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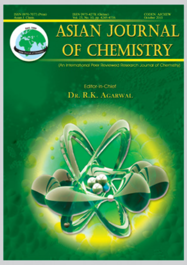

Enhancing Decolorization for Methyl Orange in Aqueous Solution by Graphene Supported Nanoscale Zero Valent Iron†

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Nanoscale zero valent iron-graphene has been synthesized *via* a simple effective chemical method. The composite nanosheets are super paramagnetic at room temperature and can be separated by an external magnetic field. The prepared nanoscale zero valent iron-graphene nanosheets were characterized by X-ray diffraction, transmission electron microscopy. The results demonstrated the successful attachment of nanoscale zero valent iron nanoparticles to graphene nanosheets. It was found that the nanoscale zero valent iron-graphene nanosheets not only show near complete methyl orange decolorization within 0.5 h under natural lighting, but they are also practically usable for methyl orange separation from water.

Key Words: Graphene, Nano zero valent iron, Methyl orange, Decolorization.

INTRODUCTION

Most of the dyestuffs are complex aromatic structures, which are difficult to dispose of by natural attenuation. Azo dyes are recalcitrant and refractory pollutants that constitute a significant burden on the environment. Removal of reactive dyes from wastewater is difficult due to their high solubility. Zero valent iron (ZVI), an environmentally friendly reducing agent, can reduce the azo bond, cleaving dye molecules into products that are more amenable to mineralization in biological treatment processes. Much attention has been paid on the treatment of azo dyes by zero valent iron in recent years[1-5]. In dye decolourization, the azo bond (N=N) of the chromophore or chromogen of the dye is broken by an electron provided by zero valent iron and the colour disappears[6]. Most research on the degradation of dyes by nanoscale zero valent iron (NZVI) has been conducted in batch experiments. However, one disadvantage of nanoscale zero valent iron is its ability to agglomerate, which can decrease the reactive contact area of nanoscale zero valent iron with the contaminants. The use of chitosan silica oxide[7], ferragel[8] or exfoliated graphite[9] may prevent nanoscale zero valent iron from agglomerating.

Recently, graphene-based composite materials with the combination of its excellent properties and inexpensive sources have attracted a great deal of attention as promising candidates for a wide variety of potential applications in catalyst supports. Graphene, a flat monolayer of a two-dimensional (2D) carbon atoms honeycomb lattice, has been emerging as a fascinating material due to the unique physical, chemical, electrical and mechanical properties. It is now well-known that many types of metals can be deposited on graphene sheets in the form of nanoparticles to impart new functionality to this increasingly popular 2D nanomaterial. For example, the combination of ferromagnetic elements such as Ni, Co and Fe with graphene could create composites with the capability of shielding electromagnetic interference and Au (or Pd)-graphene composites could be used to make ultrasensitive chemical sensors to detect hydrogen[10]. Nevertheless, very few information on the decolourization of azo dye by graphene supported nanoscale zero valent iron is available in literature. The report here is focused on the decolourization treatment of water soluble azo dye methyl orange by self-synthesized graphene supported nanoscale zero valent iron composites.

EXPERIMENTAL

Preparation of graphite oxide (GO): In brief, graphite powder (KS-6, 2 g) was dispersed in cold concentrated sulphuric acid (46 mL, 98 wt %, dry ice bath) and potassium

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permanganate ($KMnO_4$, 6 g) gradually added with continuous vigorous stirring and cooling to prevent the temperature from exceeding 293 K. The dry ice bath was removed and replaced by a water bath and the mixture heated to 308 K for 0.5 h with gas release under continuous stirring, followed by slow addition of deionized water (92 mL), which produced a rapid increase in solution temperature up to a maximum of 371 K. The reaction was maintained for 40 min in order to increase the oxidation degree of the graphite oxide product and then the resultant bright-yellow suspension was terminated by addition of more distilled water (140 mL) followed by hydrogen peroxide solution (H_2O_2, 30 %, 30 mL). The solid product was separated by centrifugation at 3000 rpm and washed initially with 5 % HCl until sulphate ions were no longer detectable with barium chloride and then washed three times with acetone and air dried overnight at 338 K.

Preparation of graphene supported nanoscale zero valent iron: Synthesis of graphene supported nanoscale zero valent iron particles were achieved by adding a 1:1 volume ratio of $NaBH_4$ (0.25M) to $FeSO_4·7H_2O$ (0.35M) and a graphite oxide (2 g), which was dissolved in 200 mL alcohol under ultrasonication (0.5 h, 1.3 × 10^5 J), according to the following equation:

$$2Fe^{2+}(aq) + BH_4^-(aq) + 2H_2O + GO \rightarrow 2Fe(0)/graphene(s) + BO_2^-(aq) + 4H^+(aq) + 2H_2(g)$$

The graphene supported nanoscale zero valent iron particles formed were washed with deionized water followed by a wash with methanol to prevent rusting. The synthesized graphene supported nanoscale zero valent iron particles were separated from the solution using magnets and dried by N_2 gas.

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. The state of the dispersed graphene supported nanoscale zero valent iron was observed using transmission electron microscopy (TEM, JEOL, JEM-2010, Japan). TEM at an acceleration voltage of 200 kV was used to investigate the number and the stacking state of graphene oxide layers on various samples. TEM specimens were prepared by placing a few drops of sample solution on a carbon grid. The clean transparent solution was analyzed by using a UV/VIS spectrophotometer. The spectra for each sample were recorded and the absorbance was determined at characteristic wavelength 460 nm for the each methyl orange solution degraded.

RESULTS AND DISCUSSION

XRD is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. Fig. 1 shows the XRD patterns of graphite oxide, graphene and nanoscale zero valent iron-graphene. The broad iron peak in Fig. 1 implied the abundance of the amorphous iron. The apparent peaks at the 2θ of 35.6, 44.7, 57.3 and 64.2° indicated the presence of both zero valent iron (Fe(0)) and iron oxide (FeO) crystalline phases. It was indicated the existence of the phase of Fe(0), which confirmed that the synthesized nanoparticles were indeed a composite of nanoscale zero valent iron-graphene.

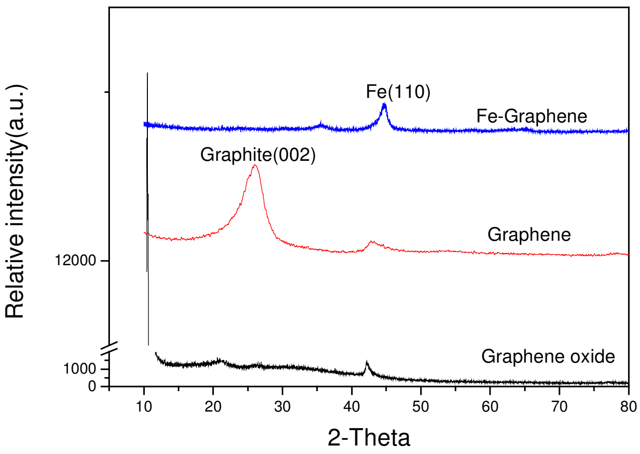

Fig. 1. XRD patterns of graphite oxide, graphene and nanoscale zero valent iron-graphene

The microstructure of the graphene supported nanoscale zero valent iron composite was characterized by TEM. The TEM image (Fig. 2) reveals that nanoscale zero valent iron particles with diameters in the range of < 50 nm are attached to the surface of graphene especially along the edges of the stacked nanosheets with thicknesses of several nanometers. These nanoscale zero valent iron particles are firmly attached to the graphene nanosheets, even after the ultrasonication used to disperse the graphene/nanoscale zero valent iron composite for TEM characterization. As shown in Fig. 2, the nanoscale zero valent iron particle is wrapped by graphene nanosheets, which helps to prevent nanoscale zero valent iron from agglomeration and enables a good dispersion of these particles over the graphene nanosheets support.

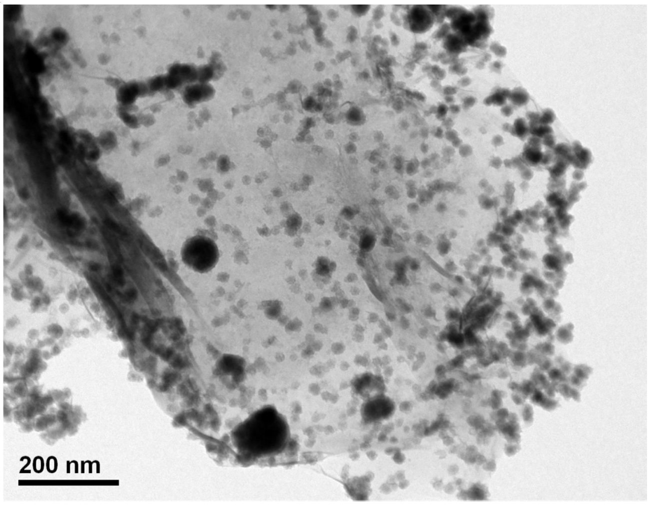

Fig. 2. TEM image of nanoscale zero valent iron-graphene

The presence of dyes and aromatic compounds in polluted water is a serious environmental problem because of their toxicities for human being and ecosystem. The nanoscale zero valent iron-graphene composite combines the high adsorption capacity of graphene and the separation convenience of magnetic nanoparticles (nanoscale zero valent iron), which makes it an excellent candidate for the removal of contaminants from water. In this study, we demonstrated a simple experiment to prove that the nanoscale zero valent iron-graphene composite was efficient to remove methyl orange in water. As shown in the above of Fig. 3, after dispersing of nanoscale zero valent iron-graphene composites in the methyl orange solution and shaking the resultant mixture by hand for only 0.5 h under natural lighting, the nanoscale zero valent iron-graphene could be easily separated from the mixture by an external magnetic field and the solution became colourless.

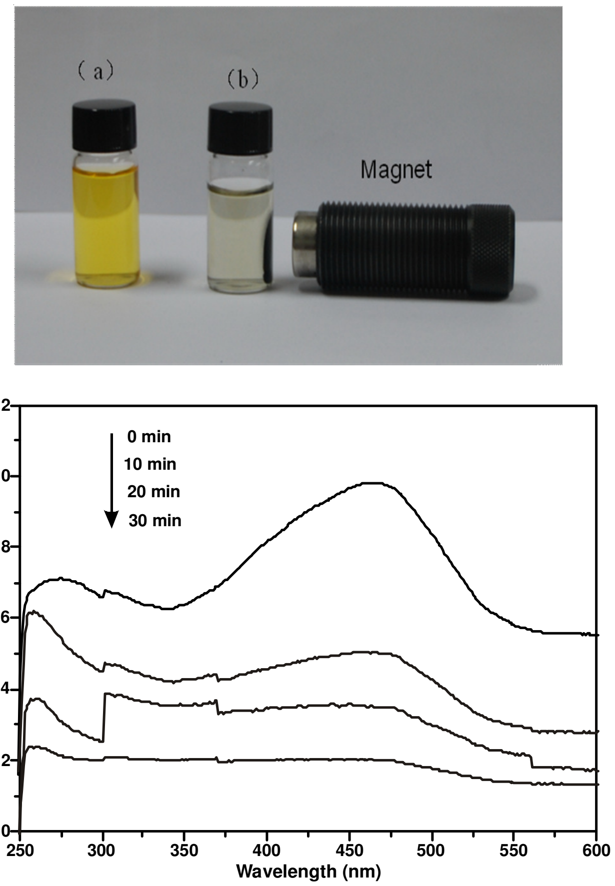

Fig. 3. UV-VIS spectra of methyl orange solution before and after adsorption by nanoscale zero valent iron-graphene. The left shows the adsorption process of nanoscale zero valent iron-graphene for methyl orange under natural lighting

Conclusion

In the present work, we prepared the nanoscale zero valent iron-graphene composites *via* a simple effective method. nanoscale zero valent iron nanoparticles are strongly attached to graphene layers or interlayers. We further found that such nanoscale zero valent iron-graphene composites had great potential as an effective absorbent for removing methyl orange in water under natural lighting. It is believed that nanoscale zero valent iron-graphene composites are particularly attractive for the design of novel composites and its detailed studies on this application are underway.

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