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# Novel method for the preparation of core–shell nanoparticles with movable Ag core and polystyrene loop shell

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**Abstract**

Core/shell nanoparticles with movable silver (Ag) core and polystyrene (PSt) shell (Ag@PSt nanoparticle) were successfully synthesized at room temperature and under ambient pressure via two steps: $\gamma$-irradiation and interfacial-initiated polymerization. Firstly, mono-dispersed Ag nanoparticles with diameters 20 nm were synthesized in inversed microemulsion by reducing silver nitrate under $\gamma$-irradiation. Then, Ag nanoparticles were coated with PSt via interfacial-initiated polymerization with cumene hydroperoxide/ferrous sulfate/disodium ethylenediaminetetraacetate/sodium formaldehyde sulfoxylate (CHPO–$Fe^{2+}$–EDTA–SFS) as the redox initiation pair. The resulted Ag@PSt nanoparticles were identified by transmission electron microscopy (TEM), dynamic light scattering (DLS), X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).


*Keywords:* Movable core; Core/shell; Interfacial-initiated polymerization; $\gamma$-irradiation

## 1. Introduction

Spherical colloids with hollow interiors have received considerable attention for their technological importance in many fields. They have potential applications such as the microencapsulation of catalyst, light fillers, low dielectric constant materials, acoustic insulation and photonic crystals as well as the controlled delivery and artificial cells [1–4]. Various procedures have been developed to prepare functional spherical colloids with hollow interiors and form a range of materials such as polymers, metals, carbons and other inorganic materials [5–7]. Notably, spherical colloids with hollow interiors have been studied with tailored properties in recent years. The spheres have mostly been synthesized by template strategies composed of the formation of an outer shell on silica or polymer spherical template and the subsequent removal of the templates.

An important aspect about hollow nanoparticles is their functionalization achieved by encapsulating guest species, which would endow them with diverse properties. Hollow nanoparticles functionalized with movable inorganic cores as novel nanostructures have been explored by several groups [8]. Xia and co-workers synthesized polymer hollow spheres having the movable interiors of gold microparticles, which is a novel functional hollow organic sphere structure [9]. Oh et al. reported another example of tin metal particles encapsulated with spherical hollow carbon [10]. Zhang et al. [11] prepared hollow $TiO_2$ nanospheres with movable silica nanoparticles inside. The hollow spherical structure prevents the aggregation of functional microparticles and provides a profitable space for the functional microparticles in the practical application.

The earlier literatures also reported the core–shell spheres with movable metal cores, including Ag(Cu) core rattle-type silica particles [12], Au@polymer [9,13], Au@silica [9,15] and Au@carbon [9,14,15]. Among them, Ag nano-particles have attracted a great deal of interest in recent years because these materials are good candidates that can be applied for optics [16], electronics [17] and

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catalysis [18]. Various silver hybrid materials have been successfully synthesized: Ag@C core/shell-structured nanoparticles [19], polystyrene (PSt) spheres coated with Ag [20], AgCl@polypyrrole-Chitosan core–shell nanoparticles [21], silver-halide/organic-composite structures [22].

Here, we report a novel method for preparing core–shell spherical colloids with movable Ag cores coated with PSt by the combination of $\gamma$-irradiation and redox interfacial-initiated polymerization. By this method, we have successfully synthesized multi-layers magetic hybrid materials of PSt/PAM core/shell particles coated with NiS clusters [23]. However, such an approach remains to be extended to other metal composites.

## 2. Experimental

### 2.1. Chemicals

Styrene (St) was distillated under vacuum and kept in a refrigerator before use. Cumyl hydroperoxide (CHPO), ferrous sulfate hydrate ($FeSO_4 \cdot 7H_2O$), disodium ethylenediaminetetraacetate (EDTA), sodium formaldehyde sulfoxylate (SFS) isopropyl alcohol, silver nitrate ($AgNO_3$), polyvinylpyrrolidone (PVP) and sodium dioctyl sulfosuccinate (AOT) are all analytical reagents and used as received.

### 2.2. Preparation of the silver nanoparticles by $\gamma$-irradiation

To prepare silver nanoparticles, $AgNO_3$ (0.003 mol), PVP (0.005 g), and isopropyl alcohol (0.025 mol) were dissolved in distilled water (4.0 ml) and the solution obtained was added into 0.15 mol/L AOT/hexane solution (40 ml) to form inversed microemulsion by the aid of a supersonic cleaner. After the microemulsion was transferred into a 50 ml container and was bubbled with $N_2$ for 40 min to eliminate oxygen, it was sealed and irradiated under $\gamma$-ray with 110 Gy/min for 24 h. The resulted microemulsion was named as emulsion A.

### 2.3. Preparation of Ag@PSt spheres via interfacial-initiated polymerization

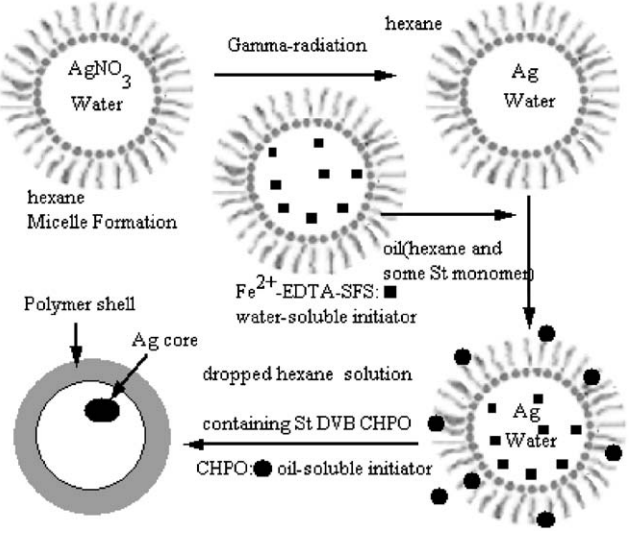
In order to introduce the reducing reagent of $Fe^{2+}$–EDTA–SFS into the dispersion phase of emulsion A, $FeSO_4 \cdot 7H_2O$ (60 mg), EDTA (10 mg) and SFS (10 mg) were dissolved in distilled water (4.0 ml). The resulted solution was added into 0.15 mol/L AOT/hexane solution (40 ml) to form inversed emulsion B. The mixed microemulsion of emulsions A and B was heated to 35 °C while being purged with nitrogen for 2 h. The oil-soluble solution of St (1.5 g) and CHPO (100 mg) in hexane (10 ml) was added into in batch or continuously with a Sp1001 syringe pump in 5 h. The water-soluble $Fe^{2+}$–EDTA–SFS of the initiation system should react with the oil-soluble CHPO of the initiation system at the oil–water interface to form the radicals initiating the polymerization. EDTA was used to chelate Fe ions and SFS to reduce $Fe^{3+}$ to $Fe^{2+}$ during the redox polymerization [24,25]. The reaction continued for another 12 h to ascertain the limiting monomer conversion. Then the microemulsion was destabilized with ethanol. The precipitate was separated by centrifugation and washed repeatedly with hexane and ethanol to remove the surfactants. The morphology was observed under TEM and FESEM.

### 2.4. Characterization

Diffraction pattern of Ag nanoparticles and Ag@PSt hybrid particles were recorded on X-ray diffractometer (Rigaku D/max $\gamma$A) equipped with graphite monochromatic Cu$K\alpha$ radiation ($\lambda = 0.154178$ nm), at a scanning rate of 0.02°/s with $2\theta$ in the range of 10–70°. X-ray photoelectron spectroscopy (XPS) was recorded on X-ray photoelectron spectrometer (ESCALAB MKII) using a non-monochromatic Al$K\alpha$ radiation (1486.6 eV) under high vacuum about $10^{-11}$ mbar. The transmission electron microscopy (TEM) and electron diffraction (ED) images were performed on a Hitachi model H-800 transmission electron microscope with an accelerating voltage of 200 kV. The morphology of Ag@PSt hybrid particles was also observed on a field-emission scanning electron microscopy (FESEM, JEOL JSM-6700) with the acceleration voltage of 5 kV. The particle size and its distribution were determined on a modified commercial laser light scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-$\tau$ digital time correlator and a He–Ne laser (output power = 10 mw at 632 nm).

## 3. Results and discussion

Ag@PSt nanoparticle were prepared by a novel method as shown in Scheme 1. This novel approach has two




Scheme 1. Schematic synthesis of Ag@PSt nanoparticle.

essential features: (1) the synthesis of silver nanoparticles by reducing $AgNO_3$ by $\gamma$-irradiation via inversed microemulsion; (2) in situ preparing PSt encapsulation around silver nanoparticles to form Ag@PSt nanoparticle through interfacial-initiated polymerization of styrene at the water–oil interface.

During the irradiation of $AgNO_3$ inversed microemulsion under $\gamma$-rays, the radiolysis of water produces many active species such as $e^-_{aq}$, $H\cdot$, and $\cdot OH$. Then, $e^-_{aq}$ could reduce $Ag^+$ to Ag. Meanwhile, isopropyl alcohol could eliminate the influence of oxidative radicals on the formation of Ag. The inversed microemulsion acted as a microreactor to form nanoparticles. The possible reactions are described as follows:

Radiolysis of water :

$$H_2O + \gamma \rightarrow e^-_{aq},\ H\cdot,\ \cdot OH,\ H_3O^+,\ \text{etc.},$$

Combination :

$$Ag^+ + e^-_{aq}(H\cdot) \rightarrow Ag,$$

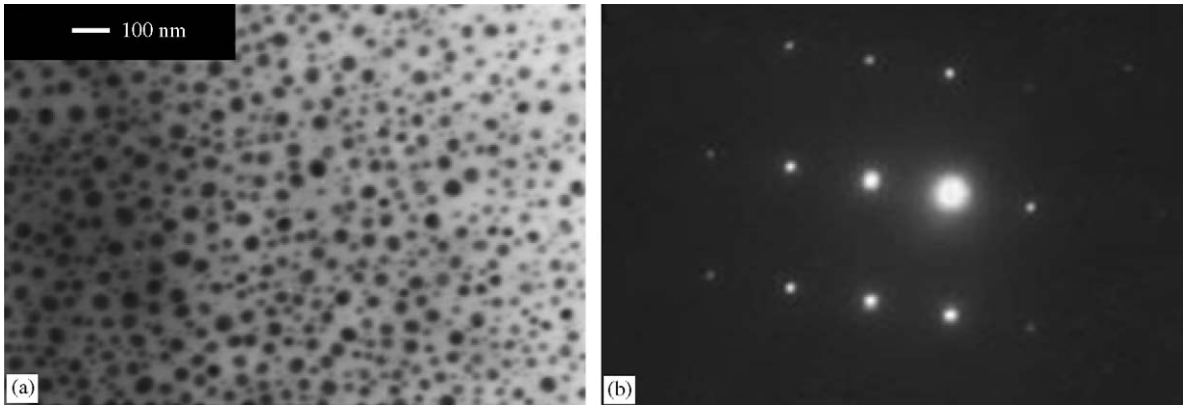



Fig. 1. TEM image (a) of and electron diffraction pattern (b) of silver nanoparticles.

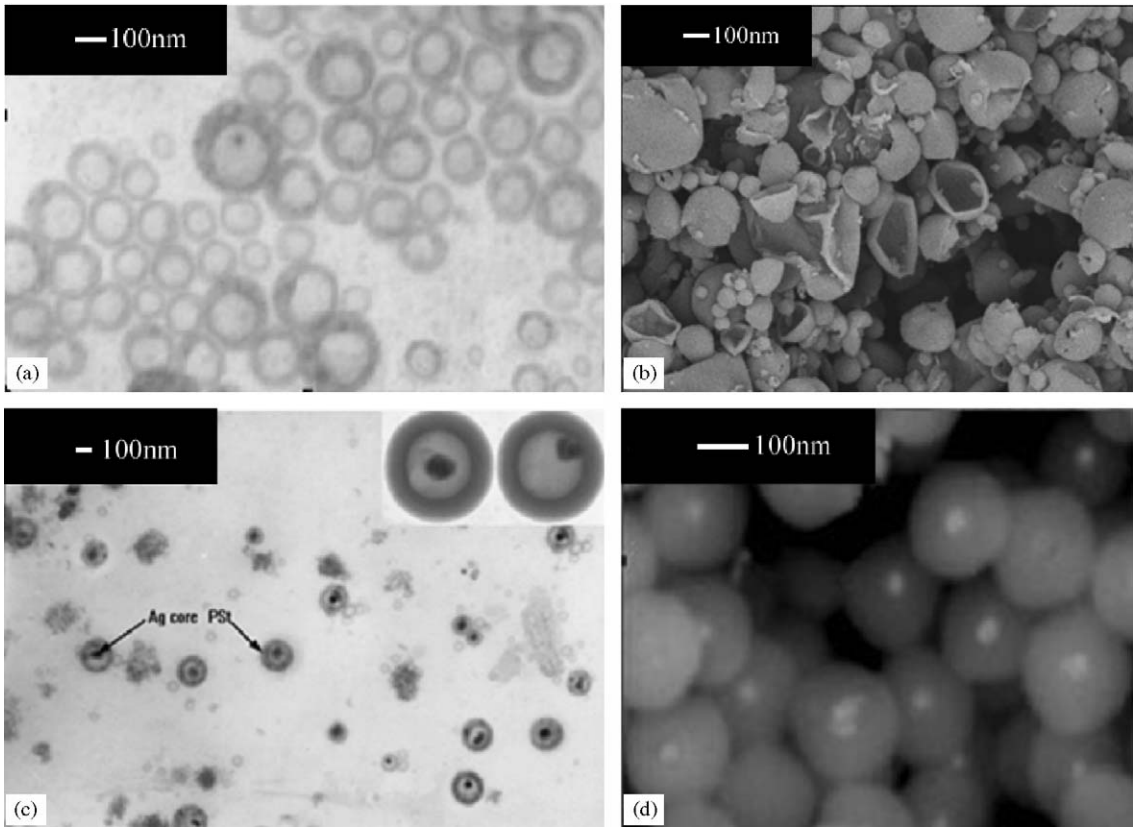



Fig. 2. TEM image (a) and FESEM image (b) of PSt hollow nanoparticles; TEM image (c) and FESEM image (d) of Ag@PSt hybrid nanoparticles.

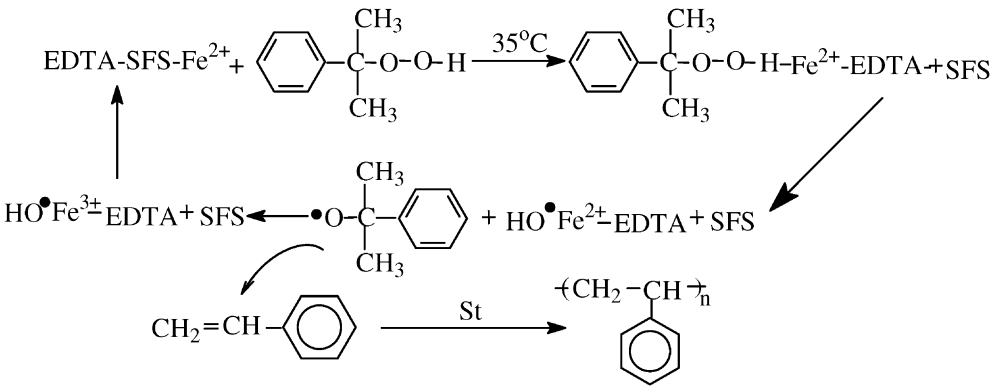



Fig. 3. Schematic representation of St polymerization by redox initiation system.

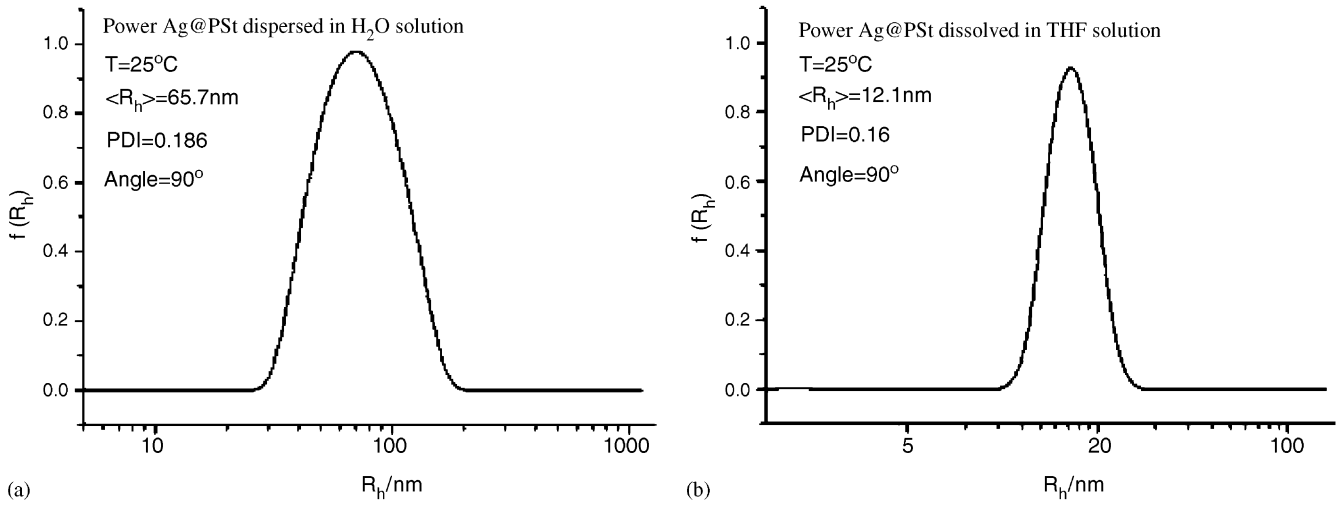



Fig. 4. Hydrodynamic radius distribution ($f(R_h)$) of Ag@PSt hybrid nanoparticles in water (a) and in THF (b).

Aggregation :

$$Ag + nAg^{+} \rightarrow Ag_{n+1}^{n+},\ Ag_{n+1}^{n+} + ne_{aq}^{-} \rightarrow Ag_{n+1}.$$

Some oxidative radicals such as $\cdot OH$ were scavenged by isopropyl alcohol:

$$\cdot OH + CH_3CH(OH)CH_3 \rightarrow H_2O + (CH_3)_2(OH)C\cdot$$

A typical TEM image of silver nanoparticles synthesized by reducing $AgNO_3$ by $\gamma$-irradiation is shown in Fig. 1a. The diameter is about 20 nm. The electron diffraction pattern of the same specimen is shown in Fig. 1b.

In our previous works, we have synthesized PSt hollow nanoparticles through this one-step interfacial-initiated emulsion polymerization [26] in the absence of silver nanoparticles. Fig. 2a shows TEM image of PSt hollow nanoparticles obtained by this method, with the diameter of hollow spheres being 70–150 nm and the shell thickness about 10–20 nm. Fig. 2b shows FESEM image of PSt hollow spheres and hollow structure with broken shell can be identified. In this article, Ag@PSt nanoparticles were

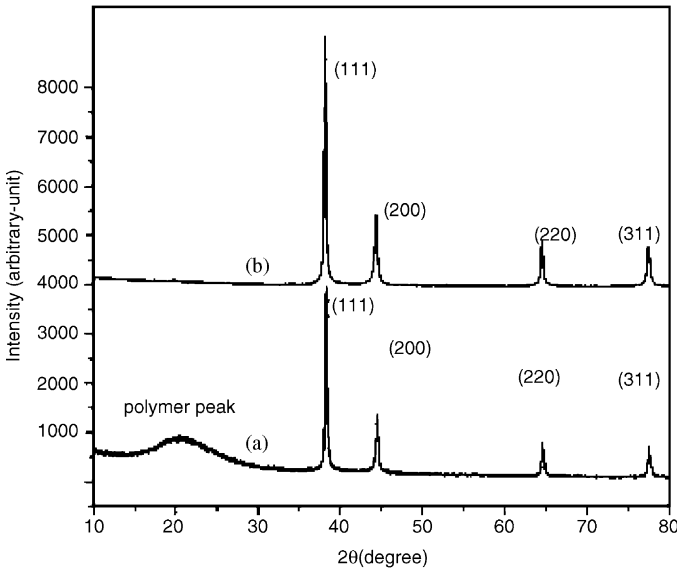



Fig. 5. XRD pattern of Ag@PSt hybrid nanoparticles (a) and silver nanoparticles (b).

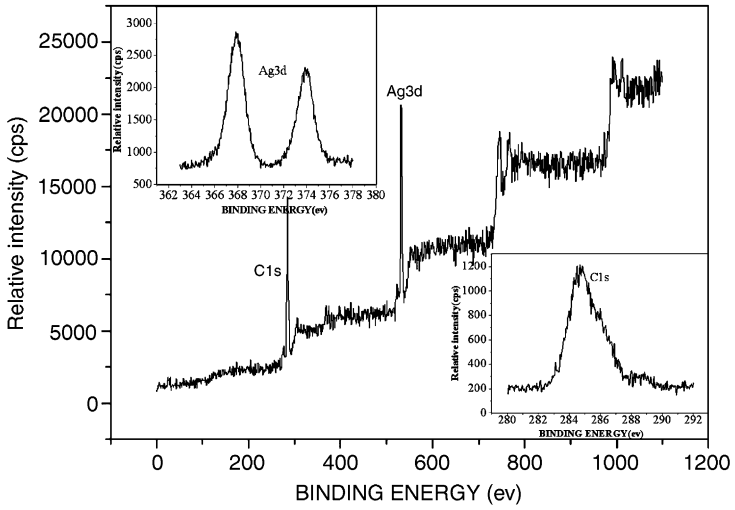



Fig. 6. XPS spectrum of Ag@PSt hybrid nanoparticles.

prepared through the same route in the presence of silver nanoparticles and their TEM image is shown in Fig. 2c, demonstrating clearly the hollow structure with Ag interior (black core) and PSt outer loop. Fig. 2d shows FESEM image of Ag@PSt hybrid nanoparticles. Compared with PSt hollow particles, Ag@PSt hybrid nanoparticles are much more uniform with the diameter of about 120 nm and the thickness of about 25 nm. The results indicate the influence of pre-existing silver nanoparticles on interfacial-initiated emulsion polymerization of St.

In this interfacial-initiated emulsion polymerization, the reducing component of $Fe^{2+}$–EDTA–SFS in the redox initiator system is water-soluble while the oxidant component of CHPO is oil soluble and has the tendency to migrate into water due to hydroperoxide group. Both the components meet each other mainly at the interface of the microemulsion reactor and produce the primary radicals, initiating the polymerization of St nearby. Due to the poor solubility of hexane, PSt chains would entangle each other to result in a PSt loop shell. A schematic representation of the reaction can be seen in Fig. 3.

Dynamic light scattering (DLS) data also offers the evidence to illuminate Ag@PSt hybrid nanoparticles. Before DLS measurement, Ag@PSt nanoparticles were re-dispersed in distillated water and THF (PSt shell will be dissolved in THF), respectively. A filter with the pore size of 0.80 μm was used to eliminate any dust. Hydrodynamic radius ($R_h$) and its distribution ($f(R_h)$) are demonstrated in Fig. 4. $R_h$ of Ag@PSt hybrid nanoparticles in water and THF was determined as 65.7 and 12.1 nm, respectively. They are in good accordance with TEM results.

The as-prepared silver nanoparticles and Ag@PSt hybrid nanoparticles were identified by X-ray powder diffraction (XRD) as shown in Fig. 5. All the four broad peaks at $2\theta = 38.2^\circ$, $44.3^\circ$, $64.6^\circ$ and $77.7^\circ$ are similar to the standard (JCPDS card file no. 4−783+), indicating the cubic phase of silver nanoparticles. The broader part in Fig. 5b may be attributed to the amorphous polymer of PSt.

The chemical composition of Ag@PSt hybrid nanoparticles was determined using XPS analysis as shown in Fig. 6, revealing that the nanoparticles are composed of Ag and C. The electron binding energy of $Ag_3d$ and $C_{1s}$ is 368.00 and 285.20 eV, respectively, confirming that the valence state of Ag is zero.

## 4. Conclusion

In conclusion, intact Ag@PSt hybrid nanoparticles with movable Ag interiors have been successfully fabricated under ambient conditions via two steps: the reduction of $AgNO_3$ to silver nanoparticles under $\gamma$-irradiation and interfacial-initiated polymerization to form PSt shell. Electron microscopy, DLS, XRD and XPS confirmed the build-up of hollow hybrid nanoparticles with movable silver particles. The results demonstrated that the reduction under $\gamma$-irradiation in microemulsion is a feasible way to synthesize metal nanoparticles and interfacial-initiated polymerization in the presence of silver nanoparticles to form a polymer loop around.

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