A strategically designed porous iron–iron oxide matrix on graphene for heavy metal adsorption†

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The iron oxide nanoparticles were transformed to a matrix of iron–iron oxide on the graphene surface at an elevated temperature in a H2/Ar atmosphere. The resultant iron–iron oxide dispersed graphene was highly porous, robust and attractive for a variety of potential applications.

In recent research, magnetite–graphene has been widely used for various applications such as catalytic activity,1 electric double-layer capacitance,2 heavy metal ion removal,3,4 drug delivery,5 biosensing6 and lithium storage.7 There are a number of reports on the synthesis and applications of magnetite–graphene employing iron oxide3,7 and only one report using zero valent iron (Fe(0)).4 With the increase in temperature, driven by the tendency to minimize surface energy, metal or metal oxide nanoparticles tend to agglomerate.1 In the previous reports on the synthesis of magnetite–graphene either iron oxide or Fe(0) nanoparticles were employed. Recently, superparamagnetic composites of a reduced graphene oxide (rGO)–iron oxide for an arsenic absorbent and rGO-supported Fe(0) (rGO–Fe(0)) for a Cr(VI) absorbent were reported.3,4 However, these materials have severe disadvantages such as low surface area, which is strongly related to their heavy metal ion removal efficiency. Furthermore, they have complicated synthesis methodology, high adsorbent concentration, long adsorption time, lower adsorption capacity and limited toxic element adsorption ability. However, for realization of practical application, a new design concept to achieve porous magnetite–rGO with a high surface area should be introduced. From this point of view, a magnetite and porous rGO structure (rGO–Fe(0)–Fe3O4) was strategically designed by employing a matrix of Fe(0)–iron oxide on graphene surfaces. The heterogeneous rGO–Fe(0)–Fe3O4 is expected to have a high porosity, fulfilling the following requisites: (1) the matrix of Fe(0)–Fe3O4 creates some surface heterogeneity on the rGO surface resulting in high surface area and consequently drastically improving the efficiency, (2) rGO nanosheets prevent the agglomeration of the nanoparticles among themselves with an increase in temperature and (3) rGO nanosheets increase the robustness and air stability of the nanoparticles. Thus, the porous rGO–Fe(0)–Fe3O4 composite can be applied for catalytic oxidation reactions.1 These substances can easily be removed from water after treatment because of their superparamagnetic nature. Furthermore, fixed-bed columns can be prepared with the composite to purify water, and the used rGO–Fe(0)–Fe3O4 composite can be easily and repeatedly regenerated by washing with 0.1 M NaOH.8 Until now, however, there have been no reports on the robust porous rGO–Fe(0)–Fe3O4 composite synthesized at lower temperature using a completely novel method for adsorbing and reducing various toxic elements like Cr(vi), Hg(II), Pb(II), Cd(II), and As(III).

In this study, we successfully synthesized the iron–iron oxide matrix dispersed on rGO, rGO–Fe(0)–Fe3O4, with high surface area and high efficiency. The Fe3O4 nanoparticles of the rGO–Fe(0)–Fe3O4 composite were assumed to be intercalated in rGO layers and subsequently converted to Fe(0) by thermal annealing at different temperatures in a H2/Ar atmosphere. At 400 °C, a matrix of Fe(0)–Fe3O4 (60/35%) was supported on rGO, whereas at 600 °C, Fe3O4 was completely converted to Fe(0) (Scheme 1). In both cases, the substances exhibited superparamagnetic behavior. The detailed synthesis can be found in ESI.† The composites were transparently characterized by XRD, Raman, Mössbauer, HRTEM and IR analyses. The final concentrations of the heavy metal ions were detected with inductively coupled plasma optical emission spectrometry (ICP-OES).

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In the small angle XRD pattern shown in Fig. 1(i), the peak (2θ = 24.4°) was attributed to the rGO (002) reflection of rGO–Fe3O4, which is very close to that of rGO–Fe(0)–Fe3O4 (2θ = 25.0°).

Surprisingly, when the sample was heated at 600 °C, the (002) reflection of rGO–Fe(0) was changed to 2θ = 26.0°, indicating the drastic reduction of the rGO interlayer distance. The rGO (002) peak became invisible (Fig. 1(ii)) due to the very high intensity of Fe(0) peaks. To observe the rGO (002) peak for the sample heated at 400 and 600 °C, the small angle XRD pattern was measured at a lower scan rate which is shown in Fig. 1(i). Gao et al. also reported this kind of shift of rGO (002) reflection.1 The wide angle XRD data for the as-made rGO–Fe3O4 showed a broad peak at 2θ = 24.4° attributed to rGO and peaks at 35.2° and 43.8° attributed to Fe3O4 (Fig. 1(ii), inset).3 In the XRD pattern (Fig. 1(ii)), 20 of 99.1° (220), 82.4° (211), 65.1° (200), and 44.5° (110) were attributed to body-centered cubic (bcc) Fe(0).9,10 These were not so prominent for the sample heated at 300 °C (Fig. 1(ii) (b)), indicating that rGO–Fe3O4 was the major component. However, the samples heated at 400 °C and 500 °C (Fig. 1(ii) (c) and (d)) showed rGO–Fe(0) as the major component along with rGO–Fe3O4 because of the 35.1° (311) 2θ value. For the sample heated at 600 °C (Fig. 1(ii) (e)), the peak at the 35.1° (311) 2θ value completely disappeared in the XRD, indicating the complete conversion of rGO–Fe3O4 to rGO–Fe(0). From the XRD patterns, it can be concluded that the samples heated at 300 °C contained a majority of rGO–Fe3O4 along with rGO–Fe(0), while the samples heated at 400 °C and 500 °C contained a majority of rGO–Fe(0) along with rGO–Fe3O4. In the sample heated at 600 °C, the rGO–Fe3O4 was completely converted into rGO–Fe(0).

To understand the characteristics of the composite materials, Mössbauer spectra were also obtained. The Mössbauer spectra (Fig. 1(iii) (a)) of the as-made rGO–Fe3O4 consisted of three components. A single doublet with narrow lines at the center (red) corresponded to rGO–Fe3O4. Two magnetic sextets with broadened lines (blue and green) were attributed to ferrous and ferric species.11 From spectra of the sample heated at 400 °C (Fig. 1(iii) (b)), three distinguishable components were observed. The magnetic sextet with narrow lines (blue) corresponded to rGO–Fe(0) (~60%). A quadrupole doublet line (red) in the central part was attributed to iron oxide. The green component corresponded to magnetically blocked superparamagnetic iron oxide particles.11 The Mössbauer spectra of the sample heated at 600 °C (Fig. 1(iii) (c)) consisted of a single magnetic sextet corresponding to Fe(0). The hyperfine parameters were consistent with those of the bcc phase of metallic iron.11 No satellite lines were observed, indicating the complete conversion of rGO–Fe3O4 to rGO–Fe(0), which was fully corroborated by the XRD results. The IR spectra of GO consisted of C=O (1735 cm−1), aromatic C=C (1625 cm−1), epoxy C=O (1216 cm−1), and alkoxy C-O (1050 cm−1) stretching vibrations. The IR spectra (Fig. 1(iv)) of the as-made rGO–Fe3O4 and the samples heated at 400 °C and 600 °C consisted of a peak at ~1590 cm−1 corresponding to the aromatic C=C stretch. In rGO–Fe3O4 and the sample heated at 400 °C, a transmittance band at around 570 cm−1 was attributed to the Fe–O bond.3,7 As expected, this band was not observed for the sample heated at 600 °C due to the complete conversion of Fe3O4 to Fe(0). The Raman, magnetic measurement data (Fig. S1) and HRTEM (Fig. S2) are explained in the ESI†

As expected, the Brunauer, Emmett, and Teller (BET) relative surface area (via nitrogen gas absorption) of the sample heated at 400 °C was the highest (384.62 m2 g−1) among those of the as-made rGO–Fe3O4 and the sample heated at 600 °C (140.70 m2 g−1 and 124.34 m2 g−1, respectively) (Table S1, ESI†). The adsorption–desorption isotherms are shown in the ESI† (Fig. S4). Until now, the BET relative surface area of our rGO–Fe(0)–Fe3O4 has been the highest in comparison with those of the rGO–iron oxide1,3 and rGO–iron composites reported in the previous literature.4 Based on our understanding, we propose that the process of integration of the removal of oxygen from dispersed/intercalated Fe3O4 nanoparticles and the formation of Fe(0)–Fe3O4 complex nanoparticles on rGO occurred sequentially and/or simultaneously. The rGO–Fe3O4 composite has maximal interlayer distance, which may be filled with intercalated water and as a result has small relative surface area.12 When the sample was annealed at 400 °C, the water molecules were removed, but not fully reduced. In addition, formation of a heterogeneous matrix of Fe(0)–Fe3O4 (60/35%) nanoparticles also increases the relative surface area. Due to this reason the rGO–Fe(0)–Fe3O4 composite may produce the highest relative surface area, compared to rGO–Fe3O4 and rGO–Fe(0). At 600 °C, the GO and Fe3O4 became almost fully reduced which led to a decrease in interlayer distance and relative surface area.

To study the arsenic adsorption efficiency, a 10 ppm solution of As2O3 was prepared by dispersing the rGO–Fe3O4, rGO–Fe(0)–Fe3O4 and rGO–Fe(0) composites individually (for details see the ESI†). From the data, as summarized in Fig. 2(i), it could be concluded that the optimal arsenic adsorption was achieved with the porous rGO–Fe(0)–Fe3O4, followed by the rGO–Fe(0) and then the rGO–Fe3O4. Aqueous solutions with different initial arsenic concentrations varying from 2 to 6 ppm were used for the experiments with pH 7, adsorption time 1 h, temperature 25 °C, and adsorbent concentration...
Adsorption isotherms of As(III), Cr(VI), Hg(II), Pb(II), and Cd(II) on rGO–Fe(0) composites (temperature 25 °C) were used as the sources of Cr(VI), Pb(II), Cd(II), arsenic adsorption capacity of the composites from water. (iv) Adsorption isotherms of As(III) on the rGO–Fe3O4, rGO–Fe(0)–Fe3O4, and rGO–Fe(0) composites (temperature 25 °C, pH 7). (iii) Maximum arsenic adsorption capacity of the composites from water. (iv) Adsorption isotherms of As(III), Cr(III), Hg(II), Pb(II), and Cd(II) (temperature 25 °C; pH 7, 1 h), and (v) maximum adsorption capacity of various elements on the rGO–Fe(0)–Fe3O4 composite. (vi) Arsenic removal efficiency of the rGO–Fe(0)–Fe3O4 from natural water samples.

0.05 g L⁻¹, as shown in Fig. 2(ii). The data for the arsenic adsorption were fitted with the Langmuir isotherm model (for details see the ESI†). A nonlinear fitting was applied to obtain all Langmuir isotherm parameters \( R^2 = 0.95 \). The adsorption constants evaluated from the isotherms of rGO–Fe3O4, rGO–Fe(0)–Fe3O4, and rGO–Fe(0) are listed in Table S3 (ESI†). The maximum adsorption capacity of arsenic ions is shown in the diagram in Fig. 2(iii). The adsorption capacity of As(III) was the highest in rGO–Fe(0)–Fe3O4 (44 mg g⁻¹), followed by that in rGO–Fe(0) (37 mg g⁻¹), and the lowest in rGO–Fe3O4 (21 mg g⁻¹) pH, temperature and time dependency (Fig. S5) are explained in the ESI†. As the rGO–Fe(0)–Fe3O4 was the most efficient in adsorbing As(III) from water, this material was further examined to evaluate adsorption efficiency of other toxic heavy metal elements like Cr(III), Pb(II), Cd(II), and Hg(II) from water. Chromium trioxide, lead nitrate, cadmium chloride, and mercuric chloride were used as the sources of Cr(III), Pb(II), Cd(II), and Hg(II), respectively. Aqueous solutions with different initial concentrations of toxic elements varying from 2 to 6 ppm were used for the experiment with neutral pH 7, adsorption time 1 h, temperature 25 °C and adsorbent concentration 0.05 g L⁻¹, as shown in Fig. 2(iv). The maximum adsorption capacities of different toxic elements are shown in the diagram in Fig. 2(v) (and Table S5, ESI†).

The rGO–Fe(0)–Fe3O4 also efficiently removed Cr(III), Hg(II) and Pb(II) compared to the Cd(II) solution. We assumed that the standard reduction potential of Cd(II) \( E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} = -0.35 \text{ V} \) was more negative than that of Cr(III) \( E_{\text{Cr}^{3+}/\text{Cr}^{4+}}^{\circ} = 1.23 \text{ V} \), Hg(II) \( E_{\text{Hg}^{2+}/\text{Hg}^{0}}^{\circ} = 0.79 \text{ V} \), or Pb(II) \( E_{\text{Pb}^{2+}/\text{Pb}^{0}}^{\circ} = -0.12 \text{ V} \).

To determine the sensitivity and validate real applications, the porous rGO–Fe(0)–Fe3O4 composite was applied to natural water samples collected from different regions of West Bengal, India ((1) Baruipur, South 24 Parganas; (2) Basirhat, North 24 Parganas; (3) Baguati, Kolkata; (4) Bansdroni, Kolkata; (5) Tollygaunge, Kolkata; (6) River Ganges) having initial arsenic concentrations ranging from 0.98 to 4.82 ppb. The data are summarized in Fig. 2(vi) and Table S6, ESI†. Amazingly, the porous material showed more than 90% adsorption efficiency up to the sub-ppb level in real water samples, indicating that the material can be realistically utilized for the purification of drinking water.

In summary, based on XRD, Raman, Mössbauer, IR, and BET data, we conclude that GO–Fe3O4 annealed at 400 °C under a 4% H2/Ar atmosphere provided a matrix of rGO–Fe0–iron oxide, creating a surface heterogeneity and leading to porous complex nanostructures. The rGO–Fe(0)–Fe3O4 composite had the highest BET relative surface area among the rGO–iron oxide and rGO iron composites. The resulting robust porous rGO–Fe0–Fe3O4 material is highly efficient in adsorbing heavy metal ions and was employed for catalytic oxidation reactions. We believe that the newly-developed approach to the rGO–Fe0–Fe3O4 composite will have both fundamental and practical significance for the development of a large variety of novel graphene-based hybrid materials for multifunctional applications.

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Notes and references