SHORT COMMUNICATION

Synthesis of Phenolic Polymer-Coated Gold Nanoparticles

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Metal nanoparticles have drawn considerable interest in various fields such as material science, organic synthesis and biology because of their unique optical, electrical and catalytic properties resulting from quantum-scale dimensions.^{1–5}

For preparation of metal nanoparticles, typical procedure is reduction of metal ions in the presence of protecting agents. Protecting agents cover metal nanoparticles and inhibit agglomeration with the formation of large particles. Colloidal metal nanoparticles have been synthesized by using protecting agents such as phosphines,⁶ thiols,⁷ amines⁸ and carbon monoxide.⁹ By using organic polymers^{10–12} such as poly(vinyl alcohol) (PVA), poly(vinylpyrrolidone) (PVP), poly(vinyl ether) (PVE) and electron donating π -conjugated polymer, colloidal suspension of metal nanoparticles was obtained.

Herein, we report on phenolic polymer-coated gold nanoparticles (PMP/Au nanoparticles, Scheme 1). Phenolic polymers, which are classically synthesized by polymerization of phenol derivatives with formaldehyde, exhibit excellent thermo-setting, mechanical properties.^{13,14} In this study, by using phenolic polymer carrying thiol moiety (Scheme 1, PMP), stable dispersion of gold nanoparticles was prepared without any tangled steps. Gibson and coworkers reported mercaptophenol modified gold nanoparticles.⁷ However, their preparation method requires tangled steps and severe conditions due to its weak thermal stability.

For the synthesis of phenolic polymer-coated gold nanoparticles, phenolic polymer having thiol moiety was synthesized. To a mixture of mercaptophenol (1.26 g, 10 mmol) and paraformaldehyde (0.30 g, 10 mmol) in 2-ethoxyethanol (10 mL), catalytic sulfuric acid (1 mL) was added. The solution was heated at 100 °C for 2 h. By reprecipitation into water, poly(mercaptophenol) (PMP) was isolated (Molecular weight:¹⁵ $M_n = 1,100$, $M_w/M_n = 2.4$, Yield: 52%). PMP was soluble in methanol, acetone, THF and DMSO and insoluble in water, diethyl ether and chloroform.

The gold nanoparticles were prepared by reduction of HAuCl_4 in the presence of PMP. As a typical preparation of PMP-protected Au nanoparticles, HAuCl_4 (5.0 mg, 12 mmol) and PMP (5.0 mg) were dissolved into 2-ethoxyethanol (13 mL). To the mixture, NaBH_4 (1.0 mg, 26 mmol) in 2-ethoxyethanol (2 mL) was slowly added. The reaction mixture was stirred at 24 h at room temperature. During the stirring, the solution changed from yellow to red, indicating the formation of gold nanoparticles. In contrast, without PMP, precipitation of bulk Au was observed during the reaction. The observations indicate that PMP acts as protecting agent for the synthesis of gold nanoparticles. By using mercaptophenol or novolak resin instead of PMP, bulk Au also precipitated from the mixture. Protecting ability of PMP to inhibit aggregation of large particles is better than that of mercaptophenol or novolak resin. For the purification of PMP/Au nanoparticles, dialysis of the solution (Cut Off = 3,000) was carried out. The trends of solubility of PMP/Au nanoparticles were similar to that of PMP.

Figure 1 shows UV-Vis absorption spectrum of PMP/Au nanoparticles in 2-ethoxyethanol. Surface plasmon adsorption band at 522 nm was observed, indicating the formation of gold nanoparticles.

From high resolution transmission microscopy (HR-TEM), uniformly-sized nanoparticles were observed (Figure 2a). The average diameter of

Scheme 1. Schematic illustration of the formation of the PMP/Au nanoparticles via reduction of gold ions by NaBH_4 .

Figure 1. UV-Vis spectrum of PMP/Au nanoparticles in 2-ethoxyethanol.

PMP/Au nanoparticles was 4 nm (Figure 2b). From expanded HR-TEM images (Figure 2c and 2d), majority of the particles exhibited the lattice fringes, which represent the individual atomic layers. The d-spacing between the fringes was 2.3 Å, which was identified (111) crystalline planes of Au. From EDX measurement, Au on carbon grid was detected. From these observations, formation of gold nanoparticles was confirmed.

From FT-IR spectra, peak for the OH band of the pristine PMP is originally positioned at 3330 cm^{-1} and shifted to 3280 cm^{-1} in PMP/Au nanoparticles, strongly suggesting formation of hydrogen bonding between PMPs on surface of Au nanoparticle. In addition, disappearing of SH stretching band of PMP around 2560 cm^{-1} indicate formation of S-Au bonds between PMP and Au surface.

Figure 3 shows the ^1H NMR spectra of PMP and PMP/Au nanoparticles in $\text{DMSO}-d_6$. Signals from phenyl (7.38–6.50 ppm) and methylene protons (4.20–3.72 ppm) were broadening and appeared corresponding to those of the parent PMP, indicating that the motion of PMP were constrained due to connection of PMP on surface of gold nanoparticles. Proton signals from phenol moiety around 9.8 ppm disappeared in PMP/Au

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Figure 2. (a) HR-TEM image and (b) size distribution histogram of PMP/Au nanoparticles. (c, d) Expanded HR-TEM images of PMP/Au nanoparticles. The d-spacing fringes (2.3 Å) were observed.

Figure 3. ^1H NMR spectra of (a) PMP and (b) PMP/Au nanoparticles in $\text{DMSO}-d_6$.

nanoparticles, indicating that inter- and/or intra-hydrogen bonding between PMPs on gold nanoparticles formed and free PMP, which did not bind to the gold nanoparticles, was not involved.

Thermogravimetric analysis (TGA) established that the content of PMP in the PMP/Au nanoparticles was 73.7 wt %. Considering that the average particle size was 4.0 nm, the numbers of PMP unit adsorbed on the surface of each gold nanoparticle was estimated to be *ca.* 4700 on average.

In conclusion, we synthesized phenolic resin having thiol moiety (PMP) and phenolic polymer-coated gold nanoparticles. To the best of our knowledge, phenolic polymer carrying thiol groups was little known and will be applied for protecting agents of the other metal nanoparticles. The obtained gold nanoparticles have phenol moiety, which are able to form hydrogen bonds with various organics and metal ions.¹⁶ Therefore, they will be applied for chemically responsive optical sensors by use of aggregation-induced color changes of the gold nanoparticles. Due to high functionality of phenol groups *via* esterification and etherification under mild conditions,⁷ various kinds of functional groups will be easily conjugated on gold surface. By crosslinking between PMP chains by adding cure agent and then removing gold nanoparticle template, hollow phenolic nanoparticles will be obtained. This is now under investigation.

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