Supporting information

A Hierarchical Adsorption Material by Incorporating Mesoporous Carbon into Macroporous Chitosan Membrane

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1. Detailed Experimental Section

1.1 Materials

CS flake (deacetylation degree = 72%, molecular weight = 850,000) was purchased from Jinan Haidebei Marine Biological Product Co., Ltd. (Jinan, China). All other chemicals were analytical grade and used as received without further purification.

1.2 Preparation of Mesoporous Carbon FDU-15

The FDU-15 carbon material was prepared according to the method reported elsewhere.[1] Typically, 1.0 g of triblock copolymer poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (Pluronic F127) was dissolved in 20.0 g of ethanol, then 5.0 g of phenolic resin precursor (20 wt% in ethanol) was added and stirred for 10 min to form a homogeneous solution. The solution was transferred into glass dishes and the ethanol was evaporated at room temperature for 5–8 h to produce transparent films. The films were then heated in an oven at 100 °C for 24 h to thermopolymerize the phenolic precursor. The products were calcined at 900 °C under nitrogen for 3 h with a temperature ramp rate of 1 and 5 °C/min below and above 600 °C, respectively, thus giving rise to the carbon sample. The resultant carbon sample was oxidized by a 5.0 mol/L HNO_3 solution at 60 °C for 6 h to get the final surface oxidized carbon for the membrane preparation.

1.3 Preparation of FDU-15/CS blend membranes

CS with 72% deacetylation degree was further deacetylated in 50 wt% NaOH solution at a ratio of 50 g/L in a stainless-steel kettle at 333 K for 24 h. The resulting CS was washed to neutral and dried for further use. The final deacetylation degree was 92% as determined by titration.[2] For the fabrication of hierarchical FDU-15/CS blend membranes, a certain amount of FDU-15 was added into a 2 wt% CS acetic acid solution under stirring. Then, porogen silica particles (300–400 mesh) and crosslinking agent glutaraldehyde solution were added. After stirring for 3 h, the mixture was poured into a poly(ethylene terephthalate) box and allowed to dry at room temperature. Then the dried membranes were immersed in a 5 wt% NaOH aqueous solution for 2 h to dissolve the silica and generate the macroporous CS/FDU-15 blend membranes. These macroporous CS/FDU-15 blend membranes were further crosslinked under mild alkaline conditions using epichlorohydrin.[2] The final membranes were washed extensively with deionized water and kept in deionized water for further use.

1.4 Batch Adsorption Measurement

Fuchsin was selected as model dye for adsorption studies. For the kinetics study, the typical macroporous CS/FDU-15 blend membrane (with 63 wt% of FDU-15 carbon content) was cut into small pieces and about 5.6 mg of the membrane was put into a test tube containing 32 mL of fuchsin solution with an initial concentration of 15.6 mg/L. Then the mixture was shaken in an oscillator at 200 r/min and 25 °C. The remaining concentration of the fuchsin in the solution after adsorption at each time interval (from 2 to 2000 min) was determined with a U-2910 UV/Vis spectrophotometer (Hitachi, Japan) at 544 nm. To compare the adsorption properties of FDU-15/CS blend membranes with different carbon content (0–63%), the membranes were put into 15.6 mg/L at for 24 h. To measure the adsorption isotherm of FDU-15/CS blend membrane, the typical membranes (63 wt% carbon content) were put into a series of fuchsin solutions with a concentration from 1 to 18 mg/L at 25 °C for 24 h. Other experimental conditions were the same as the kinetics study stated above. The adsorbed amount of fuchsin was determined by measuring the difference between the initial and the final concentrations of the fuchsin solutions. The adsorption capacity was calculated with the following expression.

$$q_e = (c_0 - c_e)V/M \quad (1)$$

where q_e (mg/g) is the equilibrium adsorption capacity, c_0 and c_e (mg/L) are the initial and final concentrations of the fuchsin solution, V (mL) is the volume of the fuchsin solution, and M (mg) is the weight of the dry CS/FDU-15 blend membrane.

1.5 Dynamic Adsorption Measurements

To evaluate the dynamic adsorption performance, three layers of the typical FDU-15/CS membrane (63 wt% carbon content) were stacked as a column and assembled into a disc holder (4 cm in diameter). After a buffer run for half an hour, 500 mL of fuchsin feed solution (10 mg/L) was continuously pumped into the membrane column with a flow rate of 2 mL/min at 25 °C. A series of elute solution with a fixed volume of 2 mL from the membrane column were consecutively collected at the preset time intervals and the corresponding fuchsin concentrations in the elute were detected with UV-Vis spectrophotometer at 544 nm. Based on the above measurement, the breakthrough curve of the fuchsin adsorption was obtained, and thus the dynamic adsorption capacity of fuchsin at 10% breakthrough was retrieved correspondingly. After an adsorption circle, 500–1000 mL of absolute alcohol was passed through the membrane column with a flow rate of 2 mL/min to desorb fuchsin and thus regenerated the membrane column.

2. Adsorption Kinetic Modelling

To analyse the adsorption kinetics of the fuchsin on the FDU-15/CS membrane, the first-order (Equation 2) and the pseudo-second-order kinetic (Equation 3) models were applied to fit the experimental data. It was found that the experimental data can be well fitted by the pseudo-second-order kinetic model.

$$dq_t/dt = k_{1,ad}\,(q_e - q_t),\ \log\,(q_e - q_t) = \log q_e - k_{1,ad}t/2.303 \quad (2)$$

$$dq_t/dt = k_{2,ad}\,(q_e - q_t)^2,\ t/q_t = 1/(k_{2,ad}q_e^{\,2}) + t/q_e \quad (3)$$

where q_e (mg/g) is the equilibrium adsorption capacity, q_t (mg/g) is the amount of adsorbed dye on the membrane at time t, and $k_{1,ad}$ (min^{-1}) and $k_{2,ad}$ (g/mg•min) are the rate constants of first-order and pseudo-second-order adsorption and.

3. Supporting Figures

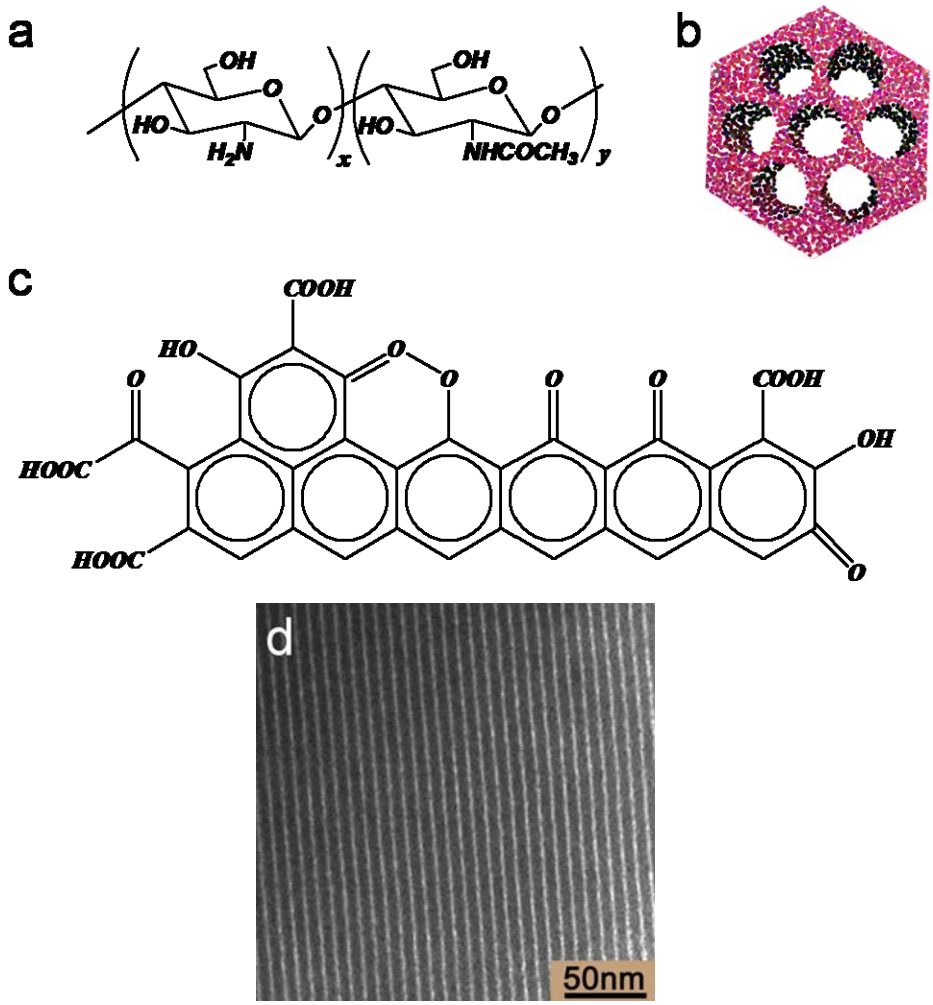


Figure S1. Structure of CS (a), models of the hexagonal mesostructure of mesoporous carbon FDU-15 (b), the oxygen-containing groups in the surface-oxidized FDU-15[3] (c), and a typical TEM image of mesoporous carbon FDU-15 particle showing the existence highly ordered hexagonal mesostructure and uniform mesopores with an estimated pore diameter of 3.3 nm (d).

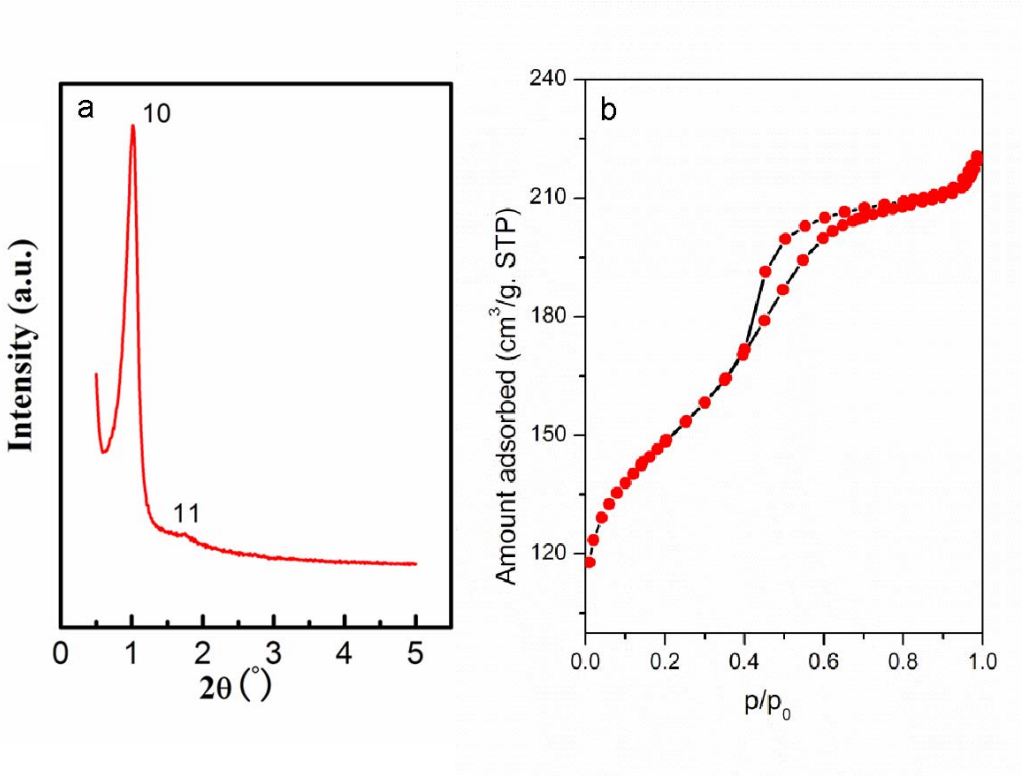
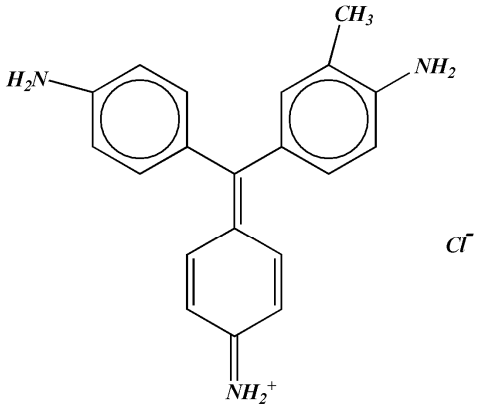


Figure S2. Small-angle X-ray diffraction pattern (a) and N_2 sorption isotherm (b) of the surface-oxidized mesoporous carbon FDU-15. The surface-oxidized mesoporous carbon FDU-15 shows one strong diffraction peak and one weak peak, which can be indexed to the 10 and 11 diffractions based on 2-D hexagonal structure with *p*6*m* symmetry. The nitrogen adsorption isotherm at 77 K of the carbon material is a combination of type-I and type-IV, indicating typical bimodal microporous and mesoporous materials.



fuchsin

Figure S3. Structure of the organic basic dye fuchsin.

4. Supporting References

(1) Y. Meng, D. Gu, F. Q. Zhang, Y. F. Shi, L. Cheng, D. Feng, Z. X. Wu, Z. X. Chen, Y. Wan, A. Stein and D. Y. Zhao, *Chem. Mater.*, 2006, **18**, 4447.

(2) Z. C. Feng, Z. Z. Shao, J. R. Yao, Y. F. Huang and X. Chen, *Polymer*, 2009, **50**, 1257.

(3) Z. X. Wu, P. A. Webley and D. Y. Zhao, *Langmuir* 2010, **26**, 10277.