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Seed-mediated successive growth of gold particles accomplished by UV irradiation: a photochemical approach for size-controlled synthesis

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Abstract

Preparation of monodispersed metal nanoparticles of different size has enormous importance in nanotechnology. Currently, the size controlled synthesis of nanoparticles is carried out either by using the capping property of a stabilizer that restrict the particle growth at the intermediate stage or by exploiting the variable size of the water pool of a reverse micelle as template. We have reported here a powerful and general method to prepare gold nanoparticles of controlled size by through UV irradiation technique. First small particles are prepared and then they are used as seed to prepare bigger particles by photoactivation technique. Metal particles of gold of different size (∼20–80 nm) have been synthesized by this method. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Gold nanoparticle; Surface development; Seed mediated growth; UV irradiation; Transmission electron microscopy (TEM)

1. Introduction

Synthesis of metal nanoclusters of desired size and shape has enormous importance in nanotechnology because of their size dependent optical, electronic, and chemical properties [1–6]. As a consequence, even the conventional noble metals, viz. silver, gold, platinum, etc. become very reactive in the nanoscale range. Further, they have very high surface energy causing them to agglomerate. Due to these facts their synthesis and stabilization has become a very difficult task. Metal particles in the ultrafine state have been prepared using various methods [7–15] such as chemical reduction, chemical liquid deposition, thermal decomposition, photochemical reduction radiolysis, etc. Until now noble metal colloids are prepared, and are stabilized by particle stabilizer such as polymer, surfactant, ligand, etc. The average size and size distribution of the nanoparticles qualitatively depends on the nature and concentration of metal ions and reducing agents [16]. The reproducibility of particle synthesis with respect to size is not quite satisfactory in many cases leading to a broad size distribution and the particles often observed to have polydispersity. A probable reason for this is the uncertainty of formation of nucleation centers, as suggested by many workers in this field. The mechanism of the particle synthesis has already been studied in detail [2,3,17–21].

The most accepted mechanism suggests a two-step process, i.e. nucleation and then successive growth of the particles. In the first step a part of the metal ions in solution is reduced by a suitable reducing agent. The atoms thus produced agglomerate to from small metal clusters. The clusters thus formed act as nucleation centers and catalyze the reduction of the remaining metal ions present in the adsorbed state or in the bulk. The result is the autocatalytic growth of the nucleation centers addressed as ‘development’ in the photographic processes. Current studies reveal further that the reduction potentials of $\text{metal}_{\text{ion}}/\text{metal}_{\text{atom}}$ and $\text{metal}_{\text{ion}}/\text{metal}_{\text{particle}}$ systems become more negative compared to that corresponding bulk metal [2,3,22–24]. For example, the reduction potential of the $\text{Au(III)}/\text{Au}_{\text{metal(aqueous)}}$ system is +1.5 V versus NHE. But for $\text{Au(III)}/\text{Au}_{\text{atom(aqueous)}}$ system it is −1.5 V versus NHE and that for $\text{Au(III)}_{\text{(aqueous)}}/\text{Au}_{\text{cluster}}$ system the reduction potential has an intermediate value. Similar results are obtained also for copper and silver and expected for other metals. This result has a great significance in understanding the mechanism of particle synthesis. The formation of metal atoms from its ions is very difficult because of the large negative potential of the $\text{metal}_{\text{ion(aqueous)}}/\text{metal}_{\text{atom}}$

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system. Conventional strong reducing agents like free radicals ($E^0 \sim -1.0$ to 1.5 V versus NHE), borohydride ($E^0 \sim -1.33$ V versus NHE) and weak reducing agents like hydrazine, alcohol may not reduce the metal ions. Thus, the uncertainty in forming nucleation center is understandable. Often trace impurities act as nucleation centers as they generally increase the reduction potential of $\text{metal}_{\text{ion(aqueous)}}/\text{metal}_{\text{atom}}$ system causing a favorable metal ion reduction [25]. Once the nucleation center is created, it acts as a catalyst for the reduction of remaining metal ions if present in the solution. The monodispersed particle formation is explained by the La Mar mechanism [26], that states initial formation of seeds and then their successive growth, i.e. development. However, under most practical conditions, growth and seed formation occurs simultaneously and sometimes aggregation [27] and formation of additional nucleation centers [28] plays a crucial role in the formation pathway. As a consequence, a broad size distribution is always observed. Metal colloids of variable size are prepared by varying the capping agent or by using a template. They restrict the particle growth at the intermediate stage and thus control the size. The most common one is the Frens' method, where different gold particles of different size are prepared by varying the gold ion to citrate ratio [29]. Citrate acts as both reducing agent as well as stabilizer. Surfactants and polymers are used in various ratios to control the particle shape and size [30–33]. Water pool of reverse micelle is also used as template for syntheses of metal particles with wide variation in size [34–37] by controlling the size of the water pool. Template synthesis has been found to be a very well suited alternative over capping agents and the dynamic aggregates of surfactants. There has been tremendous use of colloidal Au nanoparticles in recent years. Recent publications now describe interesting physical properties and possible applications of colloidal gold. Calorimetric DNA sensors based on colloidal gold [38,39], organized two- and three-dimensional arrays of colloidal gold nanoparticles are now getting attention of several scientists [40–44]. We describe here the synthesis of colloidal Au particles of different size by seeding approach. The "seed particles" were prepared photochemically by UV irradiation following a method reported earlier [45] in the presence of a neutral micelle of Triton X-100 (chemically known as poly(oxyethylene) *iso*-octyl phenyl ether and commonly known as TX-100. The seed particles were then grown to the larger size by the successive addition of metal ions and again UV irradiation under the same experimental condition. This simple photoactivation technique produces large colloidal gold particles in a reproducible and predictable way. Here particles have been observed to be nicely monodispersed in micelle. To our knowledge this is the first report where the synthesis of gold particles with controlled size have been done using photochemically prepared seed and seeding technique in conjunction with successive reduction through photo-irradiation.

2. Experimental and result

2.1. Regents and apparatus

$HAuCl_4$ and Triton X-100 are purchased from Aldrich. Double distilled water is used throughout the experiment.

Photochemical reactions were carried out in well stoppered 1 cm quartz cuvettes. Cuvettes filled with samples were placed horizontally for UV irradiation under a portable germicidal lamp (15 W; G 15 T8 UV-C, Phillips, Holand) at a distance of 10 cm.

UV–VIS spectra were measured in Shimadzu UV-160 digital spectrophotometer (Kyoto, Japan) with 1 cm quartz cuvette. Transmission electron microscopy (TEM) study of the particles were carried out at 200 kV using a Hitachi HF-2000 TEM equipped with a field emission source. An energy dispersive X-ray spectrometer (EDS) attached to the Hitachi HF-2000 TEM was used to determine the chemical composition of the samples. TEM specimens were prepared by placing microdrops of colloid solution on a carbon film supported by copper grids.

2.2. Preparation of gold seeds (S)

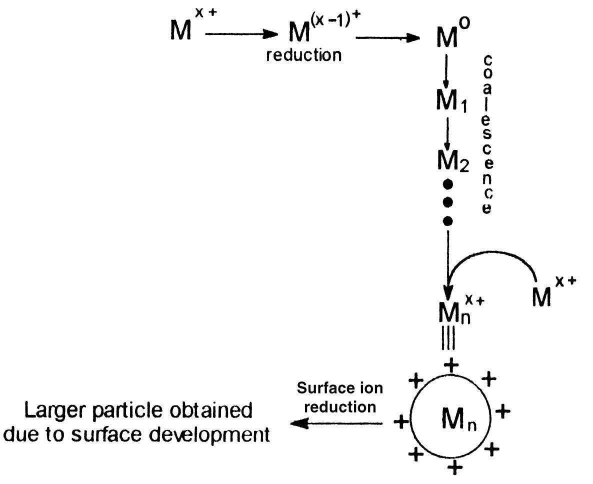
TX-100 (10^{-2} mol dm^{-3}) and $HAuCl_4$ (5.0×10^{-3} mol dm^{-3}) was taken in a quartz cuvette so that the final concentration of Au(III) ion remains 5.0×10^{-4} mol dm^{-3}. Now the cuvette is directly placed under UV light source. After 60 min irradiation, the solution turned pink and showed plasmon absorption band at 520 nm ($\lambda_{\max} = 520$ nm). This is an indication of the formation of gold particles. TEM image showed that the particle diameter lie within the range 15–20 nm. These particles were used as the seed (S) for the formation of particles of larger sizes.

2.2.1. Growth of seeds for the stepwise preparation of larger particles

Three (A–C) sets of solutions were prepared by using the following procedure.

2.2.1.1. Preparation of A. Here in the first step of particle enlargement, seed particles (S) were used for their further growth. Final concentration of metal sol and metal ion were adjusted to 1.67×10^{-4} and 3.33×10^{-4} mol dm^3, respectively, in TX-100 medium. The overall gold concentration in this mixture, i.e. $[Au(0)] + [AuCl_4^-]$ was 5.0×10^{-4} mol dm^{-3}. TEM image reflects that the average particle size was ~40 nm. It has been observed that gold ions are reduced more rapidly in the presence of seed particles. In fact, in the absence of gold particles, i.e. during seed formation, there existed an induction period for the growth of the seed particles.

2.2.1.2. Preparation of B. In this case also, particle enlargement were carried out using seed particles. Final concentration of metal sol and metal ion were adjusted to



Scheme 1. Schematic representation of the development of metal cluster.

Table 1
Condition for the preparation of gold particles for the successive growth

Metal	Sample set (prepared from)	$[M^0]$:$[M^+]$	$[M^0] + [M^+]$ ($mol\,dm^{-3}$)
Au	A (from S)	1:9	5×10^{-4}
Au	B (from S)	1:99	5×10^{-4}
Au	C (from A)	1:999	5×10^{-4}

5.0×10^{-5} and 4.5×10^{-4} mol dm^3, respectively, in TX-100 medium. The overall gold concentration in this mixture, i.e. $[Au(0)] + [AuCl_4^-]$ was 5.0×10^{-4} mol dm^{-3}. TEM image shows that the average particle size was ~60 nm. It has been noticed that gold ion is consumed more rapidly in presence of seed particles due to autocatalysis. The solution under this experimental condition became transparent and when viewed though the transmitted light the solution appeared red with blue tinge, i.e. when inspected in the direction of incident light. It appeared brown when looked perpendicularly.

2.2.1.3. Preparation of C. Here again during particle enlargement, particles prepared in the step A was used as the seeds for further growth. Final concentration of metal sol and metal ion were adjusted to 1.67×10^{-5} and 4.83×10^{-4} mol dm^3, respectively, in TX-100 medium. The overall gold concentration in this mixture, i.e. $[Au(0)] + [AuCl_4^-]$ was 5.0×10^{-4} mol dm^{-3}. TEM image indicates that the average particle size was ~80 nm. The particles are not stable enough and precipitated within 48 h. The relative particle concentration of C is very low, it is ~3 times lower than that of B and ~10 times lower than that of A.

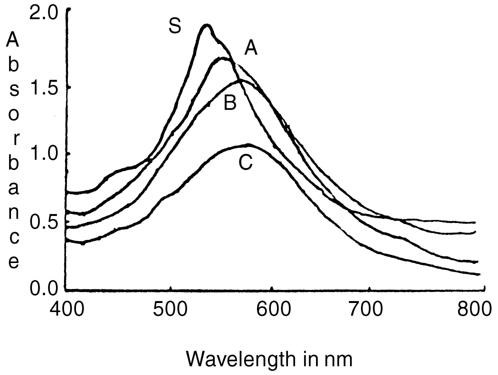


Fig. 1. UV–VIS spectra of solutions with different size Au nanoparticles (S represents the respective starter sol, i.e. 'seed'; A, B and C represent samples of increasing particle size).

3. Discussion

Our attempt is to develop a general and reproducible but simple photoactivation technique for the size- and shape-controlled preparation of gold nanoparticles. For this purpose we have used UV irradiation technique and controlled the conditions during the growth of the particles. First we have prepared smaller metal particles and latter on we used them as seeds (S)/nucleation centers for the preparation of desired particles with larger dimension, so that uncertainty of forming new nucleation centers or the importance of impurities for further creation of unwanted nucleation centers are nullified. During the addition of the chemical reducing agents the metal clusters are formed and the particles often get polydispersed due to the increase in local concentration of the reducing agent. Sometimes, new nucleation centers are formed with stronger reducing agent, despite the presence of the adsorbed metal ion onto the seed surface. Similar type of seeding method is recently used for the preparation of different silver and gold particles by chemical reduction method [19,46–48]. But this simple and reproducible approach for size controlled preparation of gold nanoparticles by UV-photoactivation technique has never been exploited earlier. The beauty of these seed

Table 2
Characteristic data for the gold system

Set	[Metal] used in the form of sol ($mol\,dm^{-3}$)	[Metal ion] added to sol ($mol\,dm^{-3}$)	Average size (nm) (calculated)	Average size (nm) (experimental)	Relative particle concentration
Seed	5×10^{-4}	–	–	18	5
A	1.67×10^{-4}	3.33×10^{-4}	33	38	1.67
B	5×10^{-5}	4.5×10^{-4}	50	59	0.5
C	1.67×10^{-5}	4.83×10^{-4}	72	79	0.17

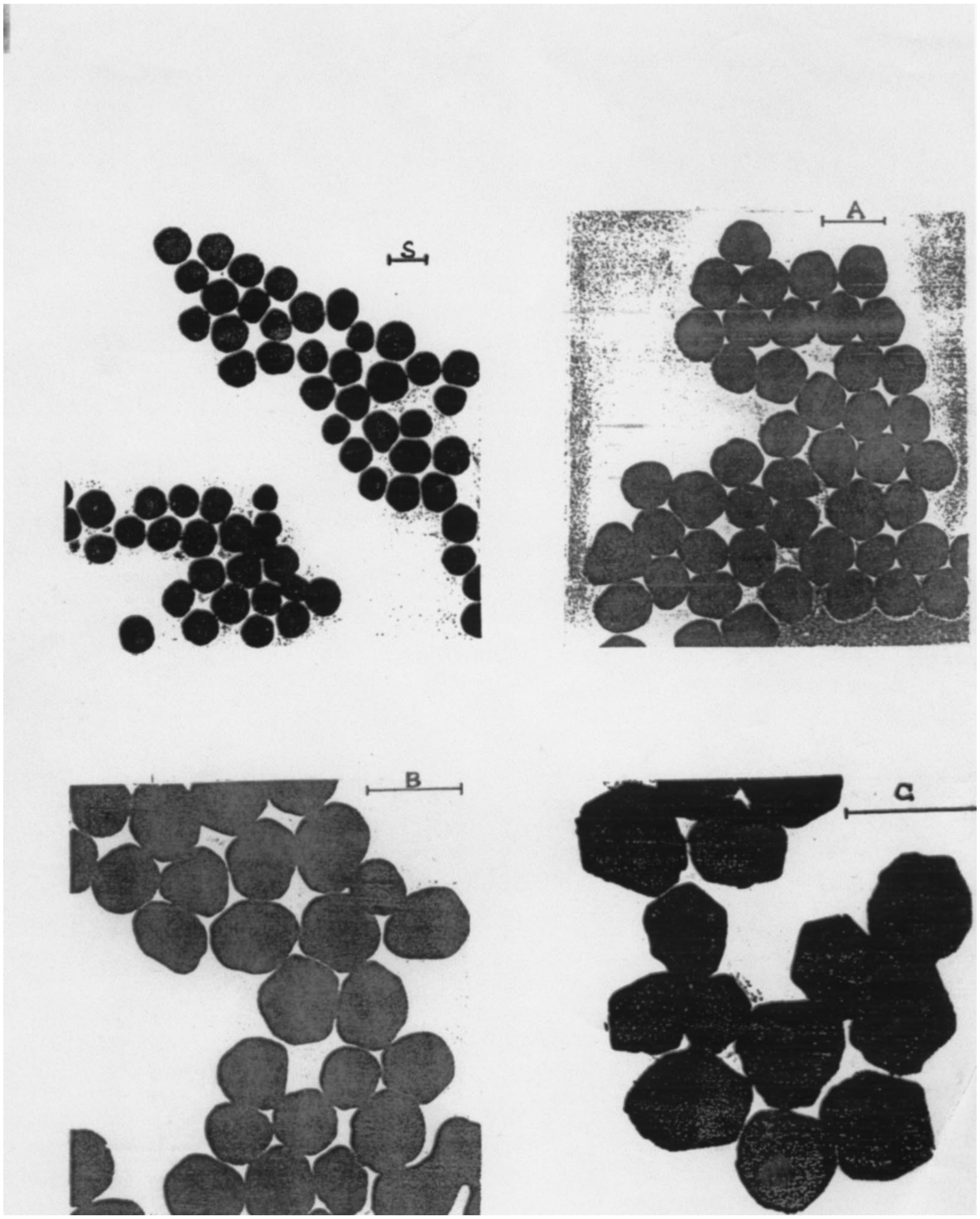


Fig. 2. TEM images with different size Au nanoparticles (S represents the starter sol, i.e. ‘seed’; A, B and C represent samples with increasing particle size). The bar represents particle diameter.

mediated method is that we can prepare a particle with desired size by varying the seed to metal salt concentration ratio. This can be calculated from the following simple equation:

$$r = r_\mathrm{s}\left\{\frac{[\mathrm{Au_a}]+[\mathrm{Au(0)}]}{[\mathrm{Au(0)}]}\right\}^{1/3}$$

where r_s is the particle radius for seed, r the particle radius for larger particle, [Au(0)] the gold concentrations in seed, and $[\mathrm{Au_a}]$ are the gold concentrations in added ion.

In this paper nanosize gold particles of better monodispersity is used as seed particles, which was prepared, by using UV irradiation method [45]. In the second step, required amount of metal seed particles, metal salt and TX-100 (playing roles of both reducing agent and particle stabilizer) were mixed and kept in UV exposure for the growth of the seed. At this stage the preformed seeds act as nucleation centers and become larger due to the reduction of the added bulk metal ions at its surface of the seeds. When trivalent gold ions $\mathrm{Au(III)Cl_4}^-$ are irradiated by UV-light the reduction occurs by successive steps (reduction into the unstable bivalent state Au(II) then disproportionation of Au(II) into Au(III) & Au(I)). However, Au(I) ions are not reduced as far as Au(III) ions are more concentrated than Au(I), nor do they disproportionate because the redox potential involving the single atom E^0(Au(I)/Au(0)) is quite negative, −1.4 [49]. Thus, $Au(I)Cl_2^-$ ions accumulate and the cluster appearance is delayed by an induction time [50]. Energy deposition throughout the solution ensures the homogeneous distribution of photolytic radicals formed by ionization and excitation of the solvent. However, direct photolysis of H_2O is UV-light source dependent.

$$H_2O \xrightarrow{h\nu} H^{\bullet} + OH^{\bullet}$$

$R{-}OCH_2CH_2{-}OH$ [R = $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_{\sim 9}{-}$] is the scavenger of $H^{\bullet}$, $OH^{\bullet}$ radicals. TX-100 on oxidation by $H^{\bullet}/OH^{\bullet}$, yields $R{-}OCH_2CH^{\bullet}{-}OH$, which has strong reducing property as H atoms. On the other hand, it has been known that photolysis of $AuCl_4^-$ may produce $AuCl_3^-$ and Cl atom in solution. The Cl atom in turn could cause abstraction of H-atom from the scavenger $R{-}OCH_2CH_2OH$ in a similar manner to $OH^{\bullet}$. They are, therefore, able to reduce metal ions.

$$R{-}OCH_2CH_2{-}OH \xrightarrow{OH^{\bullet}} R{-}OCH_2CH^{\bullet}{-}OH + {}^{\bullet}H_2O$$

$$R{-}OCH_2CH_2{-}OH \xrightarrow{H^{\bullet}} R{-}OCH_2CH^{\bullet}{-}OH + H_2O$$

$$R{-}OCH_2CH^{\bullet}{-}OH + M^+ \rightarrow M^0 + R{-}OCH_2CHO$$

The atoms are formed homogeneously throughout the solution. The binding energy between two transition metal atoms is stronger than the atom–solvent bond energy. Therefore, the atoms dimerize or associate with excess ions.

$$M^0 + M^+ \rightarrow M_2^+$$

By a multi-step process these species progressively coalesce into clusters as follows:

$$M_{n+x}{}^{x+} + M_{m+y}{}^{y+} \rightarrow M_{p+z}{}^{2+} + z \text{ with } n + m = p \text{ and } x + y = z$$

where n, m and p represent the nuclearities, i.e. the number of the reduced atoms they contain, and x, y and z represent the charge of metal ions adsorbed on the clusters (Scheme 1). The sizes of the metal particles were controlled by varying the ratio of seed to that of the added metal ions. Condition for the preparation of gold particles for successive growth (seed–ion ratio) and characteristic data for preparation of gold particles are maintained in Tables 1 and 2, respectively. Figs. 1–3 present the UV–VIS spectra, TEM images and histogram of the seeds and their successive bigger particles of gold, respectively. The gold sol has a rich plasmon band (Fig. 1). The gradual broadening and the red shifted plasmon peak position represent the growth of the gold particles in solution. Moreover, the size-dependent redox potential values of metal nanoparticles (smaller the size lower becomes

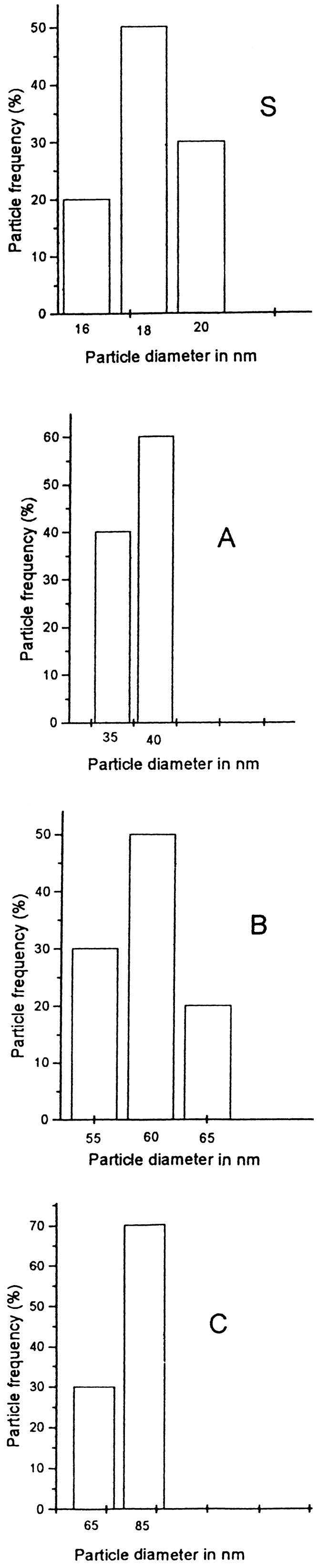


Fig. 3. Size distributed histogram (particle diameter vs. particle frequency) of Au nanoparticles (S represents starter sol, i.e. 'seed'; A, B and C represents samples of increasing particle size).

the redox potential value) speaks for the faster rate of autocatalytic growth for the small range of particles in comparison to particles of larger dimension. The photo-reduction of metal salts become reproducible with UV source because the homogeneous nature of the flux density.

4. Conclusion

The seeding effects described here will literally apply to other systems also, especially when the seed is generated as the important but first step of the size control growth of the particles. It is shown how strongly the elementary processes during the growth of small seed particles are affected by the reducing power of reducing agents/nucleophiles. We already emphasized the preparative aspects of the present work in part [51]. The selective shape-dependent growth of the particles during their successive development in size warrant further and extensive theoretical work. In our previous work [52] a new intriguing character of copper, silver and gold to become selectively cubical, spherical and non-spherical particles, respectively, at the time of their growth from the spherical seed should be looked into from the surface energy of the crystal growth. There are some important advantages to use the photochemical method for the preparation of size controlled synthesis of colloidal gold nanoparticles, first thing is that, controlled reduction of metal ions can be carried out without using excess reducing agent. Secondly the rate of reaction is well known, since the number of reducing equivalents generated by radiation is well defined and radiation is absorbed regardless of the presence of light-absorbing solutes and products. In conclusion, the novelty of this two-step seed mediated size development method (seed formation and size development) for the generation of nanoparticles lies in its simplicity and simultaneous control of both size and shape of the particles without any use of capping agent or template. The seed mediated technique or its modified version may be useful for other systems of nanoparticles for producing particles of desired sizes and shapes.

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