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 luminescence sensors are normally used. The luminescences 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) nanocomposites 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.

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 distillaries and bio-syntheses preparations in Drugs and Chemicals.

Schematic of a fiber optic based DO optical sensor

GO/ZnO nanocomposites

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

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

Figure 3. The luminescence spectral data of ZnO as is prepared ZnO nanoparticles is enriched with O2 and N2 purging. The results show the influence of DO on ZnO luminescence.

Figure 4. The luminescence spectral data 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. We significant size effect was observed.

Figure 6. The luminescence spectral data for ZnO 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 the figure new ZnO-GO sensor works as a good DO sensor as evidenced from its sensitivity to DO in wide variety of solvents.

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

Table 1. The trap state to band edge luminescence spectral data for ZnO-GO nanocomposites in different solvents as a function of O2 and N2 purging.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dissolved Oxygen (ppm)</th>
<th>As is</th>
<th>Trapping/BE lum</th>
<th>With O2 purging/BE lum</th>
<th>With N2 purging/BE lum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>10.2</td>
<td>1.1</td>
<td>1.1</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>21</td>
<td>1.2</td>
<td>1.9</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Isopropanol</td>
<td>10.2</td>
<td>1.1</td>
<td>1.9</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>40.8</td>
<td>2.7</td>
<td>3.0</td>
<td>1.5</td>
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<tr>
<td>DMF</td>
<td>29.2</td>
<td>2.6</td>
<td>2.8</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>68</td>
<td>5.6</td>
<td>5.7</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

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

References
- Advantages of new ZnO-GO nanocomposites
- Better sensing capabilities due to enhanced electron transfer
- 2D porous structure to host oxygen

Future Work
- Conducting time-resolved luminescence measurements to probe the mechanism
- Understanding 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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Mechanism of Sensing
- Electronic transfer from GO to trap
- Increased adsorption of oxygen

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 radiometric 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 O3 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