Supporting Information

Template-free fabrication of hierarchical porous carbon based on intra-/inter-sphere crosslinking of monodisperse styrene- divinylbenzene copolymer nanospheres

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Experimental details

1. Sample preparation

1.1. Materials

Styrene (St, Shanghai Chemical Reagent Co., AR) was purified by distillation under reduce pressure. Potassium persulfate (KPS, Tianjin Chemical Reagent Factory, AR) was purified by deionized water, divinylbenzene (DVB, 55%, mixture of isomers, Shanghai Chemical Reagent Co.), sodium dodecyl sulfate (SDS, Tianjin Chemical Reagent Factory, AR) and tetrachloromethane (Shanghai Chemical Reagent Co., AR) were used without further purification.

1.2. Preparation of monodisperse St-DVB copolymer nanospheres

SDS (0.1 g), pentanol (0.02 g), dissolved in deionized water (100 ml) was added in a four-necked flask equipped with a reflux condenser, mechanical stirrer, and nitrogen inlet. The solution was deoxygenated by bubbling nitrogen ten minutes and then was protected by nitrogen package to keep the nitrogen atmosphere. After that, the polymerization was carried out at 80 ^{o}C under mechanical stirring (250 rpm) according to the following three steps: (1) Nucleation: KPS (0.15 g) and St_1 (0.45 ml, 10% of the total amount of St) were added to the above reaction flask and kept for 30 min. (2) Nuclear growth: In order to realize a narrow particle size distribution, St_2 (1.36 ml, 30 %) was added in one potion and kept for 3h so as to form stable nuclear. (3) Crosslinking: We used the delayed addition method to add the crosslinking agent in emulsion polymerization. DVB (0.975 ml) and St_3 (2.72 ml, 60%) were mixed

firstly and then were added to the reaction system in one potion and kept for 12 h. After polymerization, the mixture was cooled down to ambient temperature naturally. Subsequently, methanol (300 ml) was added into the flask aimed at demulsification. The mixture was stored to -5 ^{o}C for 12 h, and then was heated until boiling and was filtrated with G4 sand funnel. After that, the resulting product was vacuum-dried at 60 ^{o}C.

1.3. Preparation of hierarchical porous polystyrene (HPP)

The St-DVB copolymer nanospheres prepared above (1.0 g) and carbon tetrachloride (60 ml) were added into a three-necked flask equipped with reflux condenser, moisture-removing trap. Then the equipment was put into a water bath (70 ^{o}C) and stirred under mild magnetic stirring speed (~400 rpm). After being totally swelled for 12 h in carbon tetrachloride, anhydrous $AlCl_3$ powder (2.8 g) was transferred into the reaction system rapidly. The crosslinking reaction was performed for 24 h. After stopping the Friedel-crafts reaction by cold mixture of acetone and 3% hydrochloric acid (v/v=1:1), the polymer was filtered off and washed successively for 12 h (4 hours per time, 3 times) with mixture solvent mentioned above, and the resulting product HPP was dried at 100 ^{o}C. It should be noted that the –CCl_2– crosslinking bridges between phenyl rings, which were formed in the process Friedel-Crafts reaction, would be transformed into –CO– crosslinking bridges during washing and drying due to the presence of H_2O.

1.4. Preparation of hierarchical porous carbon (HPC)

The as-prepared HPP with $–C_6H_4–$and –CO– crosslinking bridges was carbonized at 900 ^oC for 3 hours in N_2 flow with a heating rate of 2 ^oC min^{-1}, thus obtaining the HPC. The carbonization yield was measured to be 43%.

2. Characterization

Particle size and particle size distribution were determined by dynamic light scattering (DLS) on ZetaPALS in microemulsion at 25 ^oC; the microlatex sample was diluted by water to about 0.1 wt%. The microstructure of the samples was investigated by a JSM-6330F scanning electron microscope (SEM), a JEM-2010HR transmission electron microscope (TEM) and N_2 adsorption measurement. N_2 adsorption-desorption isotherms were obtained with an ASAP2010 (Micromeritics Corp.) instrument at 77 K. Before measurement, the samples were degassed at 150 ^oC for more than 10 h. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) was analyzed by BET theory. The total pore volume (V_{total}) was estimated from the amount adsorbed at a relative pressure P/P_0 of 0.992~0.998. The micropore surface area (S_{mic}) and external surface area (S_{ext}) were determined by t-plot theory. The pore size distribution was analyzed by original density functional theory (DFT) combined with non-negative regularization and medium smoothing. Micro-, meso- and macropore ratios (P_{mic}, P_{mes} and P_{mac}, respectively) are calculated according to the following equations: $P_{mic} = (V_{mic}/V_{DFT}) \times 100\%$, $P_{mes} = (V_{mes}/V_{DFT}) \times 100\%$, and $P_{mac} = 100\% - P_{mic} - P_{mes}$, where V_{mic}, V_{mes}, V_{mac} and V_{DFT} are the cumulative volume of micro-, meso-, macropore and total pore.