

Supporting Information

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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Experimental Section:

Ferric chloride (FeCl₃) and acetonitrile were purchased from Sigma. All reagents were used as received. Ultra-pure water (Milli-Q, Millipore) was used throughout.

The CTFNPs were prepared by the electrochemical method. In a typical preparation, the electrochemical deposition of Fe nanoparticles films were performed potentiostatically at -1.2 V using a standard three electrode cell. Pt slice was used as the auxiliary electrode while an Ag/Ag⁺ electrode as reference. The working electrode was ITO-coated glass or Pt slice. The solution for electrodeposition was 0.1 M FeCl₃ in N₂-saturated acetonitrile. During the electrolysis, the formation of black precipitates was observed. The precipitates were washed with acetonitrile and then ultrasonicated in air-saturated water at 50 °C for 1 h to get the brown CTFNPs solutions. After centrifuge (12000 rpm, 10 min) and dialysis, the highly stable CTFNPs colloidal solution was obtained. The graphene oxide used in this work was prepared from graphite according to the literature using a Hummer's method with a slight modification.^[1, 2]

The as-prepared CTFNPs were characterized by field emission SEM (FE-SEM Hitachi S-4800), TEM (JEOL JEM-2010), XRD (Rigaku D/max-2500), XPS (ESCALab 220i-XL), all XPS spectra were corrected using the C 1s line at 284.6 eV. The rate of weight loss of the CTFNPs was measured using TGA (PE TGA-7) in nitrogen atmosphere with a heating rate of 10 °C min⁻¹. Magnetic properties were measured at room temperature on a vibrating sample magnetometer (EG & G VSM Model 155). UV-visible detection was carried out on a Shimadzu UV-1601 UV-vis spectrophotometer (Japan). Zeta potential measurements (Zeta Plus, Brookhaven Instruments) were done on the stable CTFNPs colloidal solution. The hydrodynamic diameters of the nanoparticles were measured by Malvern Zeta Sizer Nano S-90 dynamic light scattering (DLS) instrument.

The reversible combination and separation experiment was carried out in glass bottles at room temperature. Briefly, a certain amount of CTFNPs was mixed with GO in water, the pH of the aqueous solution was adjusted to alkaline by sodium hydroxide for separation, and was adjusted to acidic or neutral by hydrochloric acid for combination.

Adsorption experiments were carried out in glass bottles at room temperature. 20 mL of dye's solution of a known initial concentration was stirred with 20 mg of GO. Then 20 mg of the prepared CTFNPs were added in stirring. After magnetic separation using a permanent magnet, the equilibrium concentrations of the dyes were measured with an UV-vis spectrophotometer. The adsorption capacity and removal efficiency of the dyes on the adsorbents were calculated according to the following equations [3]:

$$\text{Removal\%} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) V}{W} \quad (2)$$

where q_e (mg/g) is the amounts of dyes adsorbed onto adsorbent at equilibrium, C_0 (mg/L) and C_e (mg/L) are initial and equilibrated dyes concentrations, respectively; V (L) is the volume of added solution, and W (g) is the mass of the GO (dry).

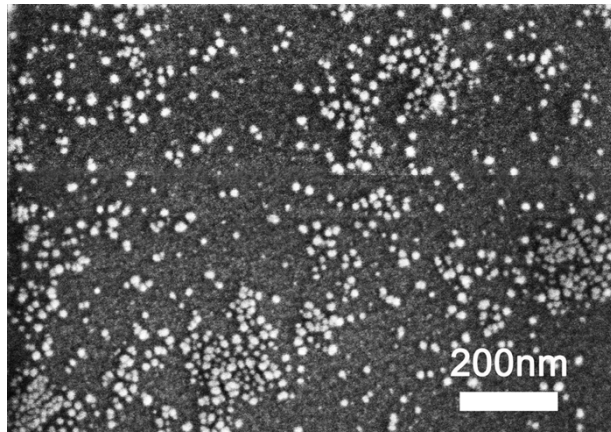


Fig. S1. SEM image of the CTFNPs.

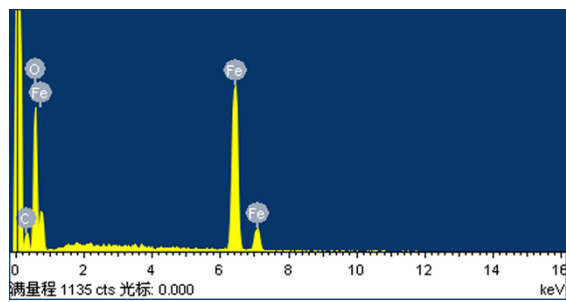


Fig. S2. EDX spectra of the CTFNPs.

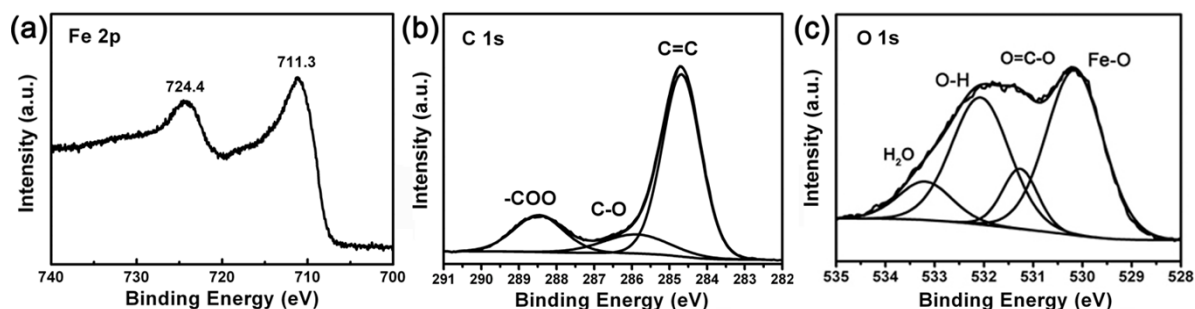


Fig. S3. XPS spectra of the CTFNPs: (a) Fe 2p, (b) C 1s, and (c) O 1s.

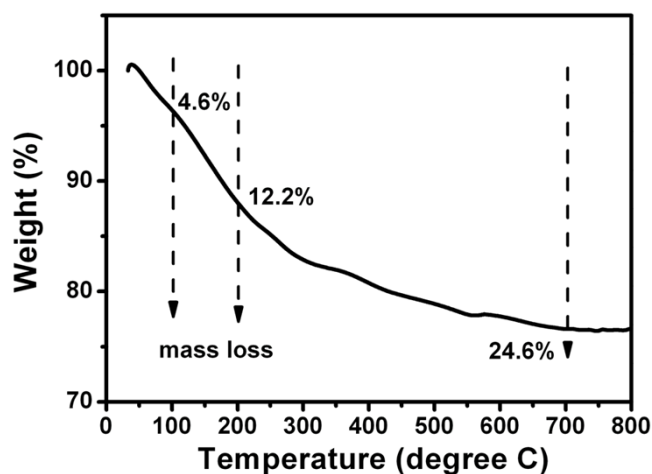


Fig. S4. The thermogravimetric analysis of the as-fabricated CTFNPs. The slight mass loss of 4.6 wt % is mainly attributed to evolution of physically adsorbed water below 100 °C, probably because of the loss of water. A mass drop around 200 °C (7.6 wt %) can be attributed to the removal of labile oxygen functional groups,^[1] while a gradual mass loss (12.4 wt %) spanning the range 250–700 °C can be ascribed to the loss of the labile carbon-containing functional groups.^[2-4]

[1] M. J. McAllister, J. L. Li, D. H. Adamson, H. C. Schniepp, A. A. Abdala, J. Liu, D. L. Milius, R. Car, R. K. Prud'homme, I. A. Aksay, *Chem. Mater.* **2007**, *19*, 4396.

[2] L. Y. Cao, Y. L. Liu, B. H. Zhang, L. H. Lu, *ACS Appl. Mater. Interfaces.* **2010**, *2*, 2339.

[3] K. L. Ai, Y. L. Liu, L. H. Lu, X. L. Cheng, L. H. Huo, *J. Mater. Chem.*, 2011, *21*, 3365.

[4] H. F. Yang, F. H. Li, C. S. Shan, D. X. Han, Q. X. Zhang, L. Niu, A. Ivaska, *J. Mater. Chem.* **2009**, *19*, 4632.

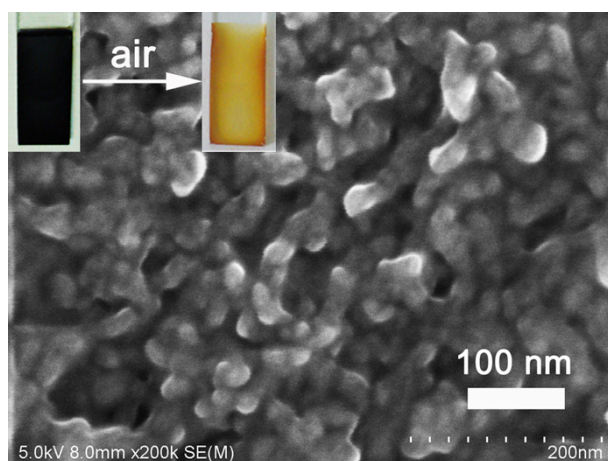


Fig. S5. SEM of the deposited film on ITO (The insets are the photograph of film before and after oxidation in the air).

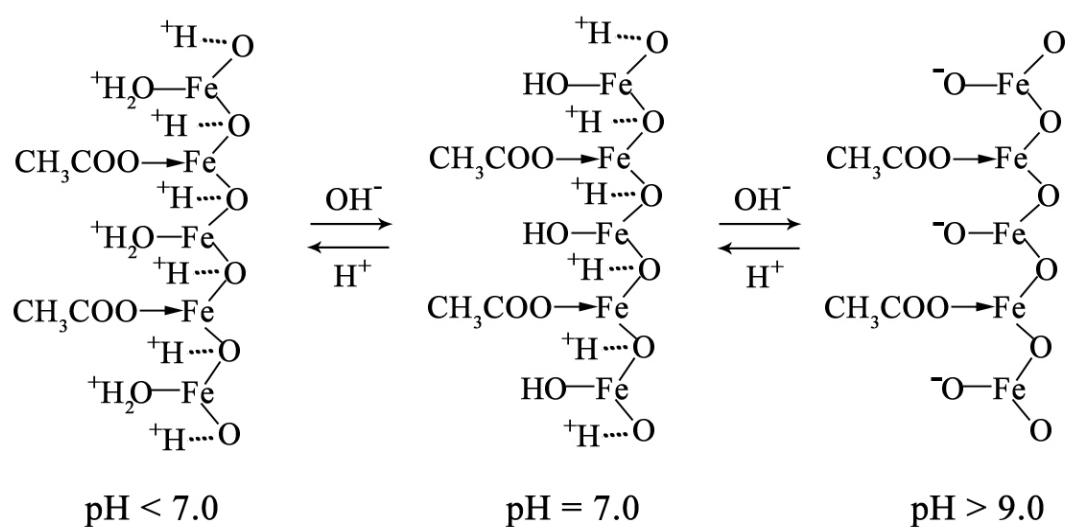


Fig. S6. The process of reversibility of positively-charged and negatively-charged surface interconversion upon pH variation of aqueous solution.

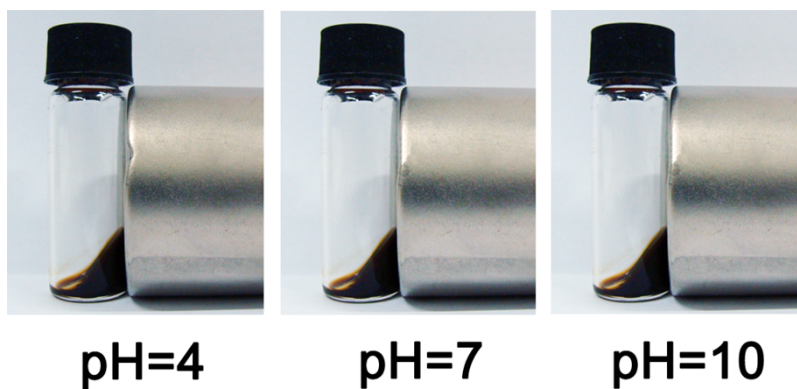


Fig. S7. The colloidal of CTFNPs in different pH with the adding magnetic field.

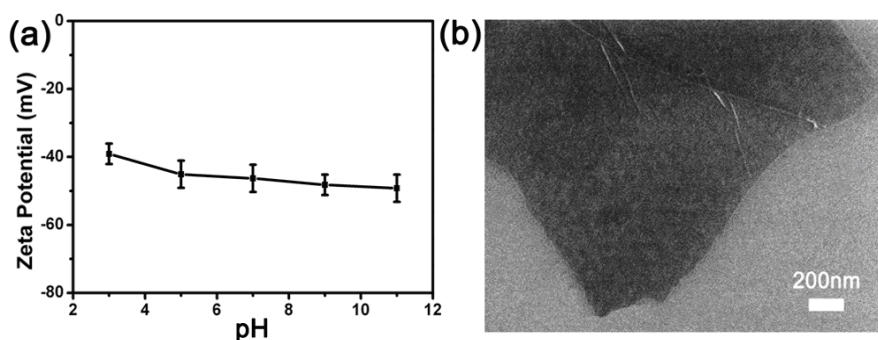


Fig. S8. (a) ζ potential of GOs under different pH conditions. (b) SEM of the as-prepared GO.

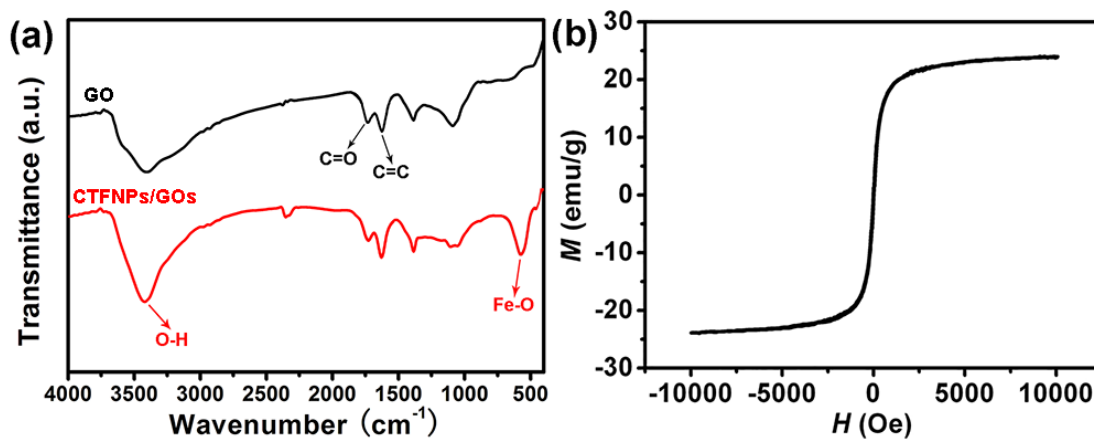


Fig. S9. (a) FTIR spectra of the GO and CTFNPs/GOs. (b) hysteresisloop of the CTFNPs/GOs.

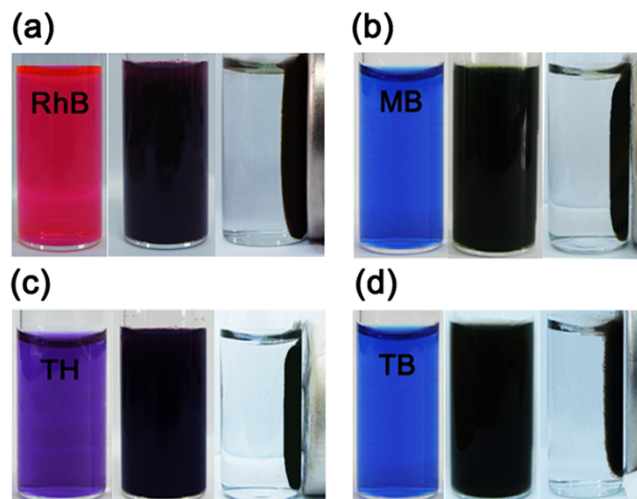


Fig. S10. Schematic illustrations for the removal of different dyes. (a) RhB. (b) MB. (c) TH. (d) TB.

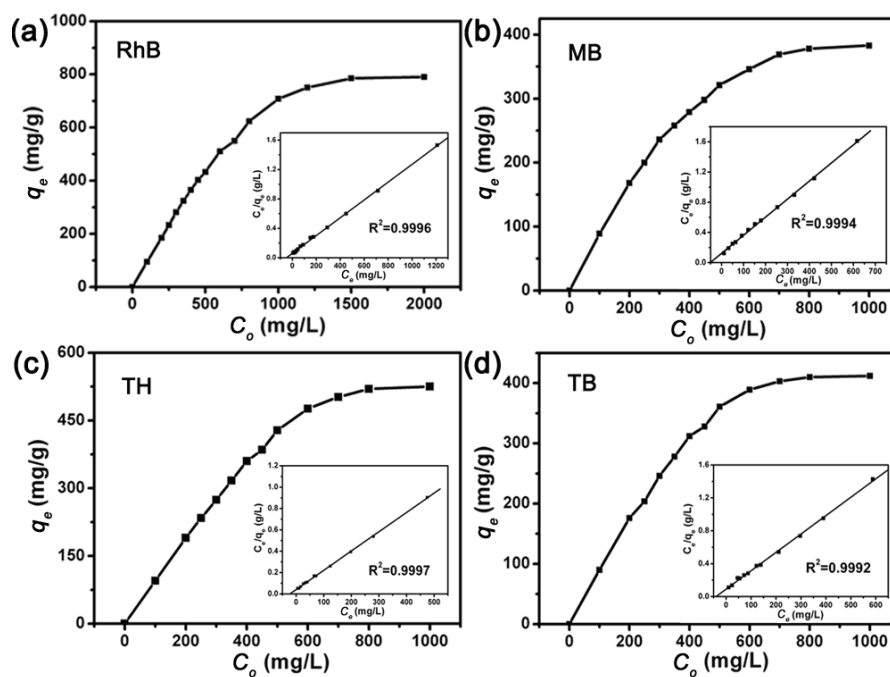


Fig. S11. Adsorption capacity of various dyes onto GOs in the presence of CTFNPs for RhB (a), MB (b), TH (c) and TB (d) respectively. (Inset is the Langmuir model for adsorption)

Movie S1. Reversible combination and separation of CTFNPs and GOs through the adjustment of pH of the solution by adding 0.1 M NaOH and 0.1 M HCl, respectively.

Movie S2. The process of dyes removal from water.

Movie S3. The recycling use of CTFNPs for dye's removal from water.