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Chemical reduction and removal of Cr(VI) from acidic aqueous solution by ethylenediamine-reduced graphene oxide

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Raw materials

Natural graphite flakes were supplied by Huadong Graphite Factory (Pingdu, China) with an average diameter of 13 μm . Ethylenediamine (ED, 99%) was purchased from Tianjin Fuchen Chemical Reagents Factory (China). Sodium nitrate (NaNO_3) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) was bought from Xilong Chemical Industry (China). Sulphuric acid (H_2SO_4 , 98%), hydrochloric acid (HCl , 37%), potassium permanganate (KMnO_4 , 99.5%), hydrogen peroxide (H_2O_2) and all the other reagents and solvents were purchased from Beijing Chemical Factory (China).

Preparation of graphene oxide

Graphene oxide (GO) was synthesized from natural graphite flakes by the modified Hummers method.¹ Briefly, natural graphite (5 g), NaNO_3 (5 g) and concentrated H_2SO_4 (150 ml) were added into a 500 ml three-neck flask at 0 °C. KMnO_4 (15 g) was slowly added with 5 portions in order to keep the temperature below 5 °C. The suspension was then heated to 35

°C and maintained for 6 h. Distilled water (200 ml) was slowly added in the suspension, and the temperature was kept at 98 °C for 15 min. The suspension was further treated by the addition of 700 ml distilled water and 20 ml H₂O₂ (30%), filtered, and then washed with 5% HCl aqueous solution and plenty of distilled water until pH ≈ 7.

Synthesis of ED-RGO sheets

GO (300 mg) was dissolved in distilled water (300 ml) and treated by a Y99-2 DN ultrasonicator (Ningbo, China) for 1 h to obtain a uniform suspension. ED (3.60 ml) and ammonia solution (900 μL) were added, and the suspension was heated in an oil bath at 95 °C for 6 h. The final suspension was filtrated by polypropylene membrane (0.2 μm). The resulting filtrate cake was washed with water and ethanol and then dried in an oven at 60 °C for 24 h.

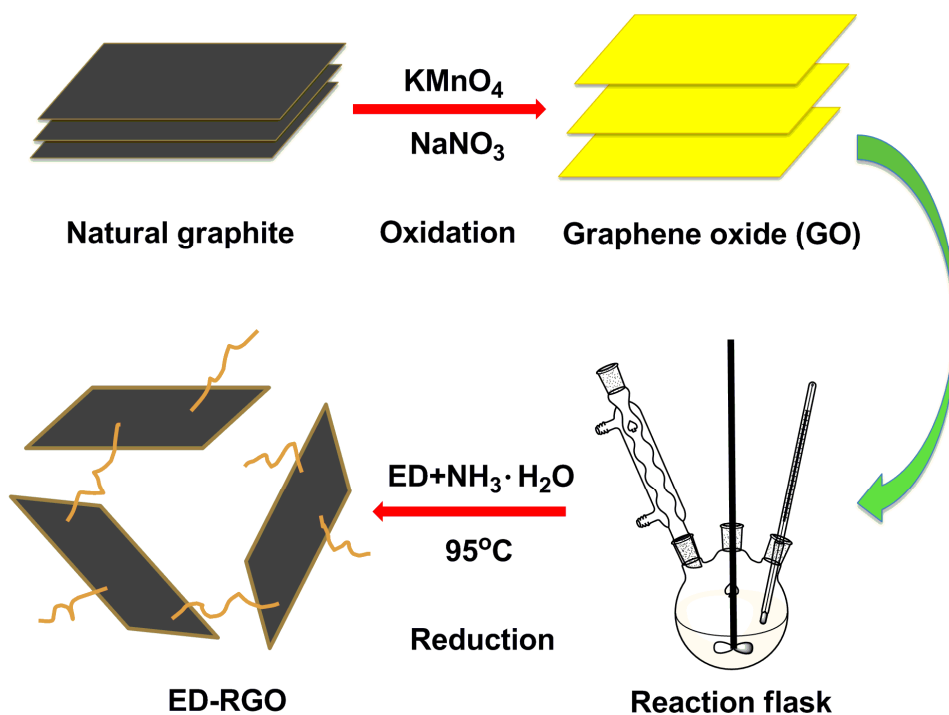
Adsorption experiments

The standard stock solution of Cr (VI) present at a concentration level of 1000 ppm was obtained by dissolving K₂Cr₂O₇ in distilled water. The stock solution was finally diluted to obtain standard solutions (100 ppm). 1 mol L⁻¹ HCl solution was used for pH adjustment using a pH meter (SevenMulti, METTLER-TOLEDO). All adsorption experiments were carried out at 33 °C. In the kinetic studies, a series of 50 mg ED-RGO was added to different 250 mL beakers containing 50 mL Cr (VI) solution (100 ppm, pH=1). The beakers were strongly shaken at a rate of 160 rpm in an oscillator to ensure a complete mixing. The contact time was in the range from 15 min to 24 h. After the shaking, the solution samples were filtered through a 0.2 μm polypropylene membrane at suitable time intervals. Other

experiments for investigating the pH and feed effect on Cr(VI) removal by ED-RGO followed a very similar procedure except that the feed in pH experiment was fixed as 0.20 g L⁻¹. Cr(VI) concentration was measured by a UV-visible spectrophotometer at 540 nm by 1, 5-diphenyl carbazide method.² The total Cr concentration was determined by a TELEDYNE Prodigy inductively coupled plasma-atomic emission spectrometer.

Characterizations

X-ray diffraction (XRD) measurements were carried out using a Rigaku D/Max 2500 diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 50 mA with a scanning speed of 4° min⁻¹. Raman spectra were recorded with a Renishaw inVia Raman microscope (Britain) at an excitation wavelength of 514.5 nm. GO and ED-RGO were characterized with a Nicolet Nexus 670 Fourier-transform infrared spectroscopy (FT-IR), a ThermoVG RSCAKAB 250X high resolution X-ray photoelectron spectroscopy (XPS) and a Hitachi S4700 field-emission scanning electron microscope (SEM) at an accelerating voltage of 20 kV.



Scheme S1. Schematic of the preparation of ED-RGO.

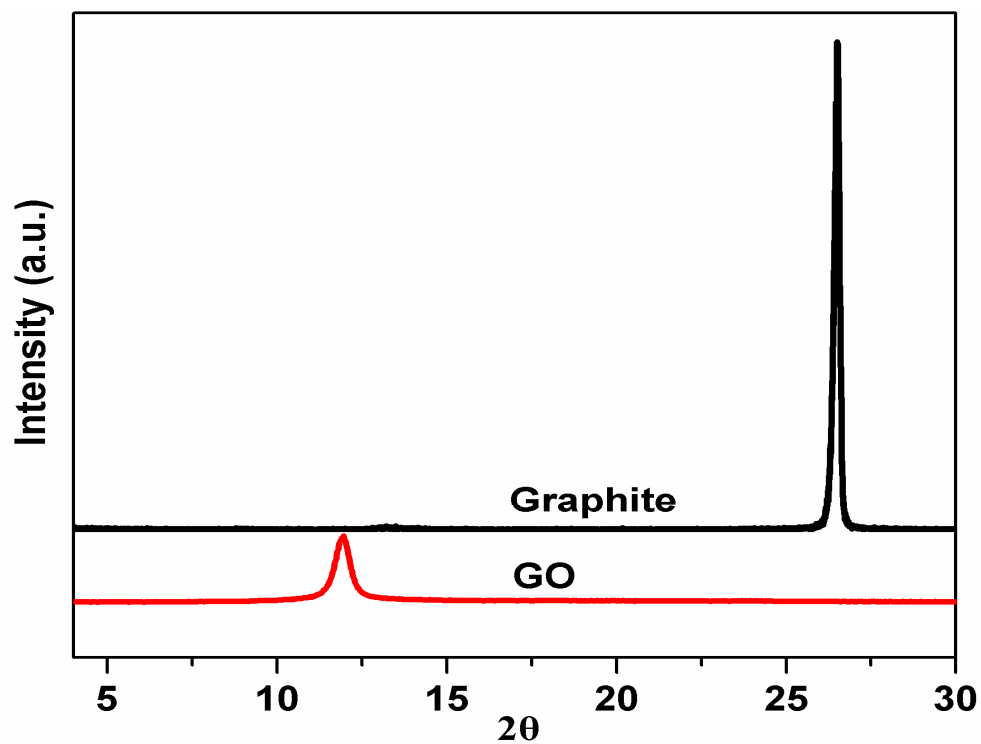


Fig. S1. XRD patterns of graphite and GO.

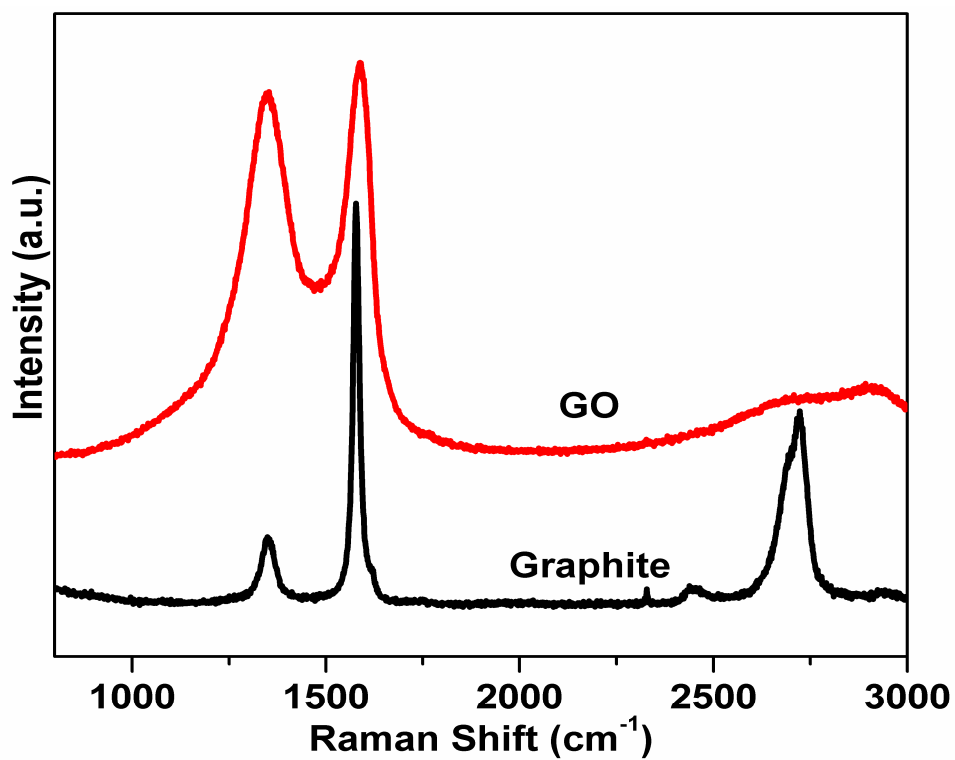


Fig. S2. Raman spectra of graphite and GO.

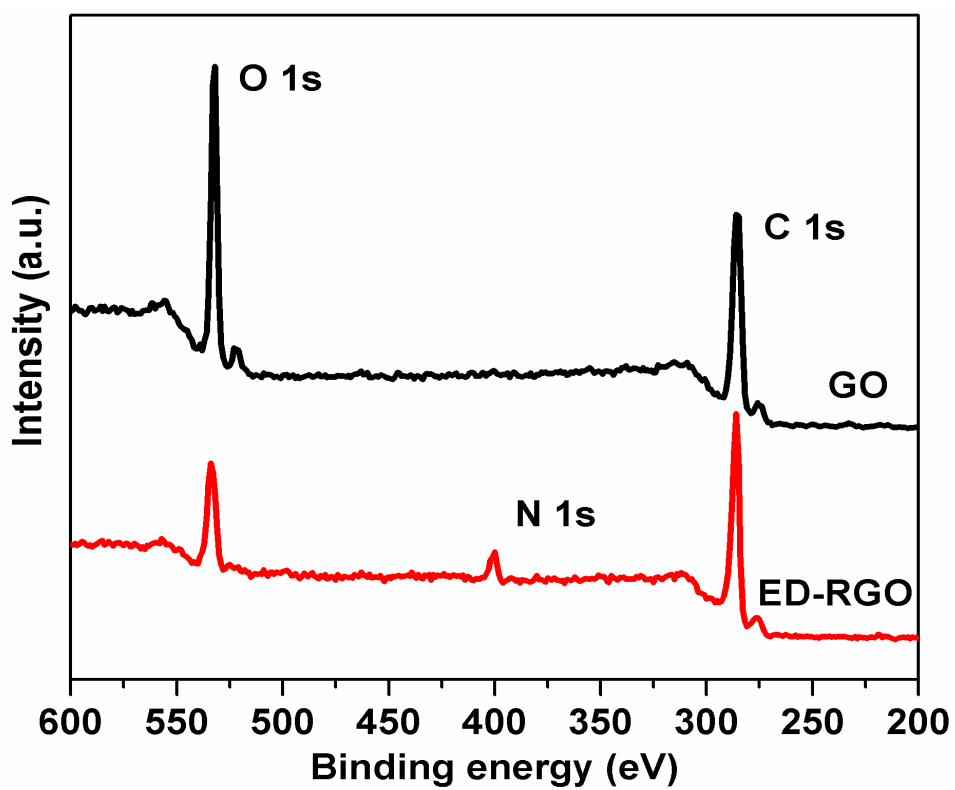


Fig. S3. XPS spectra of GO and ED-RGO.

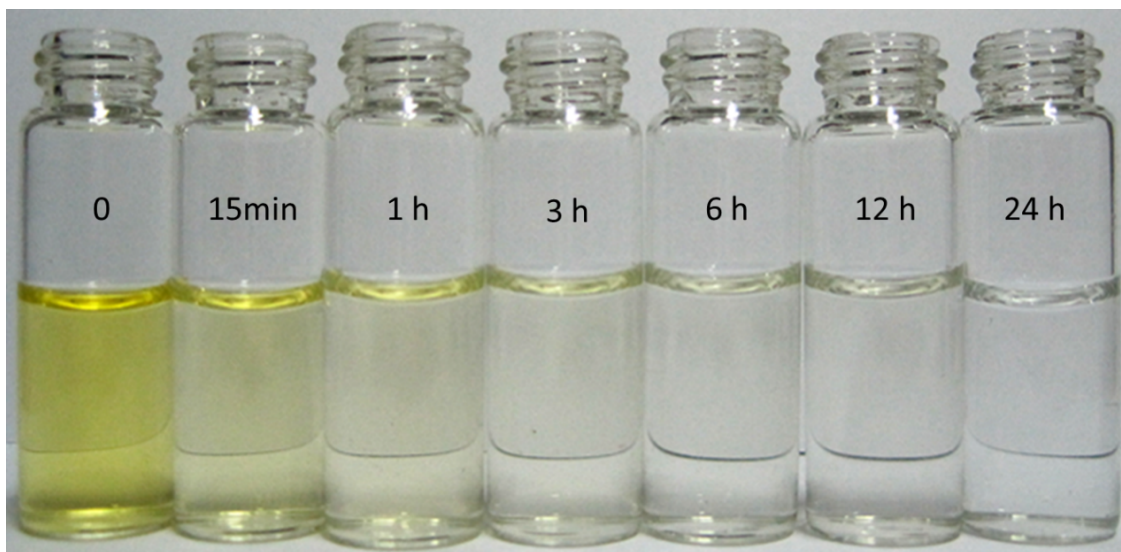


Fig. S4. Photographs of filtrates after adsorption experiments. From left to right, the contact times of the samples were 0, 0.25, 1, 3, 6, 12 and 24 h.

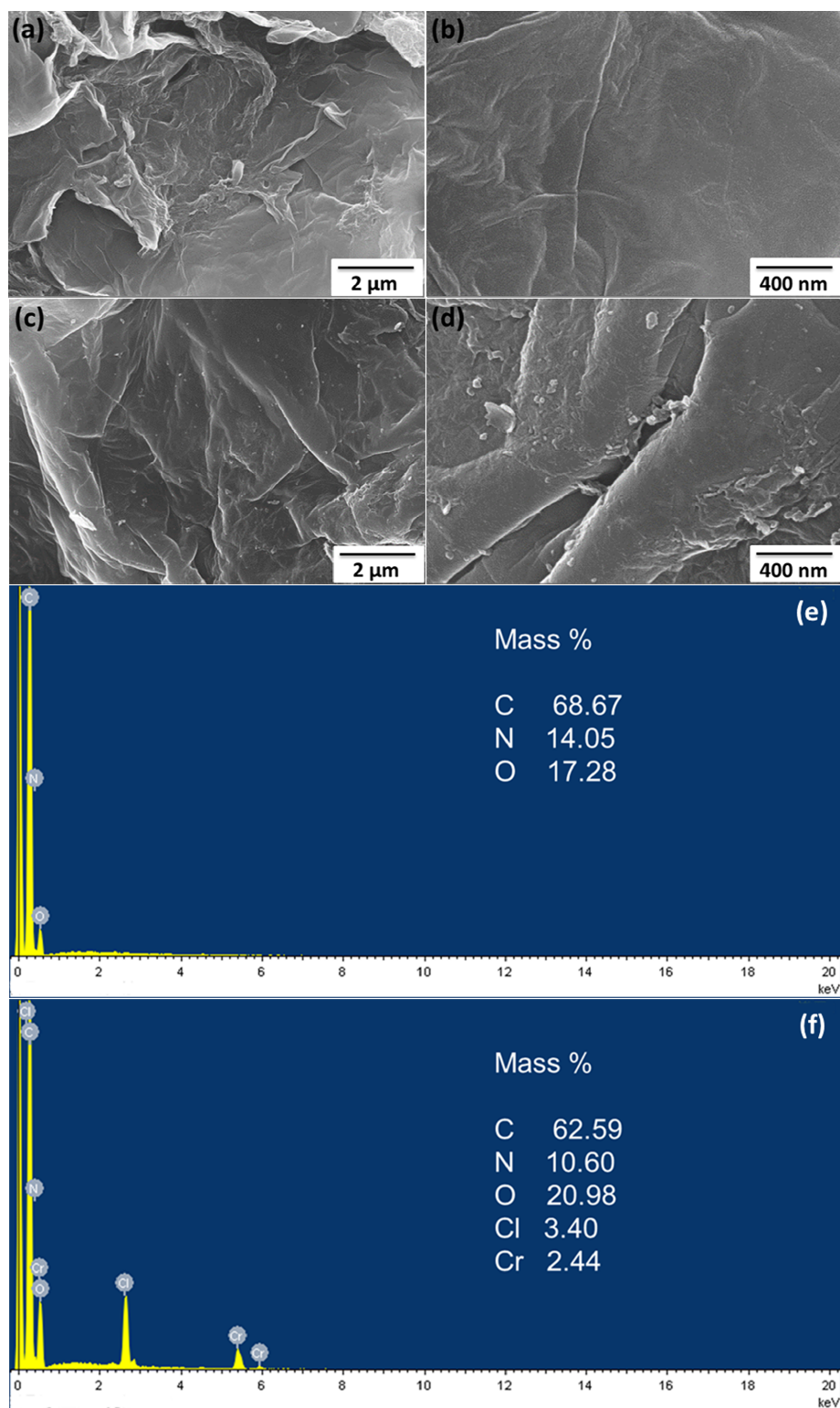


Fig. S5. SEM images of ED-RGO (a, b) before and (c, d) after Cr(VI) adsorption; EDX analyses of ED-RGO (e) before and (f) after Cr(VI) adsorption.

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
2. M. R. Samani, S. M. Borghei, A. Olad and M. J. Chaichi, *J. Hazard Mater.*, 2010, **184**, 248.