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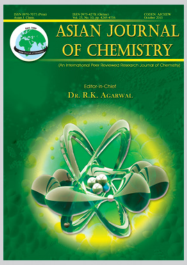

Preparation of Iron Oxide/Graphene Composites and Their Photocatalytic Properties for Methylene Blue Under Sunlight†

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Three kinds of iron oxide/graphene composites were prepared using three different ferric salts [$FeCl_3$, $Fe(NO_3)_3$, $FeSO_4$] to react with graphene oxide and followed by a heat treatment. Then, the structures of different iron oxide/graphene composites were compared and analyzed by IR spectra and scanning electron microscopy. After that the degradability using different iron oxide/graphene composites to degrade methylene blue was explored by ultraviolet spectra. The results showed that iron/graphene ($FeCl_3$ as iron source) composite has better degradability under sunlight than that of other iron/graphene composites ($Fe(NO_3)_3$ or $FeSO_4$ as iron source).

Key Words: Graphene, Iron oxide, Methylene blue, Sunlight.

INTRODUCTION

Graphene, a novel carbon-based material, possesses many unique features such as two-dimensional plane structure coupled with one-atom thickness, large surface area, as well as extraordinary electrical, thermal and mechanical properties[1,2]. 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[3,4].

To extend our interest in the preparation of graphene-based composite materials, we set out to develop a general and reproducible approach for the preparation of iron oxide/graphene composites from graphite oxide and different ferric salts. In this work, we synthesized the composite of graphene sheets decorated with iron oxide nanoparticles by a simple method. Furthermore, we demonstrated that the present iron oxide/graphene composites had great potential as an effective absorbent for removing methylene blue in water due to its rapid absorption rate and high absorption capacity.

EXPERIMENTAL

Preparation of graphite oxide (GO): In brief, graphite powder (2 g) was dispersed in cold concentrated sulphuric acid (46 mL, 98 wt %, dry ice bath) and potassium 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 iron oxide/graphene composites: Graphite oxide and three different iron salts [ferric chloride (0.1 mol/L), iron nitrate (0.5 mol/L), ferrous sulfate (0.1 mol/L)] were dissolved in ethanol solution under ultrasound for 1 h, respectively. After iron ions effectively dispersed on the surface of the graphene sheets, then dried (100 ºC, 1 h) the reaction solution and calcined at 500 ºC for 1 h in the atmosphere, we can obtain iron oxide/graphene composites. The nomenclatures of prepared samples are C/G, N/G and S/G with iron source $FeCl_3$, $Fe(NO_3)_3$ and $FeSO_4$, respectively.

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Photocatalytic activity of samples: The photocatalytic degradation was tested by iron oxide/graphene composites and an aqueous solution of methylene blue (MB) in a 100 mL glass container and then irradiation system with sunlight (location: the 4th floor balcony of chemical laboratory building in Anhui University of Architecture, China; the test time is 12:30-14:30, June 2011, sunny, outdoor temperature is 30 ºC), respectively, which was used at the distance of 100 mm from the solution in darkness box. The iron oxide/graphene composite powder (0.05 g) was suspended in 50 mL of methylene blue solution with a concentration of 1.0×10^{-5} M. Then, the mixed solution was placed in the dark for at least 2 h in order to establish an adsorption-desorption equilibrium, which was hereafter considered as the initial concentration (c_0) after dark adsorption. Experiments were then carried out under sunlight. Solution was withdrawn regularly from the reactor by an order of 30, 60, 90 and 120 min; afterwards, 10 mL of solution was taken out and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed using a UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

FTIR spectra of pure graphene, C/G, N/G and S/G are shown in Fig. 1. In case of pure graphene, absorption peaks appearing at 2361 and 2337 cm^{-1} are because of C=O, C-O stretching, respectively. It was indicated that some oxygen containing functional groups were still existed in the sample of reduced graphite oxide. In the sample C/G and S/G, on exfoliation of graphene, the intensity of C=O and C-O absorption peaks are significantly increased in intensity at the same range, but in case of N/G, we have observed the similar FTIR spectra like graphene. For the sample C/G, N/G and S/G, we also observed additional peaks at 634, 527 and 463 cm^{-1} attributed to the presence of α-Fe_2O_3[5].

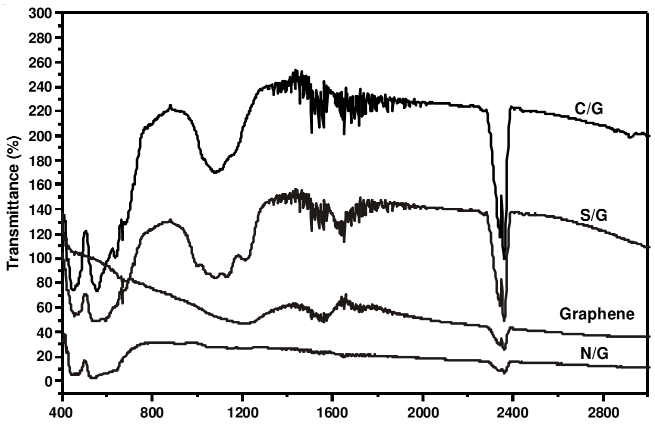
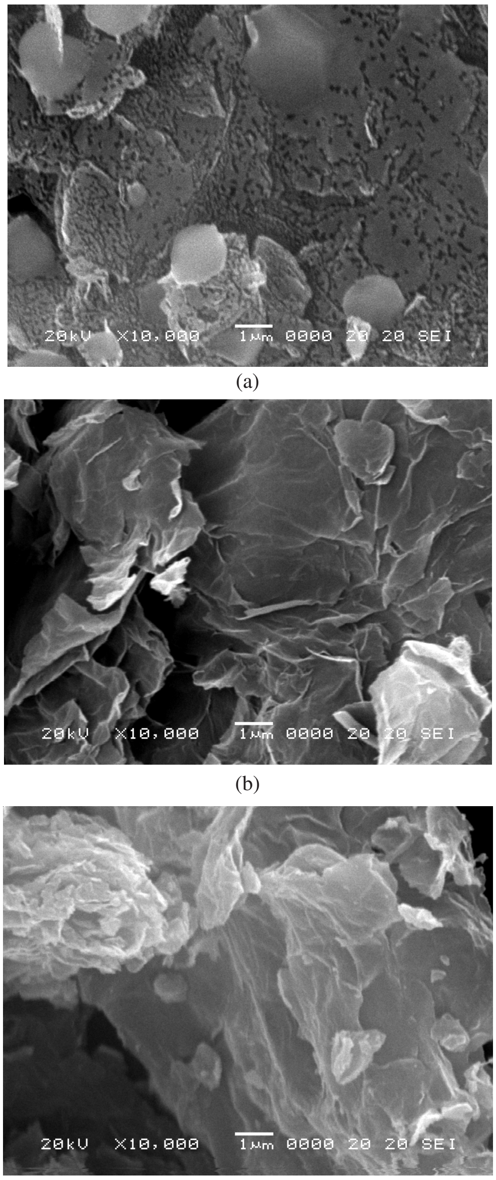


Fig. 1. Infrared spectra of C/G, S/G, N/G and graphene

In the case of graphene, because of the effect of ultrasonication treatment and heat treatment process, the graphene sheets break into pieces smaller than pristine graphite which was observed in Fig. 2. The SEM image taken from iron oxide (Fe_2O_3)/graphene composites (Fig. 2) possesses a layer-by-layer assembled structure consisting of graphene nanosheets and Fe_2O_3 particles. It reveals that Fe_2O_3 particles with diameters in the range of < 100 nm are attached to the surface of graphene in the case C/G, however, we could not find out the similar phenomena in the case of N/G and S/G. The uniform dispersion of Fe_2O_3 particles on the surface of graphene nanosheets contributes to the high absorption capacity.



(a)

(b)

(c)

Fig. 2. SEM images of (a)C/G, (b)S/G and (c)N/G

Fig. 3 shows the photocatalytic decomposition of methylene blue for C/G, S/G and N/G under sunlight irradiation. From the results in Fig. 3, among three kinds of iron oxide/graphene composite, the photocatalytic decomposition effects of the C/G composite was better than that of other iron oxide/graphene composite for the irradiation time of 90 min. It was considered that C/G have a good photocatalytic activity due to uniform dispersion of Fe_2O_3 particles on the surface of graphene nanosheets, shown in Fig. 2. At the same time, the morphology of Fe_2O_3 particles in the iron oxide/graphene composites is an important factor. It is noted that the optimization of photocatalytic decomposition of methylene blue using iron oxide/graphene composites will be studied in detail in another paper.

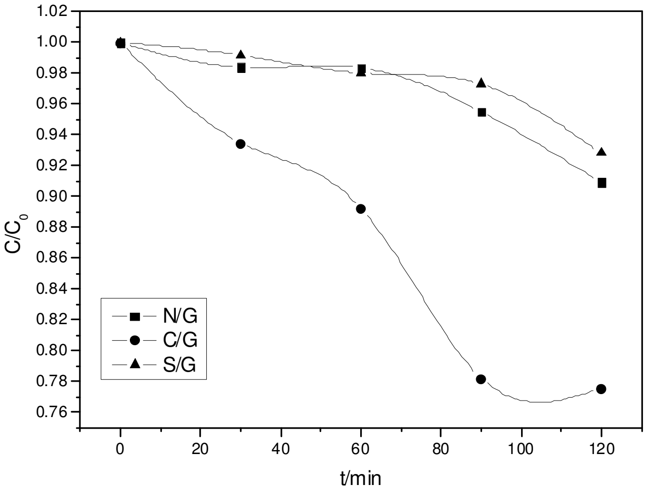


Fig. 3. Absorbance of MB solution degraded by C/G, S/G and N/G under sun light

Conclusion

In this study, iron oxide/graphene composites were produced *via* a simple method and heat treatment. The FTIR spectra show the presence of α-Fe_2O_3 for all iron oxide/ graphene composites. The SEM reveals that Fe_2O_3 particles are uniformly attached to the surface of graphene in the case C/G. The photocatalytic decomposition results show that of C/G composite was better than that of N/G and S/G composite under sunlight.

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