Supporting Information

Facile Synthesis of Asymmetric Ag-Organosilica Hybrid Nanoparticles with Tunable Morphologies and Optical Properties

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Experimental section

Materials: Ethylene glycol (EG, 99.5%), acetone (99.5%), ethanol (99.7%) and ammonia aqueous solution (28 wt %) were purchased from Sinopharm Chemical Reagent Co. (China). Polyvinylpyrrolidone (PVP, Mw=55,000) was obtained from Sigma-Aldrich Chemical Co. Silver nitrate ($AgNO_3$, 99.9%), alkoxysilanes: mercaptopropyltrimethoxysilane (SHMPS, 95%), 3-(trimethoxysilyl)propyl methacrylate (MPS, 97%), dodecyltrimethoxysilane (DDS, 95%) and hexadecyltrimethoxysilane (HDS, 97%) were purchased from Aladdin Chemical Reagent Co. Thiol-terminated methoxypoly(ethylene glycol) (mPEG-SH, M_W=5000) was purchased from Shanghai Seebio Biotech, Inc. All chemicals were analytical grade and used as received. Deionized water was used in all experiments.

Synthesis of Ag NPs. Ag NPs were synthesized as follows: 0.2 g of $AgNO_3$ was added into 80 mL of ethylene glycol solution containing 1.0 g of PVP under stirring at room temperature, and then heated up to 130 °C within 15 min and kept at that temperature for 1 h to obtain the Ag NPs. After the reaction, the as-synthesized PVP-stabilized Ag solution in EG was cooled to room temperature in an ice bath and then stored in the refrigerator for subsequent uses.

Synthesis of asymmetric Ag-organosilica hybrid particles. The asymmetric Ag-organosilica hybrid particles were synthesized based on the modified Stöber method as follows. Typically, the Ag NPs were isolated by precipitating

1.0 g of the as-synthesized Ag-EG solution with addition of 4.0 mL acetone, followed by centrifugation at 8000 rpm for 3 min. The supernatant was removed, and the Ag NPs were washed with water, centrifuged at 4000 rpm for 15 min, and redispersed into 4 mL H_2O and 2 mL ethanol. After ultrasonication for 10 min, the mixture was mechanically stirred at 60 ^{o}C in a water bath for 30 min, followed by addition of 0.30 mL ammonia (28 wt %). After 5 min, the solution of alkoxysilanes in ethanol was rapidly injected into the above mixture and the reaction was continued for 4 h to directly produce asymmetric hybrid particles. For details, there are three types of alkoxysilane mixtures used: 30 μL SHMPS (10 v% in ethanol) and 30 μL MPS (10 v% in ethanol), SHMPS/MPS; 30 μL SHMPS (10 v% in ethanol) and 30 μL DDS (6.7 v% in ethanol), SHMPS/DDS; 30 μL SHMPS (10 v% in ethanol) and 30 μL HDS (2.5 v% in ethanol), SHMPS/HDS. The resultant colloids were washed four times with ethanol and by centrifugation at 8000 rpm for 3 min. The precipitate was collected and redispersed into ethanol for characterization.

When the mPEG-SH was used as the ligand, its 1 wt % solution in water was added into the mixture immediately after the addition of the alkoxysilane mixture using the same procedure as above. The total volume of mPEG-SH and water was kept at 4.0 mL.

Characterization

Transmission electron microscopy (TEM) images were obtained using a Hitachi H-800 transmission electron microscope operating at 100 kV. The samples were dispersed in ethanol and then dried on a holey carbon film Cu grid. Dynamic light scattering (DLS) measurements were carried out on the diluted particles of average diameter and size distribution using a Nano-ZS90 (Malvern). FTIR spectra were scanned on a Nicolet Nexus 470 FTIR spectrometer with powder-pressed KBr pellets. The samples for FTIR were centrifuged and rinsed three times with ethanol and dried in an inert gas at 50 °C for 12 h before analysis. Scanning transmission electron microscopy (STEM) and element line scanning by X-ray energy dispersive spectroscopy (EDX) analyses were carried out with a JEOL-2100F field transmission electron microscope (JEOL, Japan). UV-vis absorption spectra of Ag NPs and Ag-organosilica hybrid colloidal particles (background solution: 99.7% ethanol) were recorded at room temperature on the U-4100 spectrophotometer (Hitachi, Japan) using quartz cuvettes with an optical path of 1 cm.

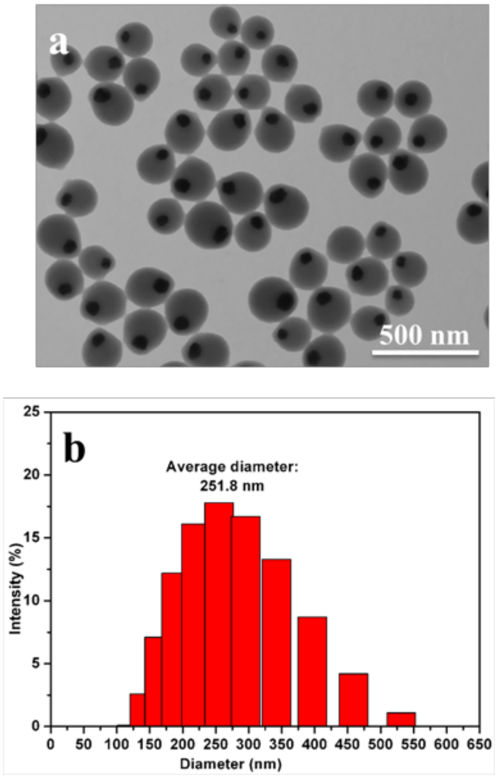

Fig. S1 (a) TEM image of eccentric Ag-organosilica particles obtained from SHMPS/MPS, (b) Size and size distribution of eccentric Ag-organosilica particles obtained from SHMPS/MPS by counting 280 nanoparticles.

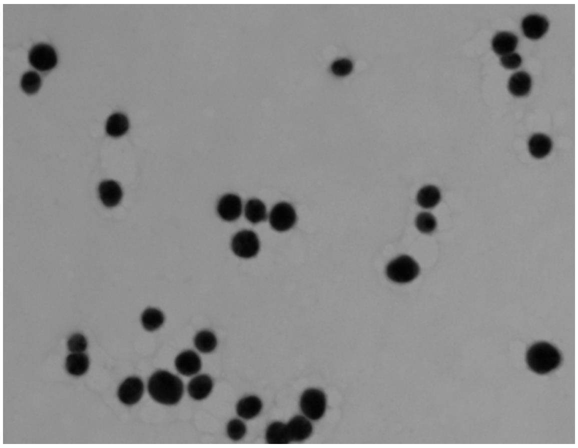

Fig. S2 TEM image of particles obtained by incubation with 400 μL mPEG-SH at 60 ^{o}C for 2 h then mixed with SHMPS/MPS

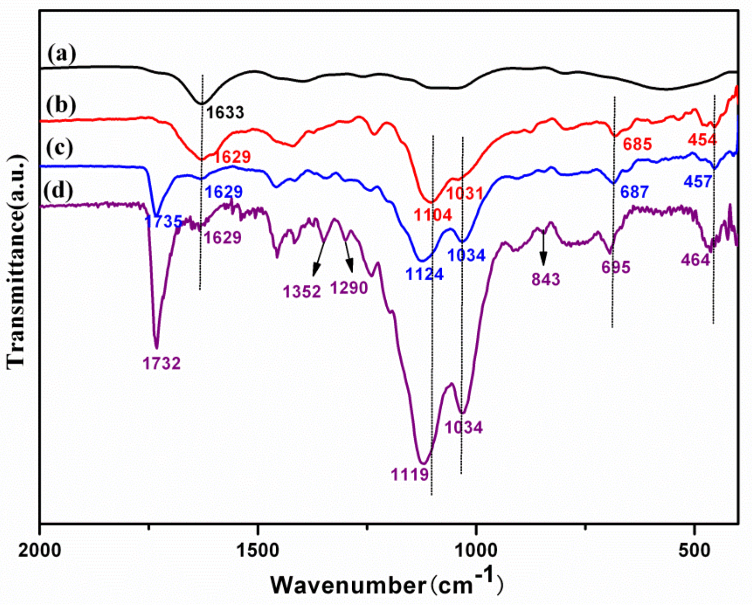

Fig. S3 FTIR spectra of colloidal particles with different compositions: (a) pure Ag NPs, (b) Ag NPs with SHMPS, (c) Ag NPs with (SHMPS/MPS), (d) Ag NPs with (SHMPS/MPS/mPEG-SH). The peak at 1633 cm^{-1} for C=O stretching vibration of PVP is observed on the surfaces of pure Ag NPs (**Fig. S3**a).[1] The bands centered at 1104 and 1031 cm^{-1} are attributed to the asymmetric Si-O-Si and symmetric Si-O-Si stretching vibrations, and the band located at 454 cm^{-1} was corresponded to Si-O-Si bending modes for the Ag NPs coated with SHMPS (**Fig. S3**b),[2] suggesting that the siloxane bonds are connected on the Ag surfaces by a cross-linking three-dimensional Si-O-Si network.[3] **Fig. S3**c displays the absorption peak of C=O groups at 1735 cm^{-1}, indicating MPS has been successfully co-condensed with SHMPS attaching onto the hybrid particles.[4] Compared **Fig. S3**d with **Fig. S3**c, the intensity of the peak at 1124cm^{-1} is enhanced and blue-shifted to 1119 cm^{-1}, this might be due to the C-O-C stretching of mPEG-SH at 1110 cm^{-1}. And all the peaks at 1352, 1290 and 844 cm^{-1} are the characteristic peaks of mPEG-SH, indicating that the mPEG-SH molecular chains exist in the hybrid particles.[5]

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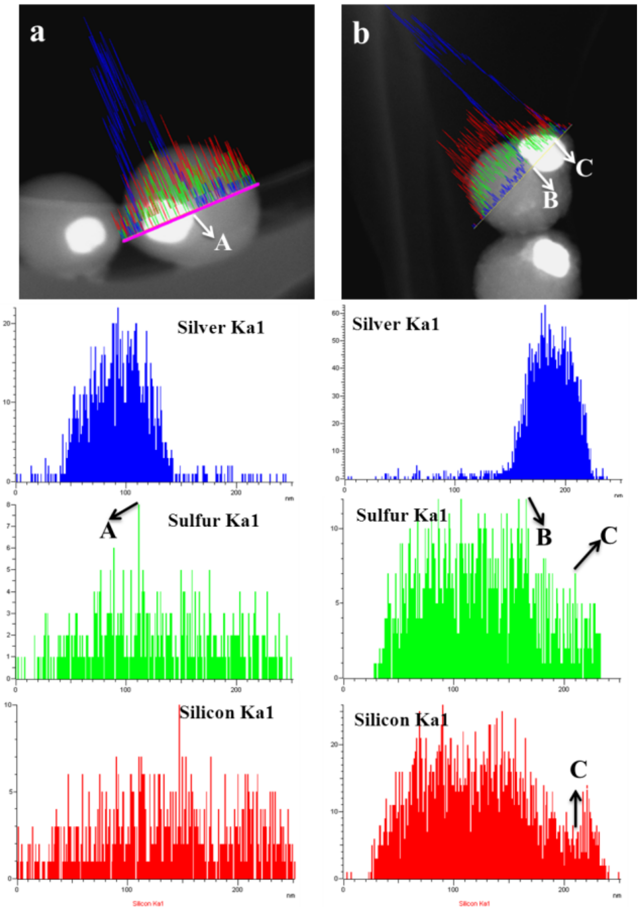

Fig.S4 STEM-EDS line scan of the typical eccentric and Janus Ag-organosilica hybrid particles obtained with SHMPS/MPS: (a) eccentric particles, (b) Janus particles. **Fig. S4**a displays that the eccentric hybrid particles have relatively higher S content at A point than at other areas, and so does the Si content. It may be concluded that the organosilica segments derived from the hydrolysis and condensation of the alkoxysilanes containing SH groups aggregate rapidly to anchor on point A of the Ag NP through strong Ag-S interaction. **Fig.S4**b shows the S and Si elemental distributions of the Janus Ag-organosilica hybrid particles. The point B corresponding to the inside edge of the Ag NPs also has a higher S elemental distribution. And the S and Si elements have nearly the same distribution trend, except the point C wherein there is a pit for the Si elemental distribution and a salient for the corresponding S elemental distribution. Theoretically, the Si content should increase with the increase of S content due to the component of SHMPS. This abnormality may be the SH groups of mPEG-SH attaching onto the point C of Ag NPs which increases the S content. This suggests that mPEG-SH is mainly distributed on the external edge of Ag NPs which is protruded from organosilica (refer to point C). Compared FigS4a with 4b, it can be found that the S elements distributed on the sides of organosilica (refer to points A and B) are always higher than the other points. Meanwhile, the addition of mPEG-SH into the reaction system has great influence on the tuning the distribution of PEG groups onto the surfaces of Ag NPs, which in turn decreases the deposition of organosilica on these sides.

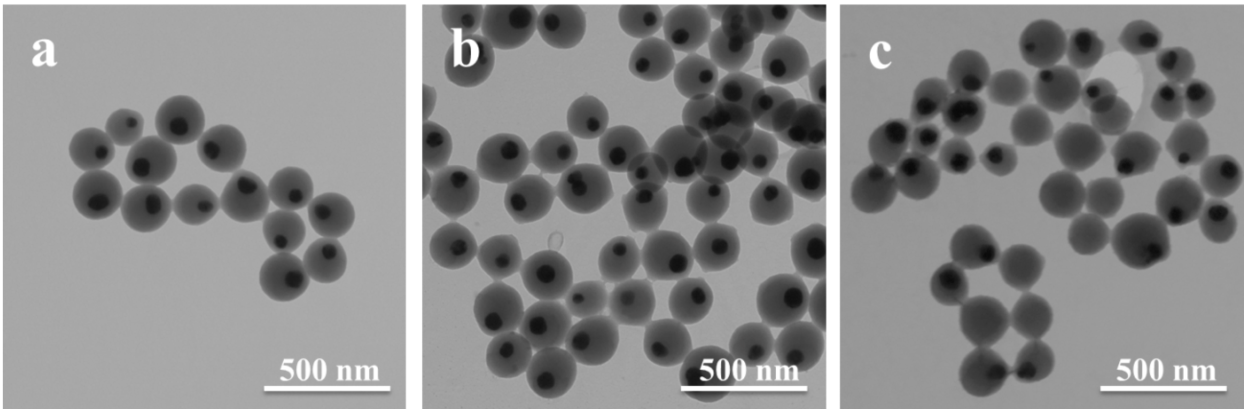

Fig. S5 TEM images of the as-obtained Ag-organosilica hybrid particles as a function of reaction temperatures: (a) 45, (b) 60, (c) 75 °C. When the reaction temperature was 45 ^{o}C (**Fig. S5**a) or 60 ^{o}C (**Fig. S5**b), almost 100% of particles was yield in eccentric form. When the temperature increased to 75 ^{o}C, the yield of the eccentric particles dropped to ~70%, accompanied by some pure organosilica spheres (**Fig. S5**c). This indicates that not all organosilica particles have been bonded with Ag NPs. It can be explained as follows: On one hand, the hydrolysis and condensation reactions of alkoxysilane precursors highly depend on the temperature to form organosilica colloids.[1] On the other hand, the organosilica coatings on the surfaces of Ag NPs by Ag-S ligand interaction are also affected by the temperature.[2] If the temperature is too high, e.g., 75 ^{o}C or higher, the alkoxysilanes produce fast hydrolysis and condensation reactions to form some pure organosilica particles by homogeneous nucleation besides attaching to the Ag seeds.

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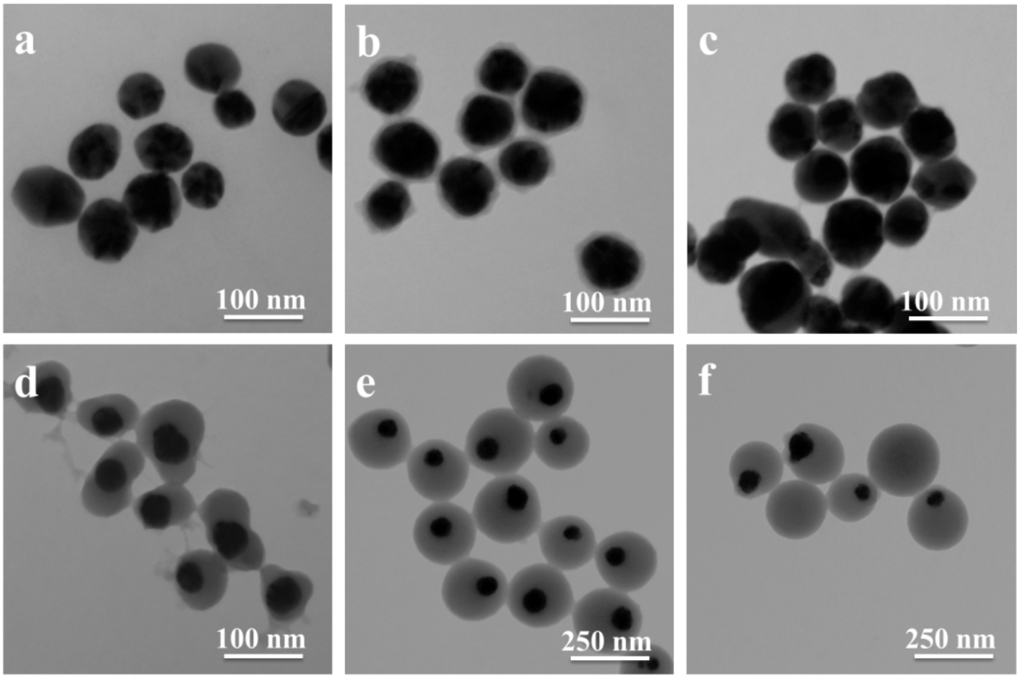

Fig. S6 TEM images of Ag-organosilica hybrid particles synthesized from different SHMPS/MPS volume ratios: (a) pure Ag NPs, (b) 30:0, (c) 0:30, (d) 30:15, (e) 30:30, (f) 30:45. The pure Ag NPs are almost spherical with the average diameter of 63 nm (**Fig. S6**a). When 30 μL SHMPS solution was used as the sole precursor, a core-shell structure with the Ag NP as the core and organisilica as the shell was obtained due to strong Ag-S ligand interaction (**Fig. S6**b). However, when 30 μL MPS solution was used as the sole precursor, these Ag NPs were not coated by organosilica because lacking of chemical interaction between MPS and Ag NPs (**Fig. S6**c). When the 30/15 volume ratio for SHMPS/MPS was used, asymmetric Ag-organosilica hybrid particles began to appear (**Fig. S6**d). When this ratio was increased to 30/30, eccentric hybrid particles were obtained with almost 100% yield (**Fig. S6**e). When this ratio was further increased to 30/45, some pure organosilica particles were observed as a result of the homogeneous nucleation of alkoxysilanes (**Fig. S6**f). This is because the higher the amount of alkoxysilanes, the faster the hydrolysis and condensation reactions of alkoxysilanes are,[1] which unavoidably produces some homogeneous nucleation and growth.

Reference：

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