

Recyclable Magnetic Nanophotocatalysts

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Literature Seminar

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For the last several decades, environmental pollution has become an increasing concern on a global scale. Therefore the development of environmental pollutant remediation and clean technologies is vital. One class of pollutant is organic contaminants in aqueous systems, which includes wastewater from pharmaceuticals, pesticides, packaging, and textile dyeing. Dyes alone account for approximately 700,000 tons per year of waste. This waste contains over 100,000 different organic compounds, of which, more than half are highly toxic azo dyes.¹ This widespread pollution warrants search for an environmentally friendly, large-scale, commercially applicable solution.

A few current solutions to this environmental problem are incineration, filtration, microbiological degradation, and oxidation.² Many of these techniques are limited or hazardous for the environment. For example, microbiological degradation is often useful for only a few select compounds and incineration has high energy and environmental costs. Alternatively, photocatalytic oxidation has proven both environmentally friendly and able to degrade a broad range of compounds.^{2,3}

Photocatalytic oxidation occurs when a photon of necessary energy excites an electron from the valence band to the conduction band leaving a hole (Figure 1). Holes may then react with water to form hydroxyl radicals which can subsequently oxidize organic compounds to H_2O and CO_2 . The energy of the photon needed to excite the electron is directly dependent on the band gap of the photocatalytic material.⁴

Currently, TiO_2 is the most common commercial photocatalyst for the oxidation of organic contaminants in an aqueous system.⁵ TiO_2 is relatively cheap and active in UV light. Although TiO_2 is cheap, utilizing UV light can be expensive. Since large volumes of waste must be purified, reducing total cost is essential. Thus, making a more efficient photocatalyst has been the focus of much research. There are two main directions researchers have taken in this field: (1) band-gap engineering; and (2) nanostructuring. The first approach attempts to change the band-gap thus changing the wavelength of light needed for activity, and the second approach seeks to increase the surface area and decrease electron-hole recombination.^{3,5,6}

These approaches have proven very successful and the efficiencies of nanophotocatalysts have improved significantly. However, one significant problem remains: nanoparticles are difficult to remove from solution. To address this issue, researchers have studied the effects of immobilizing nanoparticles on easily recoverable materials including glass beads,⁷ glass fibers,⁸ and ceramic plates.⁹ However, these studies resulted in significantly decreased photocatalytic efficiency. In the late 1990s, it was discovered that if the nanophotocatalysts contain a magnetic material, the photocatalyst could be easily recovered by applying a magnetic field.³

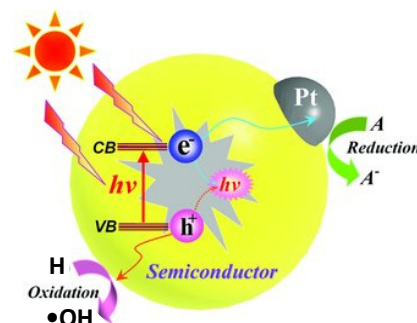


Figure 1: Basic mechanism of photocatalysis for the degradation of organic compounds.³

There have been many advances in magnetic nanophotocatalysts in the last five years. This talk will focus on three papers that study visible-light active magnetic nanophotocatalysts. The first of these papers studies the incorporation of Fe_3O_4 nanoparticles in BiOCl nanoscale flakes. BiOCl has been shown previously to be a highly efficient photocatalyst in visible light for the degradation of organic dyes.¹⁰ This study compared the photocatalytic activity of BiOCl nanoscale flakes with and without Fe_3O_4 nanoparticles added for magnetic properties. Furthermore, it compared the photocatalytic activity of the BiOCl flake with Fe_3O_4 nanoparticles to that of an $\text{Fe}_3\text{O}_4/\text{BiOCl}$ core-shell structure. The photocatalytic activity was determined by measuring the degradation of a representative dye, rhodamine B, using UV-vis absorption spectroscopy (Figure 2). The BiOCl flake with and without Fe_3O_4 nanoparticles had similar photocatalytic activity; however, the core-shell $\text{Fe}_3\text{O}_4/\text{BiOCl}$ structure was significantly less efficient. This decrease in photocatalytic activity was attributed to an increased electron-hole recombination at the Fe_3O_4 core. The study also showed that the BiOCl flake with Fe_3O_4 demonstrated good recyclability over five uses, suggesting the effectiveness of the Fe_3O_4 nanoparticles as a magnetically recyclable photocatalyst.¹¹

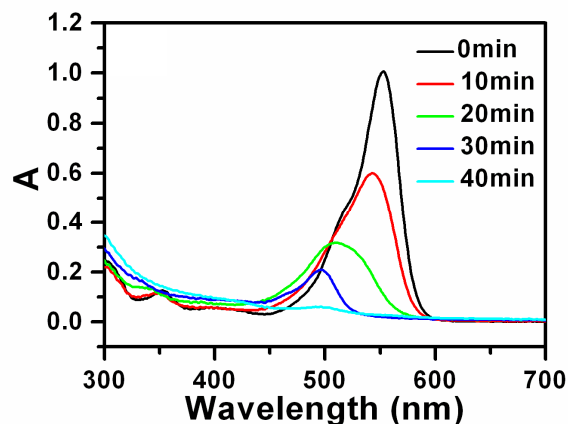


Figure 2: UV-vis spectroscopic changes of the rhodamine B solution in the presence of the nanocomposite $\text{Fe}_3\text{O}_4/\text{BiOCl}$ flake.¹¹

The second study created core-shell nanoparticles of Fe_3O_4 and WO_3 . The WO_3 shell was synthesized as a chestnut morphology, thereby increasing the surface area. Similar to the previous paper, the authors compared the degradation of rhodamine B for the $\text{Fe}_3\text{O}_4/\text{WO}_3$ core-shell structure, the hollow WO_3 structure, a commercial WO_3 photocatalyst, a Fe_3O_4 microsphere, and no photocatalyst (Figure 3). The $\text{Fe}_3\text{O}_4/\text{WO}_3$ core-shell structure had significantly superior photocatalytic activity to all other tested materials. The authors attributed this increase in activity to an increase in charge transfer at the interface of the WO_3 and Fe_3O_4 , which leads to fewer electron-hole recombinations. This material was further tested for recyclability and exhibited good recyclability over four uses.¹²

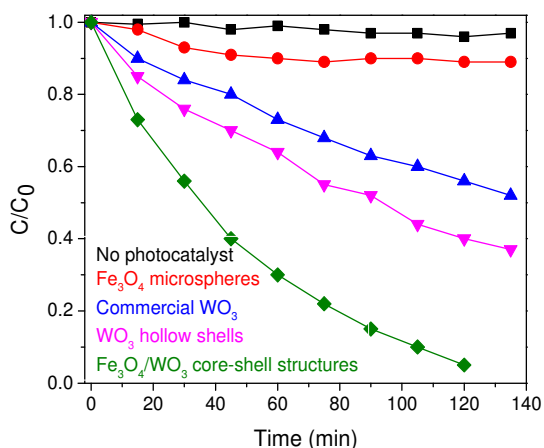


Figure 3: Photocatalytic degradation of rhodamine B.¹²

The third study also utilized the core-shell structure, but with Fe_3O_4 , SiO_2 , and $\text{AgCl}:\text{Ag}$. These nano-scale particles were similarly tested for photocatalytic activity through the degradation of rhodamine B. This was compared to the activity of no photocatalyst, a commercial TiO_2 photocatalyst, Fe_3O_4 nanoparticles, $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core-

shell nanoparticles, and $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{AgCl}$ core-shell nanoparticles. The $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{AgCl}:\text{Ag}$ structures had significantly enhanced photocatalytic activity; however, while it was easily removed from solution using a magnetic field, the efficiency of the photodegradation decreased with reuse. After eight uses, the material took eight minutes to degrade 95% of the dye, twice as long as the first use.¹³

These three studies for recyclable photocatalysts represent several of the directions pursued in this field. Easy removal of the photocatalysts from an aqueous system via a magnetic field is attractive for commercial application. While the long-term recyclability of the photocatalysts is a concern, the initial results are promising and suggest potential utility in the remediation of organic contaminants from aqueous systems. However, the materials must be highly efficient and exhibit long-term efficiency over many uses before their integration into industry is practical.

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