Graphene Oxide/Zinc Oxide Nanocomposites as Dissolved Oxygen Sensors

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Abstract

Dissolved oxygen (DO) sensors found applications in different areas such as water quality management, health care, oil spill etc. To measure the levels of DO, Clark based electrodes and luminescent sensors are normally used. The luminophores used in the probes sense the DO via the luminescence quenching due to triplet-triplet annihilation. The turn-off sensors have problems to follow minute changes in DO. Here, we present novel Graphene Oxide/Zinc Oxide (GO/ZnO) nanocomposite that can work as turn-on luminescence sensors for DO. The GO/ZnO nanocomposites are sensitive to the oxygen levels in different solvents and the luminescence is enhanced with DO. With the use of GO as a substrate, the sensitivity of ZnO nanoparticles to DO was further enhanced as the substrate works as an electron sink.

Objectives

- **To develop a novel turn-on luminescent sensor to detect DO in complex environments such as oil spills**
- **To investigate the mechanism behind the sensing of DO by GO/ZnO nanocomposites**
- **To determine the effect of synthetic conditions on the sensing abilities of GO/ZnO nanocomposites**

Introduction

Why DO?

Dissolved oxygen (DO) is present in natural water to ensure the equilibrium so that aquatic life will survive and its detection is important to maintain the quality of water.

DO detection is important for food and drug industry to guarantee DO fermentation in foods and distilleries and bio-synthetic preparations in Drugs and Chemicals.

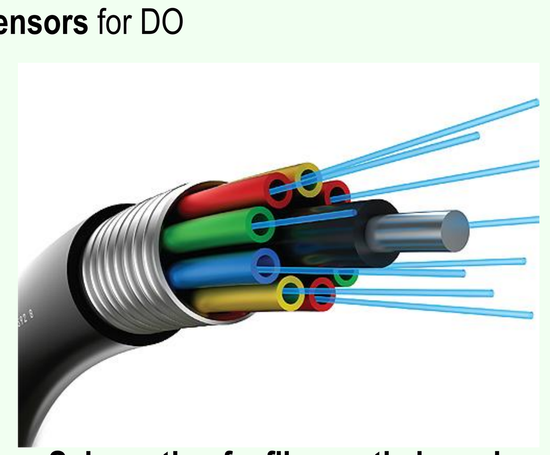
Pharma Industry: Oxygen Monitoring in Bags

Food & Beverage: Oxygen Permeation Measurement in PET Bottles

Oxygen quenching luminophores have been studied recently to optical sensors which include Clark electrodes and luminescence based electrodes. The mechanism of these methods is based on turn-off luminescence for the detection of DO.

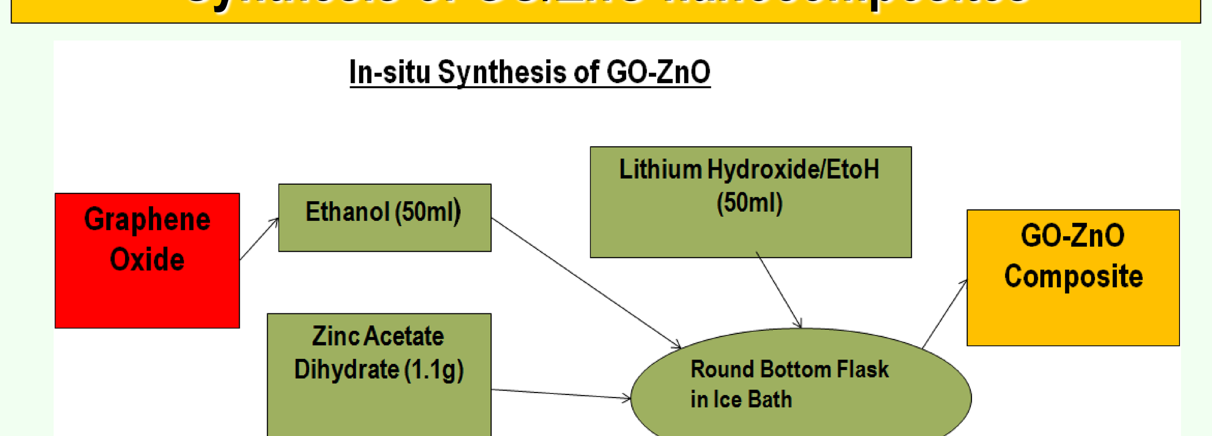
Our approach is to make **turn-on luminescent sensors** for DO

Oil spills can be detected by DO sensing

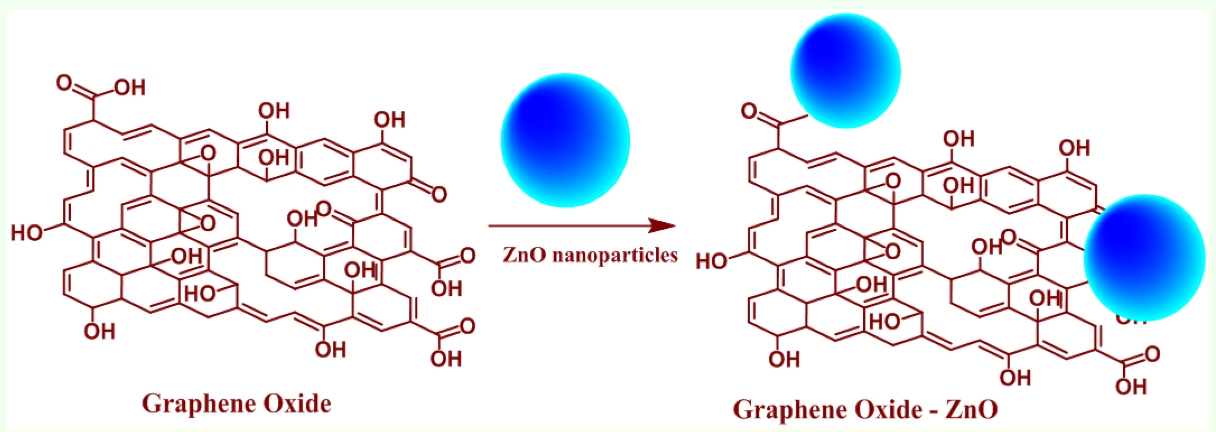


Schematic of a fiber optic based DO optica sensor

Synthesis of GO/ZnO nanocomposites



GO/ZnO nanocomposites



Scheme 1. Novel GO-ZnO nanoparticle sensor for oxygen. The ZnO nanoparticles will attach to carboxylic acid groups of the GO.

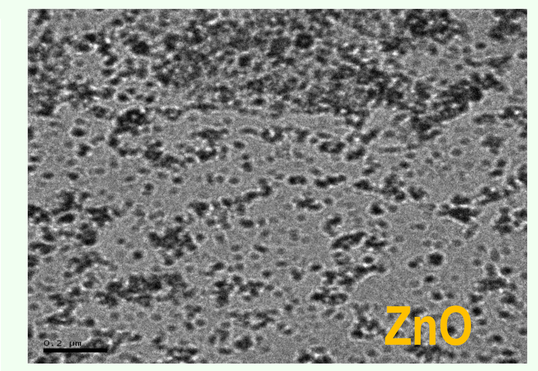


Figure 1. A TEM image of the ZnO nanoparticles at 80,000x magnification. The size of nanoparticles was determined to be around 3.7 nm..

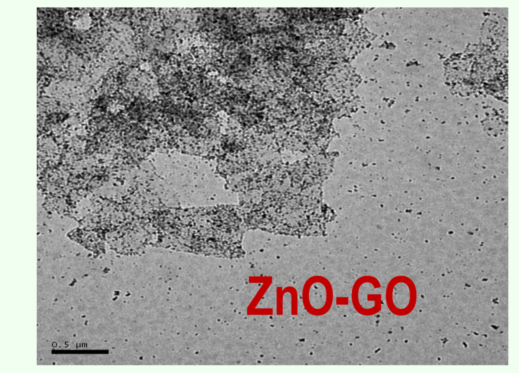


Figure 2. A TEM image of ZNO-GO nanocomposites; the GO sheets are very large, on average about 5 μm in length.

Sensing of Dissolved Oxygen – Effect of ZnO particle Size

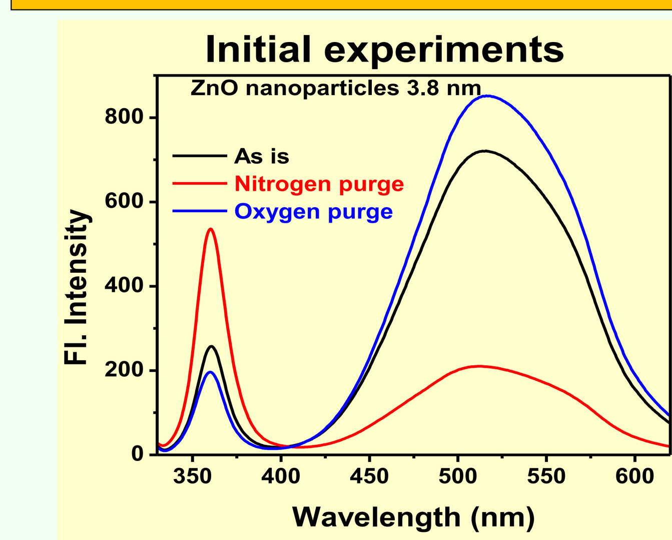


Figure 3. The luminescence spectral data of ZnO as is prepared ZnO nanoparticles in ethanol with O_2 and N_2 purging. The results show the influence of DO on ZnO luminescence

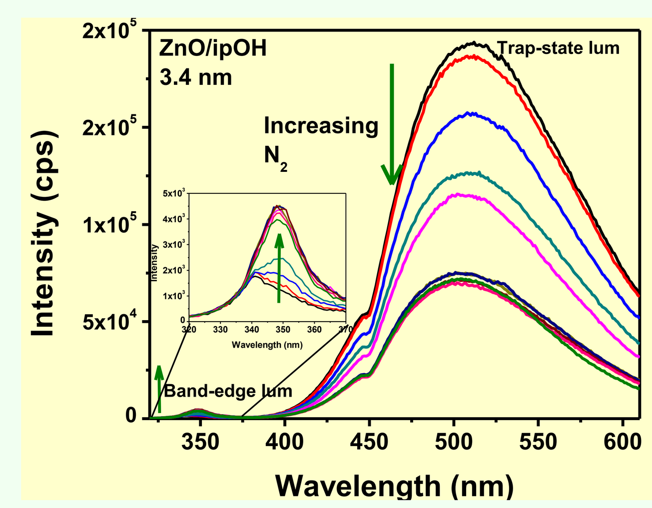


Figure 4. The luminescence quenching of ZnO with increasing N2 or decreasing DO. The band edge luminescence is increased while the trap state luminescence is quenched with nitrogen

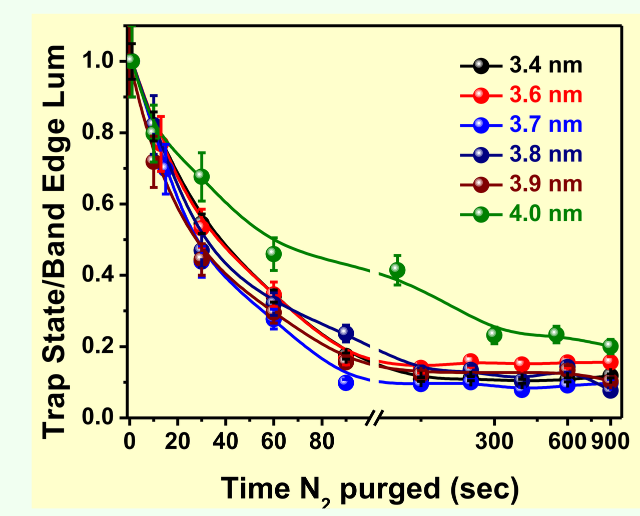


Figure 5. Influence of ZnO nanoparticles size on the sensing of DO. No significant size effect was observed

DO sensing in Different Solvents – ZnO/GO as DO Sensors

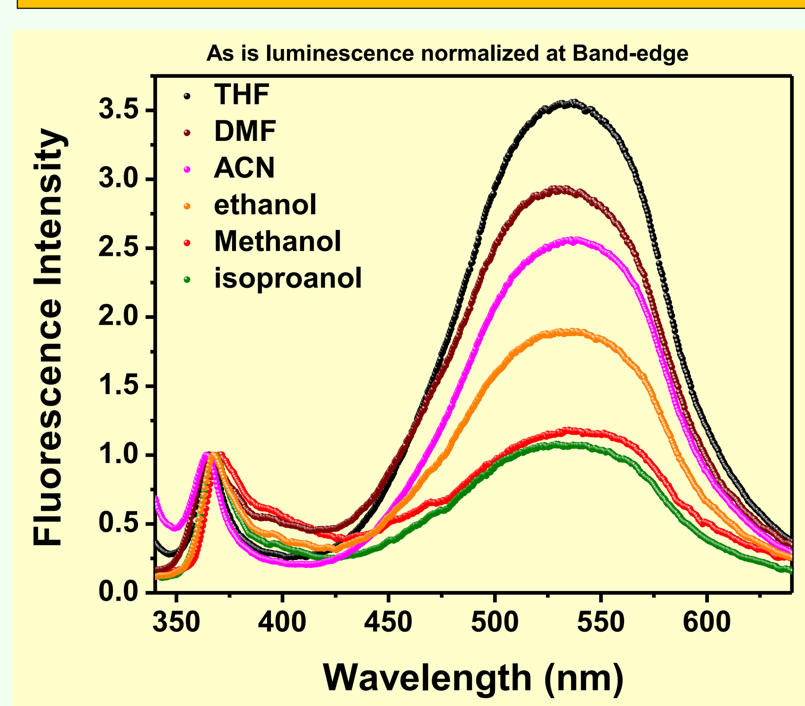


Figure 6 The luminescence spectral data for ZnO/GO in different solvents.

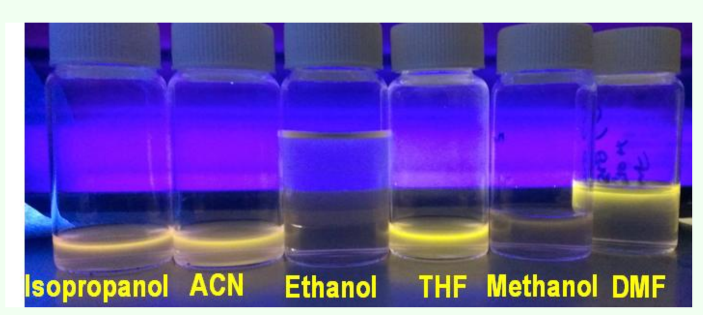


Figure 7. Luminescence images in different solvents. Different intensities can be attributed to different DO contents in solvents

Figure 8. Newly prepared ZnO/GO films with 300 nm excitation. The trap state luminescence is still observed

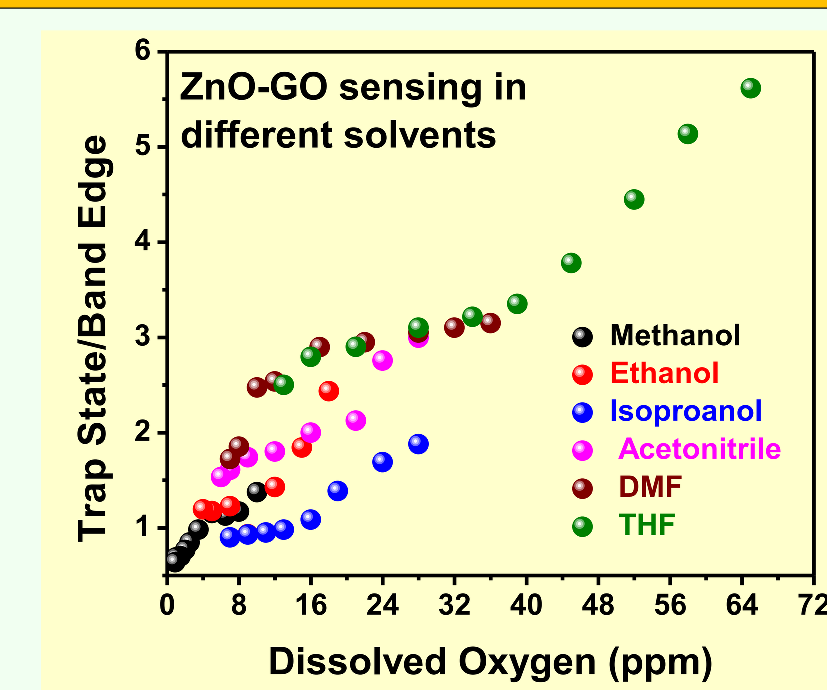


Figure 9. Trap state to band edge luminescence as a function of dissolved oxygen in different solvents. As it can be observed from Figure the new ZnO-GO sensor works as a good DO sensor as evidenced from its sensitivity to DO in wide variety of solvents

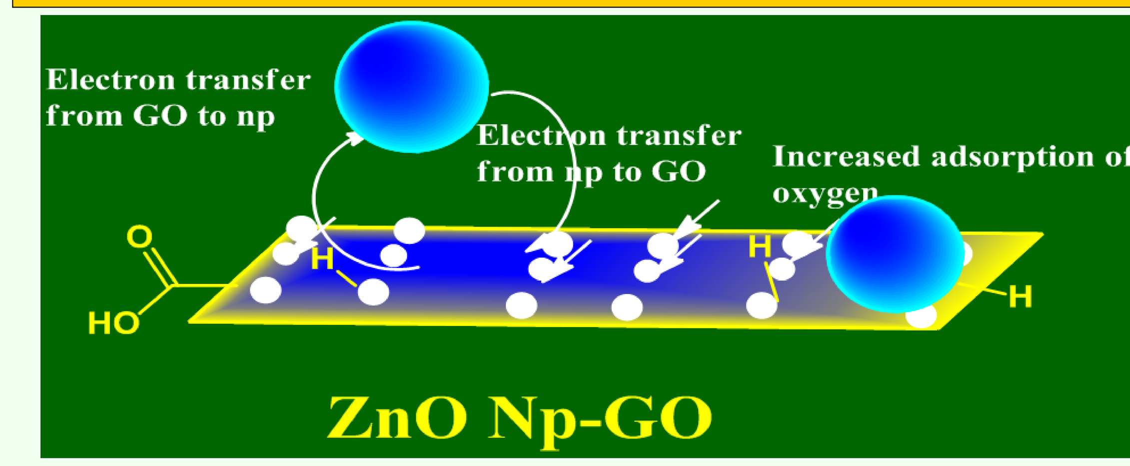
Solvent	Dissolve Oxygen (ppm)	As is Trap/BE lum	With O_2 purge Trap/BE lum	With N_2 purge Trap/BE lum
Methanol	10.2	1.1	1.3	0.6
Ethanol	21	1.2	1.9	0.9
Isopropanol	30.2	1.1	1.9	0.9
Acetonitrile	40.8	2.7	3.0	1.5
DMF	29.2	2.6	2.8	1.7
THF	68	3.6	5.7	2.5

Table 1. The trap-state to band edge luminescence data for ZnO-GO nanocomposites in different solvents as a function of N_2 and O_2 purging

Important results for ZnO-GO as DO sensors

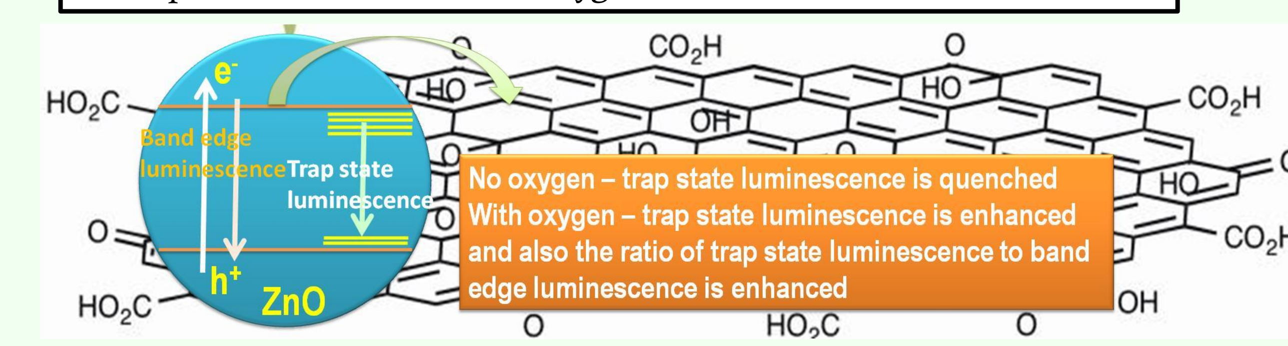
- ✓ The differences observed in different solvents is solely because of DO
- ✓ When plotted as a function of DO, the trap state to band edge luminescence ratio has increased irrespective of solvents with fairly good calibration curve

Mechanism of Sensing



Advantages of new ZnO-GO nanocomposites

- ✓ Better sensing capabilities due to enhanced electron transfer
- ✓ 2D porous structure to host oxygen

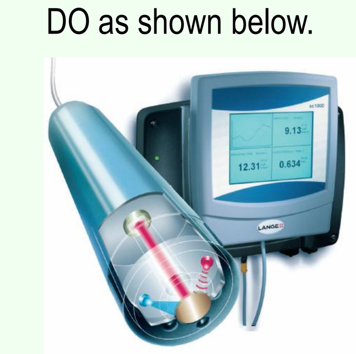


Conclusions

- ✓ **We have shown a novel way to detect DO via filling of radiative defect states with oxygen. This is one of the first study that demonstrated turn-on luminescence sensing to DO. The size influence on the sensitivity to DO (especially that of ratiometric sensing) is quite insignificant. This is probably because of the smaller size ranges studied**
- ✓ **New in-situ synthesis of ZnO decorated GO nanomaterials was developed**
- ✓ **All the solvents followed a general trend : As the O_2 level of the system drops, the trap state luminescence of the solution would decrease and the band edge luminescence would increase**
- ✓ **Present systems can be upgraded to make devices for DO sensing**

Future Work

- Conducting time-resolved luminescence measurements to probe the mechanism
- Understand the fundamental principles to generate oxygen deficient surfaces for better sensitivity and larger dynamic range towards DO
- Prepare solid state films of ZnO /GO with PDMS to create fiber optic based sensors for DO as shown below.



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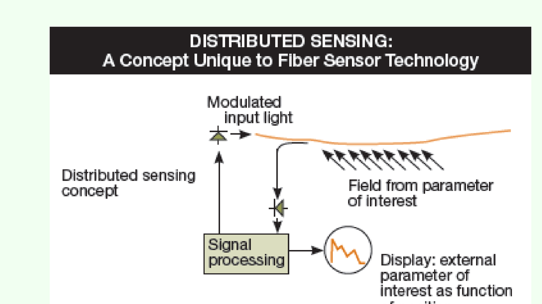

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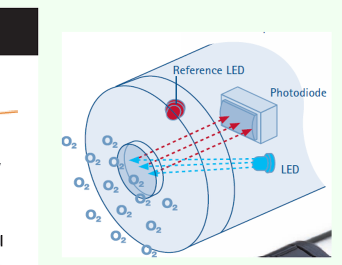

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