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Preparation and Removal Properties of Zinc Treated Fe(0)/Graphene for Methylene Blue†

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Graphene oxide as the precursor, zinc treated zero valent iron (Fe(0))/graphene functional composite materials were prepared by using wet chemical reduction method. The impact of different iron salts and zinc salts on the surface of graphene was investigated. The structure and morphology of functional composite was studied. The composition and structure of the zinc treated Fe(0)/graphene composite was compared and analyzed using XRD, SEM and a combination of different experimental conditions on the decolorization and enrichment separation performance of methylene blue. The rules of zinc treated Fe(0)/graphene composites on the decolorization of methylene blue were explored and its stability and magnetic changes were also analyzed.

Keywords: Zinc-Fe(0)/graphene composites, Methylene blue, Decolorization, Magnetic separation.

INTRODUCTION

Iron is the most common element and low cost metal in the earth. It can be naturally used as a reducing agent owing to its mild reductive ability and nontoxic property. Zero valent iron nanoparticles [Fe(0)] have high reducing power for heavy metal ion and dyes. However, the poor oxidation resistance of Fe(0) nanoparticles has been a great obstacle for further application. Moreover, bare iron nanoparticles tend to rapidly agglomerate to form larger aggregates. The nanoparticles were stabilized with carbon and polymer to prevent aggregation and oxidation[1-3].

Recently, graphene as a novel two-dimensional material was first obtained by Geim *et al.*[4] using the highly oriented graphite tape stripping method. Graphene has a large specific surface area and excellent electrical, mechanical, optical and thermal properties. In electronics, information, energy, materials and bio-medicine and in other fields graphene has great application prospects. Herein, a novel zinc treated Fe(0)/graphene functional composite material for adsorption and degradation of methylene blue is reported.

EXPERIMENTAL

Preparation of zinc treated Fe(0)/graphene: First, the graphene oxide was prepared with the modified method[5]. Second, synthesis of zinc treated Fe(0)/graphene was achieved as following: (1) adding slowly 50 mL of $NaBH_4$ (0.1 M) in 0.5 h under stirring to different iron salt (0.35 M: $FeSO_4$, $K_2[Fe(CN)_6]$) and a graphene oxide (0.1 g) solution, which was dissolved in 200 mL deionized water under ultrasonication (0.5 h, 1.3×10^5 J); (2) And then, adding slowly 50 mL of 0.1 M $Zn(NO_3)_2$ under stirring to the above solution. Finally, the zinc treated Fe(0)/graphene particles formed were washed with deionized water followed by a wash with methanol to prevent rusting. The synthesized zinc treated Fe(0)/graphene particles were separated from the solution using magnets and dried by N_2 gas. The two resulting zinc treated Fe(0)/graphene particles are designated as Zn-F/Gr(S) and Zn-F/Gr(CN), respectively. At the same condition without adding $Zn(NO_3)_2$, the Fe(0)/graphene particles were obtained. The two resulting Fe(0)/graphene particles are designated as F/Gr(S) and F/Gr(CN), respectively.

Characterizations of samples: XRD measurements were performed for graphene supported nanoscale zero valent iron at room temperature. XRD patterns were obtained with a diffractometer (Shimata XD-D1, Japan) using CuK_α radiation. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and structure of the photocatalyst composites. The clean transparent solution was analyzed by using a UV/visible spectrophotometer. The spectra for each sample were recorded and the absorbance was determined at characteristic wavelength 664 nm (methylene blue) for organic dyes solution decolorization.

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RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of Zn-F/Gr(S), Zn-F/Gr(CN), F/Gr(S) and F/Gr(CN). XRD analysis (Fig. 1) reveals the presence of crystalline Fe(0) (JCPDS card No. 06-0696) except the sample F/Gr(CN). The apparent peaks at the 2θ of 35.6, 44.7, 57.3 and 64.2º indicated the presence of both Fe(0) and iron oxide (FeO) crystalline phases. It was indicated the existence of the phase of Fe(0) as reported earlier[5]. It was confirmed that the synthesized nanoparticles were indeed a composite of nanoscale zero valent iron-graphene. For the sample F/Gr(CN), it could not find out the sharp peaks of Fe(0), the reason may be that the reactants is a complex, which is not completely dissociated during the reaction. For the zinc treated samples, it was difficult to find the characterization peaks of zinc.

Fig. 2 shows SEM images of F/Gr(S), Zn-F/Gr(S), F/Gr(CN) and Zn-F/Gr(CN). Before zinc treatment, the Fe(0) particles dispersed in the graphene layers, particle size is larger and the reunion phenomenon is more obvious. However after zinc treatment, the particle size is reduced and evenly distributed over the surface of the graphene. Obviously, zinc-treated samples will have better absorption degradation for organic dyes.

The advantages of the non-treated Fe(0)/graphene and Zn-treated Fe(0)/graphene composites for decolorization of methylene blue from solution are investigated, as shown in Fig. 3(a).

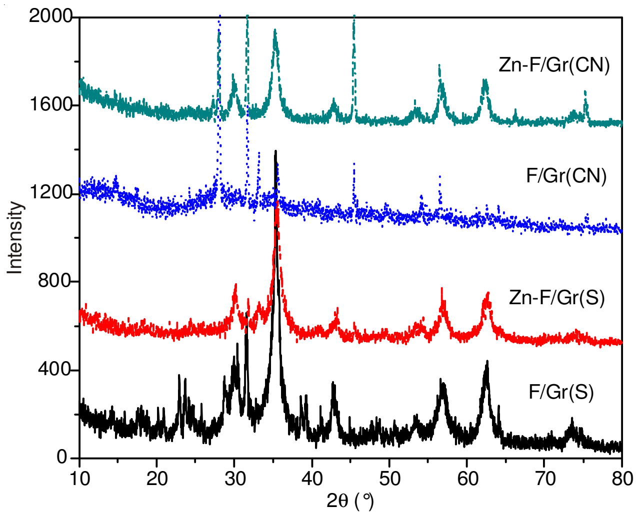

Fig. 1. XRD patterns of Zn-F/Gr(S), Zn-F/Gr(CN), F/Gr(S) and F/Gr(CN)

The data for adsorption of methylene blue by different samples were measured at the same time intervals. The results show that the Zn-F/Gr(CN) composite has fast adsorption kinetics towards methylene blue solution. The inset in Fig. 3(a) shows the adsorption process of the prepared Zn-F/Gr(CN) for methylene blue. Finally, according to most of the synthetic approaches of magnetic graphene documented so far, the thermolysis reaction mechanism for producing this material is still unclear. To confirm the stability of the high removal performance of

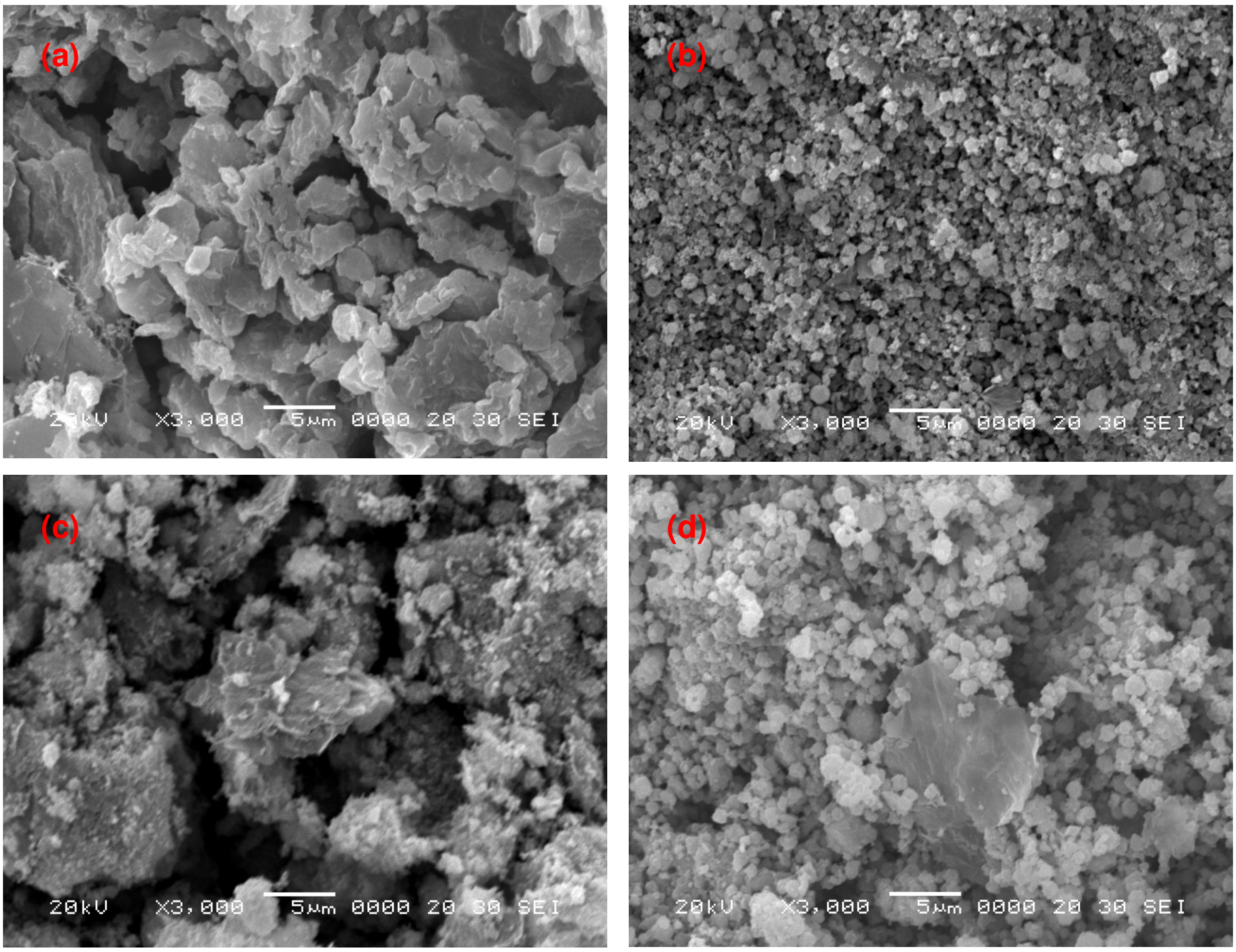

Fig. 2. SEM image of (a) F/Gr(S), (b) Zn-F/Gr(S), (c) F/Gr(CN) and (d) Zn-F/Gr(CN)

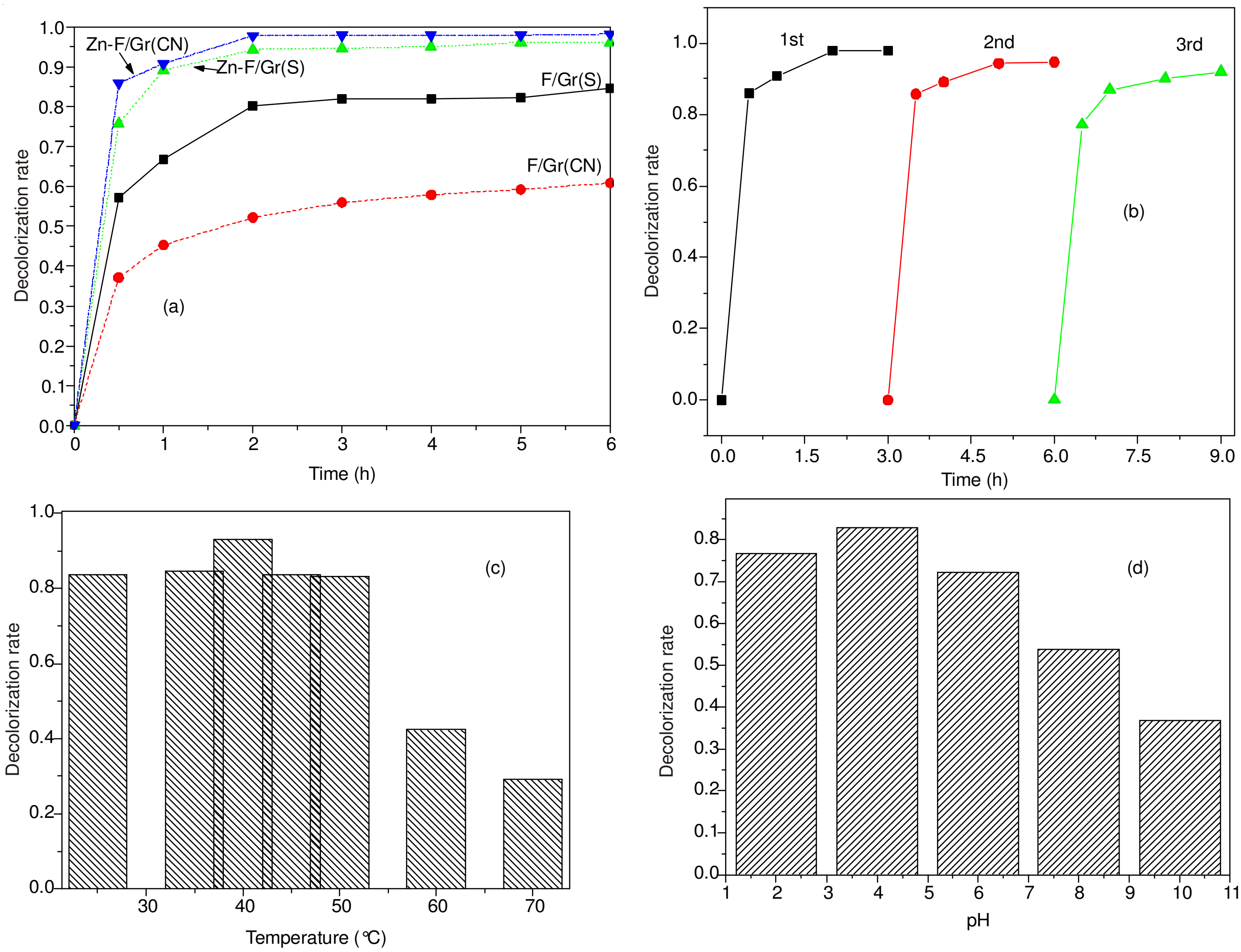

Fig. 3. Decolorization behaviours of methylene blue. (a) over F/Gr(S), Zn-F/Gr(S), F/Gr(CN) and Zn-F/Gr(CN), (b) Repeated runs of methylene blue decolorization by Zn-F/Gr(CN), (c) the effect of temperature on the methylene blue decolorization by Zn-F/Gr(CN) and (d) the effect of pH on the methylene blue decolorization by Zn-F/Gr(CN)

methylene blue from solution against the Zn-F/Gr(CN), the decolorization of methylene blue in the presence of Zn-F/Gr(CN) were performed for several cycles (Fig. 3b). The decolorization activity did not exhibit any significant loss after three recycles. It indicates that the Zn-F/Gr(CN) have high stability during the adsorption degradation, which is especially important for its application. The relationship between decolorization activity and temperature of the Zn-F/Gr(CN) is shown in Fig. 3c. It is obvious that the temperature can remarkably influence their photocatalytic activity and at 40 ℃ of temperature displays best decolorization activity. The results imply that temperature plays a vital role, possibly related to adsorption and desorption equilibrium. At pH 4, Zn-F/Gr(CN) have best decolorization activity for methylene blue (Fig. 3d). Stepwise dissociation of complexes is more favourable to zero-valent iron particles uniformly formed on the surface of graphene. Combined with zinc treatment and non zinc-treatment groups, extending reaction time and adding zinc particles on avoiding agglomeration are also beneficial.

Conclusion

Zinc treated Fe(0)/graphene has been synthesized by using a wet chemical reduction method. The results obtained in this study have also shown that the decolorization temperature and pH value of solution are effective for removal activity of methylene blue from solution. Comparison with the decolorization rate of methylene blue against the non-treated Fe(0)/graphene and Zn-treated Fe(0)/graphene composites, the Zn-F/Gr(CN) displays best decolorization activity. It can be explained that high dispersivity of zero-valent iron and zinc facilitates enhancement of dye adsorption.

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