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“One-pot” Fabrication of Ag/PMMA “shell/core” Nanocomposites by Chemical Reduction Method

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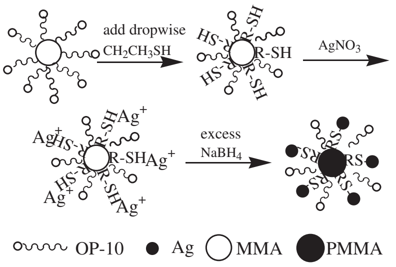
The Ag/PMMA shell/core nanocomposites were fabricated by one-pot emulsification method. $AgNO_3$ are both silver source and initiator for polymerization of MMA. The polymerization took place when the Ag^+ was reduced to Ag. The microstructures of the nanocomposites were characterized by TEM, XRD, FTIR, and AFM.

Nanosized metallic particles have been extensively studied during the past years because of their promising physical and chemical properties, which could lead to a wide range of technologically important applications. Therefore, the preparation of nanosized metallic particles of high quality is receiving much attention.[1–3] 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), catalysis, biochemistry, or potential uses as chemical sensors, etc.[4–6] Up to now, several routes have been explored for such core-shell particle fabrication, including in situ chemical reduction,[6,7] self-assembly,[8,9] LBL (layer-by-layer) technology,[10,11] sol–gel method[12] and sonochemical synthesis,[13] etc. However, in most cases, a general strategy based on a two-step process, involving the combination of surface seeding and subsequent shell growth, has been proposed. These approaches required complicated apparatus and complex process control. Here we reported a “one-pot” route to prepare metal “shell,” polymer “core” nanocomposites by chemical reduction method. In this process, Ag/PMMA “shell/core” nanocomposites were successfully synthesized without typical initiation. Compared with previous methods of preparing “shell-core” nanocomposites, the route presented here is simpler and more effective, which may stimulate technological interests.

The preparation procedure of the Ag/PMMA “shell-core” nanocomposite is as follow: 1 g of polyoxyethylene octylphenolether (OP-10) was dissolved in 20-mL of distilled water at room temperature by magnetic stirring. Then 4 mL of methyl methacrylate (MMA) was dropped into the solution under stirring for a few minutes to form an emulsion. 2 mL of 0.01 mol/L CH_3CH_2SH in ethanol was added dropwise to the emulsion under stirring for about a hour. Then 30 mL of freshly prepared 0.004 M $AgNO_3$ aqueous solution was added to the emulsion under stirring. To the resulting emulsion, 30 mL of freshly prepared 0.4 mol/L $NaBH_4$ aqueous solution was added all at once.

The formation of the “shell-core” structure is illustrated in Scheme 1. The mercaptoethanol plays an important role in the process of forming silver-shell. It functionizes the surface of the MMA droplet, which is favorable to form Ag–S covalent bond. The formation of the PMMA core may be initiated by the redox system composed of $AgNO_3$ and $NaBH_4$, which initiates the polymerization of MMA monomer. The mechanism of the polymerization is still under consideration.

FTIR spectrum in Figure 1 shows absorption bands at about 2950 cm^{-1} for the C–H stretching vibration, and at 1460 cm^{-1} for the C–H transmutation vibration of CH_3. Two strong characteristic peaks locate at 1730 cm^{-1} and 1150 cm^{-1}, can be attributed to C=O absorption bands. All these characteristic peaks are quite consistent with the IR absorption of PMMA.[14]



Scheme 1. The fabrication procedure of Ag/PMMA “shell-core” structure. (sample No. 2 in Table 1)

It can be seen from Figure 2 that the XRD pattern shows two broad reflection peaks at 2θ of ca. 38.25° and ca. 44.60°, which correspond to the 111 and 200 planes of the silver nanocrystals with cubic symmetry.[15]

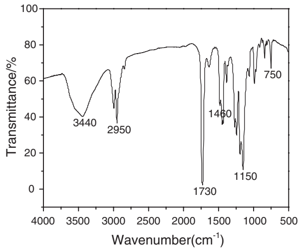


Figure 1. FTIR spectrum of the shell-core Ag/PMMA nanoparticles. (sample No. 2 in Table 1)

As can be seen from TEM image in Figure 3, the average size of the nanoparticles is about 70 nm in diameter. The strong contrast between the dark edge and the misty center exhibits its core-shell nature with the shell thickness of ca. 10 nm.

The amplitude-detection data of AFM in Figure 4 clearly show that the particles are of sphere with the particle size of ca. 90 nm, which is quite consistent with the result of TEM observation.

To record a phase image, the phase lag of the cantilever vibration compared to the z-piezo drive voltage is monitored as the probe scans the surface with a preset constant amplitude of vibration. The phase data contain additional information about the tip–sample interactions resulting from adhesion, surface

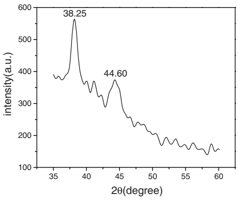


Figure 2. XRD patterns of the shell-core Ag/PMMA nanoparticles. (sample No. 2 in Table 1)

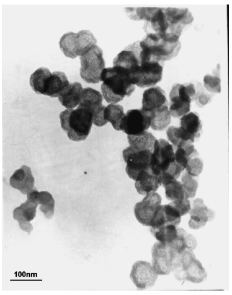


Figure 3. TEM image of the shell-core Ag/PMMA nanoparticles with the average size of ca. 70 nm and the shell thickness of ca. 10 nm. (sample No. 2 in Table 1)

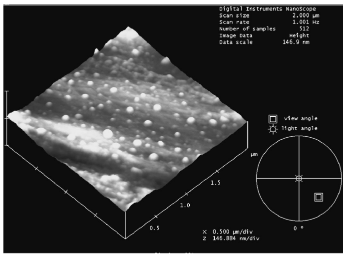


Figure 4. 3D Amplitude-detection image of AFM for the shell-core Ag/PMMA nanoparticles. The particles is of sphere with the particles size of ca. 90 nm. (sample No. 2 in Table 1)

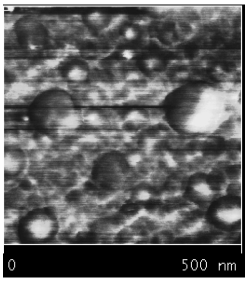


Figure 5. Phase-detection image of AFM for the shell-core Ag/PMMA nanoparticles. (sample No. 2 in Table 1)

stiffness, and viscoelastic effects.[16] It can be seen from Figure 5 that the dark and bright regions in the AFM image clearly define the two-phase structure of the nanoparticle. We estimate that the bright region is silver and the dark PMMA.

Table 1. The influence of preparation condition on the size of the nanoparticles

Sample	$AgNO_3$ (mmol/L)	$AgNO_3/CH_3CH_2SH$ (molar ratio)	Number average size (nm)	Peak width
1	30.00	6/1	70.92	19.20
2	4.30	6/1	62.39	15.91
3	4.30	1/1	50.02	12.86
4	0.43	6/1	2.46	0.66

$AgNO_3/NaBH_4$ (molar ratio) = 1:14

Dynamic light scattering (DLS) with Malven Instruments is used to measure the size and distribution of the particle. The influence of preparation condition on the size of the nanoparticles is listed in Table 1. It can be seen that the size of the particle decreases with the decreasing of $AgNO_3$ concentration at given $AgNO_3/CH_3CH_2SH$ and $AgNO_3/NaBH_4$ molar ratios. When the concentration of $AgNO_3$ reduces to 10^{-1} mmol/L , the size of the particle sharply decreases to 2.46 nm. This may be because there are not enough free radicals formed by the redox system to initiate the polymerization of MMA. Therefore, the particle obtained may only consist of pure silver. The molar ratio of $AgNO_3$ to mercaptoethanol also brings influence to the size of the particle.

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