

Photochemical Synthesis of Gold Nanoparticles by the Sunlight Radiation using a Seeding Approach

Shouan Dong, Chun Tang, Hua Zhou and Huaizhi Zhao

Institute of Precious Metals, Kunming 650221, China
E-mail: dsaw@xinhuanet.com; townkiller@21cn.com

Abstract

A novel photochemical synthesis of colloidal gold particles has been studied based on a seed-mediated growth approach under the UV solar radiation on plateau. In the HAuCl_4 solution containing certain amounts of protective agent and acetone, the colloidal gold particles with 5 nm ($\sigma=0.86$) in average diameter were prepared by UV 300 nm irradiation and used as seeds, their further growth then was carried out in the identical constituent solutions under the UV solar radiation. The results showed that to control the molar ratio of seed to Au(III) ion and use repetitive seeds can obtain different sized and surface-confined gold nanoparticles, and it is completely possible to utilize the UV solar radiation on the plateau with the higher elevation for the size-controlled synthesis of monodisperse gold nanoparticles under suitable conditions. The mechanism of the nucleation, growth and stabilization of gold particles were discussed in detail.

Introduction

During the past decade, driven by interest in unique physical and chemical properties of gold particles, the investigation of preparing gold particles and using as nanostructured materials is becoming an existing area of interdisciplinary research. Based on the properties, the ongoing and potential applications in the fields of catalysis (1-4), electronic and electrooptical devices (5-7), biomedicine (8-12) etc. extend far beyond imaging. As concerns the preparation of the colloidal gold nanoparticles which were widely used as precursors, various chemical routes, including the use of chemical reductants in both aqueous and nonaqueous solvents (13-20), electrochemical method (21-25), sonochemical method (26,27) radiolytic (28) and photochemical method (29-34) have been widely studied for different purposes of application. For producing monodisperse colloidal gold particles of 10-20nm in diameter in aqueous solution, the citrate-reduced method developed by G. Frens (13) is quite effective, which was most widely adopted or improved in a lot of published papers. However, the production of large colloidal gold nanoparticles (i.e. with diameters between 40 and 120 nm) by direct citrate reduction is unsatisfactory due to polydisperse formation. On the other hand, a representative work by M. Brust (14) on functional gold nanoparticles prepared with thiol group modification in a two-phase liquid system is very useful for assembling nanostructure, which led to wide use of chemical route for producing colloidal gold particles in nonaqueous system. Although chemical methods with various reductants for the preparation of gold nanoparticles are convenient, they are very dependent on solution conditions, including the rate and the sequence of reductant addition and the local over-concentration of reductant etc., therefore it is extraordinarily difficult to produce particles with the same mean diameter for ostensibly identical conditions. Moreover, the excess reducing agent and its oxidation products may pollute final products. For the electrochemical method, the main predominance is that it can produce anisotropic gold nanoparticles (21-25). For the preparation of size-controlled colloidal gold particles, the radiolytic and photochemical methods have recently aroused much attention because of following some important advantages: (i) controlled reduction of metal ions can be carried out without using excess reducing agent; (ii) radiation is absorbed regardless of the presence of light-absorbing solutes and products; (iii) the reduction reaction is uniformly performed in the solution, and the rate of reaction is well known, since the number of reducing equivalents generated by radiation is well defined. In addition, from the point of view of practice application, the photochemical method is more competitive without the needs of specific instrument.

In order to prevent the aggregation of the particles, the same as other chemical preparations, it is usually requisite to add protective agents such as soluble polymers, surfactants and dendrimers in the photochemical methods (29-35). The authors have studied the preparation of the colloidal gold nanoparticles by UV irradiation using linear polymer poly (ethylene glycols) (PEG) as the protective agent (34). It is found that the size, shape and disperse of the gold particles strongly depend on the degree of polymerization. Certainly, the synthesis with the photochemical method makes for the nucleation and growth; however, it is not guaranteed to form monodisperse gold particles with narrow size distribution. For this reason, T. Pal et al. recently proposed a route of seed-mediated successive growth by UV irradiation (35). The use of preformed metallic seeds as nucleation centers in nanoparticle synthesis is an important technique. M.J. Natan et al. reinvestigated the use of citrate- and borohydride-reduced gold particles as seeds for the preparation of larger gold nanoparticles of 30 to 100 nm in diameter (36,37), and utilized hydroxylamine seeding of colloidal gold nanoparticles to control the formation of conductive gold films (38). N.R. Jana et al. (39) studied the influence of adding reagent method on seed growth and promoting formation of new nucleation in detail, using 12 nm gold particles citrate-reduced by the Frens method as seeds. Although the seed-mediated nucleation can occur in the chemical reduction process of gold salts to gold nanoparticles, the improved monodispersity for the synthesis of larger size particles is still successful in the presence of seeds.

Described herein is an investigation to combine seed approach with photochemical preparation. We focused on the synthesis of size-controlled colloidal gold nanoparticles under the solar radiation on the plateau. Since solar energy is an enormous and clear energy source, the utilization of solar energy in the high-technology is a goal sought by scientists at all times. New theory and method based on modern photochemistry for the investigation of the electron excited state have provided important foundation for the utilization of solar energy, such as in the environmental protection, new reaction way and seeking new material. In this report we first prepared nearly monodisperse colloidal gold particles with UV 300nm irradiation and used them as seeds to grow into larger particles under the solar radiation by the successive addition of Au(III) ions. Based on the previous investigation (34), an aqueous solution system containing acetone was used for rapid photoreaction synthesis. The growth of the seeds under the solar radiation and influence of the UV solar energy on the growth were studied in detail. The results showed that the colloidal gold particles with different size and better monodispersity were obtained. There are some important advantages in the present investigation. Firstly, to combine seeding technique with the UV solar radiation made it possible

to utilize solar energy for size-controlled synthesis of the colloidal gold nanoparticles. Secondly, it allows smaller particles to be grown into larger particles of a predetermined size without seed-mediated nucleation phenomenon, and the surface-confined gold nanoparticles by PEG easily take place ligand exchange reactions, so that obtaining functional nanoparticles. When they were used as the precursor of preparing catalyst, chloride ions released in the photochemical reduction reaction were easily removed. Furthermore, this method is simple, convenient and cost effective.

Experimental

The colloidal gold particles with different sizes were prepared in aqueous solution system containing 5.64×10^{-2} M/l PEG, 0.5 M/l acetone and HAuCl_4 with different concentrations. All photochemical experiments were carried out in a triangle quartz container with 250ml volume. The surface area for exposure is 50cm^2 . The average molecular weight of PEG used is 400 and 600, respectively. HAuCl_4 was prepared from pure gold (99.99%) to solve in aqua regia and remove then HNO_3 with HCl. All chemical reagents used are of analytical-reagent grade. Double distilled water was used throughout the experiment. All glassware used in the experiment was scrupulously cleaned with chromic acid solution and rinsed in turn with double distilled water. The UV-Vis absorption spectra of colloidal solution were recorded generally on a MPS-2000 spectrophotometer (Shimadzu) with 1ml quartz cuvette. However, in order to trace the influence of solar radiation energy change on forming gold nanoparticle, we employed Lambda-900 UV/Vis/Infrared spectrophotometer (Parker-Elmer). Transmission electron microscopy studies of the particles were carried out at 200kV with a JEM-2000EX TEM (Japan). TEM specimens were prepared by placing microdrops of colloid solution on a carbon film supported by copper grids. Their particle sizes and distributions were determined by counting about 200 particles.

For the preparation of gold seed particles in the PEG (MW of 600) and acetone aqueous solution containing 2.44×10^{-4} M/l HAuCl_4 , an electronic dual light transilluminator (Ultra-lum com.) was used as the light source for 300 nm wavelength irradiation (48W). In the early stage of the nucleation, the solution was lightly stirred. After 10min irradiation, Ruby-red color colloidal gold solution was obtained and used as 'seed' solution.

For stepwise synthesis of larger gold particles, we utilized seed-mediated growth approach under the UV solar radiation on the plateau where the elevation is 1850 meters. The solar radiation was from 1100 to 1400 in a day and three procedures were used, the first one was to add above gold seed and Au(III) ion to PEG (MW of 600) and acetone aqueous solution, the

final concentration of gold seed and Au(III) ion remained 2.44×10^{-4} M/l, and the molar ratio of the seed to Au(III) ion was 1/11.5. The mixture solution was placed under the sunlight for about 50min until the surface plasmon absorption no change. The second procedure was the same as the first one, but the total concentration of seed particles and Au(III) ion was 1.22×10^{-3} M/l, and the molar ratio of both seed and ion was 1/57.5. In the third procedure, the total concentration and the molar ratio of gold seed to metal ion were the same as that in the first procedure. However the gold particles produced in the first procedure under sunlight radiation acted as “second generation seeds” for producing even large particles.

In addition, in order to obtain functional nanoparticles, the phase transfer method from above colloidal aqueous solution into an organic layer is effective by ligand exchange reaction.

Results and disussion; seed preparation

As mentioned above, when the gold seed particles were prepared by UV irradiation, the influence of acetone on the nucleation was studied. In the H₂AuCl₄ and PEG aqueous solution with and without acetone, the time evolution of the UV-vis absorption spectrum in the process with UV irradiation was shown in Figure 1a and 1b, respectively. It is obvious that for developing surface plasmon absorption band of being observed at around 520 nm, the induction period of forming

gold nanoparticles in the presence of acetone is quite short (~1.5min). It seems that the atoms and (or) clusters formed at the early stages of the irradiation have shorter lifetime and extremely reactive, and can promote the reduction of gold ions in the solution on their surface as autocatalytic growth center. After 10min irradiation, the solution turned ruby-red color and showed the surface plasmon absorption band with a maximum at 516 nm, and the absorbance did not increase with increasing irradiation time (Figure 1a). This is an indication of full photochemical reduction reaction of forming gold particles and shows that the nucleation of gold nanoparticles and successive growth have sufficiently rapid rate. In the absence of acetone the induction period is about 12min, after 35min irradiation, the plasmon absorption band maximum shifted to 524.5nm (Figure 1b).

For the gold seed particles prepared with and without acetone addition, TEM analyses were given in Figure 2a and 2b, respectively. It can be seen that the nearly monodisperse uniform spherical gold particles were obtained in the presence of acetone (Figure 2a), the average diameter of the particles is 5 nm ($\sigma=0.86$) with narrow size distribution (the histogram in Figure 2). However, in the absence of acetone a quite broad size distribution (4-30nm) of gold particles was obtained (Figure 2b). Therefore, it is completely feasible to use 5nm gold particles as seeds for the size- and shape-controlled synthesis of enlarging gold nanoparticles in the PEG and acetone aqueous solution system.

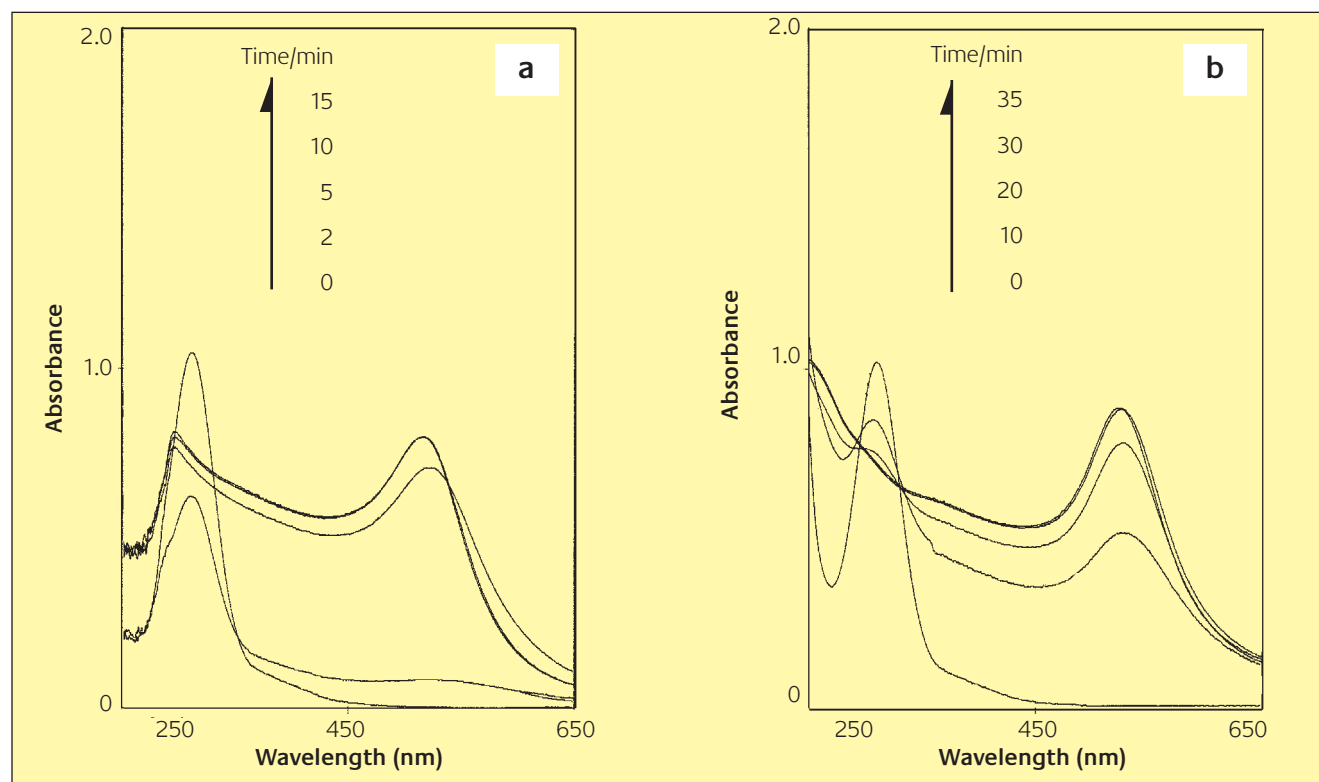


Figure 1
Evolution of UV-vis spectra of gold nanoparticles with irradiation time (a) with acetone (b) without acetone

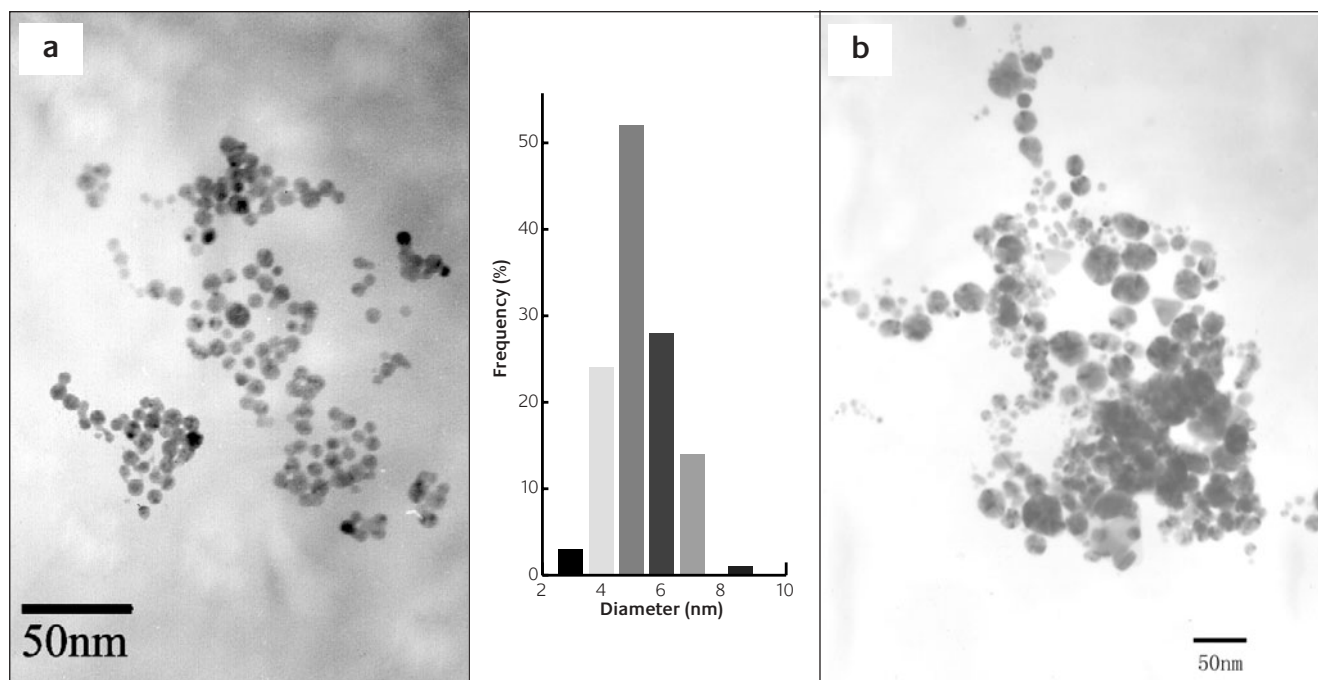


Figure 2
TEM images of gold particles (a) the system with acetone (the size distribution showed by histogram) (b) the system without acetone

Seed-mediated growth

In the HAuCl_4 -PEG-acetone aqueous solution system without and with gold seed particles of 5 nm, the nucleation and growth of gold nanoparticles were studied under the UV solar radiation. The time evolution of UV-Vis absorption spectrum recorded was shown in Figure 3a and 3b, respectively. In the absence of seed particles, after 17 min solar radiation, the solution presented light purple because of a longer induction period (Figure 3a); after 1 hour successive radiation, the plasmon absorption band appeared at around 534 nm. In the presence of gold seed particles, there was no induction period, the intensity of plasmon absorption band increased with an increase of the UV solar radiation time due to seed particles growth. The complete photochemical reduction of Au(III) was finished within 50 min radiation; the plasmon absorption band maximum is 524.9 nm (Figure 3b). Based on Mie theory, in the same medium system the red-shift of the plasmon absorption band and gradual broadening imply nanoparticle in solution to become larger. Thus, in the absence of seed particles, it is assumed that as soon as the small gold cluster formed at early stage of the nucleation under the solar radiation, their coalescence occurred quickly and grew into the larger nuclei. Through longer successive sunlight radiation these nuclei in the solution grew further into the large particles with different sizes. The TEM image of gold particles with broad size distribution (15–60 nm) showed in Figure 4a favors this conclusion. However, in the presence

of gold seeds, the particles with average diameter of 10.2 nm ($\sigma=3.12$) were obtained with narrower size distribution (Figure 4b and its histogram).

We know that it is important to control molar ratio of the seed to metal ion for obtaining desired size of particle and good colloidal dispersion (35, 36, 39). For this reason, in our second procedure the control of particle size was carried out by varying the molar ratio of seed to metal ion. When the concentration of HAuCl_4 was increased from 2.44×10^{-4} to 1.22×10^{-3} M/l in the presence of same amount of seed, the time required for complete photo-reduction reaction obviously increased under identical conditions of the UV solar radiation in a day. After 2 h sunlight irradiation, the mixture solution presented aubergine and a plasmon absorption band at 526.9 nm. The gold seeds were grown to 29.3 nm in average diameter ($\sigma=7.44$) (Figure 5). The histogram inserted in Figure 5 revealed size distribution.

In order to produce more larger colloidal gold nanoparticles under the solar radiation, we tried to use the 10.2 nm colloidal particles obtained under the UV solar radiation as next generation seeds so that their further growth can be carried out in the presence of Au(III) ions. As a result, a transparent purple solution was observed for about 50 min sunlight radiation. It is found that when using same seed solution aged for different times, the seed particles can be enlarged to 66.4 (seed aged for 15 days, $\sigma=13.3$) and 53.9 (seed aged for 45 days, $\sigma=10.3$) nm in the average diameter, respectively, and having a quite good dispersion feature (Figure 6).

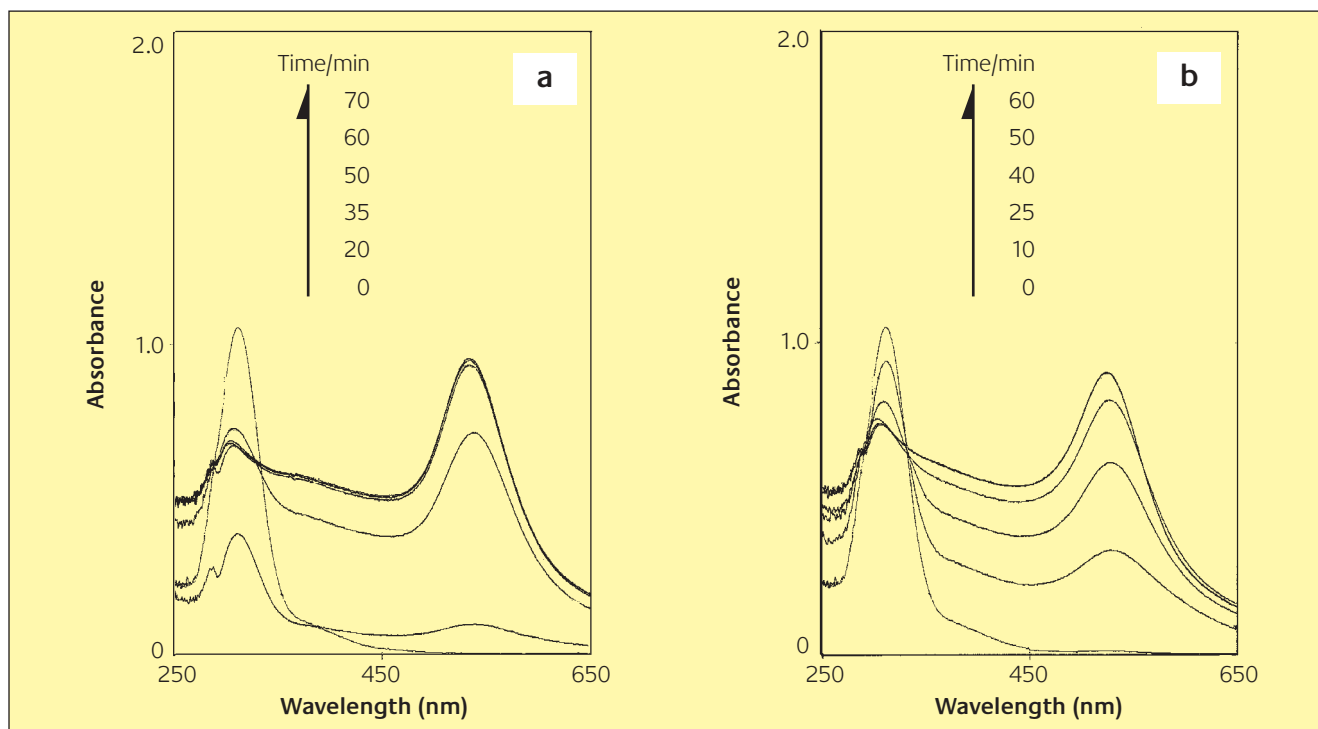


Figure 3

Evolution of UV-vis absorption spectra of gold nanoparticles with time under the UV solar radiation (a) in the absence of seed particles (b) in the presence of seed particles

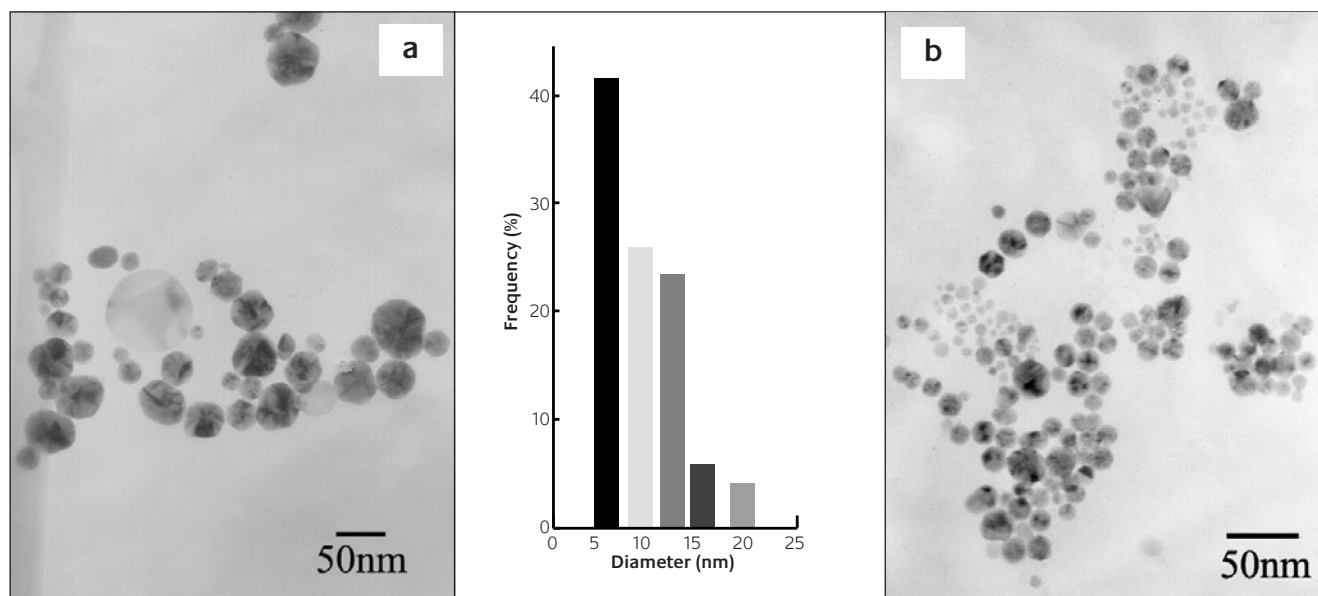


Figure 4

TEM images of Au particles growth under the UV solar radiation (a) in the absence of seed (b) in the presence of 5 nm seed particles (the size distribution showed by histogram)

Above experimental results proved that the uniform gold nanoparticle can be obtained under the solar radiation with seed-mediated growth technique. This mainly attributes that nucleation and growth process were separated in time except for the advantages of photochemical reduction method. We did not observe that the presence of seeds

appears to cause additional nucleation. The diameter of the smallest particle, as shown in figure 4b, is larger than 5 nm. It is certain that the seed particles added in the solution were acted as nucleation centers and catalyzed the reduction of Au(III) ions existed in bulk solution on their surface, avoiding new particle nucleation in the photoactivation process. The

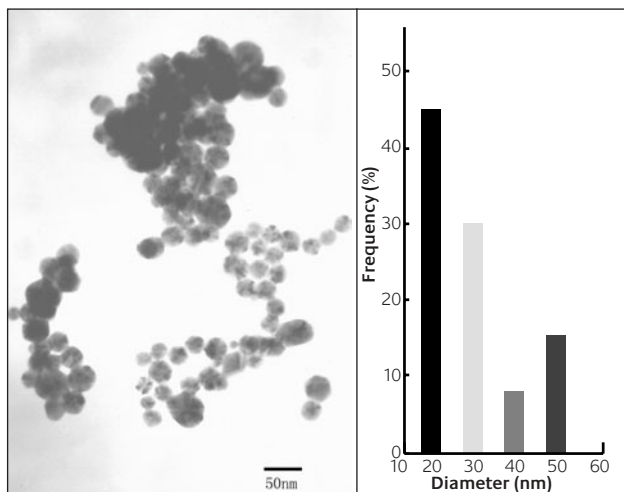


Figure 5
TEM image of Au particles obtained in 1/57.5 molar ratio of gold seed to Au(III) ion under the UV solar radiation (the size distribution showed by histograms)

seeds were thus grown to the larger particles, which depend on the initial seed particle diameter and the molar ration of seed to Au(III) ion added in the solution.

Influence of the UV solar energy on the seed growth

In previous published investigations of preparing colloidal gold particles by the photochemical reduction method, the UV lamp-house was widely used (29-35). In fact, the light source can provide UV-A, -B and -C band irradiation and has a certain wavelength range. The amount of the light source

energy consumed for the photo-reaction is easily controlled to produce a desired result. However, the solar energy is a variable and consecutive radiation, the distribution of energy presents a wide range (Fig.7). It is known that the UV solar radiation is possessed of 8.7% in spectral distribution of extraterrestrial solar radiation (40). Due to the absorption of ozone molecules which remove nearly all of the UV solar radiation, so that very little solar radiation with wavelengths less than 280nm reaches the earth's surface. Furthermore, the UV solar radiation also depends on many factors, such as the solar altitude angle (θ), atmosphere transparency, earth's latitude, local altitude, time of day and the year etc. Even now, it is still one of our aims to utilize the UV solar radiation to the photochemical synthesis of gold nanoparticles. For this purpose, it is necessary to satisfy two conditions, i.e. strong enough UV solar radiation and a sensitive photo-reaction system.

In fact, the intensity of the UV solar radiation increases with an increase of the altitude. When an altitude is 2000 meters, an increase of the intensity reaches over 10% (40). Author's laboratory locates the city of Kunming in Yunnan plateau (north latitude 25° 02'), where the elevation is 1850 meters. The atmosphere transparency here is higher. The ground receives UV radiation about 20 times stronger than sea level (41). Geographical and meteorological conditions supply rich UV solar radiation to this area, the energy of the UV solar from 280 to 320 nm, as shown in Fig.7, is strong enough. Therefore, it is completely possible to replace the UV-B band lamp-house by the UV sunlight for the preparation of stable metal colloidal dispersions under suitable conditions. On the other hand, the aqueous system selected in the present study is quite photo-sensitized for forming gold nanoparticles.

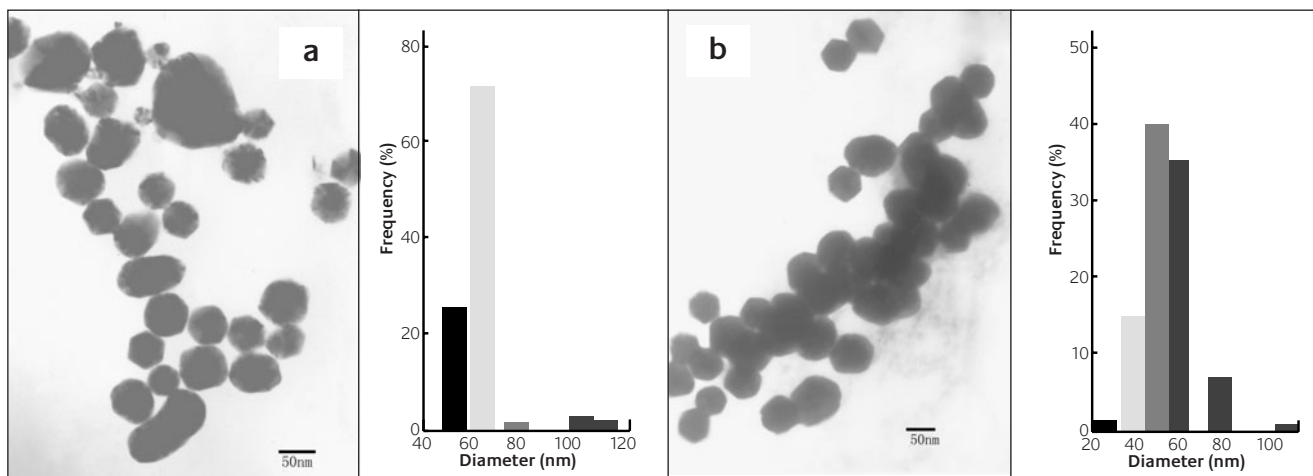


Figure 6
TEM images of Au seed particles growth with 10.2nm in diameter under the UV solar radiation (a) seed aged for 15 days (with histogram) (b) seed aged for 45 days (with histogram)

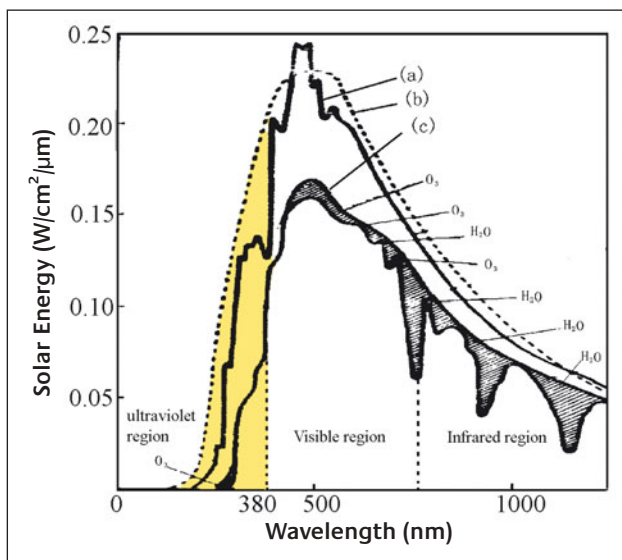


Figure 7
 Spectrum distribution of the solar radiation (40)
 (a) extraterrestrial solar radiation
 (b) black body radiation at 6000K
 (c) on sea level

In order to obtain fundamental identical energy conditions, we trace evolution of the plasmon absorption spectrum of forming gold nanoparticles with time under the solar radiation during a fine day. All results obtained at 1/11.5 molar ratio of seed to metal ions were shown in Figure 8a and 8b. It can be seen that the UV solar radiation from 1300 to 1500 (Beijing time) is the strongest in a day and from 1100 to 1200 and 1600 is stronger than that from 0900 to 1000 and 1700. After complete reduction of Au(III) ions, the plasmon absorption band was around 526nm in all cases. When we plotted the time consumed after complete reduction of Au(III) ions against the time in a day, a

histogram which indicated indirectly the change of the UV solar radiation intensity in a day was obtained (Figure 8b). This result is in accordance with the solar radiation measured by the instrument method (40). It is clear that the photochemical reaction for forming gold nanoparticles is quite rapid under the conditions of selective solar radiation.

In the experiments of the seed-mediated growth, the UV solar radiation was from 1100 to 1400 in a day and was selected in December, because the sun is far away at that time. If the experiments here are successful, then the synthesis of the colloidal gold nanoparticles can be realize at any sunny day in the year. In practice, the photochemical reduction of Au(III) ions under the UV solar radiation is similar to that with UV lamp-house irradiation of 300 nm. Therefore, on the plateau zone with the higher elevation it is feasible to utilize the UV solar radiation as energy source for the synthesis of gold nanoparticles, using the seed-mediated growth approach.

Mechanism on nucleation, growth and stability

For the nanoparticle growth a two-step process, i.e. nucleation and later successive growth of the particles, which has already been studied in detail in previous literatures, decides the mechanism of forming nanoparticles. Current studies further reveal that the reduction potentials of metal ion/metal atom and metal ion/metal particle systems are very significant for the nucleation because of size-dependent redox property. Perhaps, the mechanism for gold nucleation summarized in the literature (35) is also acceptable to the case of seed preparation herein. On the other hand, the property of colloidal particles surface-confined by protective agent is very important for explaining the mechanism of the nucleation, growth and stability of nanoparticles.

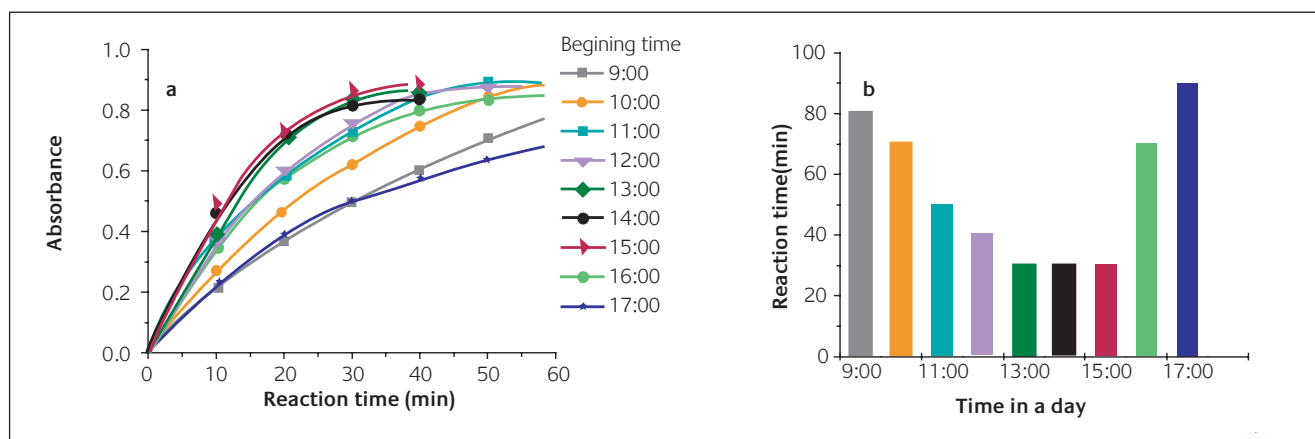
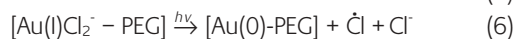
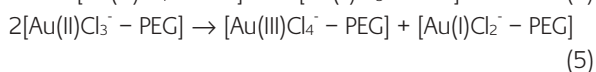
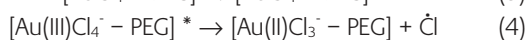
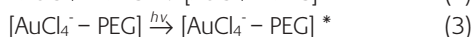
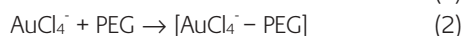
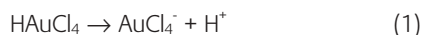


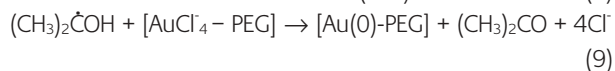
Figure 8
 a) Effect of the UV solar radiation intensity in a day on reduction reaction of Au(III) ions b) Distribution of the UV solar radiation intensity in a day indicated by reaction time

PEG used as protective agent in our study is a typical linear polymer, which presents spiral molecule with alternative anti and tortile C-O, O-C and C-C bond construction. When a space model is observed, seven or eight oxygen atoms lie on a plane, forming a cyclic molecule similar to pseudo-crown ether because of small Van der waals exclusion force and angle tension. Other oxygen atoms extend on a side of the plane. This kind of polymer possesses strong complexation (42). Au(III) can bond on the single or several molecule chain of PEG, where an intramolecularly complex formed in the dilute PEG solution or an intermolecularly complex formed in the strong PEG solution. As a result, a macromolecule metal associated-complex is formed with a synergistic 'chain effect', which led to the increase of the viscosity and the photosensitivity. When the complex was irradiated with UV light, colloidal gold nuclei were produced and enveloped in the hole of the pseudo-crown ether (18). Based on previous investigation in literature (43), we conjecture that the mechanism of forming and stabilizing gold nanoparticles by PEG can be expressed by the following equations.

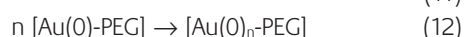
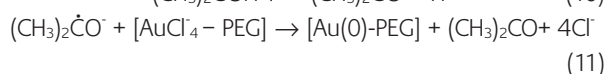
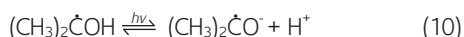
In the early stage of the nucleation of the photochemical reduction reaction,



The reduction of $[\text{AuCl}_4^- - \text{PEG}]$ associated-complex was greatly accelerated in the presence of acetone. Being similar to photochemical formation of colloidal silver particles (44, 45), acetone ketyl radical produced by excitation of acetone by 300nm light plays an accelerating role in the reduction of $[\text{AuCl}_4^- - \text{PEG}]$ ions, resulting in a faster nucleation rate:



The ketyl radical undergoes photolytic dissociation, forming a stronger reductant (46, 47):



Therefore, small gold nuclei were rapidly produced in the HAuCl_4 -PEG-acetone aqueous solution due to faster nucleation rate. That is why the induction period was much shorter than that in the HAuCl_4 -PEG solution. After the complete photoreduction, the surface-confined colloidal gold nanoparticles with small size and narrow size distribution (Figure 2a) were obtained because their aggregation was distinctly restrained by the chain effect or steric stabilization resulting from the pseudo-crown ether construction. Nevertheless, it should be emphasized that these surface-confined colloidal gold nanoparticles cannot be completely enveloped by the pseudo-crown ether and practically are "half naked" state which is more active. When they were used as seeds, these particles acted as the developing centers and catalyzed the reduction of remaining $[\text{AuCl}_4^- - \text{PEG}]$ ions in the solution under the UV solar radiation. On the other hand, the surface-confined nanoparticles easily take place ligand exchange reactions, which were confirmed by the exchange reaction of the hydrosulfuryl ligand.

For the above reaction mechanism expressed by the equations, it can be revealed more deeply only by the dynamic study of molecule excited state with transient temporal resolution absorption spectrum or Raman spectrum.

In order to further confirm the autocatalytic growth of gold seed particles in the photochemical synthesis, the kinetic curves of the absorbance of surface plasmon absorption against the irradiation time at 516nm and 525nm were plotted in Figure 9, respectively. The sigmoidal shape (curve-a and b) provides an evidence of autocatalytic growth, i.e. Au(III) ions in the solution were absorbed and reduced on the surface of forming small gold nuclei or the seed particles. In the presence of seed (curves-b and-c), the rapid increase of the absorbance in the early stage with UV or the solar radiation attributed to no existing induction period. These results are in agreement with the conclusions of the autocatalytic growth in the literatures (39, 48).

Conclusions

It is considerable successful to use a seed-mediated growth approach under the UV solar radiation on the plateau for the size-controlled photochemical synthesis of the colloidal gold nanoparticles. Different sized gold particles with improved monodispersity and uniform shape were obtained by varying the molar ratio of seed to Au(III) ion and step by step seeding method. No additional nucleation during the seed-mediated growth was observed under the UV solar radiation. A nicely colloidal gold disperse protected by PEG pseudo-crown ether structure is both considerably stable and more active. This novel route exhibits that it is feasible to synthesize gold

nanoparticles in larger scale in the selective solution system under the UV solar radiation on the plateau with the higher elevation, using a seed-mediated growth technique.

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About the Authors

Professor Dong Shouan is a Research Fellow at the Kunming Precious Metals Institute in China. His research interest is in the field of chemical material and analytical chemistry of precious metals.

Professor Zhao Huaizhi was Director of the Kunming Precious Metals Institute in China from 1984-1994. His research is focused on the precious metal materials. He has wide interests in the development and application precious metals.

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