

## Reversible Formation and Dissolution of Gold Nanoparticles through Turning On and Off Sequences of UV Light

Ki-Hyun Kim, Jong-Uk Kim, Sang-Ho Cha, and Jong-Chan Lee\*

Department of Chemical and Biological Engineering, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-744, Korea (South)

Received November 11, 2008; E-mail: jongchan@snu.ac.kr

Photochemical reduction using UV or visible light has been known to offer a very simple and effective way of synthesizing gold nanomaterials<sup>1</sup> without harsh chemical reducing agents or special or expensive equipment. Organic stabilizers or templates, including polymeric materials, have been used widely to prevent agglomeration and precipitation during photochemical reduction for the formation of monodispersed gold nanoparticles (AuNPs).<sup>1c,2</sup>

Recently, amphiphilic comb-like poly(oxyethylene)s having the hydrophilic oxyethylene backbone part and the hydrophobic alkyl side chain part were synthesized as shown in Figure 1.<sup>3</sup> Since the polymer contains electron-donating oxide (–O–) and thio (sulfide, –S–) groups in the hydrophilic region that can coordinate on the surface of gold nanomaterials<sup>4</sup> and alkyl groups to prevent coagulation, it was used as a template and/or stabilizer to prepare gold nanomaterials by UV irradiation. As an experiment, lithium tetrachloroaurate (LiAuCl<sub>4</sub>, 13.8 mg, 0.04 mmol) and poly(oxy((decyltri(oxyethylene))thiomethyl)ethylene) (D3OTP, 36.5 mg, 0.10 mmol, calculated in terms of the repeating unit) were added to a quartz reactor containing 10 mL of THF. After tightly capping the quartz reactor, the solution mixture was equilibrated for 30 min and then irradiated with a UV light (Black Lay longwave UV lamp model B-100 AP, UVP Inc.) placed 0.3 m away at room temperature. The deep-yellow THF solution of D3OTP and LiAuCl<sub>4</sub> (1) became clear and colorless (2) within 1–2 h and then turned into a deep-red color (3) with increasing irradiation time, indicating that the gold salts (Au<sup>3+</sup>) in the solution turned into AuNPs, as shown in Figure 2.

The color changes were monitored by UV–vis spectroscopy. The strong absorbance at 327 nm from the gold salt in Au<sup>3+</sup> disappears within 1 ~ 2 h, which concurs with the observed color change from yellow to colorless (Figure 3(a)). After 3 h of UV irradiation, the surface plasmon resonance (SPR) peak from the AuNPs<sup>5</sup> at 527 nm appears, and its intensity increases with increasing UV irradiation time. Therefore, the yellow Au<sup>3+</sup> solution probably transforms to a colorless Au<sup>+</sup> solution first,<sup>6</sup> and then to AuNPs. Figure 3(c) shows a TEM image of AuNPs (13.5 ± 1.3 nm) formed after UV irradiation for 15 h, which was sampled by placing a single drop of the solution onto a copper grid (without purification) followed by rapid drying. Hence, role of D3OTP as a stabilizer and/or template to synthesize monodispersed AuNPs was clearly proved. Generally, 15~20 h of UV irradiation was found to be optimal for preparing monodispersed AuNPs because irregular AuNPs were obtained in low yield with less than 15 h irradiation and gold aggregates were obtained after more than 20 h irradiation. When the UV lamp was accidentally turned off after the formation of uniform AuNPs, the deep-red colored solution became transparent and finally showed a light yellow color (4). Initially, it was thought that the AuNPs had precipitated through aggregation. However, no precipitates could be found by the naked eye, and there were no solid materials in the solution according to TEM.

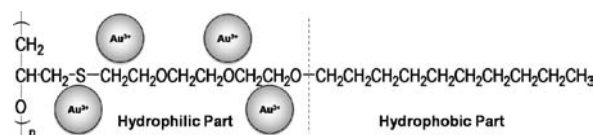
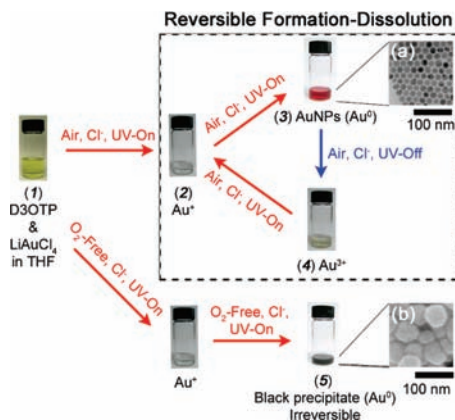


Figure 1. Molecular structure of poly(oxy((decyltri(oxyethylene))thiomethyl)ethylene) (D3OTP).

When the UV–vis spectra of the solution were measured after turning off the UV lamp, the intensity of the SPR peak at 527 nm decreased and the intensity of the Au<sup>3+</sup> peak at 327 nm increased, indicating dissolution of the AuNPs to Au<sup>3+</sup> ions. When this light yellow solution (4) was irradiated again, uniform AuNPs (13.1 ± 1.2 nm) were obtained again. Such reversible formation and dissolution of AuNPs could be repeated persistently by turning the UV light on and off. Figure 3d shows the changes of the intensity of the SPR peak (527 nm) as a function of the UV on and off time. The intensity of the SPR peak increases during UV irradiation indicating the formation of AuNPs and then decreases after blocking the UV, indicating the dissolution of the AuNPs. In all cycles, the sizes of the AuNPs were almost identical (for individual UV–vis spectra and TEM images, see Supporting Information (SI)), even though the time required for formation and dissolution varied. The reason for such time variation is unclear. This observation may have been due to differences in the chloride ion or oxygen concentration, or other environmental changes, such as temperature or brightness of the laboratory during the experiments.

Oxygen gas (O<sub>2</sub>), chloride ion (Cl<sup>–</sup>) from LiAuCl<sub>4</sub>, and polymer structure (including sulfide moiety) affect the formation and dissolution of AuNPs. O<sub>2</sub> has been known to accelerate the dissolution (or oxidation) of metal nanoparticles.<sup>1a,c,7</sup> Therefore we thought that the removal of O<sub>2</sub> in the system would shorten the reduction time during the UV irradiation process. When the solution (1) was purged with nitrogen gas before UV irradiation to generate an O<sub>2</sub>-free atmosphere, the reduction of Au<sup>3+</sup> to Au<sup>0</sup> by UV irradiation was complete within 3 h. However, no AuNPs were found, while aggregates of irregular gold nano- and/or micromaterials were observed, as shown in Figure 2b. In contrast, when the reaction mixture was purged with O<sub>2</sub>, the gold salt reduced to uniform AuNPs but took ~48 h. Under H<sub>2</sub> and Ar atmospheres, again aggregates of irregular gold crystals were obtained within 5 h of UV irradiation.

Cl<sup>–</sup> has been known to decrease the reduction potential of the metal, thus making the metal more susceptible to oxidation (i.e., dissolution).<sup>7b–d,8</sup> To examine the effect of Cl<sup>–</sup>, a trace amount of Cl<sup>–</sup> (1/100 molar amount of LiAuCl<sub>4</sub>) was added intentionally to the THF solution of D3OTP and LiAuCl<sub>4</sub> before UV irradiation. Uniform AuNPs were obtained from a longer irradiation time (>24 h), while the rapid dissolution of AuNPs was observed when the UV was off. It was also found that Cl<sup>–</sup> could dissolve small AuNPs

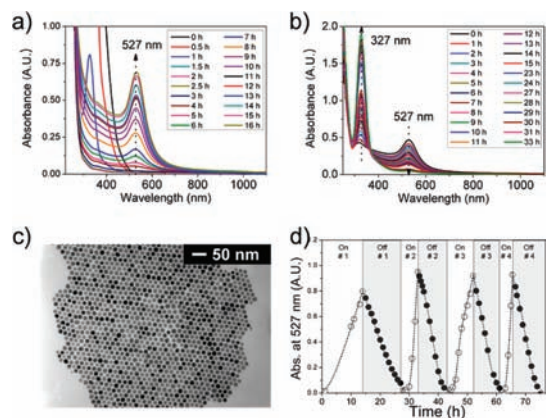


**Figure 2.** Schematic diagram of reversible formation and dissolution of AuNPs through turning on and off sequences of UV: (a) TEM image of formed AuNPs in air condition and (b) SEM image of formed black precipitate in oxygen-free condition.

having average diameter smaller than  $\sim 17$  nm prepared from other methods,<sup>9</sup> too. For example, when LiCl (50 mg) was added to the THF solution (3 mL) containing 0.1 mg of AuNPs prepared using the Brust method, they dissolved within 10 h. When UV was irradiated to this dissolved solution, only a black precipitate containing a chunk of gold particles was obtained. When a small amount of D3OTP (12.2 mg) and LiCl (50 mg) was added to the THF solution containing the Brust AuNPs, they also dissolved within 10 h, while monodispersed AuNPs were obtained by UV irradiation. Therefore D3OTP does not affect the dissolution process, while works as a template/stabilizer for the formation of monodispersed AuNPs. Furthermore  $\text{Cl}^-$  was found to be essential for the dissolution process because the dissolution behavior was not observed from the  $\text{Cl}^-$  free AuNPs solutions stabilized by D3OTP, thiols, and citric acid (details in SI).

The comb-like polymer structure containing a sulfide moiety was found to be essential for the reversible formation and dissolution of AuNPs. When (3,9,12,15-tetraoxa-6-thiapentacosane) having similar chemical structures with a repeating unit of D3OTP and low molecular weight surfactants, such as TX-100 and Pluronic P123, were examined, the reversible phenomenon was not observed (see SI); a black precipitate of gold analogous to that in Figure 2b was formed with UV irradiation, but we failed to observe the dissolution phenomenon. However, the reversible formation and dissolution of AuNPs was observed when a series of comb-like poly(oxyethylene)s with a sulfide linkage in the side chains was used instead of D3OTP. Moreover, the size of the synthesized AuNPs was found to be dependent on the length of the hydrophilic part (see SI). If the hydrophilic part (shown in Figure 1) is longer, it might contain a larger amount of gold salts, which can produce larger AuNPs.

In summary, monodispersed AuNPs were prepared by UV irradiation from a mixture of comb-like poly(oxyethylene)s and a gold salt. The prepared AuNPs dissolved to yield  $\text{Au}^{3+}$  when the UV light was switched off. The formation and dissolution of AuNPs



**Figure 3.** UV-vis spectra measured during UV irradiation (a) and after stopping UV irradiation (b) for given times; (c) TEM image of AuNPs ( $13.5 \pm 1.3$  nm) obtained after 15 h irradiation of UV; (d) Intensity changes of SPR peak at 527 nm from AuNPs as a function of time during a series of UV on and off processes.

occurred repeatedly by turning on and off the UV light. It is believed that the polymer structure of the amphiphilic comb-like poly(oxyethylene)s including the sulfide moiety, chloride ion, and oxygen are the key parameters for such a reversible phenomenon.

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**Supporting Information Available:** Detailed synthetic and experimental procedures, additional information for the dissolution process, TEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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