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 $\delta$. 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;

$\delta$ — thickness of the silver layer;

$R$ — radius of the core-shell PS/Ag composite microsphere;
$m_{\text{core}}$ — mass of the PS microsphere;
$V_{\text{core}}$ — volume of the PS microsphere;
$\rho_{\text{core}}$ — density of the PS microsphere;
$m_{\text{shell}}$ — mass of the silver layer;
$V_{\text{shell}}$ — volume of the silver layer;
$\rho_{\text{shell}}$ — density of the silver layer;
$\omega$ — mass percentage of silver layer in the core-shell PS/Ag composite microsphere.

First, $\omega$ can be related to the mass of the composite microspheres as

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

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

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

$$m_{\text{core}} = \rho_{\text{core}} \cdot V_{\text{core}} = \rho_{\text{core}} \cdot \frac{4}{3} \pi r^3$$

The mass ratio can be rewritten in terms of volumes as

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

to yield
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 μm (an average diameter of 5.6 μm) 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.

\[
\delta = r \left[ \frac{\rho_{\text{core}} \cdot \omega}{\rho_{\text{shell}} \cdot 1 - \omega} + 1 \right]^{\frac{1}{3}} - 1
\]

\[
\delta = 2.8\mu m \left[ \frac{1.05 \text{ g/cm³} \cdot 55.03\%}{10.53 \text{ g/cm³} \cdot 1 - 55.03\%} + 1 \right]^{\frac{1}{3}} - 1 \approx 109.4\text{nm}
\]
Fig. S4. The nitrogen adsorption isotherms measured at 77 K of PS/Ag-30, PS/Ag-60 core-shell microspheres and hollow Ag spheres.