Graphene oxide-based polyethersulfone core-shell particles for dye uptake

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Supporting Information

Preparation and characterization of GO

Aqueous GO dispersion was prepared by a modified Hummers' method from natural flake graphite ^{1, 2}. Firstly, Graphite (5.0 g) and sodium nitrate (3.75 g) were added to concentrated sulfuric acid (150 mL) under stirring in ice-water bath, and then potassium permanganate (20.0 g) was added slowly for over 1h. The mixture was stirred in the ice water bath for 2 h, following by a vigorous stirring for 3 days at room temperature. Then, 500 mL of DI water was slowly added to dilute the mixture, and the solution was stirred for another 20 min. The excessive potassium permanganate was decomposed by H_2O_2 (30 wt. %, 15 mL), turning the color of the solution from brown to yellow. The insoluble precipitations were removed by centrifugation. The resulted GO solution was filtered and washed with HCl aqueous solution (10 wt. %, 1 L) and DI water to remove metal ions repeatedly. The obtained brown dispersion was purified by dialysis for one week to remove the residual acid and salt impurities. Finally, the weight percentage of the GO was

10.83 mg/g, which was determined by drying the GO dispersion.

The prepared GO samples were characterized by atomic force microscopy (AFM), scanning electronic microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy analysis, as shown in **Fig. S1**. The AFM samples were prepared by dropping aqueous GO solution (\approx 0.01 mg/mL) on freshly cleaved mica surface and dried under vacuum at 60 °C. AFM images were taken on a Multi-Mode Nanoscope V scanning probe microscopy (SPM) system (Vecco Instruments Co., USA). A scanning electron microscope (FEI Sirion-200, USA) was used for the surface morphology observation. The SEM images were obtained by drop-casting the aqueous GO solution on the silicon wafer followed by vacuum drying in 40 °C. The samples for FTIR measurement were prepared by grinding the dried powder with KBr together, and then pressed into a pellet. FTIR patterns were obtained using a FTIR spectrometer (Nicolet 560, USA).

The two-dimensional single layer structure is the most crucial morphology of GO sheet. The surface structure and the height of GO sheets were characterized by AFM. **Fig. S1a** shows the typical AFM image of the prepared GO sheets on freshly cleaved mica. As shown in **Fig. S1a**, flat sheets with some wrinkles were observed clearly, verifying the characteristic single-layered 2D structure of the GO sheets. The average thickness of each single layer was about 1.1 nm; since there were some functional groups such as hydroxyl groups and epoxy groups connected on some sp³-hybridized carbon atoms on GO sheets, the layers were thicker than the single layer graphene of which the thickness was 0.35 nm ³. The morphologies of the GO sheets were further observed by SEM, as shown in **Fig. S1b**; the gossamer substance could be observed clearly, which also indicated the single-layered 2D structure of the GO sheets.

To characterize the chemical structure of the GO sheets, FTIR was applied, as shown in **Fig. S1c**. Multiple peaks in the range of 900 to 1500 cm⁻¹ were assigned to the functional groups, such as C–O–C, C–OH. The band at 1731.9 cm⁻¹ was associated with the v(C=O) in carboxylic acid and carbonyl moieties, the broad characteristic peak at 3363 cm⁻¹ was assigned to the O–H stretching vibration arising from the hydroxyl groups in GO sheets. These results indicated that hydroxyl groups, epoxy groups and carboxyl groups were presented on the GO sheets, and because of that, the surface of GO sheet showed negative charges.



Fig. S1. Characterization of the GO sheets: AFM image (a); SEM image (b); FTIR spectrum (c).

The SEM images of the cross-section of PES@GO particles

The three PES@GO particles (PES8@GO, PES10@GO and PES12@GO) have been observed by SEM, and the results showed no significant differences in the thickness or pore structure of their shells, as shown in **Fig. S2**.



Fig. S2. The SEM images of the cross section of the particles: PES8@GO (a); PES10@GO (b); PES12@GO (c).

Freundlich Isotherm

As an empirical equation, the Freundlich equation is employed to describe heterogeneous systems and reversible adsorption ignoring the formation of the monolayer. The equation may be expressed in the following form:

 $\ln q_e = \ln k_F + (1/n) \ln C_e$

where k_F is the Freundlich adsorption constant; 1/n is the heterogeneity factor; q_e is the mass of the MB adsorbed by the unit mass of the particles after the concentration reaches equilibrium (mg/g); C_e is the concentration of the MB in the solutions at the equilibrium (mg/L). The plot of $\ln q_e$ against $\ln C_e$ should give a straight line with slope (1/n) and intercept $\ln k_F$, as can be seen in **Fig. S3**. The parameters are shown in **Table S1**, the correlation coefficient values (R²) of the Freundlich model for PES8@GO, PES10@GO, PES12@GO, PES/PAA@GO and PES/GO@GO were 0.812, 0.786, 0.793, 0.811 and 0.934, respectively. The results revealed that the experimental data did not agree well with the Freundlich model.

Particles	п	$k_F(L/g)$	R_F^2
PES8@GO	4.33	161.63	0.812
PES10@GO	4.36	151.70	0.786
PES12@GO	4.45	147.48	0.793
PES/PAA@GO	3.78	151.15	0.811
PES/GO@GO	3.64	177.04	0.934

Table S1. The parameters of the Freundlich model for the particles.



Fig. S3. Application of the Freundlich model for the particles.

The adsorbed amount of MB by GO aqueous solution

The adsorption of MB onto pure GO was carried out in water at room temperature and pH 7. In general, 5 mL of 1 mg/mL GO aqueous solution was added to 20 mL of MB solution (0.1-2 mmol/L) in conical flask at room temperature. After stirring by a magnetic stirrer for 30 minutes to reach equilibrium, GO was centrifuged at 12,000 r/min for 10 min from the MB solution and the concentration of the MB solution was determined with the UV-vis spectrophotometer 756PC at the wavelength of 631 nm.

The adsorption isotherm of MB by GO aqueous solution is shown in **Fig. S4a**, where q_e is the mass of the adsorbed MB by the unit mass of GO after the adsorption reached equilibrium; C_e is the equilibrium concentration of the MB solution. With the increase of the initial concentration, the adsorbed amount increased, and when the value increased to 1053 mg/g, the adsorption capacity reached a plateau. The results fitted the Langmuir model (**Fig. S4b**) very well (R² =0.998), and the maximum adsorption amount was 1136.47 mg/g.



Fig. S4. Adsorption isotherm of MB by GO aqueous solution (a); application of the Langmuir model (b).

Reference

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