Sonochemical Synthesis, Characterization, and Photocatalytic Performance Evaluation of Au/ZnO Nanocomposite for Methyl Orange Degradation

Md. Iqbal Hossain Chowdhury
Product Development and Quality Control, Akij Venture Group, Dhaka, Bangladesh

Kaniz Fatema
Department of Applied Chemistry and Chemical Engineering, Noakhali Science and Technology University, Noakhali-3814, Bangladesh

Khodeja Afrin
Department of Applied Chemistry and Chemical Engineering, Noakhali Science and Technology University, Noakhali-3814, Bangladesh

Fariha Afrose
Department of Applied Chemistry and Chemical Engineering, Noakhali Science and Technology University, Noakhali-3814, Bangladesh

Md. Shahadat Hossain
Department of Chemistry, Noakhali Science and Technology University, Noakhali-3814, Bangladesh

Md. Abdus Samad Azad
Department of Applied Chemistry and Chemical Engineering, Noakhali Science and Technology University, Noakhali-3814, Bangladesh

Abstract:
This study examines the impact of gold (Au) incorporation on zinc oxide (ZnO) nanoparticles. Both pure ZnO and Au/ZnO nanocomposite have been synthesized using a unique and environmentally friendly sonochemical approach. The as-synthesized Au/ZnO nanocomposite was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and ultraviolet-visible (UV-vis) spectroscopic techniques. Under UV-visible irradiation, the photocatalytic effectiveness of ZnO nanoparticles and Au/ZnO nanocomposites for the degradation of dye was examined. The results demonstrated that the nanocomposite has greater photocatalytic activity than ZnO nanoparticles. This is due to the effective electron transfer from ZnO to Au prolonging the lifetime of photogenerated holes, which play the most important role in the dye degradation process.

Keywords: Sonochemical Synthesis, Photocatalysis, Nanocomposite, Au/ZnO, Methyl Orange.
**Introduction**

Pollution in the air and water is primarily caused by chemicals generated by different industries. Organic dyes such as methylene blue (MB), methylene orange (MO), and rhodamine blue are the most common sources of hazardous coloring agents. The presence of these contaminants in groundwater and surface water is harmful to both the ecosystem and living creatures (Hossain, Furusawa, & Sato, 2023). Rapid industrialization is the major source of pollutants discharged through effluents. Colorants such as organic dyes have become more prevalent in water bodies due to their use in the cosmetics, food, textile, and paper industries (Janani et al., 2021).

Many traditional procedures have been used for the decolorization and deterioration of dyes in sewage such as adsorption (Rashid, Shafiq, Akhter, Iqbal, & Hussain, 2021), membrane filtration (Anis, Hashaikeh, & Hilal, 2019), and activated sludge (Sikosana, Sikhwivhilu, Moutloali, & Madyira, 2019).

Photocatalysis is regarded as one of the most effective and adaptable approaches for the elimination of organic contaminants from wastewater. As semiconductor materials possess special photocatalytic activity, they are considered prominent catalysts for water purification under light irradiation (Liu et al., 2019). Using semiconductor materials for the detoxification of contaminants offers several benefits over conventional treatment techniques by decomposing toxic organic dyes into environment-friendly products with no waste generation (Lam, Choong, et al., 2022).

ZnO is a technologically essential semiconductor and is believed to be a competing photocatalyst among many other metal oxide semiconductors due to its high light sensitivity, large area-to-volume ratio, wide band gap (3.37 eV), low cost, and good chemical stability (Lam, Sin, et al., 2022; Mei, Zhou, Lu, & Cheng, 2020; Sivakumar, Gajendiran, & Jayavel, 2020). To be more precise, the high surface reactivity of zinc oxide tends to create a significant number of defect sites from oxygen nonstoichiometric reactions, which is one of the reasons why zinc oxide is a better electrocatalyst than other metallic nanoparticles (Shaymardanov, Rustamova, Jalolov, & Urolov, 2023).

However, photocatalysts based on ZnO encounter electron-hole recombination as a major issue (Gayathri et al., 2022). In the presence of UV light, electron/hole pairs recombine more rapidly than surface redox processes, which limits photo deterioration efficiency (Khataee et al., 2014; Pan et al., 2015). In order to improve its photocatalytic activity, a number of traditional strategies have been developed, such as doping metal (Pascariu et al., 2018) and nonmetal (Yu, Zhang, & Peng, 2016) elements, depositing noble metals (Vaiano et al., 2018; Wu, Chen, Wang, & Ji, 2017), coupling inorganic-inorganic (Faisal et al., 2015) and inorganic/organic semiconductors (Eskizeybek, Sari, Gülce, Gülce, & Avci, 2012), and modification with carbon materials (Chen, Chang, Yang, Chiu, & Lee, 2013; Wang, Qiu, Liu, & Yang, 2017).

The noble metal gold has been used in the production of ZnO-metal composite due to its strong electron attraction behavior and ability to build a large Schottky barrier between semiconductors and metals (Bora, Kyaw, Sarkar, Pal, & Dutta, 2011). Au has the benefit of not corroding in photocatalytic processes, and gold doping is a handy approach to regulate the flow of photogenerated charge carriers under UV irradiation, which helps to prevent electron–hole recombination (Long et al., 2011).

Au/ZnO has been fabricated by various conventional methods, such as co-precipitation (Y. Li, Chen, & Zhao, 2018), co-sputtering (Pal et al., 2001), ion sputtering (Dai, Ding, Chen, & Fu, 2023), microwave irradiation (M. Lee et al., 2023; Mishra & Satpati, 2022), hydrothermal (Dai et al., 2023), one-pot coordination–calcination (Lin et al., 2022), ion implantation (Macková et al., 2022), and green method (Syahjoko Saputra et al., 2021). The sonochemical method is a simple, fast, nontoxic, and environment-friendly synthesis technique (C. Li et al., 2023), where acoustic cavitation is produced when ultrasonic waves pass through a liquid media (McKenzie, Karimi, Ashokkumar,
Cavitation has three stages: the formation of microbubbles, their development, and their catastrophic collapse. Due to localized "hot spots" created by bubble collapse, the sound's diffused energy is condensed into chemically usable energy with temperatures up to 5000 °C, pressures up to 1000 atm, and a lifespan of less than a millisecond (Bhangu & Ashokkumar, 2016; Z. Li et al., 2021).

Here, we report the synthesis of Au/ZnO nanocomposite using a sonochemical method and investigate the influence of gold inclusion on the photocatalytic performance of ZnO.

**Materials and Methods**

**Materials**

All the chemicals employed were of analytical grade and did not undergo any further purification. The chemicals used in this experiment were zinc nitrate hexahydrate (Sigma Aldrich, reagent grade 98%), ethanol (Merck, Germany), ammonium hydroxide (Merck, Germany), sodium citrate dibasic dehydrate (Sigma Aldrich, USA), and gold (III) chloride trihydrate (Sigma Aldrich, USA).

**Synthesis of Au/ZnO Nanocomposite**

0.2 M aqueous solution of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) was incorporated into a mixture consisting of 200 ml of ethanol and 100 ml of water under magnetic stirring. After 10 min, 8.16 ml of NH₄OH was added to the mixture. The mixture was ultrasonically irradiated at room temperature for 4 h, and then centrifuged at 7000 rpm for 10 min. After being rinsed with ethanol three times, the residue was dried at 120 °C for 24 h. To coat the exterior of ZnO NPs with gold, 0.3 g of ZnO NP was sonicated for 10 min while being submerged in a 40 ml aqueous solution of 0.01 mmol HAuCl₄. The solution was occasionally sonicated to minimize agglomeration during stirring and brought to the boiling point. Next, 10 ml of 0.01 M sodium citrate solution was added. The hue went from white to gray. Then, the solution was agitated for 2 h at room temperature so that the Au could thoroughly modify the ZnO nanoparticles. To prevent the solution from clumping up too much while being stirred, it was occasionally sonicated.

After centrifuging the resulting powder at 8500 rpm for 10 min, it was rinsed three times with deionized water and absolute ethanol before being dried in a vacuum oven at 80 °C for 24 h. The dried nanocomposites were crushed into fine powders and calcined at 500 °C in a muffle furnace. The calcined samples were kept under an inert atmosphere until they were ready for use.

**Characterization**

The XRD spectra were recorded with a powder diffractometer (Ultima IV, Rigaku Corporation, Japan). A field emission scanning electron microscope (FE-SEM) (Hitachi Ltd., Japan) was used to study the morphological structure of the samples. The FE-SEM observations were conducted at a voltage of 5 kV and a current of 10 μA. Carbon tape was used to hold the powder prior to observation. Next, platinum was coated onto samples using a Pt-Pd ion coater (Hitachi, E-1030, Japan). A UV-visible spectrophotometer (SHIMADZU UV-1650pc, Japan) was used to record the dye concentration.

**Photocatalytic Experiments**

In a 100 ml quartz beaker, 75 ml of 5×10⁻⁴ M methyl orange solution and 0.25 g of catalyst were allowed to reach equilibrium while being agitated for 30 min in the dark. Experiments involving photocatalytic degradation were conducted under ambient conditions. For the photocatalytic stability study, pure ZnO and Au/ZnO samples were used. 3 ml of the solution was taken out at various time intervals and centrifuged to remove the catalyst from the solution. The spectra were recorded using a Shimadzu UV–visible spectrophotometer (UV-1650pc). Degradation (or elimination) % was determined according to the following equation:

\[
\text{Degradation} = \frac{A_0 - A}{A_0} \times 100\% \quad (1)
\]
where $A_0$ is the absorbance of the MO dye in solution at the preliminary stage and $A$ is the absorbance after a certain time ($t$).

**Discussion**

In XRD analysis, crystal quality was assessed for ZnO and Au/ZnO composite. The powdered XRD pattern for the synthesized compound is shown in Figure 1. Peaks appeared at $31.73^\circ$ (100), $34.38^\circ$ (002), $36.21^\circ$ (101), $47.50^\circ$ (102), $56.54^\circ$ (110), $62.80^\circ$ (103), $66.32^\circ$ (200), $67.89^\circ$ (112), $69.02^\circ$ (201), $72.48^\circ$ (004), and $76.90^\circ$ (202) agree with the standard JCPDS card no. 36-1451, suggesting that the ZnO nanoparticles have the recognizable hexagonal wurtzite structure (Kenyota, Mauagree, & Laokul, 2021).

Further, peaks at approximately $38.23^\circ$, $44.37^\circ$, $64.57^\circ$, and $77.51^\circ$ may be ascribed to the (111), (200), (220), and (311) reflective surfaces of the Au cubic crystal structure in the produced Au/ZnO sample (JCPDS card No. 04-0784) (Krishnamurthy, Esterle, Sharma, & Sahi, 2014). The XRD analysis did not reveal any unexpected stages or pollutant peaks over the entire spectrum, indicating that the final Au/ZnO product is very pure.

![Figure 1. XRD Patterns of (a) ZnO Nanoparticle and (b) Au/ZnO Nanocomposite after Heat Treatment at 500°C. * Indicates the Peaks Originated Due to Au Inclusion in the Au/ZnO Sample](image)

The crystallite size ($D$) of the samples was determined by the X-ray line broadening method using the Scherrer equation (Viter et al., 2015).

\[
D = \frac{(0.9\lambda)}{\beta \cos \theta}
\]  

(2)

where $\lambda = 0.154$ nm (X-ray wavelength), $\theta$ is the diffraction angle and $\beta$ is the full width at half maximum (FWHM). Table 1 displays the typical crystalline sizes of the ZnO and Au/ZnO specimens.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2$\theta$ (degree)</th>
<th>Crystal Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ZnO</td>
<td>36.25</td>
<td>33.58</td>
</tr>
<tr>
<td>Au/ZnO</td>
<td>36.28</td>
<td>32.11</td>
</tr>
</tbody>
</table>

Table 1. Size distribution of pure and Au-doped ZnO crystals

Initial morphological analysis of ZnO and Au/ZnO samples was conducted using FE-SEM. It can be seen from the SEM micrograph of ZnO (Figure 2a) that some spheres are aggregated and linked to one another, and their surfaces are not smooth. On the contrary, smooth spherical spheres were observed in Au/ZnO samples indicating the coating of Au on the ZnO surface (Figure 2b-2d).
Energy-dispersive X-ray (EDS) spectral peaks verify the existence of Zn, O, and Au (Figure 3).

The presence of distinct peaks suggests that the specimen is composed of Au and ZnO (M.-K. Lee & Tu, 2008).

Under UV irradiation, methyl orange (MO) was selected as a model pollutant for evaluating the photocatalytic activity of ZnO and Au/ZnO. A graph of the degradation percentages of MO using these photocatalysts is depicted in Figure 4. It shows that the decomposition of MO by Au/ZnO is much quicker than by uncoated ZnO, demonstrating the crucial role of Au as a photocatalyst in this process.

To efficiently separate photoelectron (e⁻) and hole (h⁺) pairs, it is commonly assumed that excited photoelectrons from the ZnO conduction band may swiftly and readily move to the AuNPs surface. With Au acting as an electron sink, photogenerated electron/hole pairs on ZnO surfaces are allowed to spread more evenly, thereby reducing the recombination of charges. (Verma, Tirumala Rao, Singh, & Kaul, 2021).

The rate constants were calculated according to the following equation (Vu et al., 2021):
\[
\ln \frac{C_0}{C_t} = kt \quad (3)
\]

where \(k\) is the pseudo-first-order rate constant; \(C_0\) and \(C_t\) are the concentrations of dye at initial \((t = 0)\) and time \(t\) (min), respectively.

It was found that the rate constant of \(\text{Au/ZnO}\) is considerably higher than \(\text{ZnO NPs (Table 2)}\).

### Table 2. Reaction Rate of the Selected Sample

<table>
<thead>
<tr>
<th>Serial</th>
<th>Sample</th>
<th>Reaction Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure ZnO</td>
<td>0.009</td>
</tr>
<tr>
<td>2</td>
<td>Au/ZnO</td>
<td>0.014</td>
</tr>
</tbody>
</table>

The following straightforward process, outlined in Equations (1-7), may be used to explain the degradation of MO by ZnO and \(\text{Au/ZnO composite}\).

\[
\begin{align*}
\text{ZnO} + h\nu & \rightarrow h^+ + e^- \quad (4) \\
n^+ + O_2 & \rightarrow O_2^- \quad (5) \\
h^+ + OH^- & \rightarrow OH^- \quad (6) \\
O_2^- + 2H^+ & \rightarrow 2OH^- \quad (7) \\
OH^- + MO & \rightarrow \text{colorless product} \quad (8) \\
h^+ + MO & \rightarrow \text{colorless product} \quad (9) \\
O_2^- + MO & \rightarrow \text{colorless product} \quad (10)
\end{align*}
\]

It may entail the direct interaction of the dye with photogenerated holes in a method comparable to the photo-Kolbe reaction or oxidation via sequential assaults by hydroxyl radicals or superoxide species. It has been shown that the presence of the hydroxyl radical, a particularly potent non-selective oxidant, may result in the partial or total oxidation of a variety of organic compounds. After being excited by UV light, ZnO contributes to the dissociation of water molecules into positively charged ions \((H^+)\) and negatively charged ions \((OH^-)\). The very unstable hydroxyl ions are believed to be responsible for the decomposition of the dye. It is done by repeatedly assaulting the N=N link and, as a result, gradually separating the linear chains from the rings. In the presence of dissolved oxygen, the hydroxyl group forms a new bridging with the unattached N=N in the ring opening to form NOOH. This occurs when the hydroxyl group is exposed to oxygen.

Au acts as an electron sink (receptor) (Peychev & Vasileva, 2021). During the light excitation, an electron created by the ZnO is temporarily held on the Au surface. To keep the charge/electron balance in the ZnO, the electron is transferred back to the ZnO.

### Conclusion

In this study, the sonochemical synthesis method was used to synthesize \(\text{Au/ZnO nanocomposite}\). ZnO and Au’s structural patterns were revealed by XRD spectra of \(\text{Au/ZnO particles}\). Homogeneous distribution of the Au was observed in the nanocomposite samples. In the presence of ultraviolet light irradiation, MO aqueous solution was studied for photocatalysis. Au/ZnO shows greater photocatalytic activity as indicated by the percentage of degradation and reaction rate as well.

### Acknowledgement

This research received financial support from the National Science and Technology (NST), Ministry of Science and Technology, Bangladesh.

### Conflict of Interests

No conflict of interest.

### References


Lam, S. M., Sin, J. C., Zeng, H., Lin, H., Li, H.,...


ZnO Composite Sphere Decorated with ZnO Clusters for Effective Charge Isolation in Photocatalysis. Industrial and Engineering Chemistry Research, 54(29), 7226–7232. https://doi.org/10.1021/ACS.IECR.5B01471

ASSET/IMAGES/MEDIUM/IE-2015-01471V_0009.GIF


