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Hierarchical porous polymeric microspheres for efficient adsorption and catalyst scaffold

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Experimental details

Materials. Ethanol, hexadecane, sulfuric acid (H_2SO_4, 98%), concentrated ammonia (28 %), cetyltrimethylammonium bromide (CTAB), tetraethoxysilane (TEOS), triethylamine (TEA), hydrochloric acid (HCl), ferric chloride hexahydrate ($FeCl_3$•$6H_2O$), ferrous chloride tetrahydrate ($FeCl_2$•$4H_2O$), sodium borohydride ($NaBH_4$), silver nitrate ($AgNO_3$), rhodamine 6G, and divinylbenzene (DVB) were of analytical grade and all used as received. Styrene (St) was distilled under reduced pressure over CaH and 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from ethanol. The amorphous fumed silica powders (H30) with primary particle diameters ranging from 5 nm to 30 nm was a gift from Wacker Chemie (Burghausen). Water used in all experiments was deionized and filtrated by a Millipore purification apparatus with resistivity more than 18.0 M cm.

Preparation of Hierarchical Porous Poly(St-co-DVB) Microspheres. Hierarchical porous poly(St-*co*-DVB) microspheres were produced by polymerization of the middle oil phase of double Pickering emulsion templates (W/O/W). Herein, the double Pickering emulsions were generated by a two-step method: using hydrophobic H30 as stabilizer, single Pickering emulsions were firstly prepared by emulsifying a given mount of aqueous Fe_3O_4 dispersion into a certain mount of oil phase with the assistance of ultrasonic (100 W, 40 KHz) for 5 min. Note that the oil phase consisted of St, DVB, AIBN, and hexadecane; thereafter, by

handshake, the single emulsions were further emulsified through employing hydrophilic meso-pore silica nanoparticles as emulsifiers to gain double Pickering emulsions.[1-2]

Preparation of Sulfonated poly(St-co-DVB) and poly(St-co-DVB)/Ag Nanocomposite Microspheres. Sulfonated poly(St-*co*-DVB) was achieved by the following process. Dried Poly(St-*co*-DVB) microspheres (0.1 g) were dispersed into the concentrated sulfuric acid (10 mL) at 50 ℃ for 6 h; then, the resultant microspheres were washed with a large amount of ethanol and deionized water to remove the sulfuric acid and redispersed in freshly prepared aqueous solution of $[Ag(NH_3)_2]^+$ (1 mol/L, 10 mL) shaken at a speed of 450 rpm for 24 h at room temperature. Poly(St-*co*-DVB)/Ag nanocomposite microspheres were obtained via *in situ* reduction of silver nitrate by quick addition of $NaBH_4$ (1×10^{-2} mol/L) as reducing agent.

Absorption Abilities of Sulfonated Poly(St-co-DVB) Microspheres and Catalytic Properties of Poly(St-co-DVB)/Ag Nanocomposite Microspheres. The adsorption isotherms were obtained in batch equilibrium experiments with 10 mg of different sulfonated poly(St-*co*-DVB) samples immersed in 10 mL solution of rhodamine 6G with concentrations ranging from 0.01 to 2.4 mg/mL. The amounts of the adsorbed R6G were calculated with the following equation.

$$q_e = \frac{(Co - Ce) \times V}{m}$$

Where *Co* is the initial adsorbate concentration (mg/mL); *Ce* is the equilibrium concentration (mg/mL); *V* the solution volume (mL); *m* is the dosage of sulfonated poly(St-*co*-DVB) (g).

In a typical catalytic experiment, both dye (R6G, 2×10^{-5} mol/L) and KBH_4 (1×10^{-2} mol/L) were freshly prepared as aqueous solutions. Subsequently, A series of poly(St-*co*-DVB)/Ag nanocomposite microsphere samples (20 mg) was mixed with 5 mL of 2×10^{-5} mol/L R6G aqueous solution, and 1 mL of 1×10^{-2} mol/L KBH_4 solution was rapidly injected into this mixture while stirring. In the recycle catalytic experiments, the poly(St-*co*-DVB)/Ag nanocomposite microspheres were rinsed by deionized water several times before another catalytic cycle. The concentration changes of R6G were monitored with a UV-vis spectrophotometer (Hitachi U-3010). All studies were carried out in triplicate. The calibration curve of R6G was determined by taking absorbance (526 nm) versus R6G concentration between 0 and 2×10^{-5} mol/L. For this interval, the calibration curve fits the Lambert and Beer's law:

$$A = 83750 \times C + 0.0097$$

Where *A* is the absorbance and *C* is the concentration of R6G.

Characterization. The emulsions were observed with an optical microscope (Carl Zeiss, German) and the average size of the prepared microspheres was obtained by a Malvern matersizer 2000 instrument using alcohol as solvent, infrared absorption spectra were measured in the range 400-4000 cm^{-1} by Fourier transformed infrared (FT-IR) spectrometer (Nicolet 6700) with a resolution of 4 cm^{-1}, Brunauer-Emmett-Teller (BET) surface areas were measured using a Quantachrome NovaWin2 instrument, XRD pattern was collected using a Bruker D8 Advance X-ray diffractometer with Cu target (40 kV, 40 mA) from 10° to 90°, inner structure of the microspheres was surveyed by scanning electron microscopy (SEM, Zeiss EVO-18) at the acceleration voltage of 10 kV. The specimen was firstly scattered onto a conductive adhesive, then sliced by a razor blade under the observation of optical microscope, finally sputtered with gold. TEM analysis was conducted with a JEM-100CX II operated at 200 kV. The specimen was firstly embedded in resin, after that, ultrathin section (100 nm) was obtained with a microtome (Leica UC6).

Table S1. Summary of synthetic conditions for the preparation of the hierarchical porous polymeric microspheres.

Samples	Inner water phase [a] (mL)	Middle oil phase [b]				W_F/O volume ratio	Out water phase [c] (mL)
		Monomers (St+DVB, v:v=1:1) (V_M, mL)	Hexadecane (V_H, mL)	Monomers/hexadecane (V_M/V_H)	H30 (g)		
HPPM-1	0.50	1.78	0.22	8:1	0.012	1:4	10
HPPM-2	0.50	1.60	0.40	4:1	0.012	1:4	10
HPPM-3	0.50	1.33	0.67	2:1	0.012	1:4	10
HPPM-4	0.50	1.00	1.00	1:1	0.012	1:4	10
HPPM-5	0.50	0.67	1.33	1:2	0.012	1:4	10
HPPM-6	0.50	0.50	1.50	1:3	0.012	1:4	10

[a] Aqueous Fe_3O_4 dispersion; [b] containing 1 wt % AIBN with respect to monomers; [c] with a mesopore silica content of 0.4 wt %.

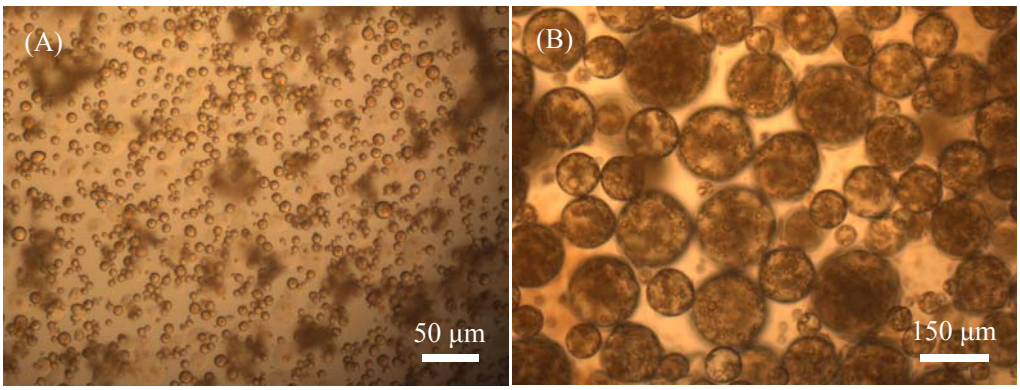

Fig. S1 Photographs of single Pickering emulsions (A) and double Pickering emulsions (B).

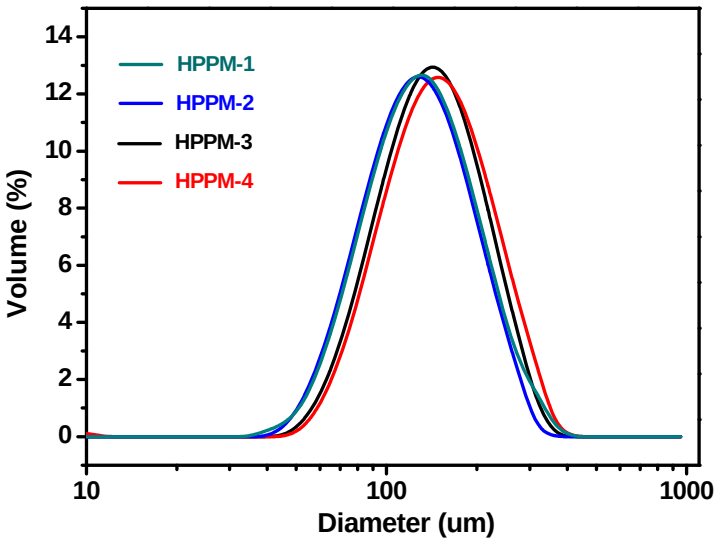

Fig. S2 Size distributions of HPPMs-1, HPPMs-2, HPPMs-3 and HPPMs-4, respectively.

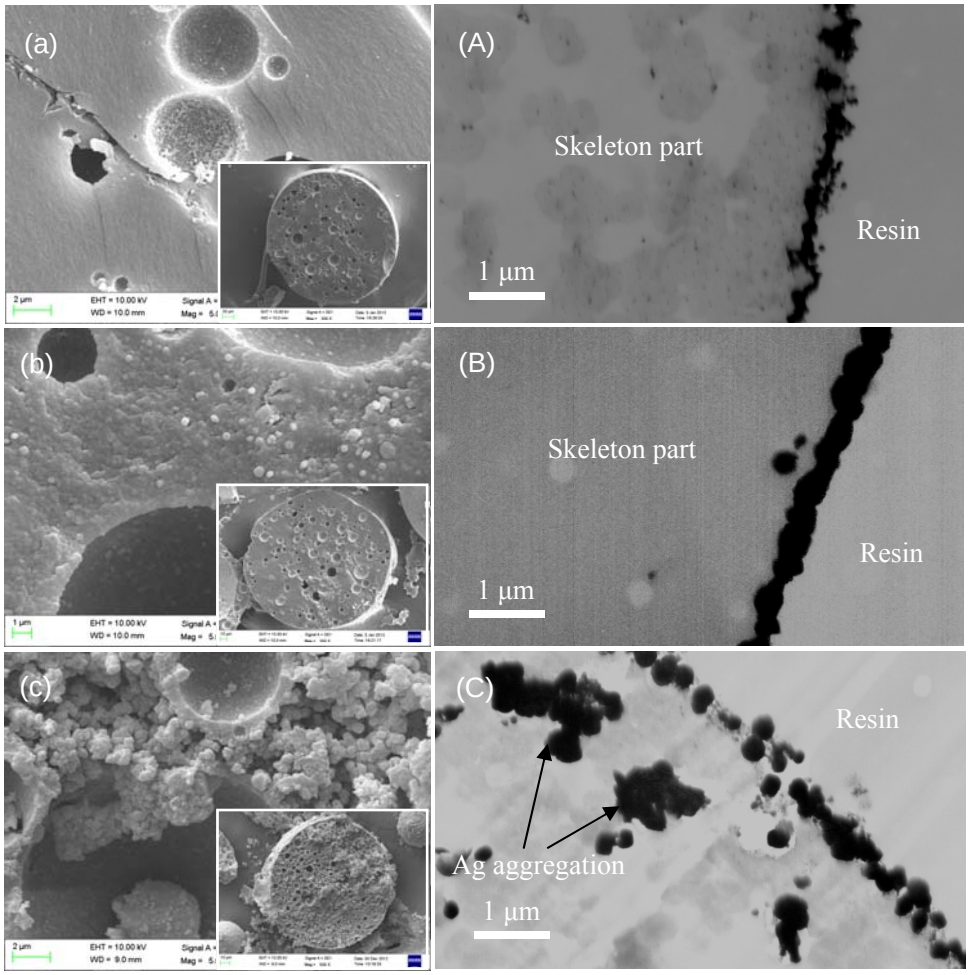

Fig. S3 Left column shows the effect of hexadecane content in the oil phase of double Pickering emulsions on the structure of the resulting microspheres: (a) HPPMs-1, V_M:V_H=8:1; (b) HPPMs-2, V_M:V_H =4:1; (c) HPPMs-4, V_M:V_H =1:1. (A) Ag-S-HPPMs-1, V_M:V_H=8:1; (B) Ag-S-HPPMs-2, V_M:V_H =4:1; (C) Ag-S-HPPMs-4, V_M:V_H =1:1. The insets represent the corresponding whole microspheres. Right column presents the TEM images of Ag loaded hierarchical porous microspheres of the left column samples.

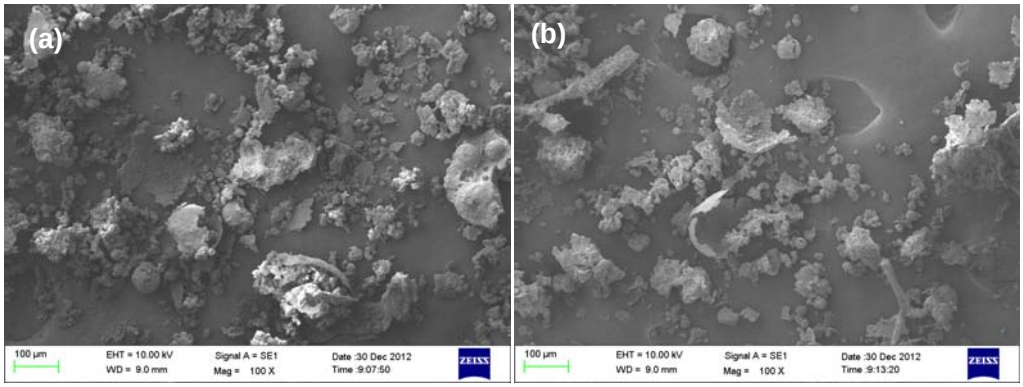

Fig. S4 Effect of V_M:V_H on the structure of polymeric microsphere. （a）V_M:V_H=1:2；（b）V_M:V_H=1:3.

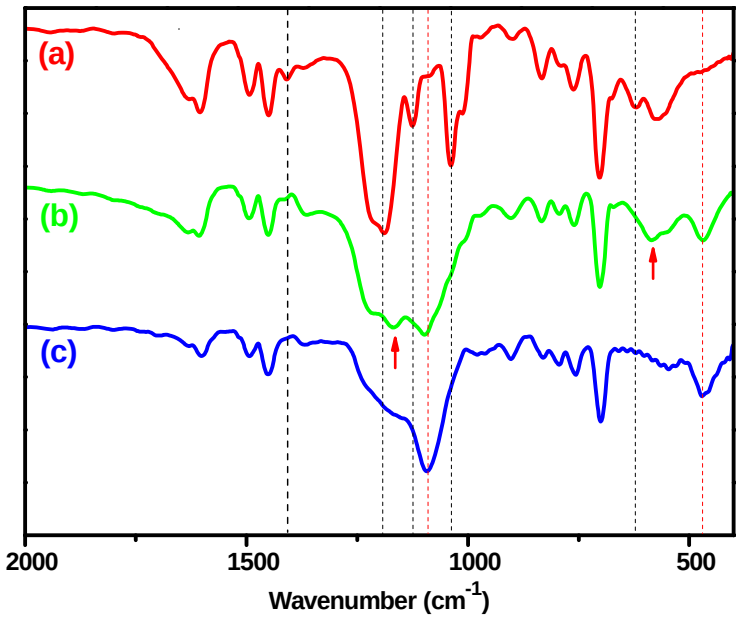

Fig. S5 FT-IR spectrums of (a) poly(St-*co*-DVB)/Ag;（b）poly(St-*co*-DVB)-SO_3H;（c）poly(St-*co*-DVB).

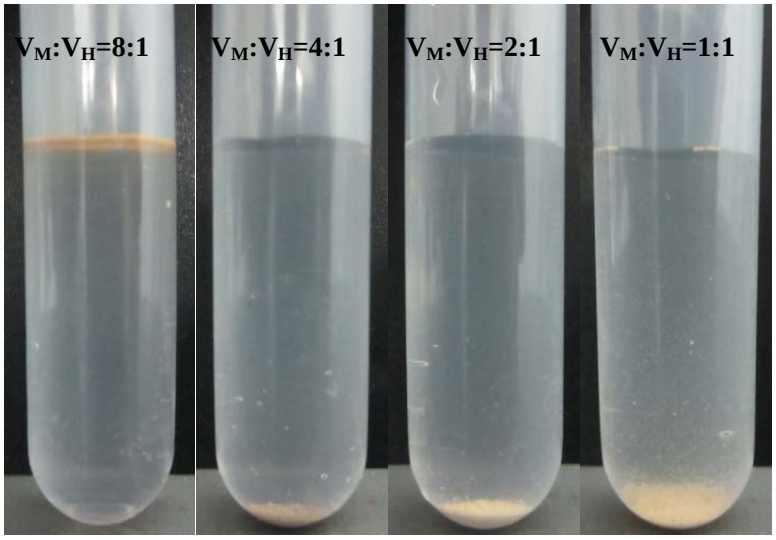

Fig. S6 Conditions of sulfonated microspheres produced under various V_M/V_H volume ratios in aqueous solution.

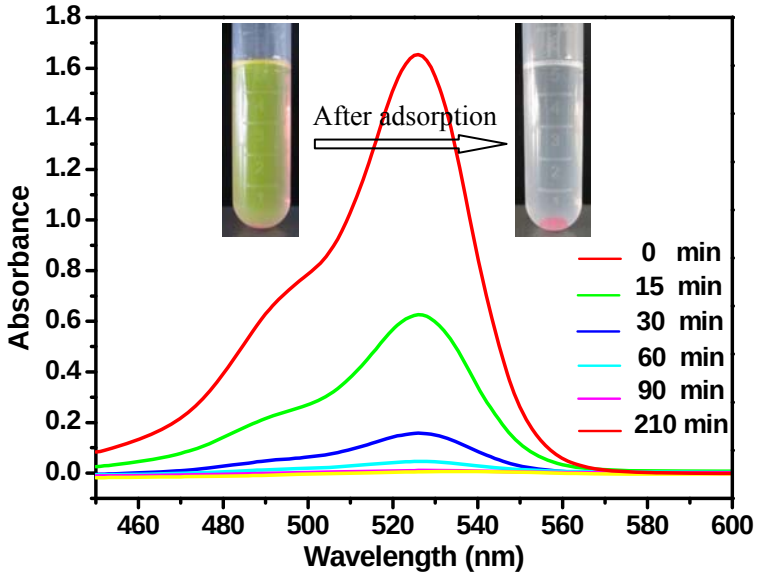

Fig. S7 UV-visible spectra of R6G aqueous solution adsorbed by S-HPPM-3 as function of reaction time, S-HPPM-3: 10 mg; R6G aqueous solution: 2×10^{-5} mol/L, 10 mL. The inset indicates photographs of R6G aqueous solution before and after adsorption.

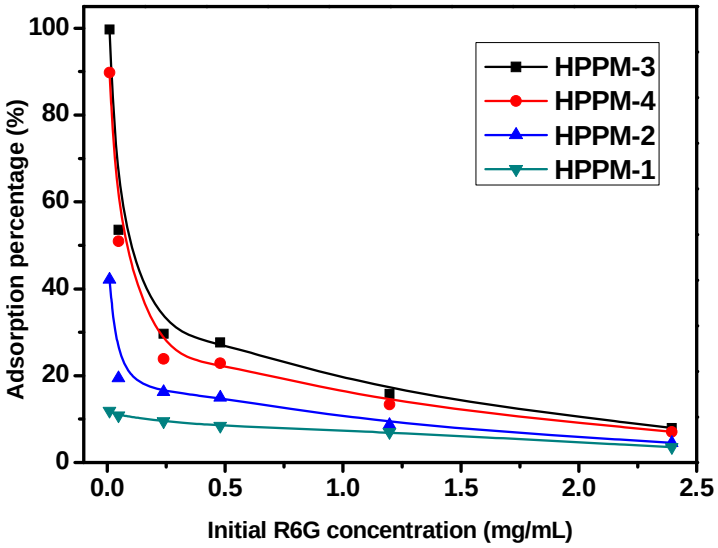

Fig. S8 Adsorption percentage of R6G by various S-HPPMs under different initial R6G concentrations.

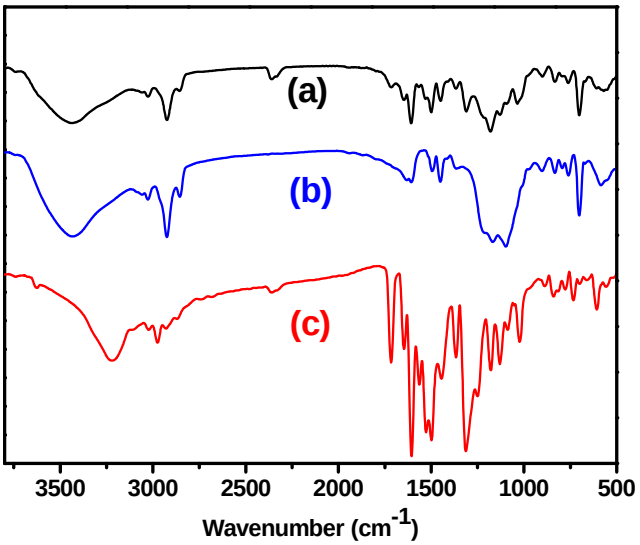

Fig. S9 FT-IR spectrums of (a) sulfonated poly(St-*co*-DVB) absorbed with rhodamine 6G; (b) sulfonated poly(St-*co*-DVB), and (c) rhodamine 6G.

We used Fourier transform infra-red technique to elucidate the interaction between the rhodamine 6G and the sulfonated hierarchical porous microsphere. IR spectra (a), (b), and (c) referred to sulfonated hierarchical porous microsphere absorbed with rhodamine 6G, sulfonated hierarchical porous microsphere, and rhodamine 6G, respectively. In spectra (c), 1313 cm^{-1},1365 cm^{-1}, 1444 cm^{-1} can be assigned to aromatic C-C and C-N stretching, 1178 cm^{-1} and 1716 cm^{-1} were associated to C-O-C stretching and C=O stretching vibration in the carbonyl phenyl group, respectively. It is worth noting that all those bands can be found in spectra (a), indicating no chemical reaction happens to these groups. However, the bands at 3221 cm^{-1} and 3624 cm^{-1} contributed to N-H vibrations were disappeared in spectra (a). It can be interpreted as the results of electrostatic interaction between secondary amino within rhodamine 6G molecules and sulfonic group from sulfonated poly(St-*co*-DVB).

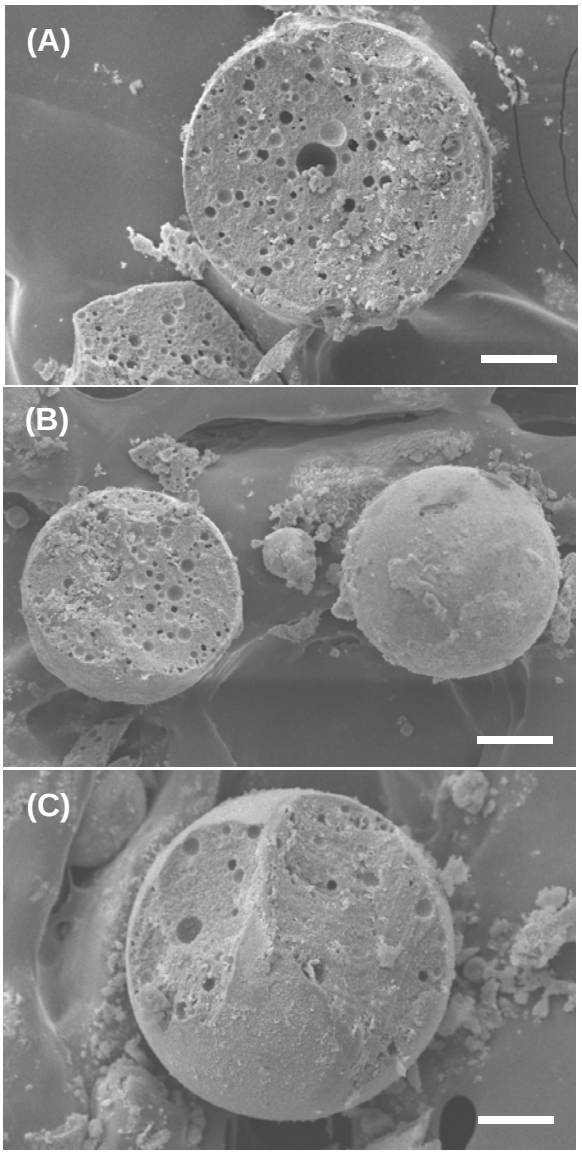

Fig. S10 SEM images of HPPMs-3 (A), S-HPPMs-3 (B) and Ag-S-HPPMs-3 (C), respectively. The scale bar equals 50 μm.

From Fig. S10, we can conclude that S-HPPMs-3 and Ag-S-HPPMs-3 can maintain their structural integrity during the sulfonation experiment and Ag loading process. Unfortunately, SEM images are not capable of demonstrating the changes of structure and composition, which, however, can be examined by TEM images (Fig. 1B and Fig. S3A~C).

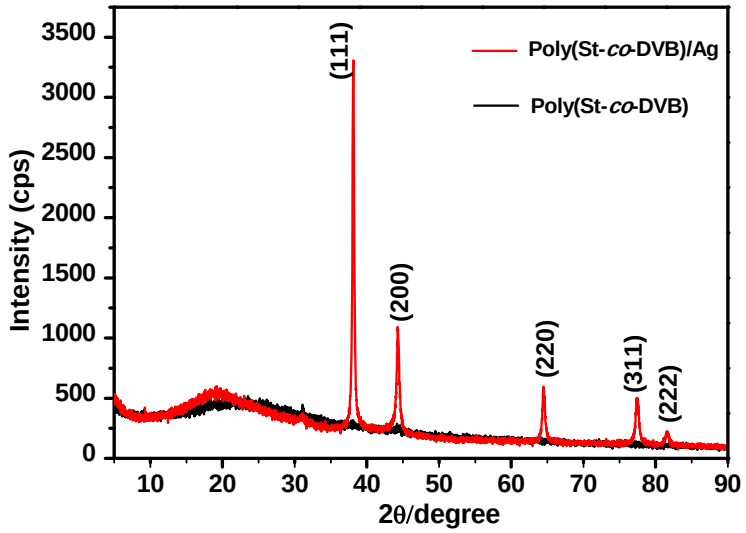

Fig. S11 XRD patterns of poly(St-*co*-DVB)/Ag nanocomposite spheres and poly(St-*co*-DVB) spheres.

The peaks at 2θ angles of 37.9, 44.1, 64.3, 77.2, and 81.4° reflect (111), (200), (220), (311), and (222) crystalline planes of the fcc structure of Ag (JCPDS No.04−0783), respectively.

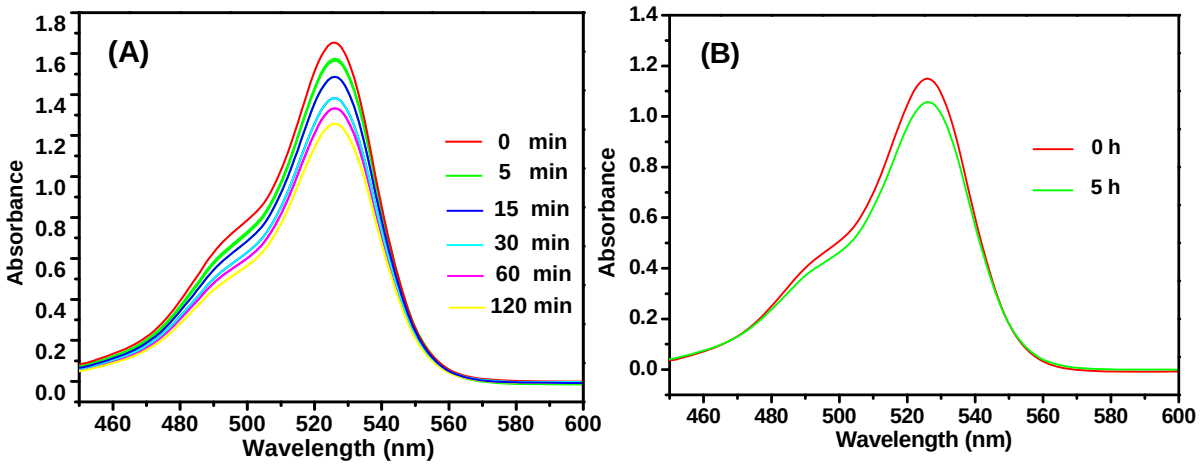

Fig. S12 (A) UV-visible spectra of R6G aqueous solution mixed with Ag-S-HPPMs-3 in the absence of KBH_4 aqueous solution. Ag-S-HPPMs-3: 20 mg; R6G: 2×10^{-5} mol/L, 5 mL; (B) UV-visible spectra of R6G aqueous solution mixed with KBH_4 aqueous solution in the absence of Ag-S-HPPMs-3. KBH_4: 1×10^{-2} mol/L, 1 mL; R6G: 2×10^{-5} mol/L, 5 mL.

References

1 Y. Ning, C. Y. Wang, T. Ngai, Z. Tong, *Langmuir*, 2013, **29**, 5138.
2 K. Möller, J. Kobler, T. Bein, *Adv. Funct. Mater.*, 2007, **17**, 605.