Synthesis of Gold Nanoparticles Using Polyethyleneglycol-Sodium Dodecyl Sulfate Cluster as Soft Template

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Abstract

Synthesis of gold nanocrystals of different diameters using a soft template of polyethyleneglycols (PEG)-sodium dodecyl sulfate (SDS) is described. The aqueous solution containing $HAuCl_4$ and PEG was sonicated to synthesize the seeds of gold nanoparticles. The seeds were then added to a series of PEG-SDS aqueous solution and mixed well, and the solution was irradiated with UV for 15 hours at 25±3 ^{0}C thereafter. Samples were characterized by transmission electron microscopy (TEM) and dynamic light scattering (DLS). The concentrations of PEG (C_{PEG}) and SDS (C_{SDS}) were found to have a dramatic influence on the formation of gold nanoparticles. At a certain concentration of PEG, when the concentration of SDS is between 0 and 31.6 mM, the more the SDS the smaller the diameter of gold nanocrystals was. SDS can capsule the gold crystals so that it stabilized the gold sols and affect the growth of gold nanoparticles. PEG was mainly used as stabilizer, and it can reduce Au^{3+}. At a certain concentration of SDS (3.16 mM), the more PEG (0.5-2 wt.%) in the solution the smaller the gold nanoparticles were. UV-vis absorption spectra indicated that the intensity of the absorption maximum (540nm) increased during the growth of gold nanoparticles. The possible mechanism of soft template was discussed as well.

Keywords: polyethyleneglycols; sodium dodecyl sulfate; gold; nanoparticle

1. Introduction

Metal nanoparticles have attracted researchers because of their size-dependent optical, magnetic, electronic, and catalytic properties. The development of synthesis method for the preparation of nanoparticles in a size- or shape-selected manner is an important and challenging task.

In recent studies some researchers used polymer, surfactant as the additives to form micelles as templates for the preparation of nanoparticles (Dykman,1998; Mayer,1998; Esumi,1998; Jana,2001; Kim, 2002; Sakai, 2004). However, using polymer and surfactant as template cannot often achieve satisfactory results. It is well known that SDS and PEG can form clusters in aqueous solution. This phenomenon has been studied for decades (Jones,1967; Benkhira,2000; Silva, 2004). There are a few reports about soft template containing polymer and surfactant used to synthesize nanoparticles (Kanjiro,1995; Leontidis,1999;). However, using PEG-SDS as a soft template to synthesize gold nanoparticles has not been reported yet.

In this work, we used PEG-SDS system as template to synthesize gold nanoparticles. There are two points of inflexion in γ-lgc curves for PEG-SDS aqueous solution (Yun Fang, 2001), where PEG and SDS can form pseudo-micelles or cluster which can guide the formation of PEG-SDS soft template. Gold nanoparticles were prepared by ultrasonic and

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UV irradiation in the presence of PEG and SDS. The gold nanoparticles have been characterized by UV-vis absorption spectra, DLS and TEM.

2. Experimental

2.1 Chemicals

Polyethyleneglycol 20000(PEG 20000, chromatographic grade) as well as $HAuCl_4 \cdot 4H_2O$(analytical reagent) were from Sinopharm Chemical Reagent Co., Ltd. SDS (99.0%, Acros Organics) were from Aldrich. Deionized water(conductivity 7.8×10^{-7} S/cm).

2.2. Preparation of Colloidal gold

A 2 mM aqueous $HAuCl_4$ solution containing 1 wt.% PEG 20000 was sonicated in an ultrasonic cleaner (SK3300H, Shang Hai Kudos Ultrasonic Instrument Co., LTD. 59kHz frequency) at a 30±1 ^{0}C for 10 min to synthesize gold seeds. Then, 0.1mL seeds solution was added to a series of PEG-SDS aqueous solution respectively; the final mixture was 0.2 mM $HAuCl_4$ containing 0-31.6 mM SDS and 0.5-2 wt.% PEG. Photochemical reactions were carried out in a well-sealed quartz cuvette with an ordinary germicidal lamp (20 W, ZWS20, Xinyate, China) for 15 hours at 25±3^{0}C. The cuvette was kept at a distance of 5 cm from the light source.

2.3. Characterization of Colloidal Gold

The above solution was centrifuged at 12000 rpm for 30 min. The precipitate was collected and dispersed in deionized water. Optical spectra were recorded using a TU-1901 spectrophotometer (Purkinje General, China). The shape and distribution of particle size were determined by TEM and DLS.

3. Results and Discussion

3.1 reaction mechanism

3.1.1 sonochemical reaction

It has been reported that the sonochemical reaction of gold (III) easily occurs in an aqueous solution by the addition of 2-propanol (Okitsu et al., 2001). In the presence of PEG, the following reactions of (1) to (4) may be suggested as the following scheme similar as Okitsu reported:

$$H_2O \longrightarrow \cdot OH + \cdot H \quad (1)$$

$$HO(CH_2CH_2O)_nH + \cdot OH(\cdot H) \longrightarrow HO\dot{C}H_2CH_2O(CH_2CH_2O)_{n-1}H + H_2O \quad (2)$$

$$HO(CH_2CH_2O)_nH \longrightarrow \text{pyrolysis radicals} \quad (3)$$

$$\text{gold(III)} + \text{reducing radicals} \longrightarrow \text{gold (0)} \quad (4)$$

After ultrasonic irradiation seeds solution turned to pink and showed plasmon absorption band. This indicated the formation of gold particles. TEM showed diameters of gold nanoparticles. From the result we can concluded that the particle diameter was in a range of 15-20 nm. These particles were used as seeds to prepare larger size particles.

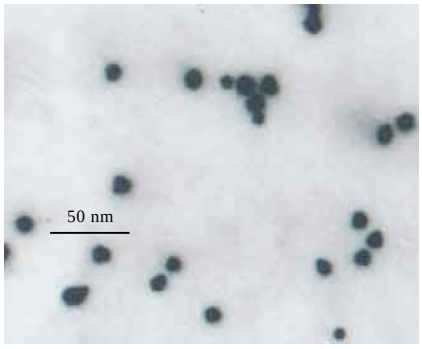

Figure 1. TEM image of gold seeds

3.1.2 photochemical reaction

It has been reported that during the course of charge transfer to solvent (CTTS) (Ming-zhang, 1998) anion was ionized by UV in aqueous solution, and $AuCl_4^-$ was deoxidized. The reaction process is as follows:

$$Cl^- + hv\ (Cl^-) \longrightarrow Cl^- + e^-(CTTS) \quad (5)$$

$$\text{gold (III)} + e^-(CTTS) \longrightarrow Cl^- + \text{gold (0)} \quad (6)$$

$$n\ \text{gold (0)} \longrightarrow \text{gold (n) (clusters)} \quad (7)$$

3.2 Effect of SDS concentration

From figure 2 it can be seen that C_{SDS} has an important influence on the results of UV irradiation. The maximum absorption band decreased with the increase of C_{SDS}. The absorption band centered at 540 nm that originated from the surface plasmon of the gold nanoparticles was monitored as suggested (Sakai, 2004). Figure 3 shows the absorption band at 540 nm increased dramatically, which indicates the initial reaction rate was high. Irradiated by UV for 200 min, the rate became slower, absorption band showed no change after 15hrs.

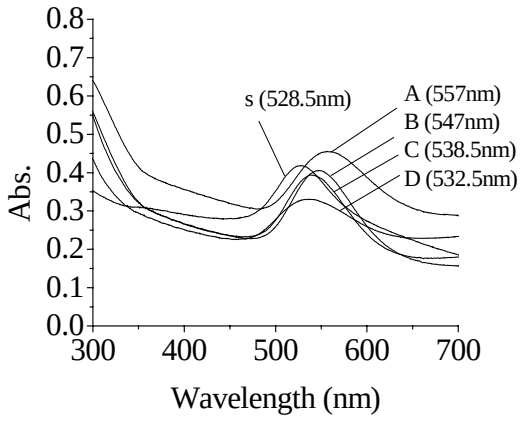

Figure 2. UV-vis absorption of gold seeds and gold nanoparticles in solutions after UV irradiation 15 hrs.
(A) C_{SDS} = 0, (B) C_{SDS} =3.16 mM, (C) C_{SDS} =10 mM, and (D) C_{SDS} =31.6 mM respectively. (S) seeds

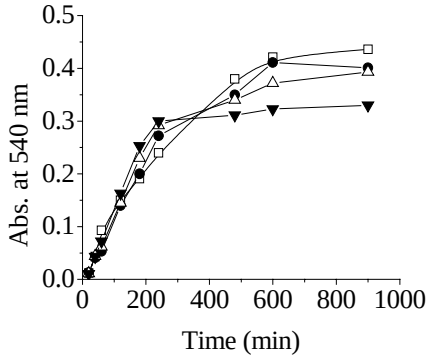

Figure 3. Absorbance at ~540 nm after irradiated with UV for 15 hrs. C_{PEG}: 1wt.% □ C_{SDS}:0; ●C_{SDS}: 3.16mM; △C_{SDS}: 10 mM; ▼C_{SDS}: 31.6 mM

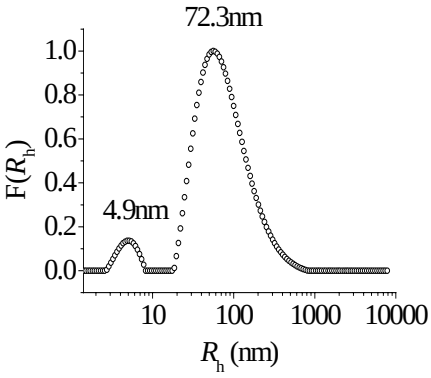

Figure 4. Hydrodynamic radius of gold nanoparticles in the solution of PEG (1wt.%) after irradiated with UV for 15 hrs

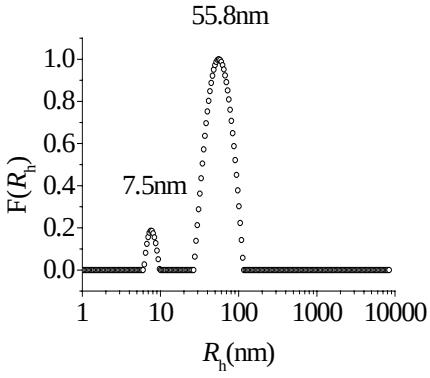

Figure 5. Hydrodynamic radius of gold nanoparticles in the solution of SDS (3.16 mM) and PEG (1wt.%) after irradiated with UV for 15 hrs.

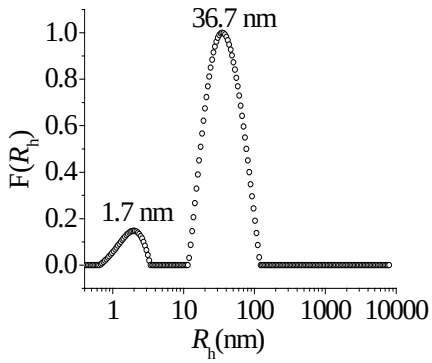

Figure 6. Hydrodynamic radius of gold nanoparticles in the solution of SDS (10 mM) and PEG (1wt.%) after irradiated with UV for 15 hrs.

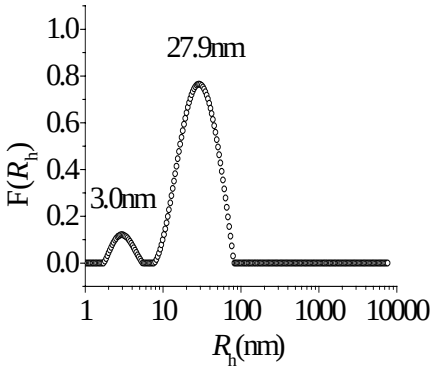

Figure 7. Hydrodynamic radius of gold nanoparticles in the solution of SDS (31.6 mM) and PEG (1wt.%) after irradiated with UV for 15 hrs.

Figures. 4-7 show that the hydrodynamic radius of gold nanoparticles reduced in the solution of PEG (1wt.%) with different concentration of SDS. R_h decreased from 72.3nm to 27.9 nm with the concentration of SDS increasing from 0 to 31.6 mM, as shown in figure 8. Obviously, once C_{SDS} exceeded 10 mM, R_h decreased slowly. Figure 9 indicates that R_h of gold nanoparticles decreased with the increase of C_{PEG}. PEG in aqueous solution can be used as stabilizer. The concentration of PEG has influence on the aggregate of gold nanoparticles. At the mean time, PEG also can reduce gold(III) (Longenberger,1995), and high concentration of PEG promoted the formation of small gold nanoparticles. Gold nanoparticles reduced by UV for 15 hrs (C_{SDS}: 10 mM, C_{PEG}: 1wt.%) is shown as in figure 10. The diameter of gold nanoparticles showed in TEM was smaller than the hydrodynamic diameter.

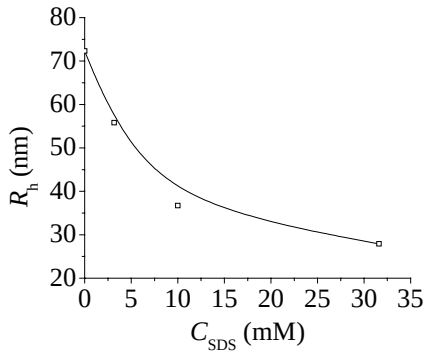

Figure 8. Hydrodynamic radius of gold nanoparticles versus C_{SDS} (C_{PEG} : 1wt.%)

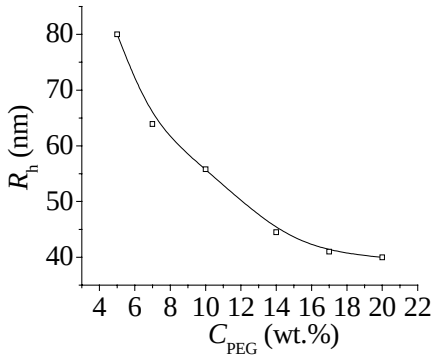

Figure 9. Hydrodynamic radius of gold nanoparticles versus C_{PEG}. (C_{SDS}: 3.16 mM)

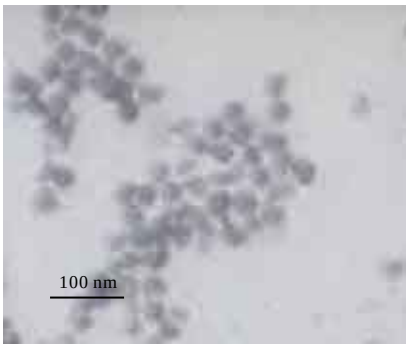

Figure 10. TEM image of gold nanoparticles made from photoreduction. (C_{SDS}: 10 mM, C_{PEG}: 1wt.%)

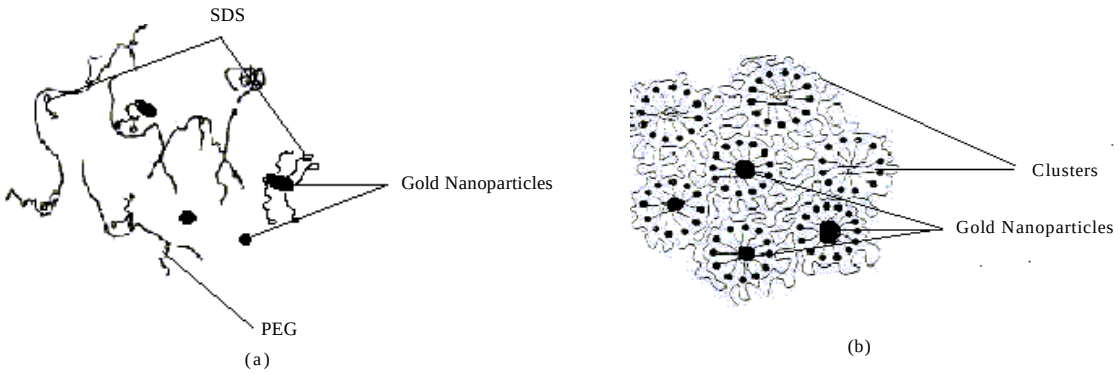

Figure 11. Schematic potential mechanism for soft template
(a) in the presence of free PEG, SDS moleculars (b) in the presence of the soft template- PEG-SDS cluster

DLS and TEM proof can suggest a potential mechanism for soft template as shown in figure11. When C_{SDS} was low (≤10 mM), it cannot form effective clusters with PEG. There were not enough clusters to restrict gold seeds' growth. When C_{SDS} was above 10 mM, there were many clusters formed and gold seeds were capped by these supermolecules. And C_{SDS} increased, the number of the clusters increased too. So the gold nanoparticles produced were smaller. C_{PEG} is another factor that has influence on the gold seeds growth. PEG as stabilizer can prevent the aggregation of gold nanoparticles and make the size of nanoparticles smaller.

4 Conclusion

We have demonstrated that the use of PEG-SDS supermolecule as template to produce gold nanoparticles. By using a seeding growth approach, gold nanoparticles with R_h ranging from 28 to 73 nm can be achieved with a relatively narrow particle size distribution. These nanoparticles typically appeared spherical. Using PEG-SDS as template to prepare other interesting or useful nanoparticles can also be realized.

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