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A Facile Method to Synthesize PS/Ag Composite Microspheres

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Abstract: A facile method to synthesize PS/Ag composite microspheres with high and uniform metal coverage was proposed to avoid synthesize the modification of PS beads. First, polyvinylpyrrolidone (PVP)-capped Ag nanoparticles (NPs) with a narrow size distribution were obtained by the modified polyol process, and then the PVP-capped Ag NPs were successfully loaded on the PS beads by a combined swelling-heteroaggregation (CSH) procedure. The size distribution of Ag NPs and the morphology of PS/Ag composite microspheres were investigated. The results show that well-dispersed and uniformly coated PS/Ag microspheres are obtained and the coverage of the Ag NPs can be controlled by changing the amount of Ag NPs.

Key words: silver nanoparticles; PS/Ag composite microspheres; combined swelling-heteroaggregation

Silver nanoparticles (Ag NPs) have been widely used due to their desirable optical, electronic, and biocompatibility properties[1-4]. In order to passivate and protect the Ag NPs from the environment, and prevent leaching of Ag NPs, Ag NPs were loaded on various substrates. Polystyrene (PS) bead was an important substrate, and has been widely served as a carrier of Ag NPs. The PS/Ag composite has been well used in many fields, such as a scattering contrast agent for biomedical imaging and labeling cells in flow cytometry[5]. The assembly of PS/Ag composite microspheres requires control over Ag NPs loading and distribution on the PS beads. Various methods have been developed to synthesize PS/Ag composite microspheres and to control the morphology of Ag NPs on surface of PS beads[6-8]. Unfortunately, there were still irregular and low metal coverage on the PS microspheres. Herein, a facile method was proposed to overcome the limitations in surface coverage and stringent treatments of classic strategies.

1 Experiment

Polymer-protected Ag NPs were synthesized as follows: poly (vinyl pyrrolidone, PVP, 1 g) was dissolved in ethylene glycol (EG, 75 mL), and silver nitrate ($AgNO_3$, 200 mg) was then added to the solution. The suspension was stirred at room temperature until $AgNO_3$ was completely dissolved. Then, the mixture was heated to 130 ℃ at a rate of 10 ℃/5 min, and the reaction was continued for a period of time (0.5~1.5 h) at this temperature. After the reaction, the dispersion was cooled down to room temperature in water. To obtain the Ag NPs, the solution was diluted with acetone, followed by centrifugation. Finally, the Ag NPs were redispersed in water for further use.

The Ag NPs were loaded on PS surface according to the following procedure: 100 μL PS (10 μm, 1.0 wt%, cross-linking degree: 8% or 80%) aqueous solution was put into a 2 mL tube and 650 μL Ag colloidal dispersion (0.04~0.15 mol/L) was added and stirred for 30 s. 750 μL tetrahydrofuran (THF) was then added dropwise to the suspension. After stirring for 10 h, the mixture was washed with deionized water via at least five centrifugation cycles to remove the THF.

Field emission scanning electron microscopy (SEM, SU-70, Hitachi, Japan) was used to investigate the size and morphology of the samples. The morphological and structural characterizations of Ag NPs were based on field emission transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN, FEI, USA) observation. The volume changes of PS beads in different solutions were observed by the optical microscopy (Nikon 80i). An oil Iris objective was used to collect only the scattered light from the samples. Ultraviolet-visible (UV-vis) absorption spectra were recorded by a Shimadzu UV-3150 spectrophotometer (Japan) in the wave-

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length range from 200 nm to 800 nm using ethanol as a reference.

2 Results and Discussions

2.1 Morphology of the Ag NPs

Fig.1 shows the TEM images of Ag NPs prepared under different reaction time. It can be seen that the particle size of Ag NPs increases with the reaction time, but the particle size distribution is widened (as shown in Fig.2). The influence of reaction time on mean particle size and coefficient of variance (CV) is presented in Fig.3. The results illustrate that the Ag NPs are quite uniform under the reaction time of 0.5, 0.75 and 1 h. The mean particle size are 26.22, 38.78 and 55.35 nm with a low CV (≤18%), respectively. When prolonging the reaction time to 1.25 or 1.5 h, the growth of Ag NPs is uncontrollable. The particles have average size of 90.07 and 103.6 nm with a CV of 26.93% and 38.13%, respectively, exhibiting poor monodisperse feature. This effect involves an Ostwald ripening mechanism. The presence of small particles in the early time is due to rapid nucleation of the Ag^0 seeds. With the progress of the reaction, part of the smaller Ag NPs slowly disappears and acts as "nutrients" for the growth of bigger Ag NPs due to the energetic factors, so the mean size of Ag NPs increases. Meanwhile, this random growth also leads to the wide particle size distribution.

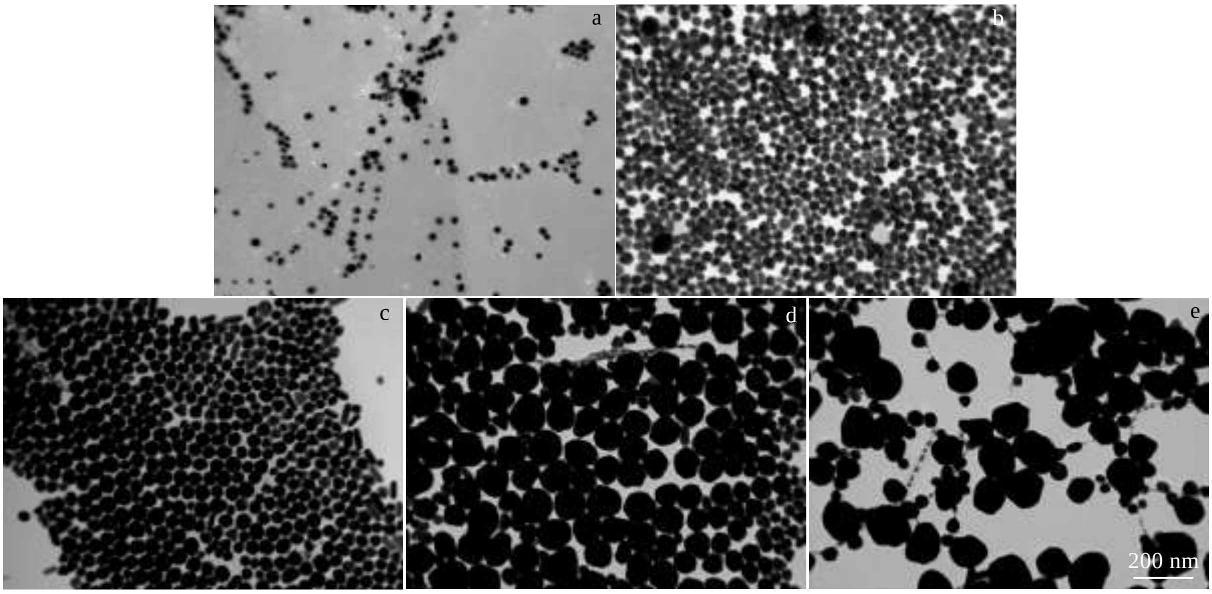

Fig.1 TEM images of Ag NPs prepared under different reaction time: (a) 0.5 h, (b) 0.75 h, (c) 1 h, (d) 1.25 h, and (e) 1.5 h

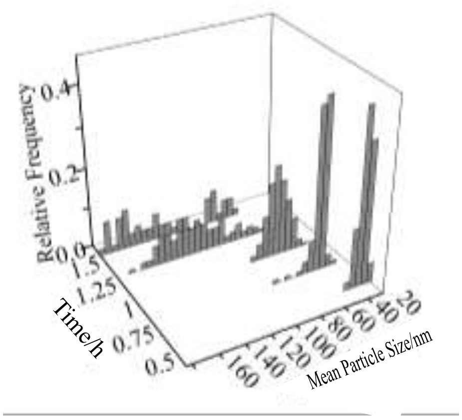

Fig.2 Particle size distribution of Ag NPs prepared under different reaction time

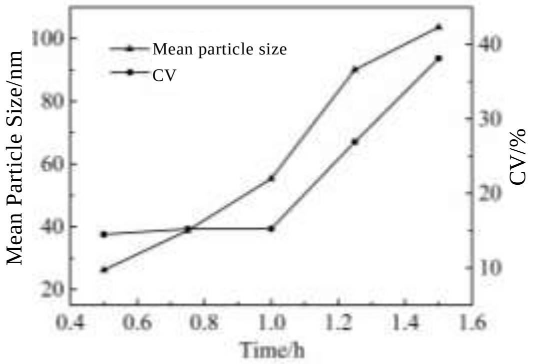

Fig.3 Plot of mean particle size and CV of Ag NPs prepared under different reaction time

2.2 Formation mechanism of the PS/Ag composite microspheres

Considering the particle uniformity, Ag NPs with mean size of 55.35 nm were selected to be loaded on PS beads. Using the combined swelling-heteroaggregation (CSH) process described in Fig.4, Ag NPs of different concentration (0.04, 0.08, 0.15 mol/L) were loaded on unfunctionalized PS beads with different crosslinking degrees (8%, 80%) by the simple addition and removal of a solvent in aqueous suspension. The process allows entanglement of PVP present on Ag NPs with the plasticized PS surface and heteroaggregation of PVP-capped Ag NPs on PS during the swelling[9]. Finally, stable PS/Ag composite microspheres are formed after shrinking.

The effect of THF in CSH process is proved by adding 50% THF to PS aqueous solution. As shown in Fig.5, THF can drive the swelling and aggregation of PS beads with crosslinking degrees of 80%. Fig.6a shows the SEM image of PS beads after the CSH process in the absence of Ag NPs. During the cycle of swelling and shrinking, some PS beads are not protected by surfactant and coalesced[10]. Fig.6b~6d show SEM images of PS/Ag composite microspheres with different levels of metal coverage. The coverage increases from approximate 25% to 80% as Ag NPs concentration increases from 0.04 mol/L to 0.15 mol/L. Ag NPs are successfully loaded on PS beads with formation of aggregation (Fig.6d, inset). This is because the effectiveness of PVP served as a stabilizer is weakened by the THF. Moreover, the crosslinking degree of PS beads is another important influencing factor on the loading of Ag NPs. Fig.6e shows that the PS beads with crosslinking degree of 80% have low metal coverage compared with the samples shown in Fig.6d. The reason is that the swelling space caused by THF is not enough for heteroaggregation.

It can be seen from Fig.7 that the PS/Ag composite microspheres show a broad plasmon resonance absorption peak at 453 nm, which is red-shifted compared with that (422 nm) of Ag NPs dispersion. The red shift is due to interparticle plasmon field coupling that occurs in the Ag NPs aggregation on the PS surface[11,12]. The plasmon coupling effect is significant for generating highly enhanced electromagnetic field on the surface of silver composite materials, which can cause the enhancement of surface-enhanced fluorescence (SEF) and surface-enhanced Raman spectroscopy (SERS) signals[13,14]. With the dependence of the plasmon resonance on particle size and shape[15,16], the features of this structure make it possible to regulate the size and density of Ag NPs to achieve more efficient structures for SEF and SERS.

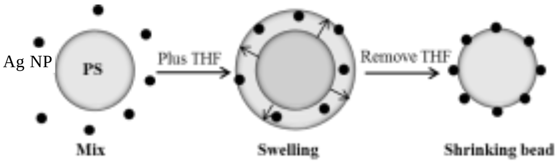

Fig.4 Schematic diagram of combined swelling-heteroaggregation (CSH) process of the loading of Ag NPs on PS beads

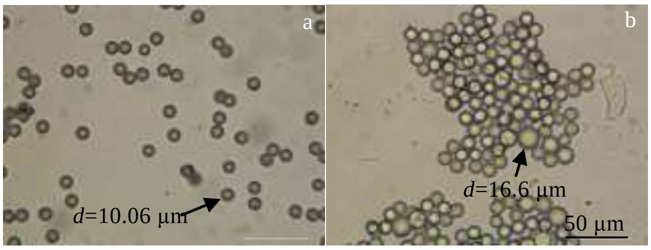

Fig.5 Optical microscopy images of PS microspheres with crosslinking degrees of 80% in DI water (a) and 50% THF-water solution (b)

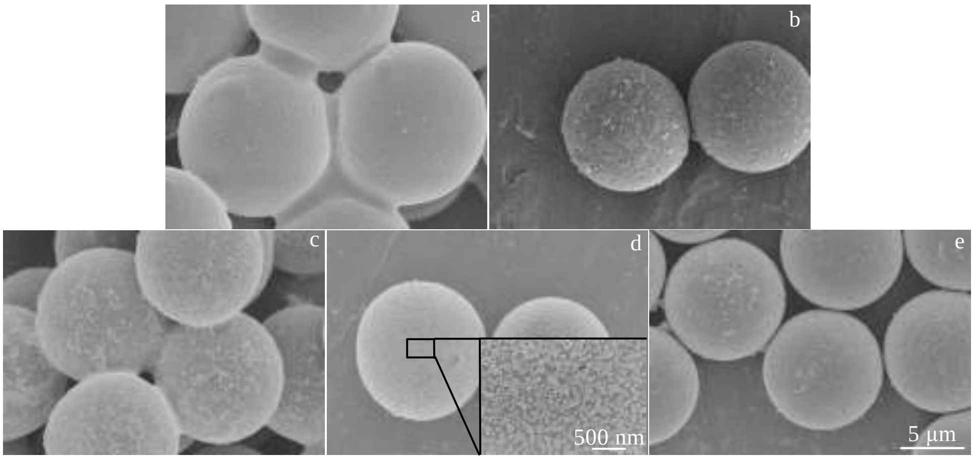

Fig.6 SEM images of pure PS beads (a), PS/Ag composites (crosslinking degree of PS is 8%) prepared from AgNPs dispersions with different concentration of 0.04 mol/L (b), 0.08 mol/L (c), 0.15 mol/L (d), and PS/Ag composite (crosslinking degree of PS is 80%) prepared from AgNPs dispersion with concentration of 0.15 mol/L (e)

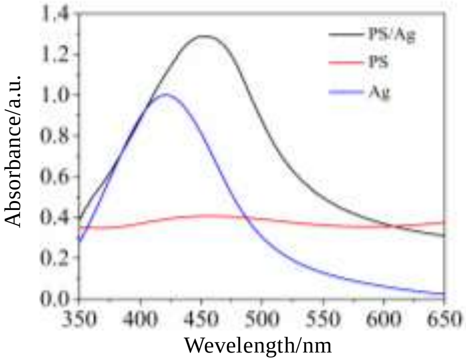

Fig.7 UV-visible spectra of PS/Ag microspheres, PS microspheres and Ag NPs

3 Conclusions

1) The morphology and size distribution of Ag NPs can be regulated by reaction time of polyol process in the presence of PVP.

2) Ag NPs can be loaded densely on unfunctionalized PS beads via CSH process.

3) The metal coverage of PS/Ag composite microspheres can be controlled by simple adjustments in Ag NPs concentration.

4) The down-top fabrication method makes the PS/Ag microspheres a potential micro-sized platform for SEF and SERS.

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一种合成 PS/Ag 复合微球的简便方法

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摘 要：提出一种制备具有高金属覆载率及良好均匀性的 PS/Ag 复合微球的简便方法，可以避免 PS 微球的表面修饰。首先通过多元醇法制备具有良好单分散性的 PVP 覆盖的 Ag 纳米颗粒，然后通过溶胀-异质凝聚法将这些 Ag 纳米颗粒负载于 PS 球上。对 Ag 纳米颗粒的尺寸分布及 PS/Ag 复合微球的表面形貌进行了研究，结果表明这种方法制得的 PS/Ag 复合微球具有良好的分散性与均一性，并且 Ag 颗粒的负载率可以通过 Ag 溶胶的加入量来调控。

关键词：银纳米颗粒；PS/Ag复合微球；溶胀-异质凝聚法

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