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Photocatalytic activity of PANI/Fe^0 doped BiOCl under visible light-degradation of Congo red dye

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ABSTRACT

A magnetic hetero-architecture PANI/Fe^0 nanofibres doped BiOCl(BPF) photocatalysts were prepared by facile chemisorptions method. The photocatalytic activity was investigated using the congo red dye in water. The presence of BiOCl and PANI/Fe^0 in the catalyst was confirmed by FTIR, XRD and EDS analysis. The morphology, size and lattice spacing of the as-prepared catalyst were investigated by SEM and HRTEM. The estimated band gap energies of the BPF composite and pure BiOCl were 1.59 eV and 3.21 eV respectively. The decrease in band gap of the BPF composite is expected to be photosensitive in visible light. The catalytic activity of the composite with 20 wt% PANI/Fe^0 nanofibres was found to be the highest (about 80%). The enhanced photoactivity can be attributed to the enlarged BET surface area, synergistic effect of PANI/Fe^0 and BiOCl as well as to the high separation efficiency of photogenerated electron-hole pairs. The VSM measurement confirmed that the composite possessed sufficient saturation magnetization and facilitated easy separation on application of an external magnetic field. Sustainability of the catalyst was affirmed by the reusability study. Based on the experimental findings, a possible mechanism is visualised and presented to explain the enhanced photocatalytic activity of the BPF under visible light.

1. Introduction

Effluents from the various industries like textiles, leather tanning, food and packaging, dye manufacturing etc. that contain dyes cause considerable water pollution and create potential risk and threat to aquatic and human life [1–3]. Therefore, the removal of these organic colored compounds prior to discharge is a big challenge to researchers worldwide. For the removal of the synthetic dyes, the most conventional methods are physical adsorption on inorganic and organic solids, biodegradation/enzymetric degradation and catalytic decomposition [4–6]. Although each of these processes has their own merits and demerits, nowadays the catalytic splitting of organic pollutants using photochemical methods provides a very efficient pathway to mineralize and convert them into harmless chemicals to decrease the damage caused by their presence [7]. After the discovery of TiO2 [8] as an effective semiconductor-based photocatalyst, throughout the globe, researchers are engaged in designing and developing other efficient photocatalysts to deal with organic pollutants.

In recent era, extensive efforts have been made to develop a large number of semiconductor materials like TiO_2, ZnO, AgCl, BiOCl, WO_3 and CdS for potential applications as photocatalysts for photodegradation of organic pollutants [9–14]. In general the photocatalytic degradation by semiconductors is based on the generation of very active in-situ free radicals as reported previously [15], such as:

$$\text{Semiconductor} + h\upsilon \rightarrow e^- + h^+ \quad (1)$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH \quad (2)$$

$$\text{Dye} + {}^{\bullet}OH \rightarrow \text{degradation product} \quad (3)$$

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$$\text{Dye} + e^{-} \text{or } h^{+} \rightarrow \text{reduction or oxidation products} \quad (4)$$

The generated free radicals mainly $^{\cdot}OH$ have high oxidizing power to degrade organic contaminates like dye molecules present in the waste water and transformed to the harmless end products. Among the semiconductor materials, BiOCl, has been known for its superior photocatalytic ability under UV irradiation and has proved to be an effective catalyst for degrading organic materials, producing CO_2 and H_2O as end products [16]. Low cost and toxicity, biocompatibility and high photocorrosion stability combined with efficient removal of pollutants make it an ideal catalyst for dealing with organic contaminants. However, the photocatalytic efficiency especially in visible light is still far from satisfactory, which limits its commercial usage in industrial water treatment. One of the main reasons, the high band gap (3.2–3.5 eV) of BiOCl limits its photocatalytic activity as it only responds to ultraviolet light (4% of solar spectrum) which limits its practical applications. Another reason is associated with the difficulty in separation and recycling of the catalyst. Also release of the catalyst to natural water resources causes secondary pollution and increases the cost of the practices. An effective mean to solve these problems can be developing easily recoverable photocatalysts, which are also active under visible light irradiation. Various strategies have been adopted to improve photocatalytic activities of BiOCl under visible light such as doping and recombination of semiconductors, attachment with graphene and incorporation of noble metals [17–19]. It is continuously explored that the modifications could effectively enhance the catalytic behaviour of BiOCl. For instance, the thickness tunable solvothermal synthesis of BiOCl nanosheets for better photoactivity under visible light has been reported [20]. Surely, the desired diversities in modification of BiOCl composites in nano/microscale for high photo catalytic activity under visible light remain to be explored for technological applications.

The photocatalytic decomposition of organic pollutants from aquatic environment using nanoscale zero valent iron (Fe^0) particles have proven to be as an effective and versatile catalyst and provided a strong platform for mechanistic studies and technological development [21,22]. Although zero valent iron is an environmental friendly green efficient catalyst with high surface specific area and in-situ activity, it highly aggregates due to having strong intrinsic ferromagnetism and limits its catalytic activity [23]. To overcome this limitation and enhance its available surface area, iron particles are dispersed onto support matrixes like carbon nanotubes, graphene and conducting polymers [24–26]. One of the most versatile supports/matrices is the conducting Polyaniline (PANI) due to its excellent environmental stability and synergistic effect [27]. The PANI polymer matrix is not only used as dispersing medium to dispersed the iron particles for the development of composite structure but also possess individual properties such as high absorption coefficient in the visible-light range and mobility to charge carrier to suppress the photocorrosion of the semiconductors and enhanced the catalytic performance [28,29].

The reuse and recovery of photocatalyst used in effluent treatment have great importance for sustainable waste management. Therefore the incorporation of magnetic particles like zerovalent iron nanoparticles with combination of synergistic effect of PANI into the nonmagnetic catalytic such as BiOCl matrices has great interest to study as it provides the combination of photocatalytic heterogeneity with an easy and efficient technique of magnetic separation [30,31]. It may also be possible to obtain some exceptional catalytic activity as a result of the concerted effect of PANI/Fe^0 into BiOCl.

Based on the recent studies of the utilization of visible light for PANI-based magnetic composites [32,33], herein, we have demonstrated a simple and straightforward solution mixing method to fabricate magnetically separable BiOCl photocatalyst doped with PANI/Fe^0. The heterarchitechture BiOCl-PANI/Fe^0 shows improved adsorption of Congo Red dye(CR) as a model organic pollutants in the waste water and highly enhanced photodegradation of dyes under visible light irradiation although individual catalysts BiOCl and PANI/Fe^0 shows inactive visible light driven catalytic effect. A possible mechanism and explanation for the enhanced photocatalytic activity of PANI/Fe^0 doped BiOCl have also been explored in present study.

2. Materials and methods

2.1. Materials

All chemicals were of analytical grade and used as received. Bismuth oxide (Bi_2O_3), aniline (ANI) monomer, sodium borohydride ($NaBH_4$) and congo red dye were procured from Sigma-Aldrich, USA. Anhydrous ferric chloride ($FeCl_3$) and ethanol (C_2H_5OH) were purchased from Merck, Germany. Ammonia solution from SRL Pvt. Ltd., India and Ultrapure water (type-2, resistivity) were used for preparation of aqueous solutions.

2.2. Synthesis of BiOCl

The BiOCl was prepared by a simple hydrolysis method as reported by Zhang et al. [12]. Firstly, in order to obtain a $BiCl_3$-HCl aqueous system, the Bi_2O_3 powder was completely dissolved in concentrated hydrochloric acid solution (40 ml). The pH of the acidic aqueous solution was adjusted between 2 and 3 by adding aqueous ammonia solution, till the white colloids appeared. The colloidal solution was heated for 30 min at 40 °C and plate-like precipitates were obtained. Then the product was centrifuged and washed several times with distilled water and ethanol and finally dried at 80 °C in an air oven till constant weight appeared.

2.3. Synthesis of PANI/Fe^0 nanofibres

PANI/Fe^0 composite nanofibres (NFs) were synthesized by rapid mixing chemical oxidative polymerization [34]. Typically, 3 g of anhydrous $FeCl_3$ was dissolved in 40 ml of ultrapure water in a three neck conical flask at room temperature. 0.4 ml aniline monomer was added and mixed rapidly in the above oxidant solution. The mixture was stirred for 5 min and kept for 2 days at room temperature without stirring. After that the synthesized polyaniline mixture was purged with nitrogen gas for half an hour followed by the dropwise addition of 50 ml of sodium borohydride solution (1 M) with continuous mechanical stirring at 200 rpm under nitrogen atmosphere. For the completion of reaction stirring was continued for another 20 min and a dark green precipitate was formed. The prepared PANI/Fe^0 nanofibres were filtered and washed several times with distilled water and ethanol. The product was dried at 60 °C in vacuum oven.

2.4. Preparation of BiOCl/PANI/Fe^0photocatalysts (BPF)

The BiOCl/PANI/Fe^0 (BPF) photocatalysts were prepared by dispersive mixing of the prepared BiOCl and PANI/Fe^0 in tetrahydrofuran. The PANI/Fe^0 was added as 10%, 15%, 20%, 25% and 30% (by weight) of BiOCl. For uniform mixing, the solution was stirred for 24 h at room temperature. The product was collected by centrifugation and washed several times with distilled water and ethanol. Finally, the BiOCl/PANI/Fe^0 composite was dried under vacuum at 60 °C for 6 h.