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Electronic Supplementary Information

Synthesis of Hierarchically Nanostructured TiO₂ Spheres with Tunable

5 Morphologies Based on a Novel Amphiphilic Polymer Precursor and Their

Use for Heavy Metal Ion Sequestration

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Fig. S1 ¹H NMR characterization of the reaction product of Ti(OiPr)₄ with equal, twice and 4 times mole ratio of PEGHE in CDCl₃. There was no obvious chemical shift for the isopropoxide group (still at 4.02ppm), indicating the addition of the second PGEHE on the Ti(OiPr)₄ had little effect on the 5 chemical shift of the residual isopropoxide group. However, the molar ratio of isopropoxide groups (4.02 ppm) to the methyl groups (0.88 ppm) decreased to only 0.32, which was close to the ratio calculated from the diadduct product of PEGHE and Ti(OiPr)₄, 0.33. When 4 times of PEGHE was used (equal with the reaction site of Ti(OiPr)₄), the peak between 4.0-4.1 disappeared completely.



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Fig. S2 DLS plot of 2 wt% dispersions of amphiphilic polymer-modified TiO₂ precursors hydrolyzed in various volume ratios of ethanol and water.



Fig. S3 XPS spectra of the O 1s peak of TiO₂ samples at different preparation stages. (a) TiO₂ precursor beads obtained from the hydrolysis of TiO₂ precursors at room temperature; (b) sample 1 5 continued to age at 75 °C for 15 h; (c) sample 1 continued to age at 160 °C for 15 h; (d) TiO₂ precursor beads obtained from hydrolysis of TiO₂ precursor at 75 °C. The change of the relative ratio of O-Ti (529.7 eV, belonging to TiO₂ and its precursor) and O-C (531.8 eV, belonging to TiO₂ precursor) indicates the changing of copolymer content on the surfaces.

a) b) b) 100 nm

Fig. S4 TEM and the inserted SEM images of TiO₂ spheres prepared from hydrolysis of amphiphilic TiO₂ precursor at 75 °C at different preparing stage. The samples were prepared in the mixed solution with volume ratio of ethanol: $H_2O = 8:2$. (a) After the amphiphilic polymer-modified TiO₂ precursor 15 was hydrolyzed in the mixture for 10 min; (b) the sample was continued to age at 75 °C for 15 h.

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Fig. S5 Effect of initial pH on the removal of Cr (VI) by hierarchical porous TiO₂. The concentration of TiO₂ beads was 2.0 g \cdot L⁻¹ and the initial Cr (VI) ion concentration was 5.0 mg \cdot L⁻¹.



Fig. S6 Time profiles of Cr (VI) removal by hierarchical porous TiO₂. The concentration of TiO₂ spheres was 2.0 g ·L⁻¹ and the initial Cr (VI) ion concentrations were 5.0, 20.0 and 200.0 mg·L⁻¹, 10 respectively.