Enhancing the Photocatalytic Activity of BiOBr Supported by Graphene Oxide for Antibiotic Degradation in Wastewater

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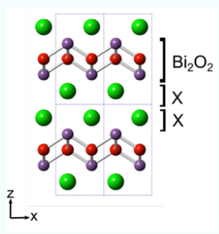
Abstract

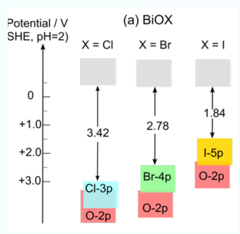
The development of bismuth-based photocatalysts offers a promising approach for wastewater treatment. In this work, bismuth oxybromide (BiOBr) was synthesized using a hydrothermal method and modified with graphene oxide (GO) at various loadings (0.5, 0.75, 1, 1.5, 2, and 3 wt%) to improve its photocatalytic performance. The photocatalytic activity of the BiOBr/GO composites was evaluated through the degradation of three antibi-otics: ciprofloxacin (CIP), tetracycline (TC), and amoxicillin (AMX) under visible-light irradiation from a 100 W LED lamp. The residual concentrations of the antibiotics after reaction were quantified using UV-Vis spectrophotometry. X-ray diffraction (XRD) analysis confirmed that BiOBr and all BiOBr/GO composite catalysts was a tetragonal phase. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses revealed that GO sheets were uniformly distributed on the square-like BiOBr microplates. UV-Vis DRS analysis showed that all synthesized material responded in the visible-light region, indicating their ability to utilize visible irradiation. Moreover, the GO/BiOBr composites demonstrated stronger visible-light absorption with increasing GO content. Among all compositions, the 2%wt-GO/BiOBr photocatalyst exhibited the highest activity, achieved degradation efficiencies of 60% for CIP, 68% for TC, and 64% for AMX within 210 minutes. Reactive species trapping experiments were carried out to identify the dominant species which is superoxide radical act as the dominant reactive species. Electrochemical measurements, photoluminescene (PL) and time-resolve photoluminescence (TRPL) analyses indicated that the incorporation of GO facilitated charge carrier separation and suppress electron-hole recombination. To confirm the reactive species that occurred during photocatalysis reaction was carried through electron paramagnetic resonance (EPR). This work demonstrates that incorporating an appropriate amount of GO into BiOBr improves its photocatalytic performance toward antibiotic degradation, demonstrating the potential of BiOBr/GO composites for wastewater treatment.

Introduction

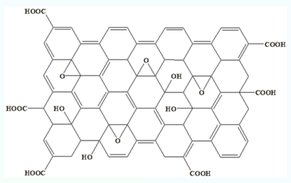
Antibiotic residues are frequently detected in wastewater due to their extensive use in medical and agricultural applications. Photocatalysis is considered an effective method for removing organic pollutants.

Bismuth oxyhalides photocatalyst





Advantages of BiOBr
- suitable band structure for visible-light photocatalysis.
- good chemical stability.
- layered crystal structure that supports charge separation.



Advantages of incorporating GO
- increase the surface area of the composite.
- facilitate charge transport.
- improve the separation of photogenerated charge carriers.

Objective: To synthesize BiOBr/GO composite photocatalysts and evaluate their photocatalytic performance for antibiotic removal.

Experimental procedure

$(Bi(NO_3)_3 \cdot 5H_2O)$ (2mmol) and KBr (2mmol) were dissolved in Di water. → Stirred until the precursor was completely dispered. → GO was added to the mixture. → Sonicate 30 min. → Stirred for 30 min. → The mixture was treated by the hydrothermal method at 160 ˚C for 12 h. → Washed 3 times with DI water and with ethanol. → The product was grounded using a mortar and collected in vial.







Figure 1. Schematic illustration of the synthesis procedure for BiOBr and BiOBr/GO composites.

Results and Discussions

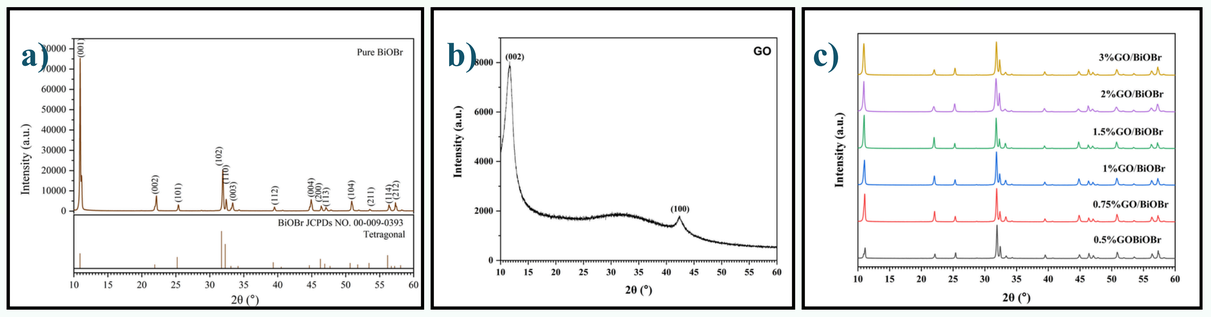


Figure 2. XRD pattern of a) BiOBr, b) GO and c) BiOBr/GO composites.

1. The diffraction pattern peaks correspond to the standard BiOBr data ($JCPD_S$ No. 00-009-0393) confirming the formation of a tetragonal BiOBr crystal structure.
2. The GO sample exhibits a board peak at 2θ = 11.6˚, which is characteristic of GO. The peak (100) at 42.395 ˚ suggested the static disorder of GO.
3. The peak of GO is not clearly visible in the composite due to the low content of GO.

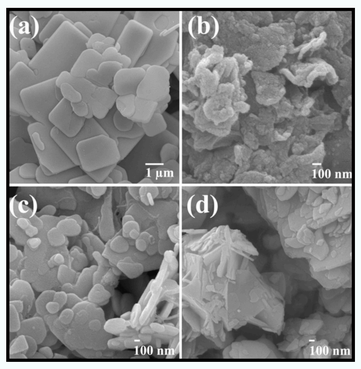


Figure 3. SEM images of **(a)** BiOBr, **(b)** GO, **(c)** 2%GO/BiOBr composite, and **(d)** 2%GO/BiOBr after 4 reuse cycles.

The BiOBr sample consists of square - like microsheets. The GO sample shows thin and wrinkled sheet structures. For the 2%GO/BiOBr composite, the BiOBr microsheets are attatch to the GO surface. After 4 reuse cycles, the composite still shows a similar structure without major morphological change.

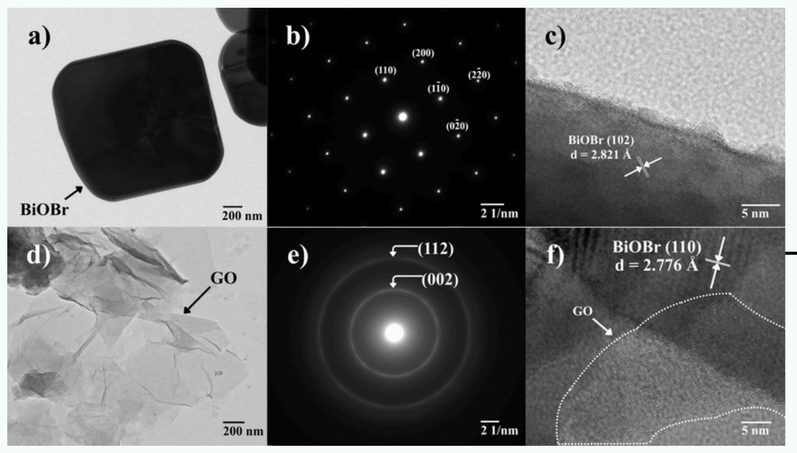
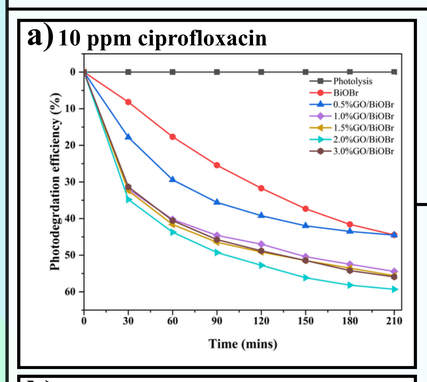
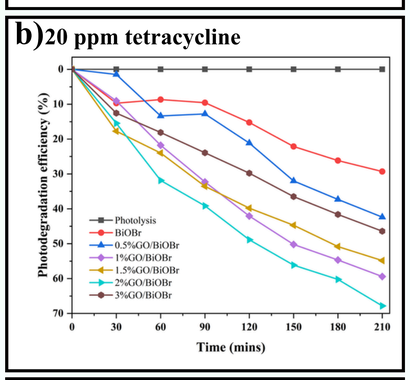


Figure 4. TEM image of **(a)** BiOBr and **(d)** GO, SAED pattern of **(b)** BiOBr and **(e)** GO, and HRTEM image of **(c)** BiOBr and **(f)** BiOBr/GO composite.

The square - like BiOBr microsheets are observed to be attached to the thin and wrinkled sheet - like GO. The HRTEM image shows lattice fringes with a spacing of 2.776 Å, corresponding to the (110) plane of BiOBr.





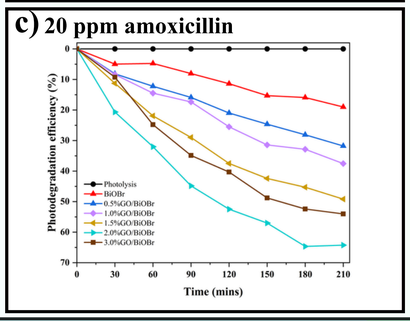


Figure 5. Photocatalytic efficiency for (a) degradation of 10 ppm CIP, (c) degradation of 20 ppm TC, (e) degradation of 20 ppm AMX.

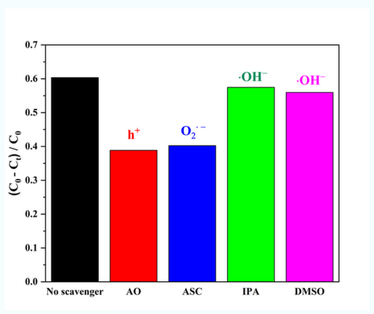


Figure. 6 Reactive species trapping experiments.

The 2%GO/BiOBr composite shows the highest photodegradation efficiency of 10 ppm CIP, 20 ppm TC and 20 ppm AMX with 60%, 68% and 64%, respectively within 210 minutes. Trapping experiments indicate that hole (h^+) and superoxide radical ($\bullet O_2^-$) are the main active species, while and hydroxyl radical (•OH) is minor specie in the photocatalytic degradation reaction.

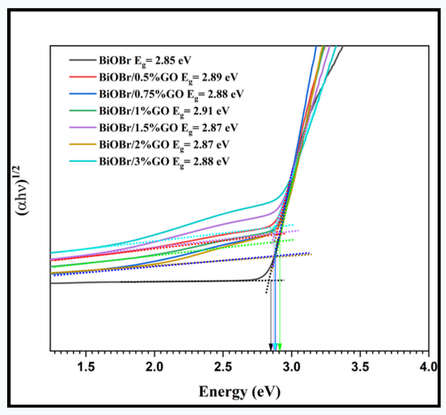


Figure 7. Tauc plots of all samples.

Band gap energies (E_g) of BiOBr and GO/BiOBr composites were estimated using the Tauc equation.

$$\alpha h\upsilon = A(h\upsilon - E_g)^{n/2}$$

Since 2%GO/BiOBr is indirect band gap semiconductor, the n value is 1. By plotting $(\alpha h\nu)^{n/2}$ versus hν, the E_g values of BiOBr is 2.85 eV while the GO/BiOBr composites show values in the range of 2.87 - 2.91 eV.

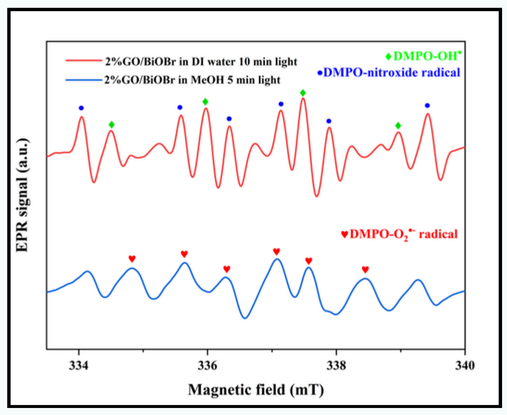


Figure. 8 EPR spectra of 2%GO/BiOBr in aqueous and methanol solution.

EPR analysis confirms the generation of $\bullet O_2^-$ and •OH as the major and minor active species in the system, respectively. The detection of a nitroxide radical resulting from the oxidation of the DMPO spin-trap highlights the system's highly oxidative environment.

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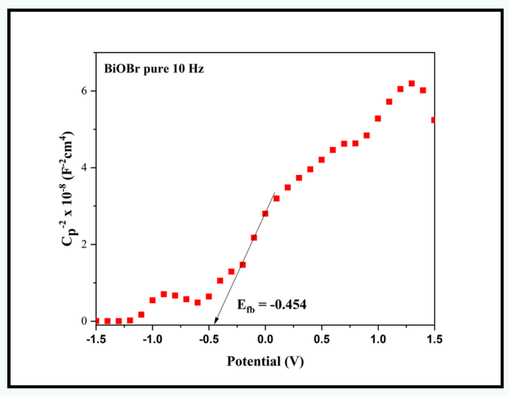


Figure. 9 Mott-Schottky plot of BiOBr.

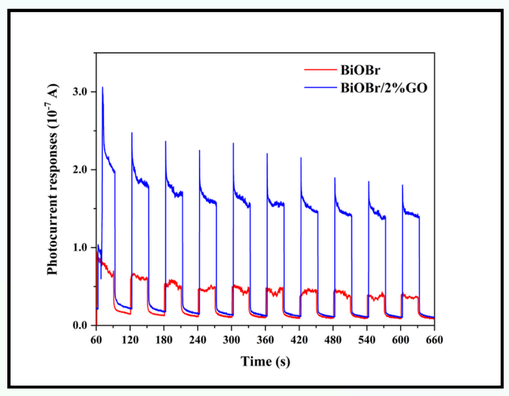


Figure. 10 Transient photocurrent responses of BiOBr and 2%GO/BiOBr.

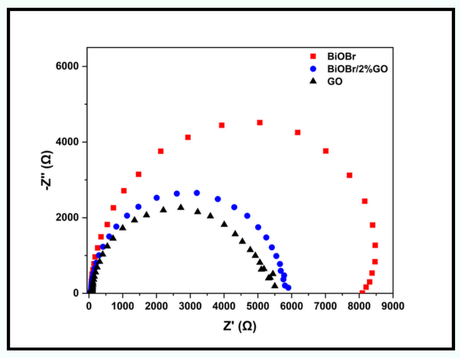


Figure. 11 EIS Nyquist plots of BiOBr, 2%GO/BiOBr and GO.

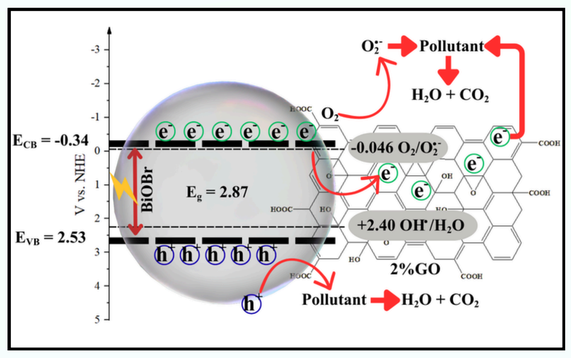


Figure. 12 Photocatalytic mechanisms for the antibiotic drugs photodegradation by 2%GO/BiOBr composite photocatalyst.

Conclusion

1. BiOBr/GO composites were successfully synthesized via a hydrothermal method.
2. The incorporation of GO improved photocatalytic activity by facilitating charge separation.
3. The 2 wt% GO/BiOBr composite exhibited the highest photocatalytic performance for antibiotic degradation under visible-light irradiation.

References

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2. Daichi K., Kenta H., Ryo M., Masanobu H., Hironobu K., Masayoshi Y., Hajime S., Hiroyuki O., Chengchao Z., Kousuke N., Ryu A., Hiroshi K., (2017) , J. Am. Chem. Soc. 2017, 139, 51, 18725–18731

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