

## A Precursor Route for the Preparation of Metal–Dielectric Composite in Large Scale

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In this paper, a novel method based on formation of a precursor was developed to fabricate metal–dielectric colloids in large scale. Metal nanoparticles formed in situ on the surface of the polyethyleneimine (PEI)-modified dielectric colloids.

The design and controllable fabrication of core–shell nanocomposites have been an active area of research in nanoscience and nanotechnology because of their fascinating properties and versatile applications.<sup>1</sup> Assembling metal nanoparticles on the dielectric core is one attractive investigation topic. Such interest stems from great advantages of these hybrid materials over conductivity, optical activity, catalytic activity as well as in biochemistry for the potential uses as chemical sensors.<sup>2</sup> Furthermore, assembly of metal nanoparticles on the support could allow them to retain high activity on recycling, enhance their pH and temperature stability, and enable easy separation from the reaction medium by centrifugation for reuse.

In general, immobilization was achieved by adsorption of metal nanoparticles on dielectric colloids with organic ligands or polyelectrolytes as “glue,”<sup>3–5</sup> “in situ” formation by dispersion copolymerization of styrene and polyamine in the presence of metal salts,<sup>6</sup> electroless plating approaches,<sup>7</sup> and solvent-assisted route.<sup>8</sup> More recently, it has been demonstrated that Ag nanoparticles could be immobilized onto the polystyrene sphere surface using polyol process.<sup>9</sup> A common feature of all these approaches is that the reductant (and/or metal precursor) and the core are separated before the formation of the core–shell composite. This can unavoidably lead to the residue of metal nanoparticles and reductant in the system or the formation of fresh metal nuclei besides particles around the core surface. Especially, a large amount of products are difficult to be obtained because of the need of a lower concentration of reagent, manipulation of complex experimental parameters, and complex operating processes. Thus, developing a simple and effective strategy to prepare metallodielectric complex with high yield still an ongoing challenge.

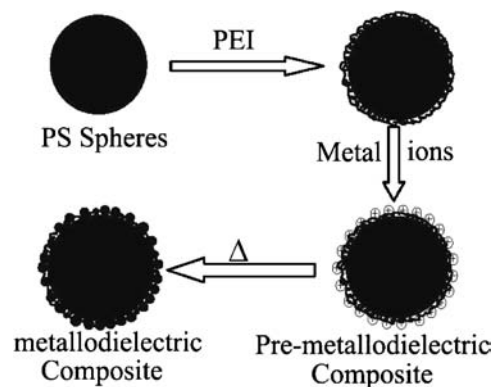
In principle, if such a composite comprising of metal ions, reductant, and core colloid exists, it should be a good precursor for the synthesis of metal–dielectric colloids because the redox reaction will only take place within the precursor. To realize the transformation of such a precursor to metal–dielectric complex, two problems must be solved. The first is constructing a “stable” precursor (pre-metallodielectric composite) that consists of metal ions, reductant, and core colloid; the second is to transform this precursor into metallodielectric composite. Here, the proposed process was realized by using polyethyleneimine (PEI) as both linker and the reductant.

PEI is a cationic polymer with branched structure in which 25% nitrogen atoms is primary amines, 50% secondary amines, and 25% tertiary amines. The plentiful amine groups in PEI can

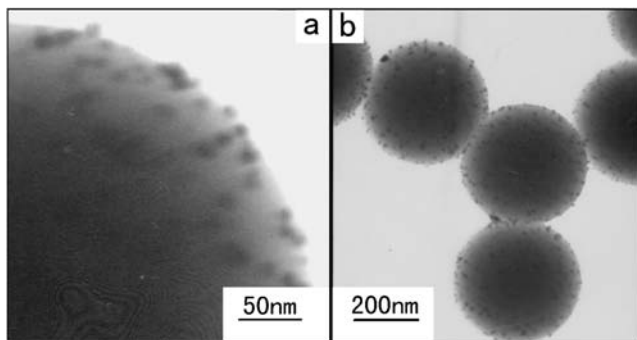
bind both with transition metal and with negatively charged colloids.<sup>4,10</sup> To the best of our knowledge, despite the previous work showed functions of PEI as linker<sup>4</sup> and reductant,<sup>11</sup> the immobilization of metal nanoparticles onto the dielectric sphere surface using the bifunctional characteristic has not been reported. In this paper, we realize large amount preparation of Ag–PS complex by using PEI as both linker and the reductant. We call such process as a “precursor route.” The procedure for the synthesis of Ag–PS composite is schematically shown in Scheme 1. Briefly, the PS colloids synthesized by emulsion polymerization<sup>12</sup> were coated with PEI in the phosphate buffer solution. After centrifugation/wash cycles, the PEI-modified PS colloids were obtained. Then, silver nitrate was dissolved in an aqueous solution containing PEI-modified PS colloids (the mass ratio of Ag to PS sphere is 1:10). After ten minutes, the colloid was washed by centrifugation/wash cycles. The solid (precursor) obtained was dispersed into water, the resulting solution was heated at 373 K for 1 h, and then silvered PS spheres were obtained.

Figure 1 shows the TEM images of as-synthesized silvered PS spheres. It can be seen that well-dispersed and nearly spherical particles are formed and immobilized on PS spheres. The particle size is no large than 15 nm as shown in Figure 1a. The XPS and XRD were used to examine particle component. The binding energy for Ag3d<sub>3/2</sub> is located at about 374.6 eV, which is close to the literature value for Ag<sup>0</sup>.<sup>6</sup> (Figure S1) In the XRD pattern shown in Figure 2, five diffraction peaks are observed at  $2\theta = 38.2, 44.3, 64.5, 77.6,$  and  $81.6^\circ$ , which correspond to the (111), (200), (220), (311), and (222) reflections of fcc structure of metallic Ag, respectively (PDF: 4-783). These measurements lead us to conclude that pure Ag phase presents in as-prepared silvered PS colloids.

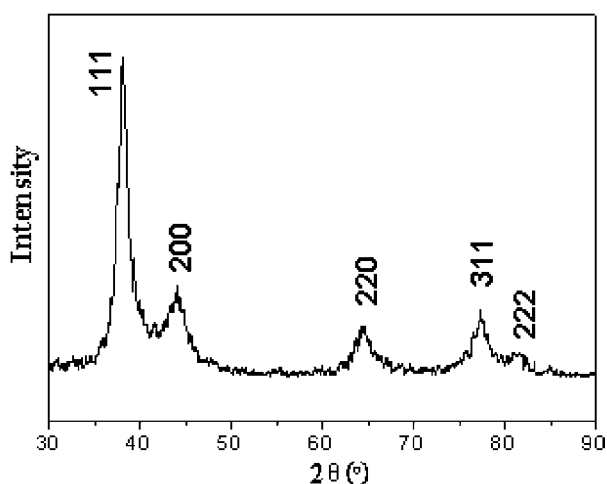
In order to confirm that the reaction only takes place within the pre-metallodielectric composite, excess Ag<sup>+</sup> was added into the solution of PEI-modified PS colloids followed by heating



**Scheme 1.** Procedure for preparing metallodielectric composite.



**Figure 1.** TEM images of silvered PS spheres: a) Higher and b) lower magnification.



**Figure 2.** XRD pattern of the silvered PS spheres.

without other treatment. The UV–vis absorption spectrum of the PS sphere after silver deposition exhibits an absorption peak at about 410 nm, which results from the plasmon resonance of isolated Ag nanoparticles. The emergence of the long wavelength peak (about 630 nm) results from plasmon–plasmon interaction between the silver nanoparticles<sup>13</sup> (Figure S2). However, the supernatant obtained from the dialyzed solution was colorless and showed no absorption peak in the range of 400–800 nm (Figure S3). The peak at about 300 nm can be contributed to absorption of excess Ag<sup>+</sup> ions.<sup>14</sup> In addition, TEM image of the product shows that no other particles rather than metal-modified PS sphere were present (Figure 1b). These results indicate that all the Ag nanoparticles were immobilized on the core surface. Similar result was obtained by Akashi group.<sup>6</sup>

The yield of Ag–polymer complex is not so limited as that of other methods. Here, the precursor of silvered PS spheres is a pre-formed “stable” pre-metallo-dielectric core–shell structure. In this process, Ag<sup>+</sup> ions coordinate with amine groups of PEI and then form a “metal-ion shell” around PEI, which prevent interaction between PEI and excessive Ag<sup>+</sup> ions. Accordingly, redox reaction only takes place between PEI and Ag<sup>+</sup> coordinated with them under heating. In addition, the coordination interaction between Ag nanoparticles formed in situ and amine groups in PEI prevents metal nanoparticles from agglomeration and detachment from PS colloid surface. Because each precursor is an individual redox reactor, the effect of the concentration of

PS colloids on the formation of the core–shell composites is expected to be small, and large quantity of silvered PS spheres can be readily obtained. For example, a reaction yielding 8 g of silvered PS spheres was performed in 100 mL water. The Ag nanoparticles on the surface of core can act as catalysts for further reduction of other metal ions (Cu, Pd, and Pt).<sup>15</sup> Therefore, this method may be indicative for the deposition of other metal particles on microspheres.

In summary, a precursor route was adopted to fabricate Ag–PS colloid composites in large scale. Metal nanoparticles formed in situ on the surface of the PEI-modified dielectric colloids. The most distinguished features of this novel preparation route, the precursor route, include simple operation, easy larger-scale production, and absence of the toxic reducing agent. The preliminary results show that this new approach developed for the synthesis of silvered PS sphere can be readily extended to other metal–dielectric and metal–semiconductor composites, such as PS@Au, SiO<sub>2</sub>@Ag, SiO<sub>2</sub>@Au, and ZnO@Au. The further work is under way.

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