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LETTER

Chemically immobilizing gold nanoparticles to the surface of polystyrene particles

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In recent years, attachment of gold nanoparticles (AuNPs) onto the surface of polymer particles of submicron or micron size has been widely investigated. Most studies in the literature enabled the anchoring of AuNPs on polymer particles via electrostatic attraction [1–4], mutual entanglement of polymer chains present on AuNP surface with those present on polymer particle surface [5, 6], and partially [7, 8] or completely [9, 10] "embedding" of AuNPs in the polymer matrix. On the other hand, it is well known that Au tends to form stable covalent bond with thiol group [11]. The Au–thiol chemistry has been extensively used to chemically immobilize the AuNPs onto various solid substrates such as silicon [12–14], carbon nanotubes [15–17], boron nitride nanotubes [18], polymer single crystal [19], and silica [20, 21]. However, there are only a few studies reporting the immobilization of AuNPs onto the polymer particles based on the Au–thiol covalent bonding [22, 23]. The prerequisite of this methodology is the successful functionalization of polymer particles with thiol group. Suzuki et al. [22] synthesized the core/shell polymer particles with core composed mainly of poly(glycidyl methacylate). Then, thiol groups were introduced by the reaction of epoxy groups with dithiothreitol. Yong et al. [23] used the commercially available carboxylate-modified polystyrene (PS) particles as the substrates for Au attaching. The PS particles were reacted with 2-aminoethanethiol hydrochloride to provide thiol groups on their surface. To these thiol-terminated PS particles, a partial layer of AuNPs was attached.

Here we report an alternative approach for preparing thiol-functionalized PS particles, to which AuNPs are immobilized via Au–S covalent bond (Fig. 1). Dithiocarbamate groups were first introduced into the PS particle surface by the copolymerization of 4-vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC) monomer in the soap-free emulsion polymerization of styrene. Then, the dithiocarbamate groups were converted to the thiol groups by the reduction with sodium borohydride [24, 25].

The synthesis of dithiocarbamate-modified PS particles was as follows. To a separated 300 mL round bottom flask equipped with a mechanical marine-type agitator and a nitrogen inlet, 5.0 g styrene monomer (Sinopharm Chemical Reagent Co., Ltd., ≥99.0%), 200 mL 0.01 M aqueous solution of $NaNO_3$ (Sinopharm Chemical Reagent Co., Ltd., ≥99.0%), and 200 mg 2,2′-azobis(2-methylpropionamidine)dihydrochloride (J&K Chemical Ltd., 98.0%) were added. The mixture was purged with nitrogen for 30 min under stirring (300 rpm) and heated to 80 °C to initiate the soap-free emulsion polymerization. After the polymerization had proceeded for 6 h, the temperature was lowered to 70 °C. Then, 200 mg VBDC monomer (dissolved in 1 mL acetone) was added dropwise. VBDC was synthesized according to the literature [26]. The polymerization was continued for an additional 4 h and then stopped by cooling in ice water. The soluble impurities were removed by dialysis against deionized water for at least 3 days.

A droplet of the PS latex thus prepared, which had been previously diluted to about 100 ppm with deionized water, was dropped onto a carbon film supported on a standard

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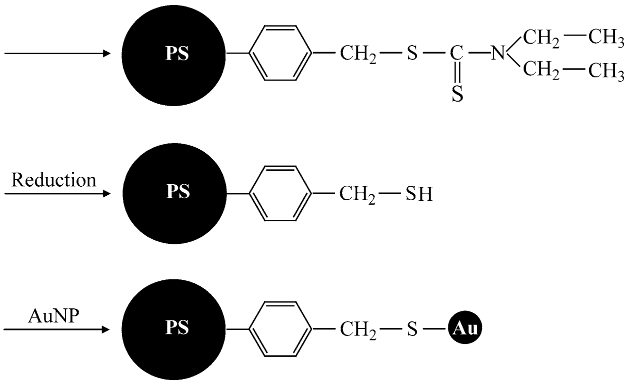

Fig. 1 Scheme of immobilization of AuNPs to the PS particle surface by chemical bonding

copper mesh grid. After being dried in a desiccator at room temperature, the specimen was examined by transmission electron microscopy (TEM, JEOL JEM-1200EXII) at an accelerating voltage of 80 kV. A typical TEM micrograph was shown in Fig. 2. The prepared PS particles were very spherical without appreciable agglomeration. The number average diameter was about 340 nm (30 particles sampled) with a high monodispersity (the coefficient of variation = 3.23%). The top surface of dithiocarbamate-modified PS particles was analyzed by X-ray photoelectron spectroscopy (XPS, Perkin–Elmer ESCA 5600) at a take-off angle of 45 °C. As expected, a weak S 2p signal at binding energy of 163.0 eV (corrected with the binding energy of C 1s, 284.6 eV) was observed in the XPS spectrum. The relative concentrations of sulfur and carbon were determined from peak-area ratios, after correcting with the appropriate sensitivity factors (S 2p: 38.321; C 1s: 17.059). This quantitative analysis gave: S, 1.2%; C, 98.8%. Based on the relative atomic concentrations, it can be calculated that the VBDC unit on the particle surface was about 5.1 mol%.

The reduction of dithiocarbamate groups and the immobilization of AuNPs were simply accomplished in a single operation. 100 mL of dithiocarbamate-modified PS latex (containing 0.08 g solid polymer) and 1 mL of 0.025 M aqueous gold chloride trihydrate (MP Biomedicals, LLC., Reagent Grade) were charged into a 300 mL four-neck flask. Then, 1 mL of 0.25 M aqueous sodium borohydride (Sinopharm Chemical Reagent Co., Ltd., ≥98.0%) was rapidly added with vigorous stirring. The dispersion turned brown immediately indicating the formation of AuNPs. After stirring for 30 min, the resulted latex was observed by TEM. It was expected that, upon addition of sodium borohydride, the dithiocarbamate groups present at the particle surface were converted to thiol groups. At the same time, AuNPs were formed in situ and chemically immobilized to the PS particle surface via strong Au–S bond. As shown in Fig. 3a and b, the PS particles were uniformly and densely coated with relatively well-defined AuNPs. The size of these AuNPs was approximately in the range of 4 nm to 20 nm. It is also obvious that no aggregates of AuNPs were present at the area outside the surface of PS particles, though no stabilizer was added during the synthesis of AuNPs. This indicates that the as-synthesized AuNPs were all effectively attached to the surface of PS particles. The prepared Au-coated PS particles precipitated from suspension after several hours, leaving colorless supernatant. However, the precipitated Au-coated PS particles could be easily redispersed by gentle shaking.

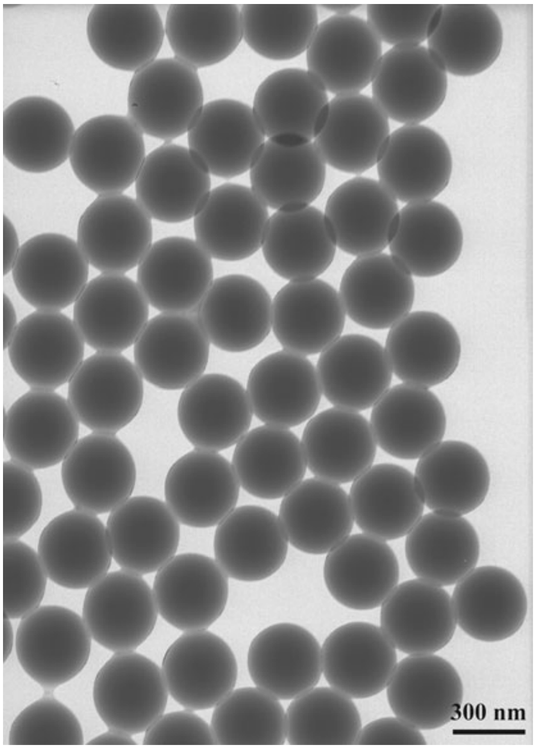

Fig. 2 TEM micrograph of dithiocarbamate-modified PS particles

Very recently, Meredith et al. [5, 6] reported a combined swelling-heteroaggregation method for the preparation of metal nanoparticle-coated PS latex beads. A range of nanoparticles (Au and Ag) with different size and shapes were successfully attached on PS beads by the mutual entanglement of polymer chains. The authors showed that the attached AuNPs did not readily detach after applying sonication. Likewise, the Au-coated PS particles obtained in this study also showed an outstanding stability against sonication. Subjecting the composite particles to the intense ultrasonic irradiation (59 kHz) at room temperature caused no appreciable change in particle morphology, even the irradiating time was as long as 1 h (Fig. 3c) and 4 h (Fig. 3d).

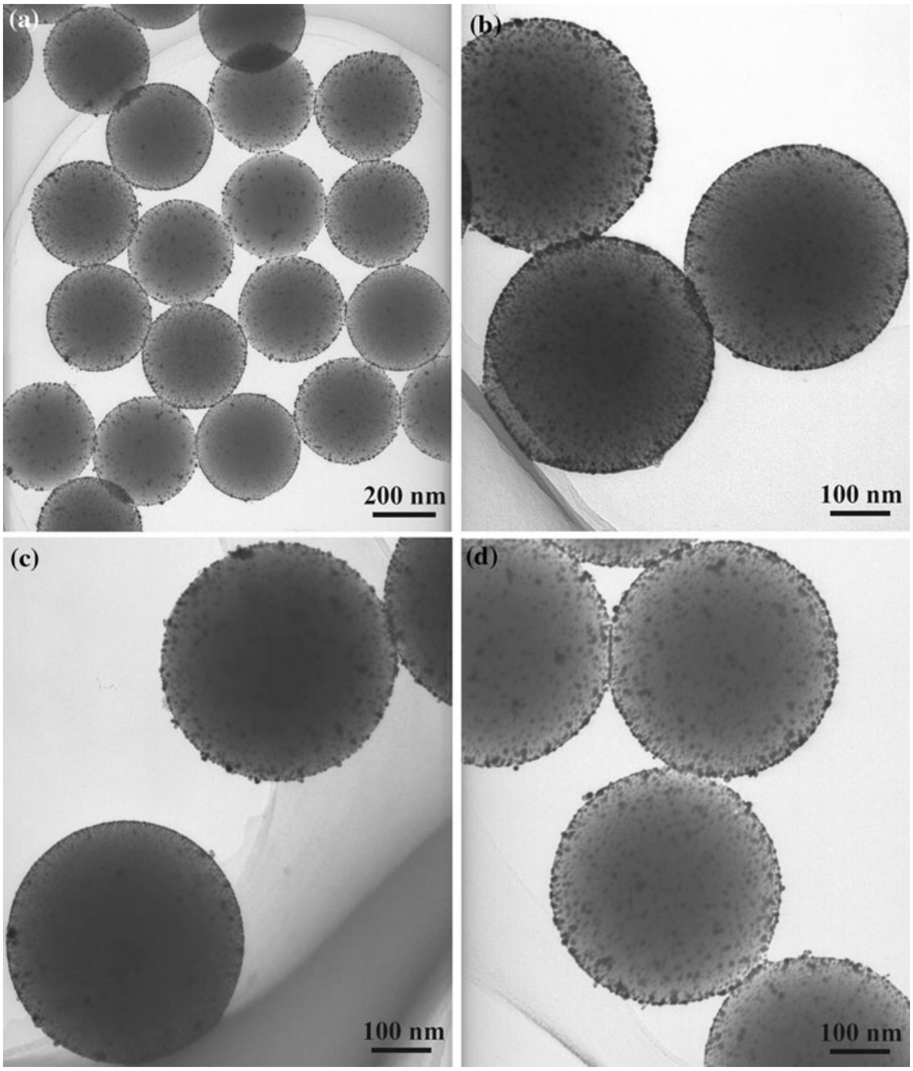

Fig. 3 TEM micrographs of Au-coated PS particles: **a** and **b** freshly prepared by the immobilization of AuNPs to PS particles, **c** after ultrasonic irradiation for 1 h, and **d** after ultrasonic irradiation for 4 h

In summary, we demonstrated a facile and effective approach for coating PS particles with AuNPs by means of chemical bonding. This approach was based on the successful functionalization of the surface of PS particles with dithiocarbamate group, which can be readily changed to the thiol group. In fact, the dithiocarbamate group has proven to be an excellent photoiniferter capable of initiating living radical polymerization [26]. Thus, this also allows for the introduction of various functional polymers to the surface of PS particles. The design and fabrication of a variety of functional PS particles via this kind of photoiniferter introduced to the particle surface are now in progress.

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