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Fabrication of compact silver nanoshells on polystyrene spheres through electrostatic attraction†

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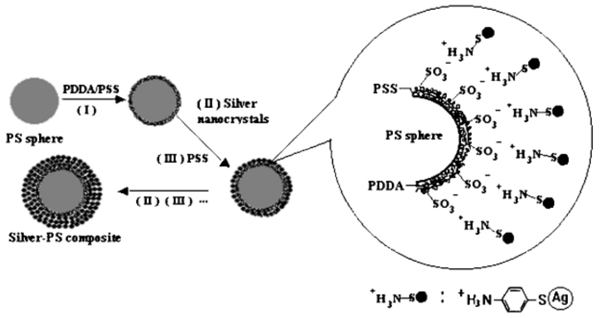
Nanoshells composed of close-packed silver nanocrystals have been fabricated on polystyrene spheres *via* direct electrostatic attraction at appropriate pH; the thickness and roughness of the shell can be readily controlled through a layer-by-layer technique.

Recently, the self-assembly of nano-sized metallic particles into pre-designed morphologies has become increasingly important due to their unique optical, electronic and catalytic properties.[1] In particular, fabrication of metal-coated latex core–shell particles is currently an attractive area of investigation because of their applications in the fields of surface-enhanced Raman scattering (SERS),[2] catalysis,[3] biochemistry[4] or potential uses as chemical sensors, *etc*. Up to now, several routes for such core–shell particles fabrication, including *in situ* chemical reduction[4–7] and self-assembly,[8,9] have been investigated. However, in most cases, the degree of surface coverage is lower than 30% and the metallic coating is non-uniform, owing to the interparticle Coulomb repulsion[8] and/or the passivation of metallic nanoparticles caused by capping agents (*e.g.* citrate).[9] More recently, a general strategy based on a two-step process involving the combination of surface seeding and subsequent shell growth has been proposed, resulting in complete and smooth gold or silver nanoshells on latex beads,[10–12] which are very helpful to explain Mie's scattering theory due to their tunable resonance. However, this strategy suffers from complex operation and difficulty to tune the thickness of the shell. In addition, in some cases, for example in SERS studies, the deposition of rough shells instead of smooth ones is more desirable, owing to the strong near-field enhancement in the vicinity of metal nanoparticles.[5] Here, we report a facile and versatile approach based on electrostatic attraction to fabricate complete silver nanoshells on polystyrene (PS) microspheres. The thickness and roughness of the shell can be readily controlled through a layer-by-layer technique. Such metal–latex particles are expected to open some new possibilities in the application of optical studies (*e.g.* SERS), catalysis and biochemistry for their more tunable features in shell thickness, roughness and composition.

Positively charged silver nanocrystals functionalized by 4-aminothiophenol (4-ATP) were prepared through a one-phase synthesis route according to the literature[13] with minor modification. 10 ml of 10^{-2} mol l^{-1} 4-ATP in ethanol was added dropwise to 30 ml of 3×10^{-2} mol l^{-1} $AgNO_3$ in ethanol. To the resulting solution, 30 ml of freshly prepared 0.4 mol l^{-1} KBH_4 aqueous solution was added all at once instead of in small portions. After purification involving high-speed centrifugation and removal of unreacted KBH_4 and 4-ATP, the as-synthesized silver particles were eventually dispersed in deionized water with appropriate pH (adjusted with HCl or $NH_3{\cdot}H_2O$) to form a silver hydrosol. The fabrication procedure of silver–latex composites is described in Scheme 1. Briefly, the PS spheres with 1.50 μm in diameter [Fig. 1(a)] were coated with two-layer polyelectrolyte films in the order of cationic poly(diallyldimethylammonium chloride) (PDDA) and anionic poly(styrene sulfonate, sodium salt) (PSS), which provided a negatively charged and uniform outer surface (**I**). Afterwards, the pre-formed modified silver nanocrystals were deposited on PS spheres through electrostatic attraction between negatively charged sulfonate groups and positively charged amine groups (**II**). To fabricate more compact and thicker silver shells, the silver nanocrystals and PSS were alternatively deposited on PS spheres (**II**, **III**…). All the above deposition steps were done with a liquid/solid volume ratio of 30 at ambient temperature for a duration of 20 min, and after each adsorption step the sample was centrifuged, washed and redispersed.

It was found that the pre-modification of silver particles with bifunctional molecules was necessary to generate suitable surface properties which could stabilize the metallic colloid and/or help the assembly of metallic nanoparticles.[1] The 4-ATP used in the present paper would act as both capping and amino-functionalizing agent which would provide the positive charge on the outer surface of the metallic nanoparticles due to the ionization of the amine groups.[14] The X-ray diffraction (XRD) pattern of as-prepared silver nanoparticles shows two broad reflection peaks which are indexed to the 111 and 200 planes, respectively [Fig. 2(a)], indicating that the silver particles are nanocrystals with cubic symmetry. The mean crystal size of the silver samples calculated from the XRD line width by the Scherrer formula is *ca.* 13 nm, which is smaller than that measured from scanning electronic microscopy (SEM) (*ca.* 40 nm), indicating that the particles seen in the SEM micrographs and used for later assembly might be agglomerates of silver crystallites. IR spectrum demonstrates that the modified silver particles have been capped by 4-ATP.

Because the ionization degree of the amine groups on silver particles is altered with pH, it is important to control the pH of the silver colloid solution in order to obtain uniform and dense nanoshells. Although the amine groups are almost fully ionized at pH lower than 3, the silver hydrosol is easier to flocculate under such conditions (probably because the Ag–S covalent bond is weakened in strong acidic medium), which leads to the low surface coverage [Fig. 1(b)]. Complete and compact nanoshells are obtained at pH of ~4.0–5.0, where the amount of positive charge on the silver nanocrystals is adequate for them to deposit. Almost all the surface of PS spheres is covered by close-packed silver nanocrystals and the metallic coating is



Scheme 1 Fabrication procedure of silver nanoshells on PS spheres.

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† Electronic supplementary information (ESI) available: Preparation and characterization of PS spheres. Fig. S1: SEM micrographs of silver–latex composites. See http://www.rsc.org/suppdata/cc/b1/b110164c/

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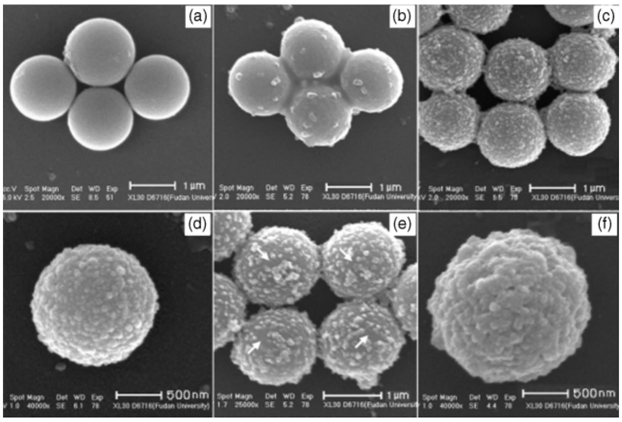

Fig. 1 SEM micrographs showing (a) original PS spheres; silver–latex composites obtained at (b) pH 2.5; (c) pH 4.5; (d) high magnification of (c); (e) pH 6.0, arrows indicate some non-coated parts on PS spheres; and (f) pH 4.5 with PS spheres coated with four layers of silver nanocrystals.

rather uniform and regular [Fig. 1(c) and 1(d)]. At pH higher than 5, the amine groups are progressively less ionized so that the amount of positive charge on the silver particles is not adequate for them to deposit compactly and densely. Only half of the surface is covered at pH 6.0 [Fig. 1(e)] and almost no silver particles are deposited on PS spheres when the pH is higher than 9. However, when PS spheres were pre-modified with just one layer of cationic PDDA, only a small portion of silver particles on PS spheres can be observed even at pH 4.5. The above facts indicate that the electrostatic attraction between the 4-ATP capped silver nanocrystals and the polyelectrolytes modified PS spheres is the basic driving force for the assembly of silver nanocrystals on PS spheres.

The layer-by-layer (LbL) technique has been widely used to fabricate core–shell particles because of its convenience to tailor the thickness and composition of the shells.[15–17] To obtain metallic shells with different thickness, silver multilayers on PS spheres were also fabricated through the LbL technique. It was found that the thickness and roughness of metallic coating were increased gradually with the increase of the depositing cycle numbers and the sample with four layers of silver nanocrystals is shown in Fig. 1(f). The increase of the shell thickness per deposition cycle is *ca.* 35 nm (calculated from the diameter change of the samples), which is slightly less than the size of the silver nanocrystals seen in SEM. By varying the number of the deposition cycles, samples with controlled ratio of core diameter to the shell thickness were easily prepared. This characteristic of the core–shell particles is expected to be beneficial for SERS studies. Moreover, by depositing various kinds of metallic nanoparticles, materials with different or hybrid shell composition are also expected to be synthesized in principle. The XRD pattern of PS spheres coated with three layers of silver particles [Fig. 2(b)] is similar with that of original silver nanocrystals [Fig. 2(a)] except for a slightly lower intensity of the diffraction peaks, confirming that the shells are composed of silver nanocrystals.

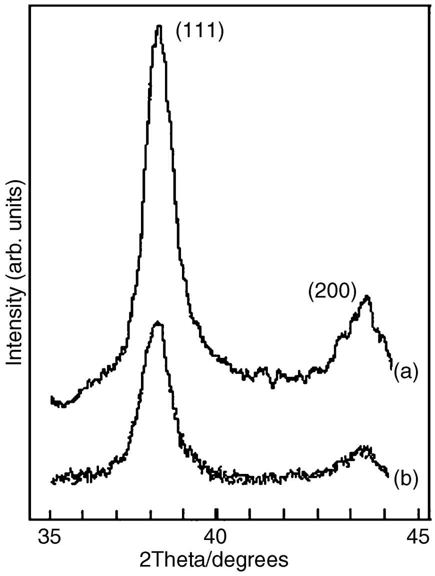

Fig. 2 XRD patterns of as-synthesized silver nanocrystals (a) and PS spheres coated with three layers of silver nanocrystals (b).

In summary, the complete nanoshells composed of close-packed silver nanocrystals have been fabricated on PS spheres through electrostatic attraction at appropriate pH. The degree of surface coverage can be controlled through the regulation of the pH of the silver colloid solution because of the tunable ionization degree of amine groups on silver nanocrystals. Furthermore, the roughness and thickness of the shell can be easily tailored by varying the number of the deposition cycles.

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The preparation route for the PS particles and their subsequent characterization and the SEM micrographs of silver–latex composites obtained under other conditions are available as ESI.†

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