

Template-assisted Synthesis of Polypyrrole Hollow Microspheres with Double-Shelled Structure

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Supporting Information:

Experimental Sections

1.1 Synthesis of Fe₃O₄ Hollow Microspheres

10 The magnetic Fe₃O₄ hollow microspheres were prepared through a solvothermal reaction. Typically, FeCl₃•6H₂O (1.35 g) and ammonium acetate (3.85 g) were dissolved in ethylene glycol (60 mL) under magnetic stirring. The obtained homogeneous yellow solution was transferred to a Teflon-lined stainless-steel autoclave (100 ml) and heated at 200 °C for 20 h. The obtained black particles were washed with ethanol several times and then dried in vacuum at 60 °C for 12 h.

1.2 Synthesis of Double-Shelled polypyrrole (PPY) Hollow Microspheres

15 Fe₃O₄ particles (0.18 g) were firstly dispersed in alcohol (15 ml) containing pyrrole (2 ml) for 2 hours, and then deionized water (70 mL) and HCl solution (15 ml, 6 M) were added into the above solution in turn, and the whole reaction system was kept under sonication for 120 minutes. The black products were collected by repeatedly centrifugation and washing in order to remove the residual pyrrole monomers and acid, and then dried in vacuum at 60 °C overnight.

1.3 Characterizations

20 The products were analyzed by X-ray diffraction (XRD), in a 2θ range from 10° to 90°, using CuKα radiation (Philips X'pert diffractometer). The morphology of the prepared double-shelled PPY hollow microspheres was studied by field emission scanning electron microscopy (FESEM, Sirion 200 FEG) and field emission transmission electron microscopy (FETEM, JEOL-2010, 200 kV). The powders were dispersed in ethanol using ultrasonic vibration. The samples for microscopy studies were prepared by deposition of dispersions of the powder in ethanol directly on the SEM stubs or holey carbon grid for TEM examination. Infrared (IR) spectra were
25 recorded in the wave numbers ranging from 4000 to 500 cm⁻¹ with a Nicolet model 759 Fourier transform infrared (FT-IR) spectrometer using a KBr wafer. The surface area of the samples was determined by using Micromeritics ASAP 2020.

1.4 Cr(VI) Removal Experiments

K₂Cr₂O₇ was used as the source of Cr(VI). The different concentrations of Cr(VI) ions were prepared and the pH value of 2 was adjusted by HCl and NaOH solutions. For each sample, 20 mg adsorbent was dispersed into the above solution (20 ml), and then the mixtures
30 were shaken at a speed of 100 rpm for 6 hours to establish adsorption equilibrium at room temperature. The adsorbent was then separated from the mixture by centrifugation. To determine Cr(VI) ions removal by the adsorbent, the Cr(VI) concentration in the remaining solution was measured by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES Atomscan Advantage).

1.5 Adsorption performance analysis

The Langmuir and Freundlich isotherm models are applied to simulate Cr(VI) adsorption on double-shelled PPY hollow microspheres,
35 respectively.

The Langmuir model is expressed as:

$$Q_e = bQ_m C_e / (1 + bC_e) \quad (1)$$

The Freundlich isotherm model can be expressed by the following formula:

$$Q_e = kC_e^{1/n} \quad (2)$$

40 where C_e is the equilibrium concentration of Cr(VI) in the supernatant (mg L^{-1}); Q_e is the amount of Cr(VI) adsorbed on per weight of PPY double-shelled hollow microspheres (mg g^{-1}) after adsorption equilibrium; Q_m represents the maximum adsorption capacity of Cr(VI) on per weight of double-shelled PPY hollow microspheres (mg g^{-1}); and b is the Langmuir adsorption constant (L mg^{-1}). The Freundlich constant k is correlated to the relative adsorption capacity of the adsorbent (mg g^{-1}), and $1/n$ is the adsorption intensity.

1.6 Cycle adsorption performance

45 The double-shelled PPY hollow microspheres (20 mg) were firstly dispersed in Cr(VI) solution (20 ml) with concentration of 150 mg L^{-1} , after the mixtures were shaken at a speed of 100 rpm for 6 hours to establish adsorption equilibrium at room temperature, the adsorbent was separated from the mixture by centrifugation. The regeneration ability of the obtained product was investigated by using alkaline and acidic solution. Typically, NaOH solution (0.5 M) and HCl solution (2 M) were used to remove the adsorbed Cr(VI) ions. The first adsorption efficiency was defined as 100%, and the efficiency in the following cycle was determined by using the first cycle as
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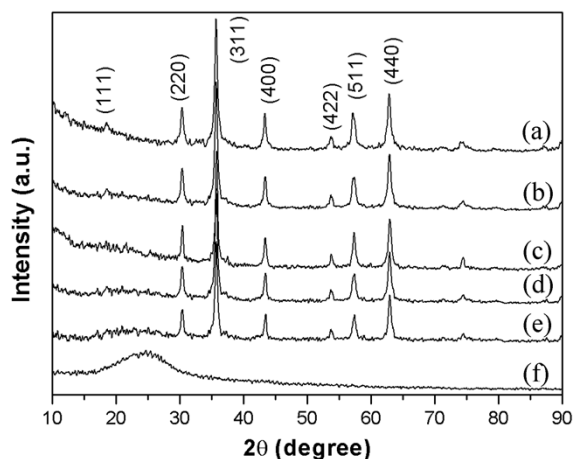


Fig. S1 XRD pattern of the products synthesized at different intervals (minutes): (a) 0, (b) 10, (c) 30, (d) 50, (e) 70, and (f) 120.

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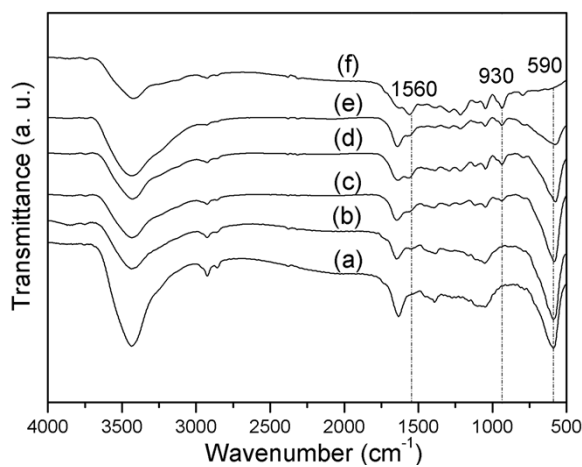
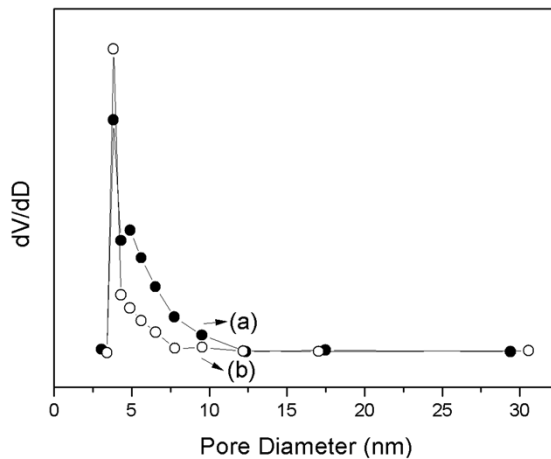


Fig. S2 IR spectra of the products synthesized at different intervals (minutes): (a) 0, (b) 10, (c) 30, (d) 50, (e) 70, and (f) 120.



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Fig. S3 BJH pore-size distribution curves of (a) the Fe_3O_4 hollow microspheres shown in Fig. 4a and (b) the Fe_3O_4 hollow microspheres shown in Fig. 2a obtained from the desorption data.

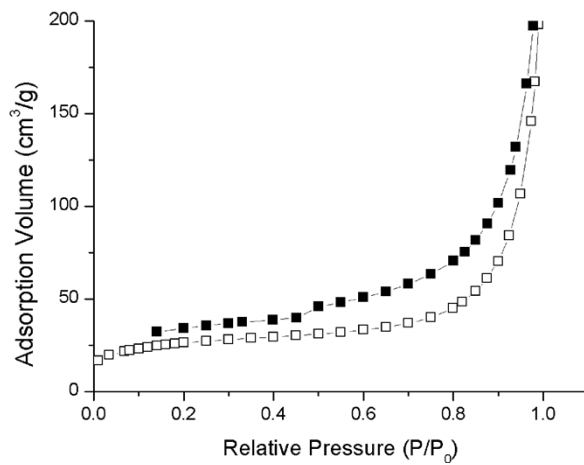


Fig. S4 N₂ adsorption/desorption isotherm for the double-shelled PPY hollow microspheres (□adsorption, ■desorption).

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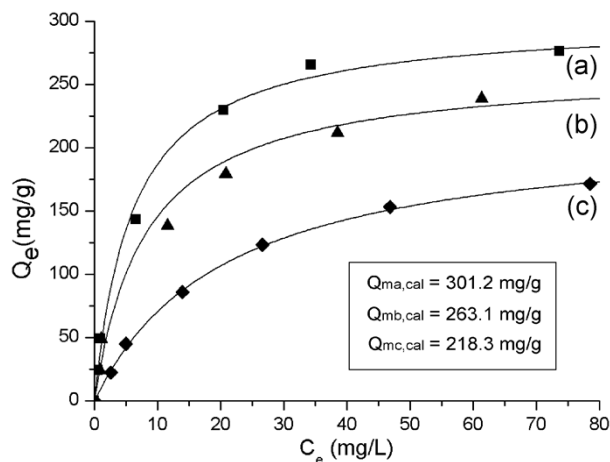


Fig. S5 The Cr(VI) adsorption isotherm of (a) double-shelled PPY hollow microspheres, (b) the product shown in Fig. 4e and (c) the product shown in Fig. 4d. (The inset values were the corresponding calculated maximum adsorption capacities.)

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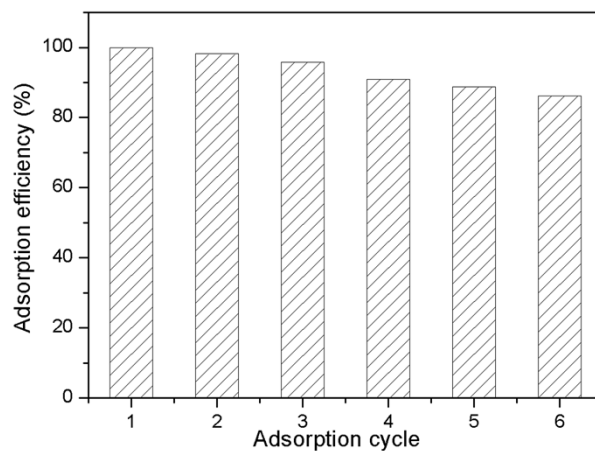


Fig. S6 The removal efficiency of Cr(VI) in six cycles.