Electronic Supplementary Information

One-pot synthesis of porous Au-nanoparticles@polymer/reduced graphene oxide composite microspheres by γ-ray radiation and their application as recyclable high-performance catalyst

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I. Synthesis of cagelike sulfonated polystyrene (SPS) microspheres

a. Synthesis of polystyrene (PS) microspheres through dispersion polymerization

PVP (1.0 g) was dissolved in the mixture of ethanol (95.0 mL) and deionized water (5.0 mL). St (27.0 mL) and AIBN (0.22 g) were added into the above solution. The system was heated to 70 °C with reflux under a nitrogen atmosphere to react 20 h. The obtained PS microspheres, as shown in Fig. S1, were collected by centrifugation (4500 rpm, 5 min), washed with ethanol thrice, and then dried in a vacuum oven at 40 °C for 20 h.

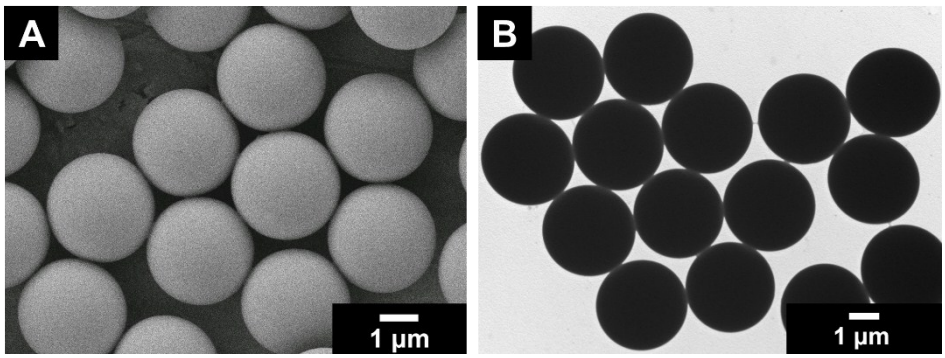

Fig. S1 SEM (A) and TEM (B) images of PS microspheres. The mean diameter is 3.1 μm.

b. Sulfonation of PS microspheres

The above prepared PS microspheres (1.0 g) was ultrasonically dispersed in concentrated sulfuric acid (30.0 mL) for 15 min. The sulfonation reaction was carried out in an oil bath at 40 °C with a magnetic stirring for 20 h. Then, the system was diluted by 200 mL of ice water. The treated microspheres were purified by centrifugation (4500 rpm, 5 min) and redispersion in ethanol alternatively for three times, and finally dried in a vacuum oven at 40 °C for 20 h. The morphology of the obtained SPS microspheres shown in Fig. S2 is almost the same with the original PS microspheres. The average diameter of SPS microspheres is 3.0 μm.

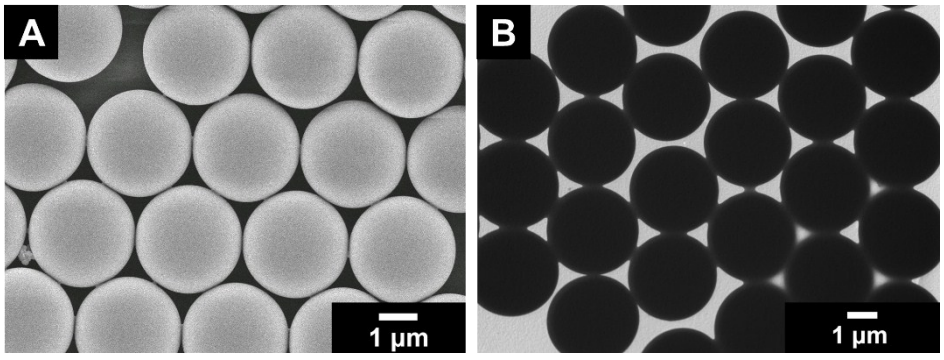

Fig. S2 SEM (A) and TEM (B) images of SPS microspheres.

The X-ray photoelectron spectroscopy (XPS) of SPS microspheres shown in Fig. S3 was carried

out on Thermo ESCALAB 250 using monochromatic Al Kα radiation (1486.6 eV) in high vacuum (5×10^{-9} Pa). Two characteristic peaks for S and C elements appear in the spectra, and the atom ratio (at.%) of S to C (S:C) of SPS microspheres is 0.58 : 97.79. The degree of sulfonation of SPS microspheres (DS_{XPS}) can be defined as the mole fraction of sulfonic groups, and be calculated to be 4.74% according to the following Equation S1:

$$DS_{XPS} = 8 \times (at.\%S/at.\%C) \times 100\% \qquad (S1)$$

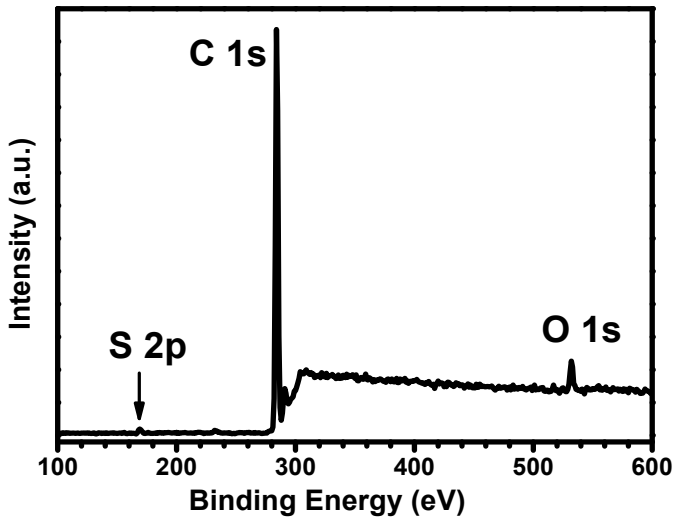

Fig. S3 XPS spectrum of SPS microspheres.

c. Fabrication of cagelike SPS microspheres

The as-prepared SPS microspheres (50.0 mg) were dispersed ultrasonically in a mixture of ethanol (5.0 mL) and water (5.0 mL). Heptane (1.0 mL) was added subsequently. Then the mixture was ultrasonically blended for 15 min, and immersed into an oil bath at 70 °C for 5 h. The product, i.e., cagelike SPS microspheres, was purified by centrifugation (4500 rpm, 5 min) and redispersion in ethanol alternatively for three times, and then freeze-dried.

II. Synthesis and characterization of primary solid SPS/AuNPs composite microspheres via γ-ray radiation

SPS microspheres (20.0 mg) were dispersed in the mixture of deionized water (8.5 mL), $HAuCl_4$ aqueous solution (1.0 mL, 5 mmol L^{-1}) and isopropanol (0.5 mL). The pH was adjusted to 3, 6 and 12 with HCl (1 mol L^{-1}) or NaOH solution (1 mol L^{-1}), respectively. The reduction of Au(III) was carried out in a field of ^{60}Co γ-ray source (located in the University of Science and Technology of China) at a dose rate of 62 Gy min^{-1} and a total absorbed dose of 55 kGy. The product was purified by alternative centrifugation (4500 rpm, 5 min) and redispersion in deionized water thrice.

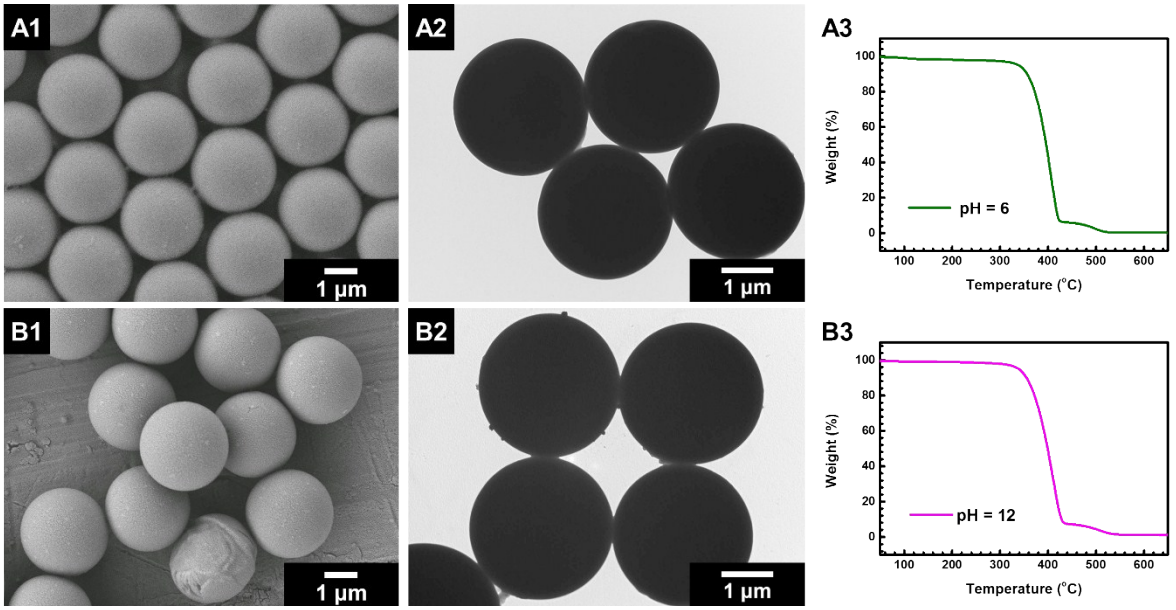

Fig. S4 SEM, TEM images and TGA curves of primary solid SPS/AuNPs composite microspheres prepared at pH = 6 (A1, A2, and A3) and pH = 12 (B1, B2, and B3).

III. TEM image and FTIR spectrum of GO

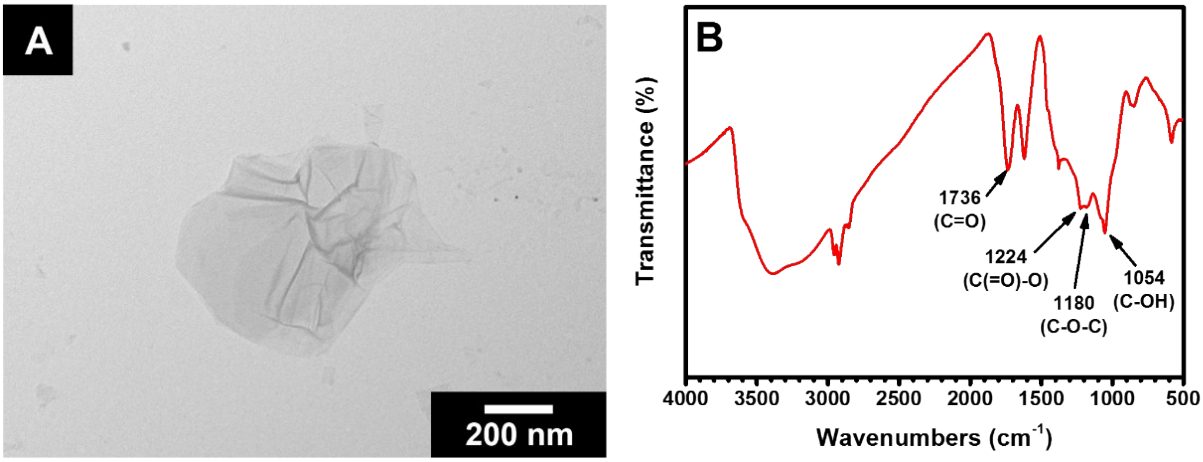

Fig. S5 TEM image (A) and FTIR spectrum (B) of GO.

IV. The morphology of AuNPs-loaded SPS/rGO composite microspheres prepared by γ-ray radiation on the aqueous dispersion containing cagelike SPS microspheres, GO, and $HAuCl_4$

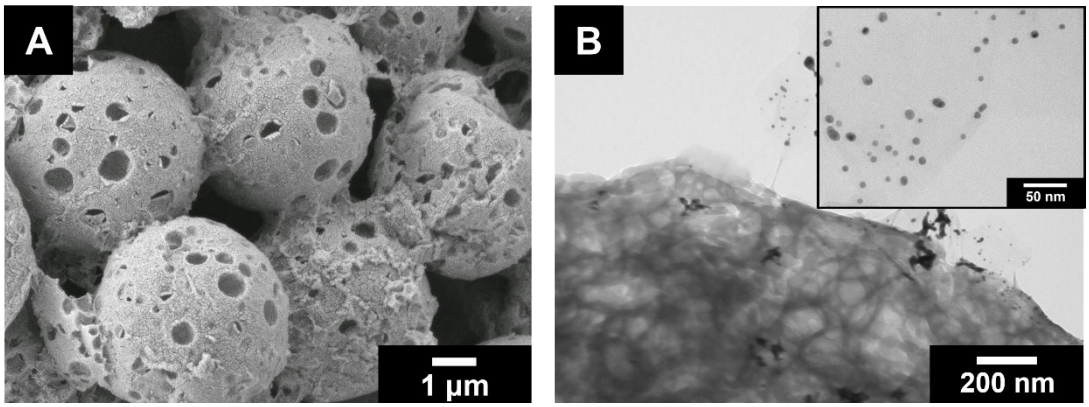

Fig. S6 SEM (A) and TEM (B) images of AuNPs-loaded SPS/rGO composite microspheres. The inset in B is the magnified TEM images of a part of the AuNPs-loaded rGO in the corresponding composite microspheres.