Highly Dispersible and Charge-Tunable Magnetic Fe3O4 Nanoparticles: Facile Fabrication and Reversible Binding to GO for Efficient Removal of Dye Pollutants

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The surface charge-tunable Fe_3O_4 nanoparticles with high dispersibility and high superparamagetism are fabricated by facile electrochemical method in acetonitrile. These nanoparticles can reversible bind to graphene oxides, which could be recycled and continually used for high-efficient removal of dye pollutants from water.

To remove dye pollutants from industrial wastewater, various technologies have been developed, including adsorption,[1-4]photocatalysis,[5, 6] coagulation,[7] extraction,[8] and chemical oxidation.[9] Among them, adsorption is still one of the most attractive technologies because of its high efficiency, low cost, and ease of operation as well as the availability of a wide range of adsorbents.[10–16] A number of materials including activated carbon,[9] carbon nanotubes,[10] chitosan beads,[11] organoclays,[12] sludge[13] and magnetic cellulose–chitosan hydrogels[14] have been explored as effective adsorbents due to their high adsorption capacity and low cost.[15]

As a new form of carbon consisting of a single layer of sp^2 network—a graphitized basal plane structure—with a high specific surface area, graphene partakes in strong π–π interactions with aromatic moieties present in most of organic dyes.[16–20] This makes graphene and its derivatives ideal adsorbent candidates for removing dye pollutants. However, there are two serious problems with the graphene adsorbents. One is the severe tendency of graphene agglomeration and restacking during operational processes, leading to a great loss of effective surface area and consequently a lower adsorption capacity than expected.[21, 22] Another is the difficulty to thoroughly separate the graphene sheets from the aqueous solutions after combining with dyes because of their small particle size.[23, 24] A number of strategies have been taken to tackle the graphene aggregation and reclamation problems by connecting magnetic Fe_3O_4 nanoparticles (NPs) to graphene oxide (GO). Particularly interesting is the one that uses functional groups, such as carboxyl (−COOH), carbonyl (−CO), and hydroxyl (−COH) groups, to bind GO to magnetic Fe_3O_4 nanoparticles through chemical bonds.[18, 25, 26] However, the utilization of Fe_3O_4 is low due to its chemical bonding to GOs, making both the GOs and the Fe_3O_4 NPs nonreuseble. Besides, the presence of Fe_3O_4 NPs on the GO surface reduces its effective adsorption area, and thus lowers its adsorption capacity.[19, 26]

Herein we provide a simple but practicable solution to the problems above by making the binding reversible between GOs and magnetic Fe_3O_4 NPs. This has been made possible by our ability to electrochemically synthesize surface charge-tunable Fe_3O_4 nanoparticles (CTFNPs) with high dispersibility and high superparamagetism. The most distinctive feature of as-prepared CTFNPs, which sets them apart from other previously reported magnetic Fe_3O_4 nanoparticles, is their tunable surface charges by changing the pH of the solution. The Fe_3O_4 NPs are positively charged in neutral and acidic aqueous solution but negatively charged in basic aqueous solution, thus they can reversibly bind to the negatively charged GOs with adsorbed dyes (GOs/Dyes) through the tunable electrostatic interaction. As a result, the separation efficiency of GOs is enhanced and the CTFNPs could be recycled and continually used for efficient removal of dye pollutants from water.

The dark brown CTFNPs solution was fabricated by electroreducing $FeCl_3$ in acetonitrile at −1.2 V, followed by ultrasonicating the obtained black film in water at 50 °C without any further surface modification (Fig. 1a). Fig. 1b and Fig. S1 in supporting information show typical transmission and scanning electron microscopy (TEM and SEM) images of the CTFNPs with diameters of about 10–20 nm. The high-resolution TEM (HRTEM) image recorded on an individual nanoparticle displays clear lattice fringes (Fig. 1c). The observed lattice plane space between the arrowheads is 2.50 Å, which corresponds to the distance between the (311) planes of Fe_3O_4. Fig. 1d shows a representative Powder X-ray diffraction (XRD) pattern, which testifies the formation of Fe_3O_4 nanocrystal of a cubic inverse spinel structure with characteristic peaks of (220), (311), (400), (422), (511), and (440).[27, 28] Magnetic measurements confirmed that the particles are superparamagnetic at room temperature. The saturation magnetization of the sample is 52 emu g^{-1} at room temperature (Fig. 1e). The elemental compositions from energy dispersive X-ray analyses (EDX) show that apart from Fe, O elements, CTFNPs contain a high content of C element. The atomic ratio of Fe, O, and C are approximately 3:6:2 (see Fig. S2). This result is confirmed by X-ray photoelectron spectroscopy (XPS) (Fig. 1f). The C 1s, O 1s and Fe 2p peaks respectively positioned at 285 (C 1s), 530 (O 1s), 711 (Fe 2p1/2) and 725 (Fe 2p3/2) eV are found to exclusively dominate the total spectra. The decomposition of high-resolution XPS spectrum (Fig. S3) and Fourier transform infrared (FTIR) spectrum (Fig. 1g) indicate that hydroxyl and acetate groups are on the surface of the CTFNPs. The FTIR spectrum exhibits the characteristic peaks of O–H ($\nu_{O\text{–}H}$ at 3438 cm^{-1}), −COO− ($\nu_{C=O}$ at 1635 cm^{-1}), and C–H ($\nu_{C\text{–}H}$ at 2900 cm^{-1}). The characteristic peaks centered at 580 cm^{-1} are attributed to lattice absorption of the magnetite.[29] The carboxyl band at about 1720 cm^{-1} for acetate is shifted to a lower wavenumber (1635 cm^{-1}) accompanied by the appearance of a new band at 1420 cm^{-1} in the spectrum of the CTFNPs indicates that the acetates were connected to the Fe_3O_4 nanoparticles through coordinate bonds between carboxy and Fe on the surface of CTFNPs.[30, 31] The structure of the above CTFNPs is shown schematically in Fig. 1h. The average weight contents of hydroxide and acetate groups anchored onto Fe_3O_4 were determined to be about 8% and 12% by thermogravimetric analysis (Fig. S4).

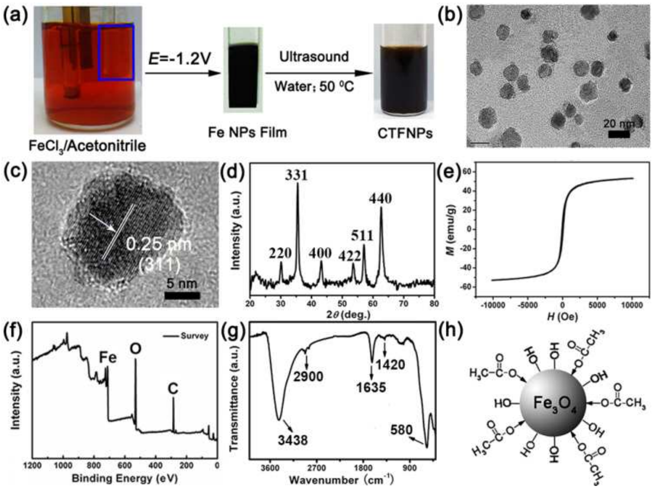

Fig. 1 (a) The route for preparation of CTFNPs. (b) TEM image, (c) High-resolution TEM image, (d) XRD pattern, (e) hysteresis loop, (f) XPS total spectral survey, and (g) FTIR spectrum of the CTFNPs. (h) The schematic representation of CTFNPs.

The obtained CTFNPs can easily be dispersed in aqueous media without any further surface modification. Dynamic light scattering (DLS) measurements reveal that the nanoparticles are highly monodisperse in aqueous media (Fig. 2a). The hydrodynamic diameter of the CTFNPs freshly dispersed in water is 28.2 nm, which remains unchanged after placement of the solution for 6 months. At a high concentration, the colloidal solution of CTFNPs appeares as a dark brown liquid that readily moves up and down following a stationary magnet, without forming any precipitate (Fig. 2b). The most important discovery about the CTFNPs, which sets them apart from other previously reported magnetic Fe_3O_4 nanoparticles, is their specific surface tunable charge with the surrounding pH in aqueous solution. As shown in Fig. 2c, Zeta potential (ζ) measurement displays that the CTFNPs are positively charged in neutral aqueous solution, and the ζ potential decreases linearly with increased pH from 5 to 11. The ζ potential is 41.6 mV at pH 5 and 22.0 mV at pH 7, suggesting that the CTFNPs are positively charged in neutral or acidic aqueous solution. At pH 9, the CTFNPs become negatively charged (−3.8 mV). Then a gradual increase of negative charge density was found at pH 11 (−23.3 mV) and pH 13 (−29.2 mV) (Fig. 2c). Moreover, when the solution was adjusted back to pH ≤ 7 by addition of HCl solution, the CTFNPs turned to positively charged again and the charge density had almost no change for pH 7 (20.2 mV) and pH 5 (39.5 mV). These results indicate that the surface charge property of CTFNPs can be readily tuned by changing the pH of the solution.

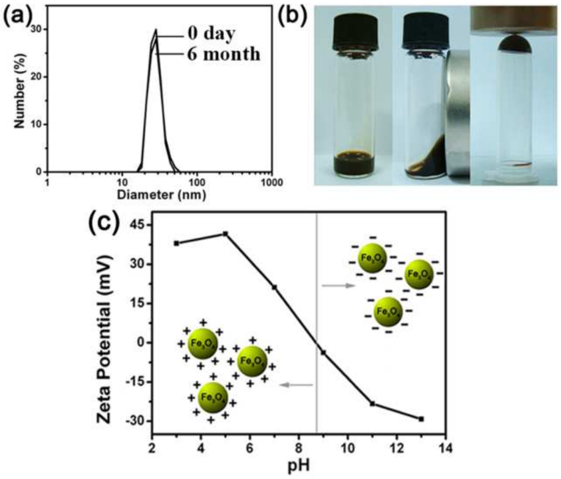

Fig. 2 (a) Hydrodynamic size distributions measured by DLS of the CTFNPs freshly dispersed in water and after shelving for 6 months. (b) Photographs of the obtained colloidal solution of CTFNPs without and with magnetic field at different direction. (c) ζ potential of the CTFNPs under different pH conditions.

In order to understand the formation mechanism of the functional groups on the surface of CTFNPs, the as-deposited black film was studied. When the black film was exposed in air directly, it was oxidized immediately to a non-magnetic yellow film, which could be determined to be Fe_2O_3 as shown in Fig.

S5. As we reported previously,[32] the black film should be composed of the metal Fe nanoparticles with very high activity by electroreduction $FeCl_3$ in acetonitrile. These active Fe nanoparticles could be oxidized to superparamagnetic Fe_3O_4 while sonicating at 50 °C in water. The surface hydroxyl groups were generated during the formation of Fe_3O_4 nanoparticles in water.[33, 34] Acetate groups should probably arise from hydrolysis of acetonitrile attached on the surface of active Fe nanoparticles during the electrolysis. Taken together, it is evident that the acetate groups are associated with the acetonitrile solvent, which is on the surface of the active Fe nanoparticles when they were first generated. In 50 °C hot water, the active Fe nanoparticles are transformed into superparamagnetic Fe_3O_4, and the surface acetonitriles are hydrolyzed to acetic acid and linked to Fe_3O_4 through the coordination bonds of O of acetate group as shown in Fig. 1h. Taking a step further, we deduce that the acetate groups are correlated with the unique positively charged CTFNPs at neutral pH by the interaction of acetate and Fe_3O_4 nanoparticles. The lone pair electrons of O atoms in the acetate group used for coordination will increase the surface negative charge density of the Fe_3O_4 nanoparticles, which may result in the very favorable adsorption of H^+ for near-surface O atoms of Fe_3O_4 and hydroxyls groups, forming the surface positively-charged Fe_3O_4 nanoparticles at neutral pH. The reversibility of positively-charge and negatively-charge surface interconversion upon pH variation of aqueous solution can be explained by adsorption or desorption of H^+ (Fig. S6).[35] Owing to the surface hydroxyl and acetate groups, the CTFNPs are positively charged and exhibit good dispersing stability in neutral aqueous solution. These acetate groups might also act as a barrier which can provide steric repulsion to prevent the particles aggregation by hydrogen bonds for dispersion of CTFNPs. These CTFNPs also have a stable magnetic property in acid or basic solution (Fig. S7).

The tunable surface charge properties of CTFNPs with the pH of solution are promising for reversibly combining and separating negatively charged GOs.[36–38] As shown in Fig. S8a, the ζ potential of the GOs is almost stable at about −45 mV in the solution of pH from 5 to 11.[39] The morphology of GO is smooth and flexible, reflecting its folding nature like crumpled silk waves (Fig. S8b). After adding CTFNPs into a GOs aqueous solution, the CTFNPs homogeneously anchored onto the surface of the GO sheets as shown in Fig. 3 and the mixture solution was well dispersed (the insets of Fig. 3a). Fig. 3b is a high-resolution TEM (HRTEM) image of the CTFNPs/GOs, in which the (311) lattice plane space corresponds to Fe_3O_4 can be well observed (Fig. S9).

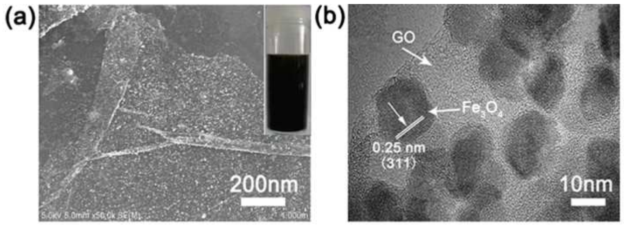

Fig. 3 SEM (a) and HRTEM (b) of the CTFNPs/GOs (inset is the photograph of mixture solution).

Most significantly, the CTFNPs adsorbed with GOs could be separated from GOs simply by treating with the alkaline solution, in which the CTFNPs could be reversibly used without losing their original properties. As demonstrated in Fig. 4 and Movie S1 in the Supporting Information, when the CTFNPs solution was added into the GOs solution below pH 7 (Fig. 4a), the well dispersed solution turned black, suggesting the positively charged CTFNPs were combined with GOs through electrostatic interaction to form CTFNPs/GOs solution (Fig. 4b). Then the GOs could be thoroughly separated from water by applying a magnetic field (Fig. 4c). In contrast, if the CTFNPs/GOs solution (Fig. 4b) was adjusted above pH 9 by adding 0.1 M NaOH, CTFNPs became negatively charged and were separated from GOs (Fig. 4d), which could be taken out from the GO solution by applying magnetic fields (Fig. 4e and 4f). It was demonstrated that the separated CTFNPs kept their properties unchanged and could be used in the next cycles.

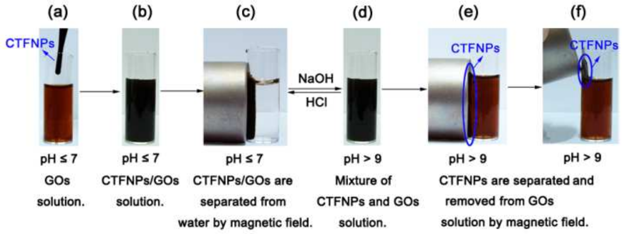

Fig. 4 Schematic illustration of reversible combination and separation of CTFNPs and GOs. (The 0.1 M NaOH and HCl solution were used to adjust the pH of the solution).

The unique tunable surface charges and high superparamagetism of CTFNPs impart outstanding properties and thus facilitate their applications for the removal of pollutants such as organic dyes. The process of dyes' removal in this work is illustrated in Fig. 5a and Movie S2. First, dyes could combine with GOs through π–π stacking interactions and van der Waals forces to form GOs/Dyes. In the presence of CTFNPs, a homogeneous colloidal solution was formed, indicating that the CTFNPs may facilitate GOs dispersion due to the formation of CTFNPs/GOs/Dyes through the electrostatic interaction between CTFNPs and GOs. Second, the CTFNPs/GOs/Dyes could be readily and thoroughly removed from water by an external magnetic field as the solution of dyes becomes colorless. What is the most significant is that the CTFNPs could be separated from the condensed CTFNPs/GOs/Dyes by the treatment with alkaline aqueous solution, which favors the recycling use of CTFNPs. To show the versatility of the CTFNPs/GOs, a series of dyes, such as rhodamine (RhB), methylene blue (MB), toluidine blue (TB) and thionine (TH) are tested as the polluting samples. Fig. S10 shows the camera images of dyes' solutions before and after adding the GOs and CTFNPs; without exception, the colors of the solutions rapidly fade within 10 min after the samples were added (each bottle of solution is placed beside a tiny magnet). It was found that the GOs in the presence of CTFNPs had a higher adsorption capacity than that of GOs alone, as shown in Fig. 5b and S11 for the maximum adsorption capacity q_m of different dyes, although the CTFNPs have little adsorption capacity for dyes(5.3 mg g^{-1} for RhB; 4.2 mg g^{-1} for MB; 3.8 mg g^{-1} for TH; 4.0 mg g^{-1} for TB), they could enhance the adsorption capacity of GOs. These results indicate that the electrostatic interaction of GOs and CTFNPs can increase the effective adsorption area of GOs for avoiding the GOs suffering from agglomeration and restacking during dyes adsorption. It is different from the covalent bonding hybrids of GOs and Fe_3O_4 NPs, in which the Fe_3O_4 NPs inevitably account for a certain percentage of the adsorption area of GOs, leading to a decrease of the adsorptive capacity of GOs. Comparing the maximum adsorption capability of CTFNPs/GOs with other graphene derivatives for dye's removal, the CTFNPs/GOs is highly competitive and its maximum quantity is over tens, even hundreds of times higher than that of many graphene derivatives (Table 1). Due to the strong superparamagnetism of CTFNPs, the GOs loaded with dyes can be easily separated from water under an external magnetic field compared with some other reported adsorbents. Remarkably, the CTFNPs could be recycled and continually used by treating the separator with an alkaline aqueous solution (Movie S3).

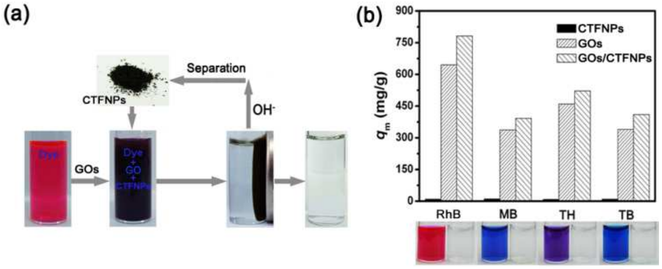

Fig. 5 (a) Schematic illustration of dye's removal and recycle of CTFNPs. (b) The maximum adsorption values for all of these dyes using CTFNPs, GO, and mixture as the adsorbents.

Table 1. Comparision of the maximum adsorption capability of various adsorbents for RhB.

Sorbents	Capacity(mg g^{-1})	Contact time(min)	Ref.
Graphitic N-doped carbon nanoparticles-decorated carbon flakes	13.7	60	40
Graphene oxide	29	180	41
Hybrid of reduced graphene oxide-Fe_3O_4 nanoparticles	50	720	25
Magnetite-reduced graphene oxide nanocomposites	13.15	120	26
Graphene oxide coated with magnetic nanoparticles	690	10	18
Graphene oxide in presence of CTFNPs	790	10	Present work

Conclusions

In conclusion, a new class of Fe_3O_4 nanoparticles (CTFNPs) has been prepared by electro-reduction of $FeCl_3$ in acetonitrile, following an ultrasound process in water at 50 °C. The nanoparticles are size-uniform, superparamagnetic, and surface charge-tunable at room temperature. The unique hydrophilic surface structures of the particles make them stable and positively charged in aqueous solution at neutral pH. Due to the binding reversibility and the positively-charge and negatively-charge interconversion upon pH variation of aqueous solution, these nanoparticles could be recycled and continually used to combine with the GOs stuffed with dyes from water through electrostatic interaction, and to easily separate from the solution by applying a magnetic field. These magnetite nanoparticles have an obvious enhancement effect for the adsorption capacity of dyes. Therefore, these novel magnetite nanoparticles have great potential as a magnetic separating material with high efficiency for the removal or retrieval of dyes and other ionic, molecular and biomolecular species.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental details; SEM, EDX, XPS of CTFNPs; The movies of reversible contribution of CTFNPs and GOs, the process of dyes removal and the recycling use of CTFNPs].

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The table of contents entry

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