Electronic Supplementary Information

Preparation of large micron-sized monodisperse core-shell polystyrene/silver microspheres with compact shell structure and their electrical conductive and catalytic properties

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Fig. S1. SEM image of SPS microspheres.



Fig. S2 SEM images of micron-sized PS/Ag core-shell microspheres prepared without Sn^{2+} ions.

Estimation of the Ag shell thickness in the PS/Ag core-shell microspheres from TGA data



Fig. S3. A model cross-section of a PS microsphere with a continuous and compact silver layer on the surface

Calculations are performed for a single PS microsphere which has the radius of r and a continuous and compact silver layer with thickness of δ . The theoretical amount of silver is calculated by dividing the mass of a single silver layer by the total mass of a core-shell PS/Ag microsphere.

The symbols represent as follows:

r — radius of the PS microsphere;

 δ — thickness of the silver layer;

R — radius of the core-shell PS/Ag composite microsphere;

 $m_{\rm core}$ — mass of the PS microsphere;

 $V_{\rm core}$ — volume of the PS microsphere;

 $\rho_{\rm core}$ — density of the PS microsphere;

 $m_{\rm shell}$ — mass of the silver layer;

 $V_{\rm shell}$ — volume of the silver layer;

 ρ_{shell} — density of the silver layer;

 ω — mass percentage of silver layer in the core-shell PS/Ag

composite microsphere.

First, ω can be related to the mass of the composite microspheres as

$$\omega = \frac{m_{shell}}{m_{shell} + m_{core}} \quad i.e. \quad \frac{m_{shell}}{m_{core}} = \frac{\omega}{1 - \omega}$$

Then, the mass m_{shell} of a silver layer on a PS/Ag composite microsphere and the mass m_{core} of a PS core microsphere are calculated as follows:

$$m_{shell} = \rho_{shell} \bullet V_{shell} = \rho_{shell} \bullet \left(\frac{4}{3}\pi R^3 - \frac{4}{3}\pi r^3\right) = \rho_{shell} \bullet \frac{4}{3}\pi \left[(r+\delta)^3 - r^3\right]$$
$$m_{core} = \rho_{core} \bullet V_{core} = \rho_{core} \bullet \frac{4}{3}\pi r^3$$

The mass ratio can be rewritten in terms of volumes as

$$\frac{m_{shell}}{m_{core}} = \frac{\rho_{shell} \bullet V_{shell}}{\rho_{core} \bullet V_{core}} = \frac{\rho_{shell}}{\rho_{core}} \bullet \frac{(r+\delta)^3 - r^3}{r^3} = \frac{\rho_{shell}}{\rho_{core}} \bullet \left[\left(1 + \frac{\delta}{r}\right)^3 - 1 \right]$$

to yield

$$\delta = r \left[\left(\frac{\rho_{core}}{\rho_{shell}} \bullet \frac{\omega}{1 - \omega} + 1 \right)^{\frac{1}{3}} - 1 \right]$$

The density of the PS microspheres and silver is known of about 1.05 g/cm³ and 10.53 g/cm³, respectively. The radius *r* of a PS microsphere is also known of 2.8 μ m (an average diameter of 5.6 μ m) from the SEM images shown in Figure 2a and b. For the sample of PS/Ag-30 core-shell hybrid microspheres, the mass percentage of silver layer is 55.03% given by TGA data in Figure 9. Finally, the silver shell thickness of PS/Ag-30 microsphere is calculated by the above formula.

$$\delta = 2.8 \mu m \left[\left(\frac{1.05 \text{g/cm3}}{10.53 \text{g/cm3}} \bullet \frac{55.03\%}{1 - 55.03\%} + 1 \right)^{\frac{1}{3}} - 1 \right] = 109.4 \text{nm}$$



Fig. S4. The nitrogen adsorption isotherms measured at 77 K of PS/Ag-30, PS/Ag-60 core-shell microspheres and hollow Ag spheres