ABSTRACT

To avoid the loss of precious metal catalysts on carriers, a simple approach is introduced for silver colloids having 'anchorages' hooked onto inorganic substrate surfaces. This method is based on the nanoreactor of solubilized copolymer micelles for the fabrication of Ag sphere particles. The hydrolysis of tert-butyl acrylate yields acrylic acid and a tri-block copolymer polystyrene-\(b\)-poly(acrylic acid)-\(b\)-poly(\(\gamma\)-methacryloxypropyltrimethoxysilane) (PS-PAA-PMPS), with PMPS as active functional moieties, was synthesized and characterized which can play strong interaction with inorganic substrates surface as an "anchorage". The PS-PAA-PMPS copolymer solution was prepared to solubilize metal salts to prepare nanoparticles as nanoreactors for in situ reduction. The degree of solubility increased with the increased hydrophilic PAA units but it was also restricted by its dimensional size resisting solubilization. Spherical particles in diameters of 10~30 nm were well dispersed and SEM images showed the hybrid silver colloids remaining on the glass substrate due to their firm adherence after elution. It was demonstrated that this special polymer-protected system provides a successful way for nanoparticles to form anchorage onto the glass surface with firm adhesion and stable properties. This kind of silver colloids conveniently form firm and stable coatings onto the glass substrate which might give longer service life as catalysts to be used in electromagnetic interference shielding, anti-microbial uses and catalytic reduction of p-nitrophenol.

INTRODUCTION

Metal nanoparticles which provide important building blocks for the construction of functional structures have been extensively investigated for their unique properties [1]. Metal colloids have valuable properties for preparing films, coatings, fibres, etc., to extend the prospects of potential applications [2].

There are many works focused on amphiphilic copolymers and their assemblies in selective solutions. It is shown that carrier systems could be designed for noble metallic nanoparticles to adjust their catalytic activity [3]. Nano-size particles of Ag and Au [4], Co and some alloys were synthesized as micellar copolymers or colloidal grid networks [5]. Silver nano-particles (Ag NPs) have excellent electrical conductivity, electromagnetic interference shielding, anti-microbial effects [6,7], optical properties and surface-
enhanced Raman scattering (SERS)\[8,9\]. Supported silver catalyst is commonly used in oxidation catalysis process [10] and medical sensors or photothermal cancer therapy [11].

Chemical reduction, UV irradiation [12,13], ultrasonication technique [14], radiolytic process [15] and polyol method [16] have been studied and developed in order to obtain silver particles with narrow size distribution and uniform shape [17]. Chemical reduction [8] has been widely studied since it is economical and convenient. Hypermolecular system has been used to achieve catalytically stable metal colloids, though deficient interaction adhering to the carrier leads to the lapse of ingredients. Silane block was introduced into the copolymer system as reacting groups to connect colloids onto surfaces [18].

Ag NPs are obtained by various methods [19], especially when micelles are produced as nano-reactors are considered as efficient method [20]. In the present study, we synthesized Ag colloids in PS-b-PAA-b-PMPS micelles. Many other research works mainly focus on the preparation and performance of metal colloids. However, we have paid attention to another problem, i.e., "protection from lapsing". γ-Methacryloxypropyltrimethoxysilane (MPS) is a useful silane which can achieve strong interfacial bonding to the substrate. The introduction of MPS blocks has provided "anchoring points" for adhering to the silicate substrates to enhance the interaction, thus, increased the possibility of strengthening the anti-lapse performance when used as catalyst and carriers [21].

Poly(γ-methacryloxypropyltrimethoxysilane) (PMPS) is usually synthetized via Wurtz-coupling reaction. In this case ATRP [22] was used for its polymerization in mild condition and simple operation, and besides it has been proved that PMPS has tendency to graft onto the fibres surface [23,24]. A solution of PS-b-PAA-b-PMPS was prepared to solubilize AgNO₃ and triethylsilane (Et₃SiH) was used to conduct a chemical reduction process. By use of a coupling agent such as block PMPS as "hook-up", it performs as modulus transfer uniformly to deeper layers and effectively bond to the inorganic substrates such as metals, silicate and ceramics. Ultimately, it shows the ability to reduce the lapse of active ingredients and improve the efficiency of the colloid catalysts.

**EXPERIMENTAL**

**Materials**

Styrene, NaBH₄, and petroleum ether, analytically pure (AP) were purchased from Lingfeng Chemical Reagent Co. Ltd., Shanghai, China. Lunar caustic (AP) was stored in brown reagent bottle. tBA and Et₃SiH were purchased from Sigma-Aldrich (USA) with a purity of 99% and used without further treatment. MPS (98%, Kexing Chemical Reagent Co., Shanghai, China) was used directly. Xylene and dioxane (AP, Sinopharm Shanghai Medical Instrument Co. Ltd.) were dried over 3Å molecular sieve and stored in a freezer after vacuum distillation. Hydrochloric acid (36.5 wt%) and phosphotungstic acid (2 wt%) were used as aqueous solutions.

**Synthesize of PS₁₅₃-b-PAA₄₁-b-PMPS₁₅**

A sample of PS₁₅₃-b-PtBA₄₁-b-PMPS₁₅ was synthesized according to a process reported in literature [25]. In brief, a solution mixture of polymers made in dioxane with a three-fold excess of concentrated hydrochloric acid was heated to reflux for 24 h. After precipitation in petroleum ether (boiling range 90~120°) the final product PS₁₅₃-b-PtBA₄₁-b-PMPS₁₅ was obtained and dried under vacuum at room temperature till constant weight. ¹H NMR (Bruker DPX-500, Germany) was conducted to testify the structures of the hydrolysis products, using CDCl₃ as solvent and TMS as the internal standard.

**Solubilization of AgNO₃ and Chemical Reduction of Silver Colloids**

An amount of PS₁₅₃-b-PAA₄₁-b-PMPS₁₅ was dissolved in dioxane/xylene whose volume fraction was 1/9. AgNO₃ was added to the solution in brown-coloured reactor and surged by ultrasonic sufficiently. The solubilization was studied by "Mohr method". Et₃SiH was added (n Et₃SiH/n AgNO₃ = 20/1) and the residual AgNO₃ was removed by a centrifuge. The samples were stained with phosphotungstic acid before conducting transmission
electron microscopy (TEM) using TECNAI F2 (FEI Company, USA).

**Coating on Glass Substrate**
The solution containing silver particles was coated on a glass substrate and dried repeatedly for about 5 times. It was then eluted with dioxane for 2 days, exposed in air and protected from light for a week. Scanning electron microscopy (SEM) (Jeol JSM-6360LV, Japan) was conducted and Fourier infrared laser spectroscopy (FT-IR) spectra were recorded using a Nicolet 550 IR, USA.

**RESULTS AND DISCUSSION**

**Synthesis of PS\textsubscript{153-}b-PtBA\textsubscript{41}-b-PMPS\textsubscript{15}**
A sample of PS\textsubscript{153-}b-PtBA\textsubscript{41}-b-PMPS\textsubscript{15} was synthesized by ATRP. Table 1 presents the characterization of the copolymer by a Waters 150C gel permeation chromatogram (GPC) (USA). During the hydrolysis process, PtBA block was absolutely hydrolyzed into PAA block, meanwhile, a tiny amount of PMPS block was unavoidably hydrolyzed because this coupling agent is sensitive to water. Figure 1 displays a typical \textsuperscript{1}H NMR spectrum of PS\textsubscript{153-}b-PtBA\textsubscript{41}-b-PMPS\textsubscript{15} in CDCl\textsubscript{3}. The incorporation of the PS block is illustrated by the appearance of a polymeric phenyl proton (Ph) peak at 6.3-7.25 ppm. The appearance of CH\textsubscript{3}O-peak at 3.5-3.8 ppm demonstrates that the PMPS block has not been hydrolyzed completely and therefore it can be used in suspension form.

As a result, Si-O-CH\textsubscript{3} group disappeared after γ-MPS hydrolysis where the reactive Si-OH groups were produced [26]. Here, the fraction was very low and therefore it was ignored and the structure of hydrolytic product PS\textsubscript{153-}b-PtBA\textsubscript{41}-b-PMPS\textsubscript{15} may be given as in Scheme I.

**Solubilization of AgNO\textsubscript{3}**
Most metal ions can be exchanged with the H\textsuperscript{+} in the carboxylic acid groups, since the formation of bond between metal ions and carboxylate ions is thermodynamically favourable [17]. During the solubilization process, AgNO\textsubscript{3} was added to the copolymer solution and carboxylic acid groups acted as functional groups

### Table 1. Characteristics of PS\textsubscript{153-}b-PtBA\textsubscript{41}-b-PMPS\textsubscript{15}.

<table>
<thead>
<tr>
<th>Structures of polymer</th>
<th>$\bar{M}_w$</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w/\bar{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS\textsubscript{153-}Br</td>
<td>1.68$\times$10\textsuperscript{4}</td>
<td>1.6$\times$10\textsuperscript{4}</td>
<td>1.049</td>
</tr>
<tr>
<td>PS\textsubscript{153-}b-PtBA\textsubscript{41}-Br</td>
<td>2.25$\times$10\textsuperscript{4}</td>
<td>2.12$\times$10\textsuperscript{4}</td>
<td>1.063</td>
</tr>
<tr>
<td>PS\textsubscript{153-}b-PtBA\textsubscript{41}-b-PMPS\textsubscript{15}</td>
<td>2.63$\times$10\textsuperscript{4}</td>
<td>2.29$\times$10\textsuperscript{4}</td>
<td>1.149</td>
</tr>
</tbody>
</table>

![Figure 1. \textsuperscript{1}H NMR Spectrum of PS-b-PAA-b-PMPS.](image)

![Scheme I. Structure of hydrolytic product of PS-b-PAA-b-PMPS.](image)
to chelate metal ions. The method is widely used for the synthesis of silver particles [27]. Figure 2 presents the FTIR spectrum of PS-b-PAA-b-PMPS/Ag⁺ solution. With formation of carboxylates, the original C=O stretching, O-H stretching and asymmetrical bending vibrations almost disappear. The sharp bands at 1455.8 cm⁻¹ and 1376.8 cm⁻¹ indicate the presence of carboxyl groups, corresponding to the formation of a complex between the carboxyl and silver ions.

Micelles were assembled in dioxane/xylene to form a nanometer-sized reactor [28]. By increasing the concentrations of the micelles or the Ag⁺ ions the system is favourable for the formation of the Ag particulate shape [29] we used micelle solution to enhance the migration of greater number of Ag⁺ into the core.

Figure 3 shows that AgNO₃ is insoluble in organic solvent such as dioxane/xylene and it dissolves gradually because of the formation of micelles. Micro-titration was conducted taking potassium chromate as tracer agent and silver chromate precipitate as end point of the titration, and the solubilization capacity of AgNO₃ was then calculated. The degree of solubility increases with the increased hydrophilic PAA units but also restricted by dimensional size resisting solubilization.

**Reduction of Silver Ions**

Chemical reduction process was conducted under reducing rate using Et₃SiH and nano-sized silver particles were obtained. The XRD pattern (Figure 4) is displayed to prove the presence of Ag nanocrystals. As previously studied, silver oxide has peaks at 2θ = 26.7°, 32.8°, 38.2° and 32.3°, 34.2° and 37.9° [30].

Figure 4 is the XRD pattern of the colloids after eluted with dioxane for 2 days. It is shown in Figure 4 that three diffraction peaks are observed at 2θ = 38.2°, 44.3°, 64.5° which correspond to (111), (200) and (220) of the given order face centered cubic (fcc) structure of metallic Ag particles. The peaks at about 27° and 32° are due to the presence of a trace amount of Ag₂O caused by high temperature of above
100°C when being eluted with dioxane. As there are no other Ag₂O peaks and the intensity of these two peaks is relatively low, it may be concluded that the metal colloids have strong anti-oxidation characteristics.

Representative TEM result of silver particles is shown in Figure 5. Silver colloids in 1 mg/mL PS₁₅₃-PAA₄₁-PMPS₁₅ (n Et₃SiH/n AgNO₃=20/1) in Figures 5a and 5b are presented as before and after reduction, respectively. Obviously, spherical particles with diameter of 10-30 nm are well dispersed. The mechanism of this process can be explained by the micelle effect. It is well known that self-assembly occurs when amphiphilic copolymers dissolve in selective solvents to form micelles with different morphology like spheres, rods, wires, vesicles or layers. In this system, functional groups take part in the formation of the cores. As a result, reduction process occurs inside the micelles.

From TEM images, we can observe that spherical micelles are formed during the dissolution of PS₁₅₃-PAA₄₁-PMPS₁₅ in dioxane/xylene. The blocks constitute the shell and steric and shielding effects prevent particles from aggregation. As low reducing rate is favourable for maintaining the micelle morphology, stable silver colloids are obtained and therefore particles of high chemical stability are formed under the polymer protection.

**Adhesive Effect on Glass Substrate**

Here silane coupling agent was used to interact with the hydroxyl groups of glass surface for firm adhesion. Scanning electron microscopy (SEM) was conducted to examine the morphology of the surface of the glass substrate coating with colloid solution. Obviously shown in Figure 6, in contrast to the blank untreated glass, we can see that even after elution, the hybrid silver colloids have remained on the glass substrate.

**Figure 5.** Silver colloids reduced in 1 mg/mL PS₁₅₃-PAA₄₁-PMPS₁₅ (n Et₃SiH/n AgNO₃=20/1): (a) before and (b) after reduction.

**Figure 6.** SEM Micrographs of silver colloids suspended on glass substrate: (a) glass coating by silver colloids and (b) empty glass substrate.
substrate due to firm adherence. The morphology of most silver colloids takes a spherical shape and some partly collapse because of the volatilization of solvents. In conclusion, the polymer-protected nanoparticles with stable properties are successfully suspended inside the inorganic substrate.

FTIR was conducted to analyze the suspension effects. Figure 7 presents the proof that the "hook-up" plays an important role in adhering silver particles onto the glass surface. At 1020 cm\(^{-1}\) there is a strong absorption peak of Si-O-R skeletal vibration and the peak at 3361 cm\(^{-1}\) is assigned to stretching vibration of intermolecular association of hydroxyl groups between Si-OH groups.

Scheme II presents the formation of hydrogen bonds and stable covalent bonds (Me-O-Si). These interactions lead to the adherence of silver particles onto the substrate and uniform transfer of any applied stress. It was obvious that surface bond conjugations between PMPS blocks and the surface must have occurred as expected.

CONCLUSION

A sample of PS\(_{153}\)-PAA\(_{41}\)-PMPS\(_{15}\) with carboxyl functional groups was prepared by the hydrolysis of PS\(_{153}\)-PtBA\(_{41}\)-PMPS\(_{15}\), itself synthesized by ATRP, and nano-sized micelles were obtained using these well-designed amphiphilic copolymers. A solution of PS\(_{153}\)-PAA\(_{41}\)-PMPS\(_{15}\) was used for solubilization of AgNO\(_3\). The solubilization of micelles for AgNO\(_3\) was also dependent on the molecular structure and concentration of the polymers. The degree of solubility increased with the increase of hydrophilic units but still restricted by dimensional size resistance. Using Et\(_3\)SiH as a reducing agent, the regions of aqueous phase aggregation can be avoided which lead to more efficient protection of particles from aggregation. Hence, in this way nano-sized silver colloids were obtained. As a result of compact coverage of silver particles, the metal colloids have strong anti-oxidation characteristics. Consequently, by involving the silane coupling blocks as "hook-up", the colloids were conveniently adhered to the silicate substrates to enhance the interaction thus, increasing the possibility of strengthening the anti-lapse performance when being employed as catalysts and carriers. Our colloids not only help with the composition of nano-particles by uniform dispersion and morphology, but also protect the colloids from disintegration. In this way, there would be less wastage of active ingredients, increased shelf life and improve the efficiency of the colloid catalysts.

REFERENCES

1. Kazimierska EA, eCiszkowska M, Thermorespon-


