Enhanced Visible Light Photocatalytic Decolorization of Azo Dye using Magnetic PANI/CuFe$_2$O$_4$/ZnO

Abstract
In this study, novel magnetic hybrid of PANI/CuFe$_2$O$_4$/ZnO was synthesized by in situ oxidative polymerization of aniline in the presence of CuFe$_2$O$_4$ as magnetic component and ZnO as photoactive component. The prepared sample was characterized by using X-ray diffraction, Fourier transform infrared spectroscopy, field emission scanning electron microscopy and UV-vis spectroscopy. The catalytic activity of PANI/CuFe$_2$O$_4$/ZnO was investigated by degradation of methyl orange (MO) in aqueous solution under visible light. The results indicated that the as-prepared PANI/CuFe$_2$O$_4$/ZnO show highly enhanced photocatalytic activity. Moreover, the PANI/CuFe$_2$O$_4$/ZnO can be easily separated from the aqueous solution by an external magnet and reused for several cycles.

Keywords: Polyaniline; Magnetic; visible light; Photocatalyst; ZnO

Introduction
Semiconductor research has demonstrated the main application in areas such as hydrogen production through photocatalytic water splitting [1], dye sensitized solar cells [2] and photocatalytic treatment of harmful organics from air and water [3]. Developing of efficient visible light responsive photocatalysts for environmental remediation has become the main area in photocatalysis research because of the usage of solar light [4]. For the actual applications, ZnO photocatalysts are usually not suitable due to the inconvenient and expensive separation [5], high photocorrosion [6], and low quantum efficiency resulted from its wide band gap ($E_g = 3.37$ eV) and the rapid recombination of photo-generated carriers [7]. In this regard, the modified ZnO-based photocatalysis with conducting polymers such as PANI can respond to visible light region effectively [8]. Moreover, ZnO-based photocatalysis coupled with conducting polymers are difficult to separate and recover from aqueous solution. In this regard, CuFe$_2$O$_4$ as the important magnetic materials have been utilized with photocatalysts and allowing easy separation of the photocatalysts from the liquid after the photocatalytic process [9].

Synthesis of PANI/ZnCrFeO$_4$/ZnO Photocatalyst
The PANI/ZnCrFeO$_4$/ZnO sample was prepared by in situ polymerization of aniline on the surface of the ZnCrFeO$_4$ and ZnO samples that reported previously. In this procedure, 10mL of 0.1M aniline, 10mL of 0.125 ammonium peroxysulfate and 30mL of 0.1M nitric acid solutions were added to 0.25g of synthesized ZnCrFeO$_4$ and 0.1g of ZnO at room temperature. Then, the mixture was stirred during the polymerization of aniline, which was completed within 24 h. Finally, the prepared PANI/ZnCrFeO$_4$/ZnO was dried at 60°C.

Photocatalytic activity
The control experiments were performed under visible light irradiation in the absence of the photocatalyst and in the presence of ZnO, CuFe$_2$O$_4$, PANI/CuFe$_2$O$_4$/ZnO and polyaniline as photocatalysts under visible light irradiation.

Mechanism of photocatalytic activity
The photogenerated electrons of PANI can transfer to the conduction band of ZnO and CuFe$_2$O$_4$, and the holes from the valence band of ZnO and CuFe$_2$O$_4$ can transfer to HOMO of PANI. The photogenerated electrons can be captured by dissolved O$_2$ to yield the O$_2^•−$, HOO• and •OH radicals and have been involved in the degradation of dye.

Conclusion
We provide a simple method to synthesize the magnetically recyclable PANI/CuFe$_2$O$_4$/ZnO photocatalyst by an in situ oxidative polymerization. The resulting sample show an enhanced photocatalytic activity for degradation of Methyl orange (MO). The photocatalytic decolorization percent of MO dye on the surface of the samples was determined about 45%, 5%, 98% and 55% for ZnO and CuFe$_2$O$_4$, PANI/CuFe$_2$O$_4$/ZnO and polyaniline samples, respectively. Also, PANI/CuFe$_2$O$_4$/ZnO sample can be reused three times with only gradual loss of activity.

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Conflict of Interest
None.

References
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