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## UV-light induced shape changes of gold nanoparticles

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### ABSTRACT

Gold nanoparticles prepared via laser ablation in aqueous micellar solution and by chemical method was studied under UV-light. The results showed that, no effect of light was observed on the nanosphere in micellar solutions. While in case of nanoparticles prepared by laser ablation in distilled water, the aggregations was observed. This may be due that the capping micelles prevent the nanoparticles from aggregation during the irradiation time courses. On the other hand the gold nanorods (Nds) of aspect ratios of L/d(length divided width)= ~2.6, 3.1,3.6, and 3.8 with absorption maxima at 700, 730, 760 and 780nm, respectively, have been found to change their shape after irradiation. The rat of photodecomposition decreases with decreasing the aspect ratios. The critical photodecomposition was at aspect ratio of 2.3. The decreasing was explained in the dissolution of the surfactant around the gold nanorods. © 2008 Trade Science Inc. - INDIA

### KEYWORDS

Gold nanoparticles;  
Micellar solutions;  
Critical photodecomposition;  
Nanorods;  
UV-light.

### INTRODUCTION

Ultrafine noble metal particles have been prepared by various methods and the studies of their physico-chemical properties have been a very active field of research due to their potential applications in optics, electronics, and catalysis. In particular, optical properties of gold, silver, and copper have been extensively studied since they strongly absorb light in the visible region due to the surface plasmon resonance<sup>[1-4]</sup>.

The preparation of anisotropic metal particles has been reported; they show unique optical propertie<sup>[5]</sup>. Anisotropic gold<sup>[6]</sup> have been prepared by using cationic micelles and microemulsions which are called “soft templates”. On the other hand the preparation of gold nanoparticles by UV-irradiation were carried out in micelles and the results obtained illustrated that the for-

mation depends on the concentration of Au ions and the cationic surfactants as well as UV-irradiation time<sup>[6,7]</sup>. The study of reshaping of gold nanorods by thermal effect and under femtosecond laser pulses can cause fragmentation of the gold nanorods into smaller spherical particles<sup>[8]</sup>. Furthermore, it was reported by Chang et al.<sup>[9]</sup> that after irradiation with low power nanosecond pulses a high abundance of spherical shaped nanoparticles was produced which were suggested to be an early stage of the shape transformation from a rod to a sphere<sup>[10]</sup>. The effect of temperature on the gold nanorods encapsulated in micelles<sup>[11]</sup> with an average aspect ratio 3.3 was carried out. The results obtained showed that the mean aspect ratio of the nanorods in the solution decreases with increasing temperature while the average width remains approximately constant. The results showed also differences in the ther-

mal stability of micelles of different lengths. The kinetic study of the thermal reshaping is carried out. The activation energy of the nanorods reshaping (micelles decomposition) is found to be  $21.0 \text{ k cal mol}^{-1}$ . The most stable rods shaped micelles is found to have an aspect ratio 2.0<sup>[12]</sup> gold nanorods with different aspect ratio of  $L/d$  (length divided width) = 4, 3.5, 2.8 were studied in binary solvents of aqueous glycerol water ratio (25-75%) and different temperatures (35-100 C°). The results showed that, the longitudinal surface plasmon resonance ( $SP_L$ ) is strongly dependent on the temperatures. The activation energy was found to be  $12.9 \pm 1.0 \text{ K cal mol}^{-1}$ <sup>[13]</sup>.

In the present study we reported the effect of UV-light on the shaping of gold nanoparticles and gold nanorods with different aspect ratios.

## EXPERIMENTAL

Gold nanoparticles were prepared by laser ablation of a metal gold plate in aqueous micellar solution of cetyltrimethylammonium bromide (CTAB), (pures,Fluka). Double distilled water was used. As shown in figure 1, the gold plate (>99.9%) was placed on the wall of a glass tube filled with 3mL of a solvent. Laser pulses ( $\tau = 8 \text{ ns}$  at 10 HZ) from a Nd-YAG laser (continuum SLI-10) at  $\lambda = 1064 \text{ nm}$  were focused onto the surface of a gold plate using a fused silica cylindrical lens ( $p = 100 \text{ nm}$ ). The focused region on the gold plate has a rectangular shape of 6 nm length and 0.5nm wide. The position of the laser beam on the surface of the pre polished metal plate could be varied, to obtain a fresh surface and help to provide ~homogeneous nanoparticles. The energy of Nd-YAG laser was 100 mJ/pulse measured by power energy meter (molelectron-EPM 2000:Tar5). The colored solution was measured by Perkin Elmer Lambda-40 spectrophotometer after irradiation courses.

Gold nanosphere were prepared by borohydride reduction of the gold salt in the presence of citrate as capping agent<sup>[14]</sup>. The different sizes of gold nanorods were prepared by variation the ratio of the seed mediated growth according to Nikoobakat and El-Sayed<sup>[15]</sup>. The samples prepared by laser ablation technique or by the chemical method were irradiated by using UV-light source (Analamp mod. 81-105-7-01,230 nm,

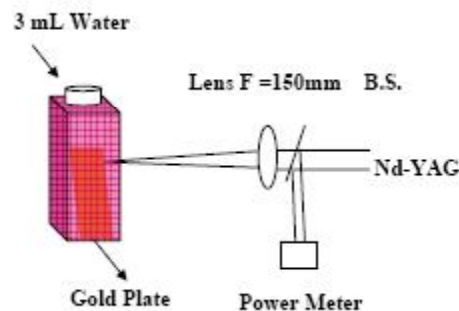


Figure 1 : Schematic diagram of the experimental set up

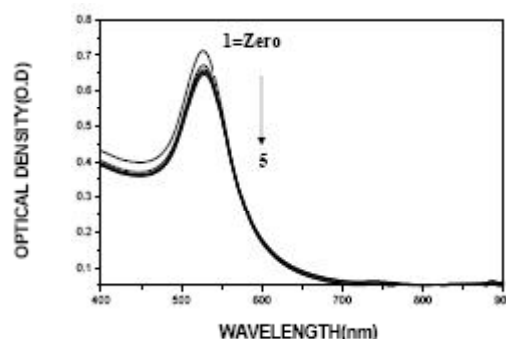


Figure 2 : Dependence of the absorption spectra of gold nanoparticles prepared by chemical method in CTAB micellar solution on UV-irradiation: interval times (1-5) 20 minutes

USA) 3ml colloidal solution of the nanoparticles were put at 5cm under the UV-light source and exposed to different irradiation time.

## RESULTS AND DISCUSSION

It is well known that, the optical absorption spectrum of gold nanoparticles is due to the surface plasmon (SP) resonance(s) and the nanoparticles of sizes of 5-50 nm showed a sharp band in the 520-530 nm regions<sup>[14]</sup> and is known transverse band. With increasing the length of the nanoparticles, the absorption spectra are characterized by two bands. The first band is an intense band at longer wavelength and corresponding to the longitudinal resonance band and the other is a much weak transverse resonance band at ca.  $\lambda_{\text{max}} = 528 \text{ nm}$ <sup>[16,17]</sup>. The position of the longitudinal band undergoes red shift with increasing the gold nanorods aspect ratio. The mean transverse diameter of Au nanorods is typically equal to ca. 10 nm, while its mean longitudinal length is variable<sup>[14]</sup>.

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### Effect of irradiation by UV-light

By irradiation the spherical nanoparticles that prepared by chemical method or by laser ablation technique in micellar solution as a function of time, the optical density showed a very slightly decreasing without any remarkable shifts in the corresponding wavelengths of each nanoparticles, figures 2 and 3. This may be due that the capping micelles prevent the nanoparticles from aggregation during the irradiation time courses. On the other side, the study of the effect of the irradiation on the gold nanorods encapsulated in micelles with an average aspect ratios of ( $L/d=2.6, 3.1, 3.6, 3.8$ ) with the absorption maxima at 700, 730, 760 and 780 nm, respectively was carried out. Figure (4-a,b) shows the absorption spectra of the changes of gold nanorods of ( $L/d= \sim 2.6$ ) before and after irradiation by UV-light. The optical density at both longitudinal and transverse plasmon bands decreases with increasing the irradiation time and the absorption maxima was gradually shifted to shorter wavelengths ( $\lambda_{max} = 700-672$  nm), figure (4a). It is clearly observed from the absorption spectra that no significant changes in the width of the nanorods. The optical density at  $\lambda_{max} = 533$  nm was decreases without changes in the band width in the range 511-550 nm. Therefore, the decreasing in the absorption spectra and the blue shifts in  $SP_L$  are caused by decreases in the length of the nanorods. Figure (4b) illustrate that the normalized absorption spectra changes in linear way. This may be due to the regular reshaping of the nanorods inside the capping micelles with the decomposes of micelles around the gold nanoparticles and accordingly the decomposes of the gold nanoparticles in regular way and precipitate in the solution. The thermal stability of gold nanorods in aqueous micellar solution and in binary glycerol/water micellar solutions was studied<sup>[12,13]</sup>. The results showed that such change in configuration requires the breaking of bond between the micelles and the gold surface, which could lead to either the breaking of the micelles around the long rods or the annealing of the micelles around the shorter rods. At this point the long rods break faster than the shorter one as the temperature increases. The activation energy in case of micellar solution was  $21.0 \pm 1$  k cal/mol<sup>[12]</sup>, while in case of binary glycerol/water micellar solutions it was found to be  $12.9 \pm 1$  k

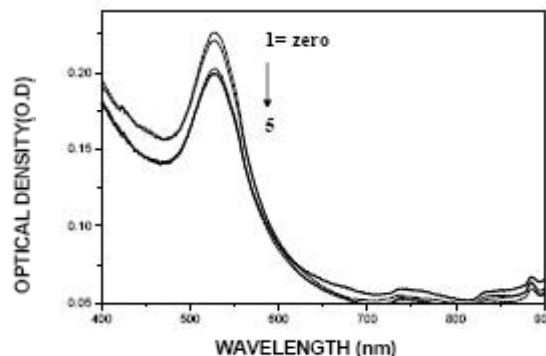


Figure 3: Dependence of the absorption spectra of gold nanoparticles produced by laser ablation in micellar solution on UV-irradiation: interval times (1-5) 20 minutes

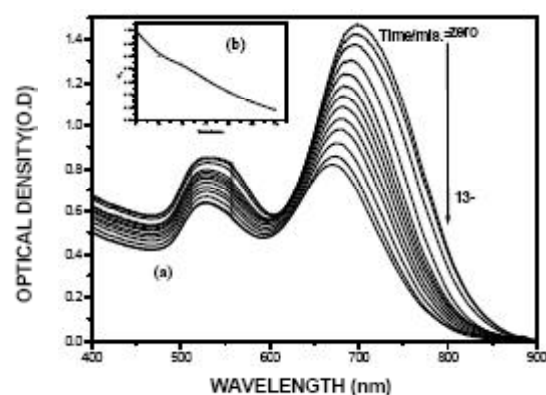


Figure 4 : (a) Dependence of the absorption spectra of gold nanorods on UV-irradiation: interval times (1-13) 20 minutes, (b) Dependence of the normalized of gold nanorods at  $\lambda=700$ nm. on the irradiation time

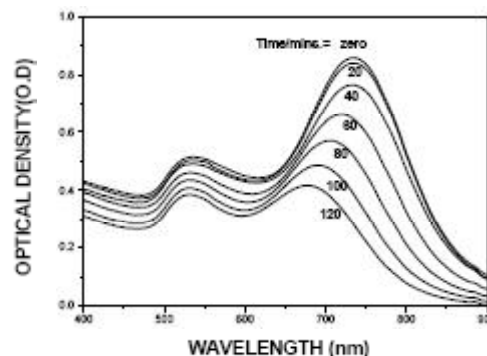


Figure 5 : Dependence of the absorption spectra of gold nanorods on UV-irradiation,  $\lambda= 730$ nm

cal/mol<sup>[13]</sup>. The lowering of the activation energy may result from the lowering of the dielectric constant of aqueous glycerol/water micellar co-solvent. The smaller the dielectric constant of the organic solvent, the more easily it can break the micelles by lowering the overall dielectric constant of medium<sup>[18]</sup>. It is worthwhile to

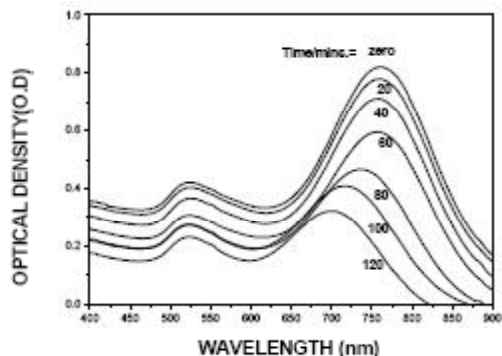


Figure 6 : Dependence of the absorption spectra of gold nanorods on UV-irradiation,  $\lambda = 760\text{nm}$

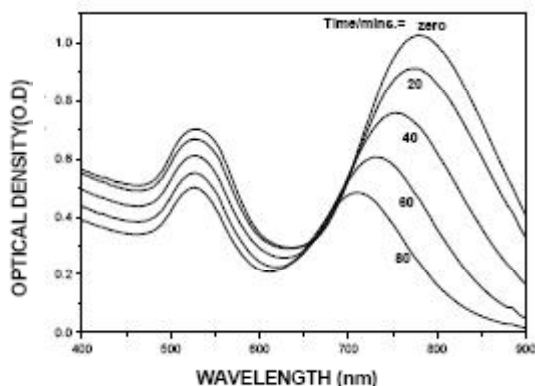


Figure 7 : Dependence of the absorption spectra of gold nanorods on UV-irradiation,  $\lambda = 780\text{nm}$

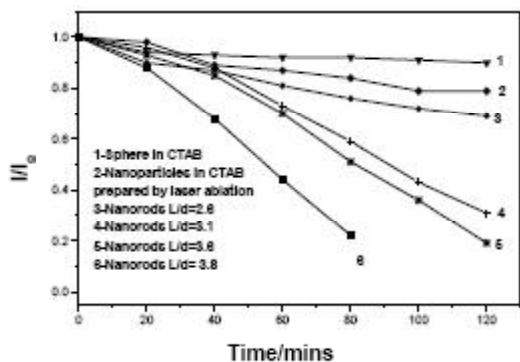


Figure 8 : Normalized absorption spectra of gold nanoparticles at different irradiation time

mentioned that with increasing the irradiation time of gold nanorods, the rate of decomposition decreasing with decreasing the length, figures (5-7). Figure 8 illustrate the normalized absorption spectra of the gold nanoparticles at different aspect ratios and different irradiation time courses. The figure showed that the rate of photodecomposition depend on the aspect ratio. As observed from the figure a slightly decreasing in the rate in case of nanosphere and high increases in linear way

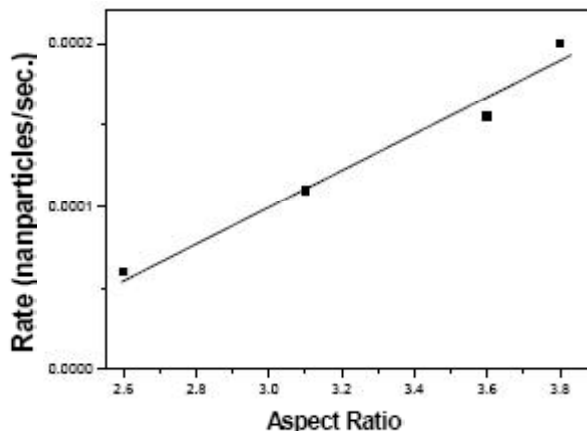


Figure 9 : Rate of photodecomposition of gold nanoparticles at different ratio L/d

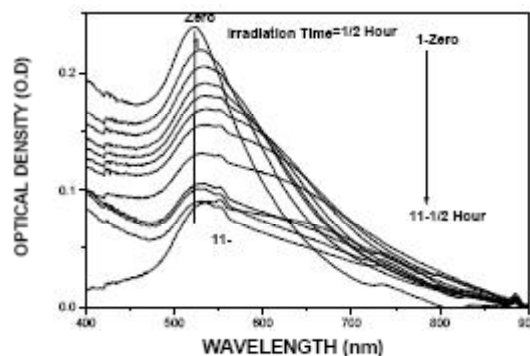


Figure 10 : Dependence of the absorption spectra of gold nanoparticles prepared by laser ablation technique in distilled water on UV-irradiation

with increasing the aspect ratios. The effect of the aspect ration on the photodecomposition rate was calculated from the slope of different aspect ratios in figure 8. The relation between the rate of photodecomposition and the different aspect ratios in figure 9, could be calculated according the following equation.

$$R = x + B \cdot X \tag{1}$$

$$R = -2.3 + 1.1 \cdot X$$

Where R is the rate of photodecomposition, x is the critical photodecomposition of gold nanorods ratio given by inter-section of the linear curve with the x axis, B is the slope of the linear curve and X is the aspect ratio.

The figure showed that at aspect ratio 2.3 the nanorods may be difficult to decomposes by light. It is also showed that, the rate of photodecomposition increases by 1.14 with increasing the L/d by 0.1. Figure 10 Showed the absorption spectra of gold nanoparticles prepared by laser ablation technique in distilled water on UV-irradiation. By irradiation the nanoparticles as a

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function of time, the absorption maximum of the surface plasmon resonance (SP) shows a red shift and accompanied with a decreasing in the optical density and a broadening of the absorption spectra from ~600-850nm. The broadening may be due to the light scattering. The observed red shifts from  $\lambda_{\text{max.}} = 521\text{nm}$  to  $\lambda_{\text{max.}} = 540\text{nm}$  with the decreasing in the optical density of the absorption maximum can be ascribed to the aggregation of the gold nanoparticles. It is worthwhile to maintain that the capping micelles prevent the spherical nanoparticles from aggregation during the irradiation time courses.

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