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Evolution, dissolution and reversible generation of gold and silver nanoclusters in micelle by UV-activation

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Abstract. Gold and silver nanoparticles were produced separately by UV photoactivation (with variable flux density) in the presence of nonionic micelle, TX-100. Even their cyano complexes break down in TX-100 under UV and hence dissolution and reevolution of almost monodispersed nanoparticles (~ 3 nm) are possible.

Keywords. Nanoparticle; micelle; photolysis; electrolytic effect.

1. Introduction

In this brief communication, we have highlighted for the first time the *in situ* preparation, dissolution and reversible generation of gold and silver nanoparticles from their cyano complexes by the UV-light. Here we have exhibited the preparation of gold and silver nanoparticles by UV-photoactivation method and then their dissolution in the presence of cyanide ion (cyano complexation of Au and Ag indeed!). The cyano complexes on further irradiation with UV-exposer regenerated the corresponding metal nanoparticles. The dissolution and regeneration steps were carried out reversibly up to a certain concentration of gold (7×10^{-5} M) and silver (3×10^{-5} M). For the evolution of gold, a catalytic amount of pre-formed Au(0) particle was needed but for silver there was no need of any trace element. A probable mechanism has been proposed for the reduction of Au(III) ion. The extent of formation of gold particles has also been investigated as a function of flux density (100–850 Lux) of the UV-light.

2. Experimental

Photochemical reaction was carried out in 1 cm quartz cuvette in a photoreactor with a variable flux density of 100–850 Lux. The flux density was measured using a Digital Lux Meter (model LX-101), Taiwan. UV-visible spectra were measured in Shimadzu UV-160 digital spectrophotometer (Kyoto, Japan) with 1 cm quartz cuvette. Transmission electron microscopy (TEM) studies of the particles were carried out at 200 kV using a Hitachi HF-2000 TEM equipped with a field emission source. Aqueous 10^{-2} M TX-100, 5×10^{-3} M $HAuCl_4$, 10^{-2} M $AgNO_3$ and 10^{-2} M sodium cyanide (NaCN) solutions were used as stock solution.

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3. Results and discussion

3.1 *Preparation, dissolution and reversible generation of Au(0) and Ag(0)*

Nanoparticle of Au(0) was obtained by the reduction of $HAuCl_4$ in TX-100 medium by UV-activation following the reported method (Pal 1998) and the solution showed the plasmon absorption band having a l_{max} at 523 nm. The photo produced gold particles were dissolved using NaCN in the nonionic micelle in air (Jana *et al* 2000). The dissolution reaction is

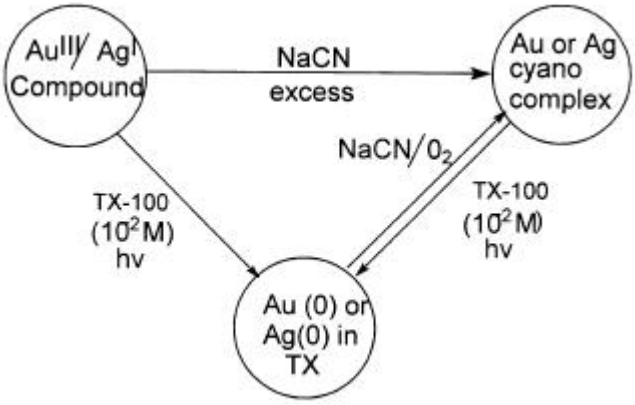
$$4Au(0) + 16NaCN + 6H_2O + 3O_2 \rightarrow 4Na[Au(CN)_4] + 12NaOH. \quad (1)$$

When the cyano complex of Au(III) was again photolysed in the presence of trace amount of gold, surprisingly same amount (same absorbance value at 523 nm) of Au(0) was produced. The process can be carried out time and again for a gold concentration up to 7×10^{-5} M and cyanide concentration up to $3{\cdot}3 \times 10^{-5}$ M. Higher concentration of $HAuCl_4$ or cyanide ion led to the aggregation of particles (electrolytic effect), which was concluded from red shifting of the peak position. Similar was the case of silver without the need of any trace metal.

The evolution, dissolution and reversible generation of Au and Ag nanoparticles in TX-100 micelle are depicted in scheme 1.

Ultra fine size (~ 3 nm) of gold and silver particles were produced which were authenticated from transmission electron microscopy (TEM) and are shown in figure 1.

A probable mechanism has been proposed for the reduction of Au(III) ion (Gachard *et al* 1998; Fraccois *et al* 2000). The trivalent gold, Au(III) is reduced by the hydroxymethyl radical generated by the photolysis of TX-100 [R–0–CH_2CH_2OH, where R = $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_{\sim 9}$–] into Au(I). The next step is the fast disproportionation of Au(I) and Au(III). Then, accumulated aurous ions Au(I) are reduced by the hydroxymethyl



Scheme 1. Overall reaction steps showing the evolution, dissolution and reversible generation of Au or Ag nanoparticles.

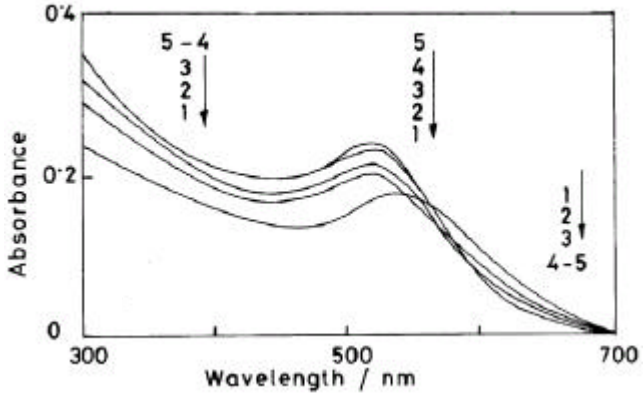


Figure 2. (1–5) Successive evolution of gold nanoparticles from $HAuCl_4$ ($7{\cdot}4 \times 10^{-5}$ M) in TX-100 medium ($0{\cdot}99 \times 10^{-2}$ M) with variable flux density (100–850 Lux) maintaining constant time of irradiation (12 min).

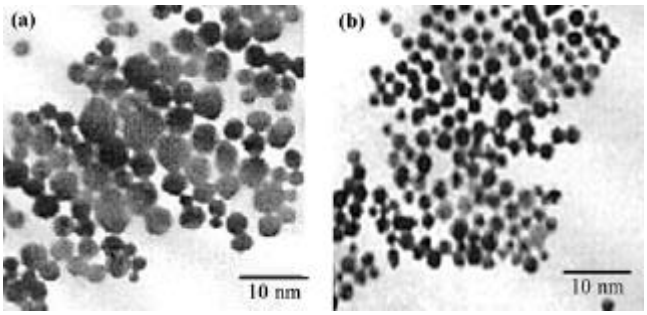


Figure 1. Transmission electron micrograph of **(a)** gold nanoparticles and **(b)** silver nanoparticles.

radical to Au(0). The atoms are formed with a homogeneous distribution throughout the solution. The atoms, then, tend to dimerise when encountered in pairs or associated with excess ions. But the micellar structures formed by the TX-100 molecules inhibit this association and thus act as particle stabilizer.

3.2 *Formation of Au(0) as a function of flux density*

Lastly, the formation of Au(0) nanoparticles was investigated as a function of flux density (100–850 Lux) keeping the irradiation time constant (12 min). For a particular concentration of TX-100 and $HAuCl_4$, at a lower flux density (~ 100 Lux), the plasmon absorption band for Au(0) appeared at 536 nm. With the successive increase in flux density**,** the plasmon absorption band shifts progressively to the blue region with concomitant increase in absorbance value. Finally, at high density (~ 850 Lux), the absorption band shifts to 519 nm. The successive generation of gold nanoclusters is shown in figure 2.

4. Conclusion

Nanoparticles of gold and silver can be generated reversibly from their cyano complexes. Smaller nanoparticles can be generated in comparison to the other methods. Variation in flux density brings about changes in the size of particles.

Acknowledgement

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