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Preparation of gold nanoparticles on poly(methyl methacrylate) nanospheres with surface-grafted poly(allylamine)

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Abstract

A facile method for in situ anchoring of gold nanoparticles onto the surface of polymer nanospheres was successfully developed in this study. As polymer nanospheres, amphiphilic poly(methyl methacrylate) (PMMA)/poly(allylamine) (PAA) nanospheres were prepared by graft copolymerization of methyl methacrylate from PAA. The gold nanoparticles anchored were spherically symmetric and the average sizes were ~12 nm for all samples. It was found that surface-grafted PAA effectively anchored and stabilized gold nanoparticles for a long period of time.

Keywords: Gold nanoparticles; Poly(methyl methacrylate) nanospheres; Poly(allylamine)

1. Introduction

The anchoring of metal nanoparticles onto the surface of polymer microspheres is drawing great attentions because it has potential applications in chemical, electronic, and optical sensors [1]. Chen et al. [2–5] in situ synthesized platinum or silver nanoparticles on poly(*N*-isopropylacrylamide)-coated polystyrene microspheres. They also showed that platinum nanoparticles had a higher activity than the commercial Pt/C catalyst. Dokoutchaev et al. [1] anchored various metal colloids onto the surface of polystyrene microspheres functionalized with amine or carboxylic acid groups.

Among the metal nanoparticles, gold nanoparticles have been extensively studied due to their potential applications in optoelectronics, electronics, catalysis, and other areas [6]. In order to prepare gold nanoparticles with small sizes, narrow size distributions, and stability, various stabilizers having a good interaction with their surface have been investigated [6–16]. Dokoutchaev et al. [1] reported that microspheres having a net positive charge after protonation of surface amine groups exhibited excellent adhesion of gold colloids. Leff et al. [7] used alkylamines to prepare organically soluble gold nanoparticles. Gold nanoparticles were also prepared with poly(amidoamine) dendrimers with surface amino groups, which act as a very effective protective colloid for stabilizing gold nanoparticles in the range of 2–3 nm with lower concentration compared to other linear polymers [11–14].

Recently, Li et al. [17] developed a novel method for the preparation of amphiphilic core-shell polymer nanospheres via graft copolymerization of methyl methacrylate (MMA) from water-soluble polymers containing amino groups such as branched polyethyleneimine, poly(allylamine) (PAA), chitosan, gelatin, bovine serum albumine, etc. They were prepared via one-step synthesis without any surfactant under concentrated conditions.

In this study, in situ anchoring of gold nanoparticles onto the surface of polymer nanospheres was investigated. As polymer nanospheres, amphiphilic poly(methyl methacrylate) (PMMA) nanospheres with surface-grafted PAA (PMMA/PAA nanospheres) were prepared via graft copolymerizations of MMA from PAA and gold nanoparticles were synthesized on their surface. It is expected that surface-grafted PAA would effectively stabilize gold nanoparticles for a long period of time.

2. Experimental

PAA (20% solution in water, M_w 65,000), *tert*-butyl

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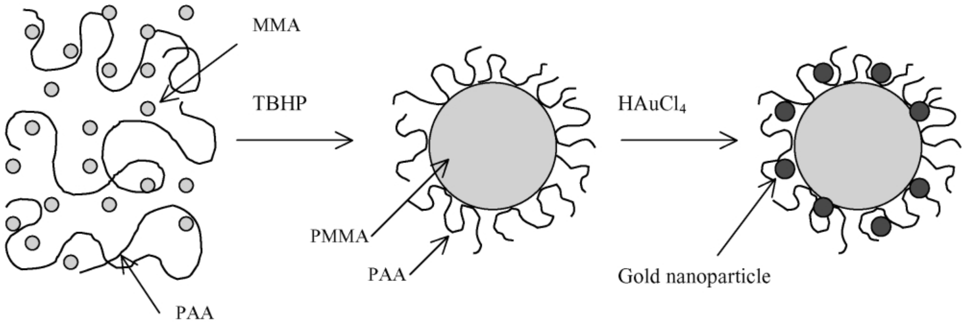

Fig. 1. Schematic representation of the formation of PMMA/PAA nanosphere and gold nanoparticles.

hydroperoxide (TBHP, 70% solution in water), MMA, sodium borohydride ($NaBH_4$), and hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$) were purchased from Aldrich Co. MMA was purified by vacuum distillation and freshly distilled and deionized water was used for the medium of graft copolymerization. PMMA/PAA nanospheres were prepared via direct graft copolymerization of MMA from PAA in the absence of surfactant. One gram of PAA solution was dissolved in 50 ml of water and mixed with 1 g of purified MMA. The mixture was sonicated for 10 min and purged with nitrogen for 30 min. 0.1 mM of TBHP was added to the mixture and stirred at 80 °C for 6 h under nitrogen. In order to prepare gold nanoparticles on PMMA/PAA nanospheres, 3 ml of a 1.0 N HCl solution was added to 5 ml of the solution of PMMA/PAA nanospheres to give a positive charge on the surface of PMMA/PAA nanospheres. To this solution was added 1, 2, or 3 ml of a $HAuCl_4 \cdot 3H_2O$ solution (6.0×10^{-3} mol) with vigorous stirring and then added an excess of $NaBH_4$ solution to reduce $HAuCl_4$. Gold nanoparticles not anchored on PMMA/PAA nanospheres, PMMA homopolymer, and unreacted PAA were removed by centrifugation at 10,000 rpm for 10 min. The centrifuged residue was redispersed in water and centrifuged two more times. The average diameter and distribution of PMMA/PAA nanospheres were determined by dynamic light scattering measurement (Brookhaven Instruments Inc.) with a He–Ne laser (673 nm) at a fixed scattering angle of 90°. The results were calculated using a non-negative least squares algorithm. When the difference between the measured and calculated baselines was less than 0.2%, the correction function was accepted. UV–vis. absorption spectra were obtained using a Perkin–Elmer UV–vis. spectrometer (Lambda 20). The formation and average particle sizes of gold nanoparticles were determined using a transmission electron microscope (Philips CM200).

3. Results and discussion

Fig. 1 shows schematic representation of the formation of PMMA/PAA nanosphere and gold nanoparticles on its surface. Li et al. [17] reported that amino radicals in PAA chains generated by TBHP initiated MMA graft copolymerization. The resulting amphiphilic copolymers act like polymeric surfactants and thus PMMA emulsion polymerized within the hydrophobic domains forms the core and PAA the shell. Dense and hairy hydrophilic shells of PAA on the PMMA particle, which should be expanded in the solution, were clearly observed under high TEM magnification [17]. In this study, the average diameter of PMMA/PAA nanospheres obtained was ~200 nm and they were monodisperse. PMMA/PAA nanospheres prepared were first treated with a 1.0N HCl solution to give a positive charge on their surface and then a $HAuCl_4$ solution was added with vigorous stirring, which was reduced to form gold nanoparticles with a $NaBH_4$ solution. During the reduction, the color of the solution changed immediately from yellow to red. In

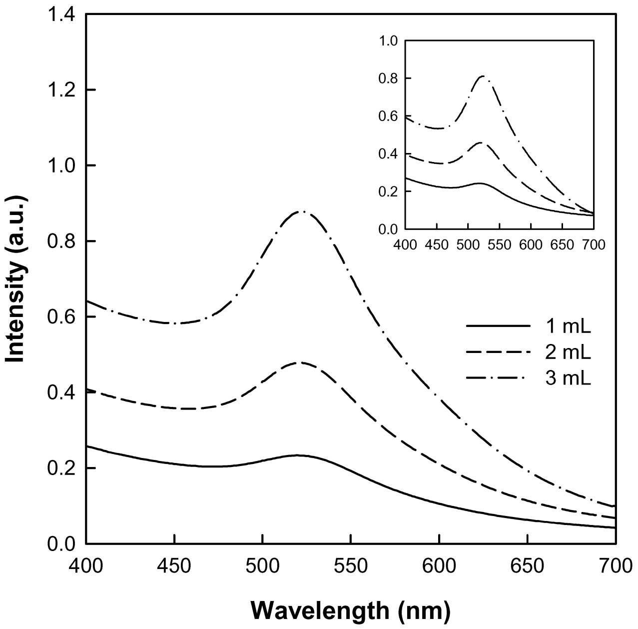

Fig. 2. UV–vis. absorption spectra of gold nanoparticles anchored on the surface of PMMA/PAA nanospheres with different amounts of the $HAuCl_4$ solution.

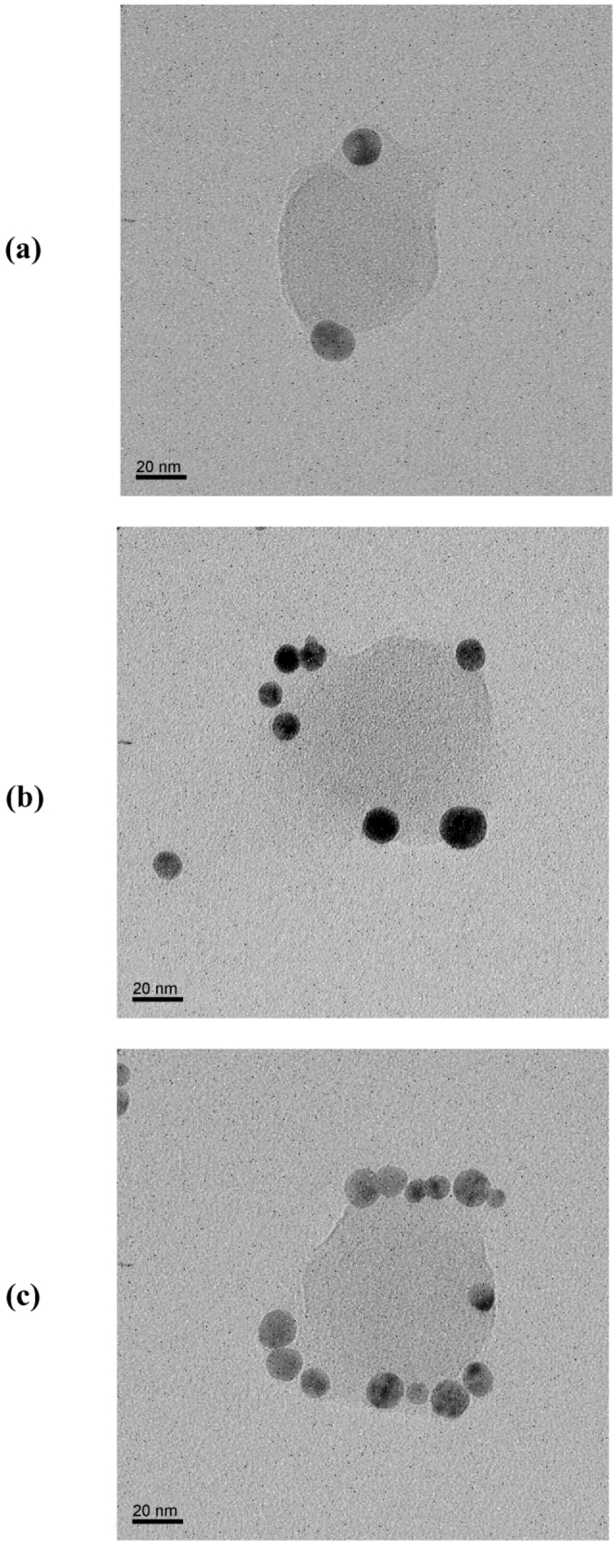

Fig. 3. TEM micrographs of gold nanoparticles on PAA/PMMA nanospheres synthesized with different amounts of the $HAuCl_4$ solution: (a) 1 ml, (b) 2 ml, and (c) 3 ml. The scale bars correspond to 20 nm.

order to remove gold nanoparticles not anchored on PMMA/PAA nanospheres, the solution was centrifuged. The centrifuged residue was completely redispersable in water, indicating surface-grafted PAA successfully not only stabilized gold nanoparticles but also prevented the flocculation of PMMA/PAA nanospheres.

Fig. 2 shows UV–vis. absorption spectra of gold nanoparticles anchored on the surface of PMMA/PAA nanospheres with different amounts of the $HAuCl_4$ solution. The distinct gold surface plasmon peak at around 520 nm was clearly observed for all samples. They showed almost the same peak position irrespective of the amount of the $HAuCl_4$ solution added, indicating they have almost the same average size of gold nanoparticles. Their intensity was increased with increasing the amount of the $HAuCl_4$ solution, although it is impossible to quantitatively compare them due to the centrifugation process employed to remove free gold nanoparticles in this study. The insert in Fig. 2 shows UV–vis. absorption spectra of gold nanoparticles on PMMA/PAA nanospheres obtained after 6 months. The gold surface plasmon peaks were not shifted with time, reflecting that gold nanoparticles were successfully stabilized by PAA chains.

The average size of gold nanoparticles on PMMA/-PAA nanospheres was determined by TEM. Fig. 3 shows TEM micrographs of gold nanoparticles on the PAA/PMMA nanosphere synthesized with different amounts of the $HAuCl_4$ solution. The average diameter of PMMA/PAA nanospheres was smaller than that measured on dynamic light scattering. It is considered that dense and hairy hydrophilic shells of PAA were well expended in the solution. All of the gold nanoparticles were spherically symmetric and the average sizes were ~12 nm for all samples. It was reported that the average size of gold nanoparticles was dependent on the interaction between stabilizer and gold surface rather than its architecture [9,12,16]. Interestingly, as the amount of $HAuCl_4$ solution added was increased, the number of gold nanoparticles anchored on the surface of PAA/PMMA nanospheres was increased rather than their size. This indicates that dense and hairy hydrophilic shells of PAA effectively stabilized $AuCl_4^-$ and the resulting gold nanoparticles. Although the centrifugation was carried out to remove free gold nanoparticles, some of them were observed in TEM analysis. However, extremely large gold nanoparticles remaining in the centrifuge residue were not detected.

In conclusion, gold nanoparticles were in situ synthesized on the surface of PAA/PMMA nanospheres. The surface-grafted PAA chains not only stabilized gold nanoparticles but also prevented the flocculation of PAA/PMMA nanospheres. It is expected that the size and number of gold nanoparticles can be controlled by changing the molecular weight of the starting PAA and remaining amino groups can be further derivatized to incorporate other important molecules.

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