Master’s Thesis Engineering Technology

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Photocatalytic degradation of an organic pollutant (Rhodamine B) under visible light irradiation using a bismuth iodide oxide, iron(II,III) oxide and (reduced) graphene oxide photocatalyst

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Introduction

The Hanoi University of Science and Technology (HUST), founded in 1956, is the first multidisciplinary technical university of Vietnam. HUST is a university which holds high regards for academic excellence and effectiveness. The institute where this academic research takes place is the International Training Institute for Materials Science (ITIMS). Scientific education, research and transfer of technological knowledge in the field of materials science are accomplished in this establishment. My line of research falls under conducting research on a material called graphene.

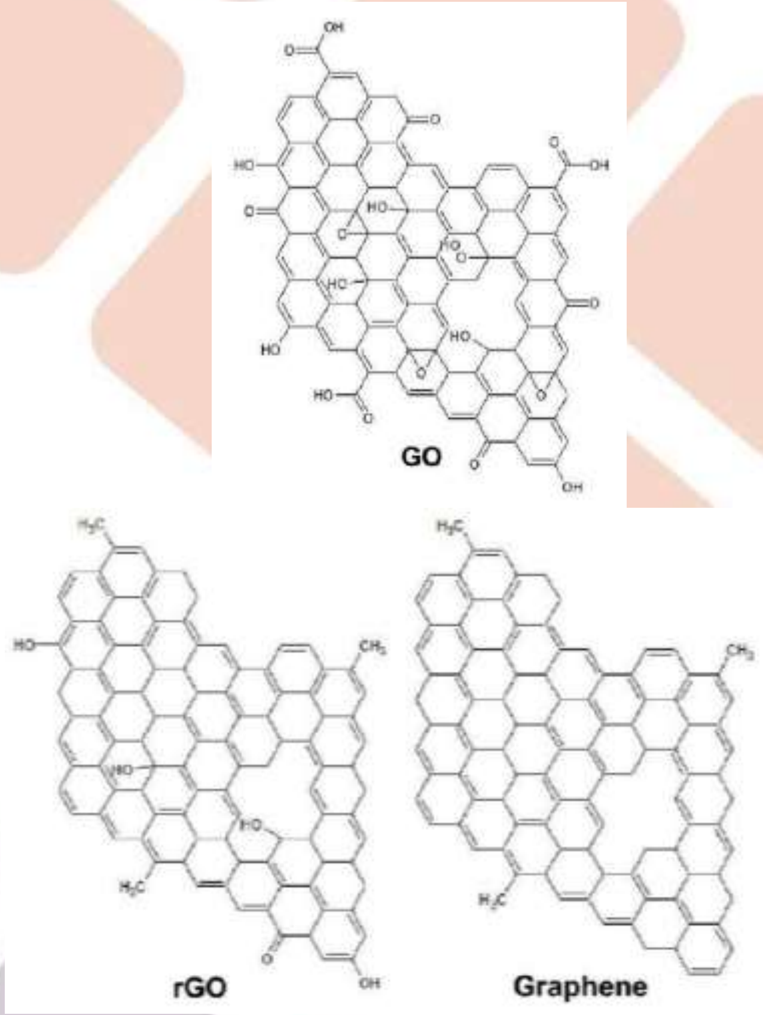

Figure 2. Different structures of graphene

Problem definition

Graphene is a 2D carbon-based material with a honeycomb sp^2 carbon lattice. It was first isolated in 2004 by Andre Geim and Konstantin Novoselov, they succeeded by using a method now known as the “Scotch tape method”.

Graphene possesses remarkable properties:

- Strongest material on earth, yet very flexible;
- Thickness of 1 atom;
- High thermal and electrical conductivity.

Because of these properties graphene has applications in composites, coatings, sensors, electronics...

In the form of composites, graphene has an application as a photocatalyst. Photocatalysts are catalysts that utilize energy from light to drive chemical conversions. Semiconductors such as metal-oxides absorb a photon of light to promote an electron from the valence band to the conduction band leaving a hole in the VB. This system of electrons and holes is necessary to enable photocatalysts to work as a degradation method because they are responsible for the redox reactions that need to take place.

There are a number of drawbacks to popular photocatalysts:

Low activity in visible light;

Quick recombination of electron-hole pairs.

Composites of graphene and metal-oxides show promising results for both disadvantages.

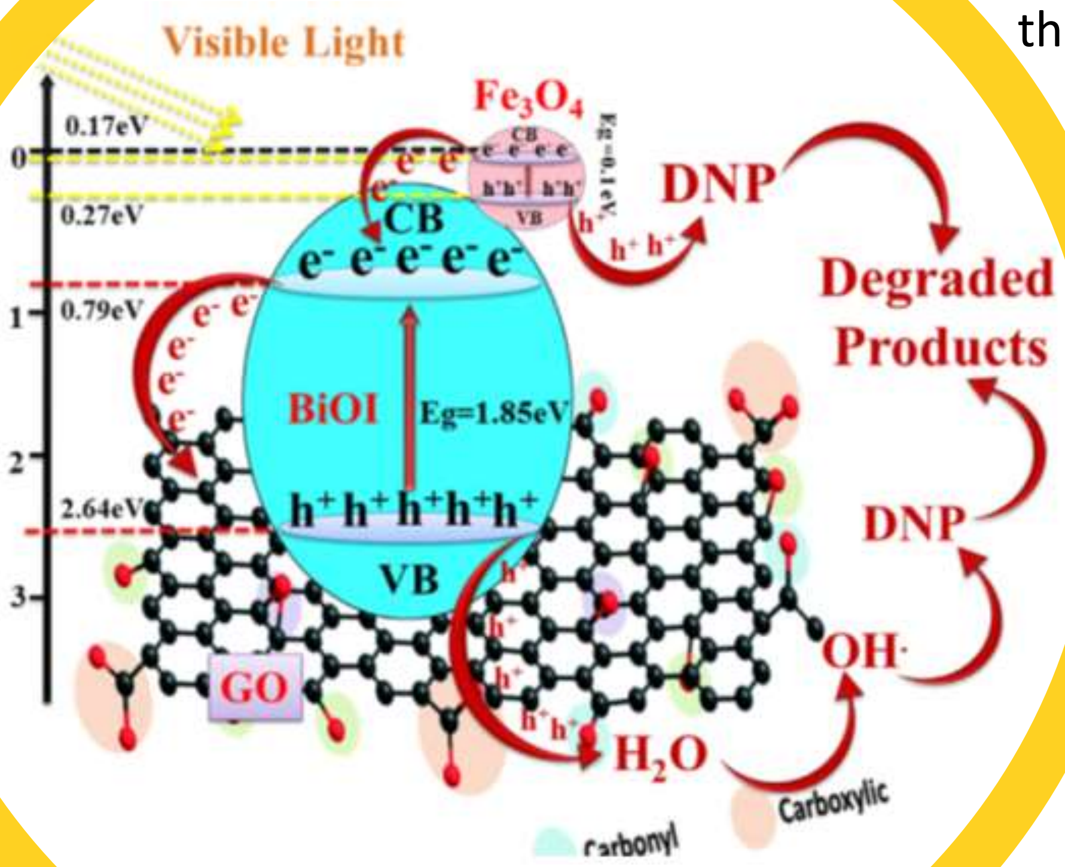

Figure 1. Photocatalytic mechanism of Fe_3O_4/BiOI@(r)GO

Photocatalyst in question

Bismuth oxyhalides possess eminent photocatalytic behaviour thanks to their suitable electric and optical properties. Their crystal structure is a tetragonal matlockite structure. This structure provides very good separation of formed electron-hole pairs. Bismuth iodide oxide has the lowest band gap out of all the BiOX’s, which means that it shows the best degradation efficiency under visible light irradiation.

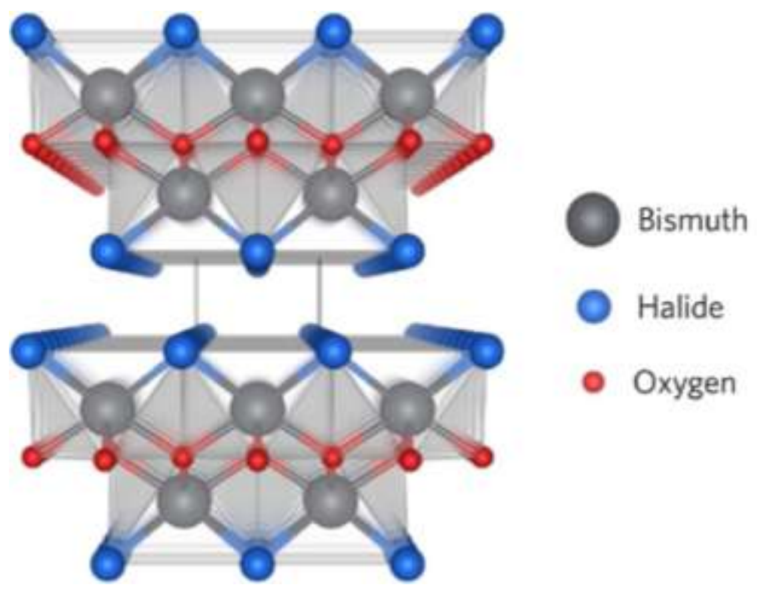

Figure 3. Tetragonal matlockite structure of bismuth oxyhalides

In order to improve the photocatalysts, metal/non-metal doping and coupling with other semiconductors were sought as a solution. BiOI was coupled to graphene and reduced graphene oxide. Optimal results of these combinations were six times better than naked BiOI due to the excellent electron mobility of graphene.

Coupling with other semiconductors is also a promising way to improve BiOI photocatalysts. Semiconductor/semiconductor heterojunctions can appear. The combination of BiOI and Fe_3O_4 is a Type III heterojunction, so at first sight, before contact, a composite of these two semiconductors does not offer any advantage. Yet, this is what would be tested because the bands will reform and Fe_3O_4 as a magnetic component offers a different advantage to the system. By adding Fe_3O_4 as a magnetic semiconductor, the photocatalyst can be magnetically separated to reduce synthesis time while this would normally be done via sedimentation and centrifugation, which are time-consuming processes.

Singh et al. [1] explored the photocatalytic mechanism of Fe_3O_4/BiOI@GO in their work. Both BiOI and Fe3O4 will generate holes and electrons through photoexcitation. The narrow band gap of Fe_3O_4, located between 0.17 and 0.27 eV, enhances the absorption of visible light.

When appropriate/adequate light energy is introduced into the composite, the electrons can be transferred from the CB of Fe_3O_4 to the CB of BiOI because of the reformed bands. This leads to the separation of charge carriers in Fe_3O_4. The electrons in the CB of BiOI can then be transferred to the (r)GO leading to separation of charge carriers in BiOI as well. Radicals will then be produced, and the pollutant will be degraded.

Planned experiments

Synthesis: (r)GO and Fe_3O_4 must be synthesized separately. The synthesis of GO is performed using an Ultrasonication-assisted modified Hummers' method. When both (r)GO and Fe_3O_4 are synthesized, BiOI/Fe_3O_4@(r)GO can be synthesized. BiOI/Fe_3O_4 is synthesized for comparison.

Characterization: In the second part of the experiments, the formed composite will be characterized.

Scanning and Transmission Electron Microscope	Morphological and compositional information
X-ray Diffraction	Analysis of the crystal structure
Fourier-Transform Infrared spectroscopy	Information on functional groups
Energy-Dispersive X-ray spectroscopy	Elemental analysis
Photoluminescence	Characterization of electronic and optical properties

Verification of the photocatalytic activity: The photocatalytic activity of the composite will be verified under visible light irradiation in a degradation experiment with Rhodamine B using optical absorbance measurements. The concentration of Rhodamine B can be obtained by measuring the absorbance at various times and the degradation percentage over time can be calculated. Verification tests must be carried out for different pollutant starting concentrations (10 - 50 mg/L Rhodamine B), with different catalyst loadings (0.5-5 g/L catalyst) and for different catalysts. For BiOI/Fe_3O_4@(r)GO, the reusability will also be tested by performing multiple tests with the same catalyst sample.

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[1] P. Singh, A. Sudhaik, P. Raizada, P. Shandilya, R. Sharma, and A. Hosseini-Bandegharaei, “Photocatalytic performance and quick recovery of BiOI/Fe 3O4 @graphene oxide ternary photocatalyst for photodegradation of 2,4-dintirophenol under visible light,” Mater. Today Chem., vol. 12, pp. 85–95, 2019.