 shows a drastic reduction of the photocatalytic activity of this sample. This issue can be addressed by combining of TEM, XPS and TGA results. According to the XPS results, the 400 °C sample has a BE peak at 168 eV (Fig 4·7 (c)). This discloses the existence of oxidized sulfur species in this sample. Therefore, the surface effect from sulfur towards oxidation reaction is similar to that of
the 260 °C sample. TEM images of the 400 °C sample shows that the cluster size has become considerably larger after the thermal treatment (Figure 4-8).

Figure 4-8 TEM image of 3wt%AuMPC-TiO$_2$ sample after thermally treated at 400 °C. Inset shows the size distribution and average size of MPC on TiO$_2$. The bigger clusters are capable of absorbing more incoming radiation and block the active sites on TiO$_2$ surface. As a result, the 400 °C sample exhibits lower charge separation which in turn reduces its catalytic efficiency. The larger clusters are capable of accumulating large number of electrons. Therefore, the larger clusters also can act as electron-hole recombination centers.
The above experiment concludes that 260 °C is the optimum temperature for the thermal treatment and the following experiments were carried out by treating the sample at that temperature.

4.3.3. Effect of gold loading

The amount of gold loading is the other important parameter that controls the maximum quantum efficiency of the photocatalytic reaction. Since the composites heated at that temperature showed promising activity during the previous experiments, composites with different loading of MPC were subjected to thermal treatment at 260 °C. Figure 4-9 shows photocatalysis results of Rd 590 in presence of the thermally treated composite and bare TiO₂. Bare TiO₂ was also subjected to the thermal treatment and its catalytic activity was measured as a control experiment.

The results show that thermal treatment dramatically increases the catalytic activity of the composites. When the gold loading is increased, the photocatalytic activity becomes enhanced accordingly, up to 6wt % of gold loading. Further increase of gold loading reduces the photocatalytic activity (9wt%Au-TiO₂). It has been reported that a large number of negatively charged gold particles on TiO₂ will act as charge recombination centers by accepting holes.\textsuperscript{21,22} This will reduce the efficiency of charge separation when the gold content is above its optimum percentage. The same behavior also has been observed with Pt nanoparticles\textsuperscript{22,23} and gold nanoparticles.\textsuperscript{21} MPC also
interact with the light by absorption and scattering. When gold is deposited on TiO₂, it occupies the active sites, obstructing the light path, and preventing interaction of the light with TiO₂. This also will contribute to the lower photocatalytic efficiencies at higher surface coverage of gold.

The activities of TiO₂ before thermal treatment and after the thermal treatment were compared. There is some enhancement of the activity toward Rd 590 oxidation but enhancement with the gold is remarkably higher than that of bare TiO₂. The activity enhancement of bare TiO₂ may be ascribed the surface changes of the titania during the thermal process.

![Photocatalytic activity of thermally treated samples](image)

Figure 4-9 Photocatalytic activity of thermally treated samples
The previously mentioned dye sensitization experiment, the anoxic condition experiments, the SCN⁻ experiment and the IO₃⁻ experiment were carried out with 6wt%Au·TiO₂, to confirm the fact that the same mechanism of photocatalytic degradation of Rd 590 is occurring at Au·TiO₂ composites after the thermal treatment. According to the results, the reactions of Au·TiO₂ composites also showed similar mechanistic characteristics to bare TiO₂.

4.3.4. Mechanism for enhanced activity by gold

The possible mechanistic aspects of the reactions of the composite, before and after the thermal treatment are proposed and shown in Figure 4-10. When the TiO₂ absorbs photons of energy greater than or equal to its band gap, photoelectrons are promoted from the valance band to conduction band, leaving behind holes in valence band. These electron-hole pairs will recombine, unless they are subjected to further reactions. The presence of metal nanoclusters on TiO₂ is believed to retard fast electron-hole recombination.
Figure 4-10 Photocatalytic reactions of AuMPC-TiO₂ nanocomposites before (A) and after (B) the thermal treatment at 260 °C

The enhancement of the photocatalytic activity of TiO₂ by anchoring metal clusters has been demonstrated using gold²⁴-²⁸ as well as other metals like platinum.¹²,²⁹ From the comparative photocatalytic measurements, and from the TGA and XPS results, it is apparent that the tiopronin monolayer is preventing gold from its facilitating role in the catalytic processes of the TiO₂. When the nanocomposite is heated at 260 °C, the capping organic layer on the gold is partially removed. The XPS data and the TGA analysis support the hypothesis of ligand removal. This will expose the gold surface to TiO₂ and to the reaction environment. Consequently, gold is actively participating in the photocatalytic reaction by accumulating electrons.

Metal nanoparticles on TiO₂ also can enhance the photocatalytic activity by providing catalytic sites. In the present study, the gold surface also may be
participating in the electron transfer reaction between the composite and Rd 590.

Excessive heat during the thermal treatment does not improve the activity due to melting of the ligand and due to the formation of oxidized sulfur species on the TiO$_2$ or MPC surface.

4.4. Conclusion

The possibility of using the composite material in the oxidative pathway was demonstrated. The thermally treated sample displays dramatically higher activities. The mechanistic aspects of the photocatalytic reaction was also elucidated by analyzing the participation of dissolved O$_2$ and holes. The effect of the thermal treatment was analyzed by XPS measurements.
4.5. References

(12) Choi, W. *Catalysis Surveys from Asia* 2006, 10, 16.


CHAPTER 5

PHOTOCATALYTIC DEGRADATION OF NAPROXANE

5.1. Introduction

A large number of synthetic and naturally occurring chemical species are not commonly monitored nor reported in waste waters. But the adverse health and ecological effects of these compounds cannot be underestimated. Therefore, the development of methods to identify those compounds and the design of elimination or treatment strategies is extremely important. A nationwide investigation by US Geological Survey has determined the occurrence of 82 compounds as organic waste water contaminants. These emerging trace contaminants include pharmaceuticals (both human and veterinary medicine), natural and synthetic hormones and many persistent organic waste water contaminants. Importantly, 80% of streams have shown the presence of traces of these compounds. Although there is little concern about short term effects, lifetime accumulation of sub-therapeutic doses are harmful.

Non-steroidal anti-inflammatory drugs (NSAIDs) can be commonly found in inland water bodies. They are one of the most widely used drug categories in the world. NSAIDs have been detected in hospital waste water, sewage treatment plants, inland water bodies such as lakes and rivers, marine waters and soil.
Carballa et al. have described the removal of NSAIDs with common water treatment methods such as adsorption, coagulation, and filtration. Some compounds are not easily biodegradable and cannot be degraded through conventional methods. Therefore the expansion of new strategies, that have a potential of extending towards large scale applications, is essential. Removal of the above contaminants through heterogeneous photocatalysis process plays a key role in this regard.

Trotz et al. recently summarized the photocatalytic removal of pharmaceuticals and endocrine disrupting compounds in waste water. Photocatalytic degradation routes for the 10 dominant pharmaceutical compounds have been summarized. Merck TiO$_2$ and ZnO are the common catalysts that have been used to eliminate the above contaminants. Few approaches have analyzed the byproducts of the reactions. Trotz et al. have summarized the effect of the pH, photocatalytic concentration, the light source and the intensity of the radiation. According to the article, the identification of the byproducts of the catalytic reaction is important to evaluate the kinetics, stability and the toxicological effects.

Photocatalytic reactions can be complex and involves multiple reaction byproducts. Sometimes the products can be more toxic than the parent compound. Therefore, elucidation of the reaction pathways and the identification of the byproducts are important.
Liquid chromatography with mass spectrometry (LC-MS), LC with UV detection or fluorescence detection, NMR, gas chromatography mass spectrometry (GC/MS) and infrared spectroscopy have all been used in the process of identification of the photocatalytic pharmaceutical byproducts. Among these methods, LC-MS has gained special favor owing to its versatility.\textsuperscript{36}

5.1.1. LC-MS analysis of pharmaceutical byproducts

LC-MS is a very sensitive method for selective identification of pharmaceutical products in trace levels.\textsuperscript{37} It also has been utilized for the monitoring and identification of photocatalytic transformation products of common pharmaceutical compounds.\textsuperscript{35} The most important capability of this method is to carry out the separation and identification of a mixture of compounds, simultaneously. The Key technological features behind LC-MS are as follows.

![Figure 5-1 Major components of LC-MS system](image)

Figure 5-1 Major components of LC-MS system
High pressure liquid chromatography (HPLC) is used to separate a mixture of compound to their individual components. It has a stationary phase, which is bound to the column and a mobile phase that takes the analytes through the stationary phase. Removal of the solvents and the ionization of the analyte molecules take place in the interface. Electrospray Ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI) are commonly used during the analytical procedures for pharmaceutical compounds. Mass Spectrometry (MS) is a gas phase method of examining compound via their mass to charge ratio (m/z). Since HPLC is a liquid phase method, an interface is a vital part that processes the liquid to gaseous transformation of the analytes. The present experiments use ESI as the interface. During the ESI method, the liquid sample is pressurized through a capillary with a nebulizing gas under a high electric field. Initially, charged droplets are formed and eventually the ions are evaporated. The polarity of the system can be changed in order to obtain negative or positive ions depending on the analyte of interest. ESI is a soft ionizing technique that only yields molecular ions. Typically, the positive ionization mode gives protonated, sodiated or ammoniated species of the molecules. The negative mode yields deprotonated species.
MS part consist of a mass filter (mass analyzer) and a mass detector.

Figure 5.2 Components of MS

After the ionization process, the ions are accelerated through a mass analyzer under a high vacuum. The quadrupole mass analyzer is commonly used. It consist of four parallel rods that are polarized in different electrics fields. Depending on the quadrupole voltage, while some ions reach the detector, some combine with the quadrupole. The voltage of the quadrupole can be manipulated to separate the charged species. If there is a prior understanding about the molecular species under analysis, the voltage of the quadrupole can be adjusted to filter those ions. This method is called Selective Ion Monitoring (SIM) mode. During the SIM mode the detector is exposed to particular species of the ions and high sensitivity can be always obtained with this method.
5.1.2. Photocatalytic degradation of Naproxane

This chapter aims at exploring the photocatalytic degradation of NSAID called naproxen. Naproxen, 2-(6-methoxy-2-naphthyl)propanoic acid was initially introduced by Syntex Research. Naproxen and its water-soluble sodium salt are extensively used drugs for their analgesic and antipyretic properties. However, an increased risk of heart attack and strokes has been observed in the patients taking this drug. Pharmacokinetic research has shown that 95% of the dose is excreted in urine. Therefore naproxen can be considered as a major pollutant. The drug has been identified in rivers at concentrations higher than 26 µg/L. Therefore the development of new approaches to complete elimination of this compound in water, the evaluation of the byproducts and the analysis of the toxicological effects of the byproducts are vital.

Studies with heterogeneous photocatalysis of naproxane have been carried out previously. Oxidation of naproxen by means of TiO₂ has been accomplished by hydroxyl radical generation. A number of byproducts have been formed and they have been qualitatively identified by LC-MS. Even though the different reaction parameters such as dissolved oxygen concentration and pH were studied, complete mineralization has not been achieved. Therefore, the development of new photodegradation strategies that produce high yields of hydroxyl radicals towards complete
mineralization is important. If the method produced less byproducts during the process, that would be an added advantage.

This chapter illustrates the application of previously prepared 6wt% Au-TiO$_2$ nanocomposite system for the photocatalytic degradation of naproxen. According to chapter 4, 6wt% Au-TiO$_2$ (thermally treated) exhibits the highest activity towards the oxidative degradation of the compounds. Therefore, 6wt% Au-TiO$_2$ is utilized for the photocatalytic reaction. This is the first study where a metal-semiconductor nanocomposite was used for the photocatalytic degradation of a pharmaceutical compound. Promising results have been obtained with the composite system compared to TiO$_2$ and the importance of the study is that the experimental procedure can be extrapolated towards structurally similar pharmaceutical products such as Ibuprofen and Clofibric acid.

5.2. Experimental

5.2.1. Materials

Gold(III) chloride trihydrate (ACS reagent), tiopronin, acetonitrile, sodium borohydride, naproxen sodium salt, LC-MS grade water, LC-MS grade methanol and ACS grade methanol were purchased from Sigma Aldrich. TiO$_2$ nanoparticles was purchased from Acros Organics. Acetic acid (A.C.S grade) was purchased from J.T.Baker.
5.2.2. Photocatalytic experiment

The photocatalytic reaction was carried out using the previously mentioned setup. A stock solution of 27.7 mg/L of TiO₂ and the nanocomposite was prepared by simultaneous shaking and sonicating. The pH was adjusted to 3.0. According to previous publications, higher catalytic efficiencies have been observed at lower pH values due to higher adsorption of naproxen to the catalyst. Lower pH values also yields reproducible results. The variation of the catalytic activity due to aggregation of TiO₂ can also be minimized by lowering the pH. A stock solution of naproxen was prepared and the desired amount of the stock solution was added to the above photocatalyst solution to obtain a final concentration of 11 ppm of naproxen. The mixture was magnetically stirred for 30 minutes to facilitate reaching the adsorption equilibrium. A 3 ml sample of the solution was transferred to a glass cuvette. Photolysis with TiO₂ and 6%Au-TiO₂ was carried out for 5, 10, 15 and 20 min intervals. The reaction mixture was magnetically stirred during the photocatalytic reaction. The resulting solutions were filtered through a membrane filter (20 nm). Each photocatalytic experiment was carried out 3 times to ensure the reproducibility. The collected filtrates were subjected to chromatographic analysis. Chromatographic analysis results were used to determine the concentration of remaining naproxen in the sample.
5.2.3. Chromatographic analysis

HPLC apparatus and conditions

A Shimadzu HPLC pump system (LC-10ADvp) equipped with a Shimadzu photo diode array detector (SPD M10Avp), a Shimadzu SIL-HT auto sampler and an Aligent Zobex reverse phase column (5\(\mu\)m, C18) with 150 x 2.1 mm were used with a mobile phase of acetonitrile:water (pH=3.0) (40\%:60\%). The flow rate was 0.20 ml/min.

LC-MS apparatus and conditions

A Shimadzu HPLC pump system (LC-10ADvp) equipped with a Shimadzu MS analyzer (LCMS 2010A), a Shimadzu SIL-HT auto sampler and an Aligent Zobex reverse phase column (5\(\mu\)m, C18) with 150 x 2.1 mm were used with a mobile phase of acetonitrile:water (0.1% formic acid) (40\%:60\%). The flow rate was 0.15 ml/min.

5.3. Results and Discussion

5.3.1. Comparison of photocatalytic activity

HPLC analysis

Calibration standards of naproxen were made and the HPLC analysis was carried out to determine the retention time and the area of the peak. The linearity of the chromatographic signal was assessed over 4 ppm to 20 ppm. A calibration curve was constructed by plotting the naproxen peak area vs
concentration. The precision of the method was assessed by carrying out triplicates of each standard. The naproxen concentrations of the unknown photolysis samples were measured by using this calibration plot. The UV visible spectrum of naproxen shows an intense band with a peak maximum at 228 nm. Therefore, during the HPLC experiments, the chromatogram at 228 nm absorbance was extracted from the PDA results.

Control experiments for naproxen degradation

Preliminary experiments were carried out to determine the extent of hydrolysis and adsorption during the photocatalytic experiments. According to the experiments performed in the dark, in the presence of TiO₂, negligible decay of naproxen was observed due to adsorption occurs over a period of 20 minutes. Hydrolysis experiments were carried out by stirring a solution of naproxen for 20 minutes in the presence of the light source used in previous experiments. Negligible degradation of naproxen due to hydrolysis was observed.

Comparison of the photocatalytic efficiency

The time-dependent chromatographic analysis of the naproxen degradation in TiO₂ depicts the degradation of naproxen and the evolution of byproducts. According to Figure5·3, the retention time of naproxen was found to be 11.9 min. Four byproducts are being formed during the degradation and they elute at 7.9, 9.5, 13.4 and 17.5 min.
Figure 5-3 Naproxen photocatalysis in the presence of TiO$_2$
Figure 5.4 Naproxen photocatalysis in the presence of 6wt% Au-TiO$_2$
The peak areas of the byproducts initially increased with the time. The Naproxen peak diminished accordingly. The time-dependant relationship between the naproxen concentration and byproduct concentrations confirms the formation of the byproducts as a result of the degradation of naproxen.

A similar experiment was carried out with 6%Au-TiO₂. The degradation of naproxen was observed. Formation one dominant photoproduct was observed during the reaction. It elutes at 9.5 min in HPLC experiment. This behavior is different from TiO₂ experiment.

A detailed analysis of the byproducts will be made in later sections.

The initial naproxen concentration, before stirring, was 11 ppm. During the stirring process, the naproxen concentration dropped to 9.7 ppm and 9.3 ppm of TiO₂ and 6wt%TiO₂ respectively. This shows that naproxen was adsorbed on TiO₂ surface. Furthermore, the composite adsorbs more naproxen than TiO₂. Therefore, it can be speculated that the gold surface behaves as a platform to binding of naproxen. Figure 5.5 shows the time dependant concentration change in the presence of TiO₂ and Au6%-TiO₂.
Figure 5-5 Time evolution concentration change of naproxen in the presence of TiO$_2$ and 6wt%AuTiO$_2$

Figure 5-5 indicates that the degradation of naproxen occurs rapidly in the presence of the TiO$_2$-gold composite, compared to bare TiO$_2$. Comparison of the initial slopes of the decay curve indicates that 6wt%AuTiO$_2$ is 55% more efficient than bare TiO$_2$.

5.3.2. Effect of gold on mechanism

Previous studies of the photodegradation of naproxen$^{33}$ and the photocatalytic studies of similar analogs, such as diclofenac$^{40}$ have confirmed that the
oxidative degradation of these molecules take place in the aqueous solution in the presence of TiO₂ via hydroxyl radical attack. Therefore the previous explanation (chapter 4) for the oxidative degradation of Rd 590 can be extrapolated to explain the elemental catalytic processes in the current experiments. Moreover, previous experiments on the photocatalytic degradation of pharmaceutical compounds have revealed the importance of oxygen. A great enhancement of the reaction was observed in oxygen-saturated solution, confirming the role of oxygen as the key electron accepter species in the previous studies. Previous studies also have observed quenching of the photocatalytic activity due to fast recombination of electrons and holes in the absence of oxygen.

In the present study, the degradation process of naproxen was greatly accelerated in the presence of gold clusters on TiO₂. This indicates that gold is playing a facilitating role on the degradation process. Gold can participate in the reaction in two ways. Firstly, it behaves as a capacitor and accepts electrons during the irradiation process. As results, the hole producing process would be more efficient and consequently enhanced production of hydroxyl radicals can be expected. Hydroxyl radicals in turn transform naproxen to its byproducts.
Secondly, it can be speculated that the exposed gold surface can participate in the reaction. During the adsorption process, the composite adsorbed more naproxen than plain TiO₂. This further validates the above explanation.

![Mechanism](image)

Figure 5.6 Mechanism for the photocatalytic activity of TiO₂ (a) and 6wt%AuTiO₂ (b)

5.3.3. LCMS analysis of the photocatalytic byproducts

**Reaction with TiO₂**

Previously, LCMS has been utilized in order to probe the reaction intermediates of naproxen during the photocatalytic degradation processes. The filtered reaction mixture is separated through the column and individual compounds are directed to MS. The greatest advantage of ESI-MS is that the soft ionizing usually gives molecular weight information. Fig 5.8 shows the
LC-ESIMS of naproxen. The retention time is 11.9 min. The mass spectrum of the peak at 11.9 is given below. 231 m/z of the mass spectrum is due to the molecular ion of naproxen.

Figure 5-7 LC-ESIMS of naproxen

Figure 5-8 Mass spectrum of the peak at 11.9 minutes

The photocatalytic reaction mixture obtained after 10 minutes of reaction with TiO$_2$ was injected to LCMS. The LC-ESIMS and the mass spectrum of the peak of interest are as follows.
Figure 5-9 LC-ESIMS of byproducts of TiO$_2$ reaction after 10 minutes

Figure 5-10 Mass spectra of the peaks of the chromatogram of Figure 5-10.

Structure elucidation was carried out using the literature report which has identified the photoproducts of naproxen. The peak at 9.9 min has a molecular ion peak of 185 m/z. This has been identified as 1-(6-
methoxynaphthalen-2-yl)ethanol (a). The peak at 11.9 has a molecular ion peak of 231 m/z. This is due to unreacted naproxen (b). Two peaks appears at 14 min and 18 min and they have same molecular ion peaks of 201 m/z. UV absorbance of the peaks also considered to assign the molecular structures to these two peaks (Figure 5-11). Species of Fig d of 5-11 has UV absorbance peaks at higher wave lengths. This should be due to the extended conjugation of the product molecule. Considering MS results and UV absorbance results, c was identified as 2-(1-hydroperoxyethyl)-6-methoxynaphthalene and d was identified as 1-(6-methoxynaphthalen-2-yl)ethanone. The mole structures and the peak positions are given in table 5-1.

![Figure 5-11 UV-visible spectrum of c and d compounds](image)

Figure 5-11 UV-visible spectrum of c and d compounds
Table 5-1 Structure elucidation of the naproxen photoproducts

<table>
<thead>
<tr>
<th>Compound</th>
<th>m/z</th>
<th>Retention time/min</th>
<th>Charged species</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>185.1</td>
<td>9.8</td>
<td><img src="image" alt="Chemical structure of compound a" /></td>
<td><img src="image" alt="Chemical structure of compound a" /></td>
</tr>
<tr>
<td>b</td>
<td>231.1</td>
<td>12.0</td>
<td><img src="image" alt="Chemical structure of compound b" /></td>
<td><img src="image" alt="Chemical structure of compound b" /></td>
</tr>
<tr>
<td>c</td>
<td>201.1</td>
<td>13.9</td>
<td><img src="image" alt="Chemical structure of compound c" /></td>
<td><img src="image" alt="Chemical structure of compound c" /></td>
</tr>
<tr>
<td>d</td>
<td>201.1</td>
<td>18.0</td>
<td><img src="image" alt="Chemical structure of compound d" /></td>
<td><img src="image" alt="Chemical structure of compound d" /></td>
</tr>
</tbody>
</table>
Reaction with 6wt%Au·TiO$_2$

After following the same procedure, the reaction by products of 6wt%Au·TiO$_2$ after 10 min was injected to LC-MS. According to the results, the chromatogram was significantly different from the previous experiment. Naproxen peak could not be distinguished in the chromatogram due to low concentration at 10 min. The other noticeable difference is the absence of c in the reaction mixture.

![Figure 5-12 LC-ESIMS of byproducts of 6wt%Au·TiO$_2$ reaction after 10 minutes](image)

Selective ion monitoring analysis was carried out by to confirm the above results. Ions at 185, 210 and 231 m/z were analyzed by changing the quadrupole voltage. Significantly higher intensities of the signals were observed due to selective ion monitoring. Figure 5-13 and Figure 5-14 display the difference in the product formation.
These results are similar to the previous results of TiO₂ catalysis reactions.\textsuperscript{41} This confirms the hydroxyl radical attack for the degradation of naproxen. In both cases it is apparent that the reaction has taken place on the carboxylic acid end on the molecule rather than ring structure. This behavior is consistent with the previous work on the similar types of molecules. Quinta
et al.\textsuperscript{42} reported that they did not observe the degradation of the aromatic rings due to hydroxyl radical attack of similar molecular species.

According to the comparison between LC-ESIMS of the two reaction environments, the composite yields fewer byproducts than pure TiO\textsubscript{2}. This is an advantage of using the composite. Moreover, the formation of the 185 m/z ion is favored in the reaction of the composite.

5.4. Conclusion

The photo-induced degradation of a pharmaceutical pollutant using metal-semiconductor nanomaterial has been demonstrated for the first time. The sensitivity and selectivity of modern LC-MS have been utilized to investigate the applicability of the newly developed nanocomposite. The comparison of the degradation rates revealed that the composite is 55\% more efficient than TiO\textsubscript{2}. Byproducts of the reaction have been identified and these results can be used to elucidate the degradation pathway of the molecule.
5.5. References

(12) Choi, W. *Catalysis Surveys from Asia* 2006, 10, 16.