Supporting information

A Strong adsorbent for Cu²⁺: graphene oxide modified by triethanolamine

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1. Materials, method and characterization

Preparation of graphene oxide (GO)

GO was prepared following the modified Hummers method. Briefly, a mixture of graphite (2.0 g), $K_2S_2O_8$ (1 g) and P_2O_5 (1 g) was added into 15 mL of H_2SO_4 and stirred at 80 °C for 4.5 h. After cooling and stirring in ice water for 0.5 h, the suspension was diluted with 1000 mL deionized water and then filtered. The filter cake was washed with deionized water (pH=5.5) and dried. Then KMnO₄ (10 g) was added slowly while vigorous stirring. The reaction was carried through at 35 °C for 2 h. After addition of 250 mL deionized water, the mixture was stirred for another 2 h. Then 500 mL deionzed water and 8.3 mL H_2O_2 (30% wt%) were added into the mixture. After filtration, the residue was washed by HCl (10% v/v) and deionized water until pH value of the solution is neutral. The obtained dark and viscous liquid was donated as GO.

Synthesis of TEA-GO

Typically, a mixture of GO (100mL, 2mg/mL), TEA (5mL), deionized water (50mL) was added into a 250mL three-necked flask, and stirred at 80 $^{\circ}$ C for 2h. A few minutes later, GO suspension changed from yellow-brown to black. The suspension was then centrifuged, and the precipitate was washed with distilled water. Repeat centrifuging process till pH 7 and then dried under vacuum at room temperature. And the black TEA-GO powder was obtained.

Adsorption experiment of TEA-GO for Cu²⁺

TEA-GO (0.02g) was mixed with Cu^{2+} solution with a specific concentration. Then, the suspension was placed into thermostatic water bath oscillator under room temperature for 3 h. Finally, the suspension was filtered, and filtrate was collected to measure the concentration of Cu^{2+} by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Characterizations

Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrophotometer using KBr pellets. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB 250Xi X-ray Photoelectron Spectroscopy. Transmission electron microscopy (TEM) was carried out using JEM-2100F. The concentration of Cu²⁺ was determined by an Optima 5300 ICP-AES.

2. Supporting results and discussion

The dispersion of TEA-GO (0.2 mg/mL) in various solvents is shown in Fig. S1. Homogeneous colloidal suspensions of TEA-GO nanosheets are easily produced in H₂O, ethanol, glycol, and N, N-dimethylformamide (DMF). And these colloidal suspensions are stable for several months.



Fig. S1 Digital photos of GO (a) and TEA-GO dispersed in different solvents: H₂O (b), ethanol (c), and DMF (d).

Fig. S2 shows the TEM images of GO and TEA-GO. TEA-GO exhibits the typical wrinkle-like thin sheet morphology as GO, which is the feature structure of graphene nanosheets. But TEA-GO has more corrugations and scrolling than GO, which may result from increased amount of hydroxyl produced from modification of GO by TEA.



Fig. S2 TEM images of GO (a, b) and TEA-GO (c, d)

The Langmuir and Freundlich adsorption isotherm models are both widely used in adsorption studies. We try to fit the adsorption data of TEA-GO with these two models. But the Langmuir adsorption isotherm model (R=0.742) and Freundlich adsorption isotherm model (R=0.890) cannot fit the adsorption data of TEA-GO to Cu^{2+} well (shown in Fig. S3a, b). Moreover, when the adsorption progress is divided into two parts and simulated with Langmuir adsorption isotherm model, the adsorption data of TEA-GO cannot be fitted well (R1=0.987, R2=0.861, shown in Fig. S 3c, d).



Fig. S3 Fitting of Langmuir adsorption isotherm model for Cu²⁺ adsorption on TEA-GO

The adsorption isotherm of Ni²⁺ on TEA-GO is shown in Fig. S4.



Fig. S4 The adsorption isotherm of Ni²⁺ on TEA-GO

Fitting of Freundlich adsorption isotherm model for Ni^{2+} adsorption on TEA-GO is showed in Fig. S5. The adsorption progress is regarded as two stages, and each stage can be also fitted by Freundlich model well (R1=0.918, R2=0.964).



Fig. S5 Fitting of Freundlich model for Ni²⁺ on TEA-GO

The survey XPS spectra and N1s XPS spectra of TEA-GO-Cu²⁺ is shown in Fig. S6.



Fig. S6 The survey XPS spectra (a) and N1s XPS spectra (b) of TEA-GO-Cu²⁺.