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Facile synthesis of asymmetric Ag–organosilica hybrid nanoparticles with tunable morphologies and optical properties[†]

Yangyi Sun,^a Min Chen,^a Zengbo Wang*^b and Limin Wu*^a

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This study reports a simple and novel wet-chemical method for synthesizing asymmetric Ag-organosilica hybrid nanoparticles with finely-tuned morphologies and optical properties.

Design and fabrication of colloidal particles with asymmetric geometry and anisotropic material compositions have drawn great attention in recent years. These particles are not only vital for exploring important scientific issues in the assembly mechanism and chemical-physical properties at the nanoscale, but also for holding great promise for potential applications in optics,¹ magnetics,² surfactants,³ catalyses,⁴ self-assembly devices,⁵ *etc.*

Generally speaking, asymmetric colloidal particles can be divided into three categories: organic-organic, organic-inorganic, and inorganic-inorganic hybrid spheres.⁶ In particular, the metalbased asymmetric nanoparticles are interesting because of their novel properties. Typically, they belong to the multiple-component systems synthesized by depositing growth material on the metal seeds.7 The growth mode, for concentric-eccentric core-shell, Janus or other structures, is mainly determined by the interfacial reaction between the metal seeds and other growing materials.8 However, although the inherent lattice mismatch between metal and material or the extrinsic chemical interaction of the ligands can be used to tune the metal-material interfacial energy,⁹ it remains a challenging task to precisely tune the interfacial reaction to fabricate metal-metal, metal-metal oxides based asymmetric materials,¹⁰ and even harder work for metal-nonmetal oxides due to their difficulty in tuning surface energy and lack of lattice match between metal and nonmetal oxides.¹¹

In this communication, we present a simple and novel wetchemical method for the fabrication of asymmetric Ag–organosilica hybrid particles with fine-tuned nanostructures in eccentric,

Ag SH-MPS,MPS SH-MPS,DDS SH-MPS,HDS SH-MPS,HDS MPEG-SH

Scheme 1 The design and fabrication process of asymmetric Ag–organosilica hybrid particles.

Janus and peanut-like morphologies. As shown in Scheme 1, in this approach, the alkoxysilanes containing mercaptopropyltrimethoxysilane (SHMPS) and 3-(trimethoxysilyl)propyl methacrylate (MPS), or dodecyltrimethoxysilane (DDS) or hexadecyltrimethoxysilane (HDS) were added into the system consisting of the PVPstabilized Ag nanoparticles (Ag NPs), ethanol, water, and ammonia solution. The hydrolysis and condensation reactions of these alkoxysilanes caused the coating of organosilica on the surfaces of Ag NPs, generating Ag–organosilica hybrid particles in eccentric, Janus and peanut-like morphologies due to the strong Ag–S covalent bond between SHMPS and Ag NPs. Moreover, the nanostructure of Ag–organosilica hybrid particles can be further modified and modulated by a hydrophilic thiol-terminated polymer, methoxypoly(ethylene glycol) (mPEG-SH).

Fig. 1 demonstrates the typical TEM images of the as-prepared Ag–organosilica hybrid colloidal particles as a function of alkoxysilanes and mPEG-SH. Each particle has shown an asymmetric structure in which the Ag composition appears black in color. The asymmetry strength is however different. When SHMPS–MPS was used as the alkoxysilane mixture, the hydrolysis and condensation of the alkoxysilanes produced the organosilica coating on the surfaces of Ag NPs, resulting in an eccentric core–shell structure with each Ag nanoparticle encapsulated inside one organosilica particle (Fig. 1a). The whole hybrid particles were spherical in shape with the mean diameter of 185 nm and the mean distance of the Ag NP core to the shortest surface of organosilica particles was about 30 nm based on

^a Department of Materials Science and State Key Laboratory of Molecular

Engineering of Polymers, Fudan University, Shanghai 200433, China. E-mail: lmw@fudan.edu.cn

^b School of Electronic Engineering, Bangor University, Dean Street,

Bangor LL57 1UT, Gwynedd, UK. E-mail: zwang@bangor.ac.uk

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Fig. 1 TEM images of asymmetric Ag–organosilica hybrid particles with different systems: (a) SHMPS–MPS, (b) SHMPS–MPS–MPEG-SH, (c) SHMPS–DDS, (d) SHMPS–DDS–mPEG-SH, (e) SHMPS–HDS, (f) SHMPS–HDS–mPEG-SH.

TEM images and with the mean diameter of 252 nm from dynamic light scattering (DLS) measurement in ethanol with a very narrow polydisperse index of 0.063 (Fig. S1, ESI⁺). Very interestingly, when mPEG-SH solution was immediately added following the two alkoxysilanes, the Ag NPs protruded from the surfaces of the organosilica spheres, forming a snowman-based Janus structure (Fig. 1b). When SHMPS-DDS was used as the precursor, the Ag NPs were much away from the center of the organosilica sphere, as compared with the SHMPS-MPS system. Here, the Ag NPs nearly touch the interior walls of the organosilica spheres; some of the Ag NPs even tried to jump out of the spheres (Fig. 1c). When mPEG-SH solution was added, a snowman-based Janus structure was also obtained (Fig. 1d). When SHMPS-HDS was used, a snowmanbased Janus structure was directly obtained (Fig. 1e). Addition of the mPEG-SH solution led to the generation of asymmetric Ag-organosilica hybrid particles with peanut-like morphology. The size differences of the organosilica particles in three alkoxysilane mixture systems can be attributed to the different alkoxysilane concentrations having been used. These results clearly suggest that the alkoxysilanes with different hydrophobicity, e.g., MPS, DDS and HDS, have played a critical role in determining the morphologies of the final hybrid particles, and the hydrophilic mPEG-SH can help promote the formation of Janus structures.

To understand the growth mechanism, we used the SHMPS– MPS mixture as the model system. Fig. 2 displays the morphological evolution of the colloids as a function of reaction time. After the Ag NPs were mixed with alkoxysilanes for only 1 min, some organosilica floccules that derived from the hydrolysis and



Fig. 2 The morphological evolution vs. reaction time of the as-obtained particles: (a) 1, (b) 2, (c) 4, (d) 15 min, (e) 4 h.

condensation of the alkoxysilanes started to form on one side of the Ag NPs (Fig. 2a).¹² After 2 min, these soft floccules grew into small organosilica bumps on the surfaces of the Ag NPs (Fig. 2b). As the reaction time increased from 4 to 15 min, these organosilica bumps became particles, producing eccentric core-shell Ag-organosilica hybrid particles (Fig. 2c and d). Extension of reaction time would help increase the formation of perfect eccentric core-shell hybrid colloidal particles (Fig. 2e).¹³

Fig. 3 demonstrates the TEM images of the Ag–organosilica hybrid particles obtained when different amounts of mPEG-SH were used following the addition of SHMPS–MPS. All the hybrid particles have a snowman-like Janus structure. As the amount of mPEG-SH solution increased, the Ag NPs tended to protrude further away from the surfaces of the organosilica spheres, leading to a more obvious Janus structure. When the Ag NPs were first incubated with 400 μ L mPEG-SH at 60 °C for 2 h and then mixed with SHMPS–MPS, almost no organosilica was coated on the Ag NPs (Fig. S2, ESI†). This is because the mPEG-SH chains can also bind to the surfaces of Ag NPs *via* thiol groups, forming a layer of hydrophilic PEG around the Ag NPs. This polymer layer could block the diffusion of organosilica chains derived from the sol–gel reaction of alkoxysilanes onto the Ag surfaces.¹⁴

Comparison of FT-IR scans (Fig. S3, ESI[†]) of the pure Ag NPs, the Ag NPs coated by only SHMPS, the as-obtained eccentric and Janus particles indicates that the siloxane bonds are connected on the Ag surfaces by a cross-linking three-dimensional Si–O–Si network,¹⁵ and the mPEG-SH molecular chains exist in the hybrid particles.¹⁶ The STEM-EDX line scans (Fig. S4, ESI[†]) of typical eccentric (Fig. 1a) and Janus (Fig. 1b) particles further demonstrate that organosilica



Fig. 3 TEM images of Ag–organosilica hybrid particles prepared with different amounts of mPEG-SH solution: (a) 200 μ L, (b) 400 μ L, (c) 600 μ L.



Scheme 2 Schematic illustration of the formation of eccentric and Janus Ag–organosilica hybrid particles.

segments derived from the hydrolysis and condensation of the alkoxysilanes containing SH groups aggregate rapidly to anchor on the interior side (to organosilica) of Ag NPs, while mPEG-SH is mainly distributed on the external edge (to medium) of Ag NPs which protrudes from organosilica.

Based on the above results and discussion, a possible mechanism for the formation of eccentric and Janus hybrid particles can be proposed as follows (Scheme 2): when alkoxysilanes were added into the system with Ag NPs, two competitive reactions occurred. One was the heterogeneous nucleation and growth of organosilica on Ag seeds to form hybrid particles, another was the homogeneous nucleation and growth of organosilica to form pure organosilica particles, which could be avoided by adjusting the reaction temperatures and chemical compositions as shown in Fig. S5 and S6 (ESI[†]). For the heterogeneous nucleation, the Si-O-Si oligomers obtained from the hydrolysis and condensation of alkoxysilanes quickly attached onto the surface of Ag NPs via the strong Ag-S interaction, forming a small organosilica domain on one side of Ag seeds. This domain has high Si content (see Fig. S4, ESI† for silicon Ka1) which tended to adsorb more Si-O-Si groups.17 Thus the subsequent oligomers would be preferentially deposited on this newly formed organosilica domain to form a large organosilica particle. On the other hand, another side of Ag seeds could also have some Si element to adsorb more or less Si-O-Si groups and formed small organosilica domains although this reaction was slow. Thus, the eccentric Ag-organosilica hybrid particles were yielded. The fast hydrolysis rate of alkoxysilanes and quick attachment of the forming oligomers to the Ag NPs by Ag thiol reaction can benefit the synthesis of asymmetric structures. When the hydrophilic mPEG-SH was added in the system, these mPEG-SH chains were bound onto the surfaces of Ag NPs via strong Ag-S bonds to form a hydrophilic layer around the surface of the Ag seed. Because the mPEG-SH is much larger than SHMPS, this bonding rate for mPEG-SH chains was slower than that for thiol-terminated Si-O-Si oligomers.18 As a result, the thiol-terminated Si-O-Si oligomers were quickly attached on one side of the Ag seed, while the mPEG-SH chains were mainly distributed on the another side of the Ag seed. Because the hydrophilic PEG chains tended to contact the aqueous phase and reduced the Ag NP-solution interfacial energy,^{11,19} the Ag seed protruded from the surface of the organosilica sphere, forming a Janus hybrid structure. When the DDS and HDS were used, the oligomers derived from hydrolysis had a reducing surface wetting ability with Ag NPs due to the increasing hydrophobicity of alkoxysilanes, facilitating the formation of more obvious asymmetric structures. Further addition of mPEG-SH changed the organosilica nucleation sites on the Ag seed to form a peanut-like structure.



Fig. 4 (a–e) Schematic illustration of different morphology particles: (a) pure Ag NP, (b) eccentric particle, (c) Janus particle – Fig. 3a, (d) Janus particle – Fig. 3b, (e) Janus particle – Fig. 3c, (f) experimental extinction spectra of (a–e) particles and (g) simulated extinction spectra.

Fig. 4 shows the experimental (f) and theoretical (g) extinction spectra of particles with different morphologies and asymmetries (a–e). The theoretical calculation was performed using the FEM method.²⁰ Refractive indices of silver and organosilica materials were taken from the work of Palik and Seet,²¹ respectively.

The original Ag NPs display an intense, sharp peak at around 430 nm, which is consistent with calculation and the literature.²² After being encapsulated with organosilica particles, all the SPR peaks became broad and red-shifted which can be explained by the increasing refractive index of the medium surrounding the Ag NPs from the Mie theory.²³ However, the Ag-organosilica hybrid particles with different symmetries show various SPR peaks. For the eccentric Ag-organosilica hybrid particles wherein Ag NPs are still inside the organosilica particles, the major SPR peak is located at 510 nm. For these Janus Ag-organosilica hybrid particles, as the amount of mPEG-SH solution increased from 200, 400 to 600 µL, the Ag NPs tended to protrude more from the surfaces of the organosilica spheres and produced more obvious Janus structures, as shown in Fig. 3, the SPR peaks gradually blue-shifted to 502, 500 and 494 compared to eccentric hybrid particles. The main SPR peaks and blue-shift tendency are confirmed in our calculation, as evidenced in Fig. 4g. The theoretical results have shown good matches with experimental results, except some small difference in peak positions. The tunable wavelength feature of synthesized particles is attractive for applications in solar energy harvesting, conducting polymer devices, drug delivery and biosensors.²⁴

In summary, we have reported a simple and facile wet-chemical method for the synthesis of asymmetric Ag–organosilica hybrid nanoparticles with controllable morphology. The asymmetric structures can be easily tuned from eccentric core–shell, to snowman Janus and peanut-like morphologies, depending on the properties of alkoxysilanes and the addition of mPEG-SH. The HS-groups of alkoxysilanes can ensure the fast attachment of the organosilica on one side of the Ag seed by strong S–Ag interaction, while the hydrophilic mPEG-SH is propitious to decrease the Ag NP-solution interfacial energy, increasing the asymmetry of Ag–organosilica hybrid nanoparticles. The present method is simple and versatile, and can be extended to fabricate some other metal-inorganic compound asymmetric particles. The rich thiol groups on the surfaces of the asymmetric hybrid nanoparticles and the metallic feature can make the as-obtained hybrid nanoparticles find some important applications in biomaterials, sensors, optoelectronics, *etc.*

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