UV–visible light reshaping of gold nanorods

Article in Materials Chemistry and Physics - May 2010
DOI: 10.1016/j.matchemphys.2010.01.048

CITATIONS
9

READS
51

1 author:

Alsayed A M Elsherbini
Cairo University
59 PUBLICATIONS 411 CITATIONS

Some of the authors of this publication are also working on these related projects:

- Exfoliation of graphene sheets via high energy wet milling of graphite in 2-ethylhexanol and kerosene
  View project

- Photocatalysis of selected drugs using TiO2-based nanomaterials View project
UV–visible light reshaping of gold nanorods

El-Sayed A.M. Al-Sherbini

Department of Measurements, Photochemistry and Agriculture, National Institute of Laser Enhanced Science (NILES), Cairo University, P.O. Box 12613, Al-Gamaa, Cairo, Egypt

A R T I C L E   I N F O

Article history:
Received 28 June 2009
Received in revised form 3 January 2010
Accepted 25 January 2010

Keywords:
Gold nanoparticles
Localized surface plasmon resonance (LSPR)
Photostability
Laser ablation
Micellar solutions

1. Introduction

Gold nanoparticles have unique optical and chemical properties that make them ideally suited for a number of applications in biotechnology, including optical probes, targeted drug delivery, and programmed material synthesis. The optical response of gold nanoparticles is often characterized by the presence of a strong absorption band that is absent from the spectrum of the bulk. This is attributed to a resonance in the collective motion of the conduction electrons in response to an incident electromagnetic field and is called the localized surface plasmon resonance (LSPR). LSPR is dependent on the size, shape and degree of particle–particle coupling of the nanoparticles, dielectric properties of the metals from which the nanoparticles are composed and dielectric properties of the local environment in which the nanoparticles are immersed [1–4].

Gold nanoparticles in different modifications (e.g. spherical, rods, shells) are the most promising candidates for photothermal (PT) sensitizers, since they are strong absorbers, nontoxic, easily conjugated to antibodies or protein and have adjustable optical properties. It has been discovered that an accumulation of gold nanoparticles on a cell membrane leads to an increase in bubble formation efficiency, resulting in more severe cancer cell damage at relatively low laser fluence of 60–80 mJ cm⁻², which is safe for normal tissues [5,6].

Nanophotothermolysis with pulsed lasers and absorbing nanoparticles attached to specific targets has recently demonstrated great potential for selective damage to cancer cells, bacteria, viruses and DNA. When nanoparticles are irradiated by short-laser pulses, their temperature rises very quickly leading to irreversible cell target damage, without damaging the surrounding healthy tissues.

The effect of temperature on the gold nanorods encapsulated in micelles [7] was investigated and the results showed that the absorption maximum of the longitudinal band SPₐ of the nanorods decreases and blue shifted with increasing the temperature time courses while the average width remains approximately constant [8–10]. This might be due to the differential thermal instability of rods or the capping micelles. The temperature could reshape the individual nanorods inside the micelles, or the long micelles could dissolve as the exposure time of temperature increases. The later leads to precipitate of the longer gold nanoparticles out of the solution being studied. The effect of short-laser pulses on the stability of gold nanorods was studied. The results showed that the final products strongly depend on the energy of the laser pulse as well as on its width. At high laser fluences (∼1 J cm⁻²) the gold nanorods was melted into spherical nanoparticles (nanodots). Upon decreasing the energy of the excitation pulse, only partial melting of the nanorods takes place. Shorter but wider nanorods are observed in the final distribution [11–13].

In the present study the photostability of the gold nanoparticles prepared via laser ablation in water or in aqueous micellar solution and by wet chemical method was studied using different low power laser sources and UV-light conventional lamps.
2. Experimental section

Gold nanoparticles were prepared by laser ablation of a metal gold plate in aqueous micellar solution of cetyltrimethylammonium bromide (CTAB) (Puress, Fluka). Double distilled water was used. As shown in Fig. 1, the gold plate (>99.9%) was placed on the wall of a glass tube filled with 3 mL of micellar solution. Laser pulses (τ = 8 ns at 10 Hz) from a Nd-YAG laser (continuum SLI-10) at λ = 1064 nm were focused onto the surface of a gold plate using a fused silica cylindrical lens (ϕ = 100 nm). The focused region on the gold plate has a rectangular shape of 6 nm length and 0.5 nm wide. The position of the laser beam on the surface of the 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⁻¹ measured by power energy meter (molelectron-EPM 2000:Tar5). The colored solution was measured by PerkinElmer Lambda-40 spectrophotometer after irradiation time courses. The samples prepared by laser ablation technique or by the chemical method were irradiated under different diode laser sources of different wavelengths of 620, 560, 520, 460 nm and or by using UV-light source (Analamp mod. 81-105-7-01, 230 nm, USA). 3 ml colloidal solution of the nanoparticles were put at 5 cm under the UV-light source and were exposed at different irradiation times.

Gold nanospheres were prepared by borohydride reduction of the gold salt in the presence of cetyltrimethylammonium bromide (CTAB) as capping agent [14]. Gold nanorods were prepared according to method reported by Nikoobakht et al. [15]. Gold nanorods prepared by using seed-mediated method. Seed and growth solutions were made as described below.

3. Seed solution

Cetyltrimethylammonium bromide (CTAB) solution (2.5 ml, 0.20 mol dm⁻³) was mixed with 2.5 ml of 5 × 10⁻⁴ mol dm⁻³ HAuCl₄. To the stirred solution, 0.3 ml of ice-cold 0.01 mol dm⁻³ NaBH₄ was added. The brownish yellow solution was vigorously stirred for 2 min and was kept at 25 °C.

4. Growth solution

CTAB (2.5 ml, 0.20 mol dm⁻³) was added to specific amount of 4 × 10⁻³ mol dm⁻³ AgNO₃ solution at 25 °C. To this solution, 2.5 ml of 5 × 10⁻³ mol dm⁻³ HAuCl₄ was added, and after gentle mixing of the solution 70 μl of 0.0788 mol dm⁻³ ascorbic acid (freshly prepared) added. Ascorbic acid as mild reducing agent changes the growth solution from dark yellow to colorless. The final step was the addition of the seed to the growth solution at 27–30 °C. The color of the solution gradually changed within 10–20 min. For longer NRs, the color changes takes place more slowly. The temperature of the growth medium was kept constant at 27–30 °C in all the nanorods preparations. By adjusting the amount of silver ions or gold seed concentrations the different aspect ratios can be obtained.

5. 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 that the nanoparticles of sizes of 5–50 nm show a sharp band in the 520–530 nm regions [14] where it is known a 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 it is corresponding to the longitudinal resonance band and the other is a much weak transverse resonance band at ca. λ max = 528 nm [16–18]. 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 lengths are variables [14].

5.1. Effect of irradiation by diode laser sources and by UV-light

Nanoparticles such as gold when stimulated with the right frequency of laser light can act as tiny, precise and powerful heaters, which potentially could be used in biomedical applications. The problem is that the stability during irradiation by different laser sources is a crucial parameter. Thus, the study of the photostability of special interest to evaluate how the gold nanoparticles can be applied in the field of biotechnology.

By irradiation the spherical nanoparticles, that are previously prepared by chemical method or by laser ablation technique in micellar solution, using diode lasers (620, 560, 520, 460 nm; 150–250 W m⁻²) or UV lamp as a function of time, the optical density showed a slight decrease in the intensity without any remarkable shifts in the corresponding wavelengths of each nanoparticles, Figs. 2 and 3. This may be due that the capping micelles prevent the nanoparticles from aggregation during the
irradiation time courses. Also an aqueous solution of gold nanorods with the absorption spectra of $\lambda_{\text{max}} = 730$ nm was irradiated under the same conditions by using diode lasers at 620 nm, Fig. 4. The figure demonstrates insignificant decrease in the optical density with increasing the exposure time. The same results were obtained when the samples were irradiated at 560, 520, 460 nm, are not shown here.

Fig. 5 shows the absorption spectra of the changes of gold nanorods of ($L/d = \sim 3.1$) before and after irradiation by UV-light at 365 nm. 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 ($\lambda_{\text{max}} = 730–691$ nm). The optical density at $\lambda_{\text{max}} = 533$ nm decreased without changes in the band width in the range 511–550 nm.

When a new sample of the same aspect ratio ($L/d = \sim 3.1$) irradiate by UV-light source at 230 nm, Fig. 6. The figure showed that the rate of the photodegradation increases and it was also blue shifted to $\lambda_{\text{max}} = 677$ nm. Therefore, the decreasing in the absorbance and the blue shifts in SPL are caused by decreases in the average length of the nanorods and the absorption spectra changes in $\sim$ linear way, Fig. 9-5,6. This may be due to the regular reshaping of the nanorods inside the capping micelles. The rod shape capping CTAB micelles is unstable, and they decompose much faster than the short rod shape micelles. Accordingly, the long gold nanorods decompose and precipitate out in the solution.

Structural transformation of gold nanorods is investigated by using low-energy femtosecond and nanosecond laser pulses in colloidal solution [13]. The observation results suggested that, short-laser pulsed photothermal melting begins with the creation of defects inside the nanorods followed by surface reconstruction and diffusion, in contrast with the thermal melting of the rods, where the melting starts at the surface. The thermal stability of gold nanorods in aqueous micellar solution and in binary glycerol/water micellar solutions was studied [9,10]. The results indicated 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 longer rods break faster than the shorter one as the temperature increases. With increasing the aspect ratios of gold nanorods, the rate of photodecomposition increases with increasing the length, Figs. 7 and 8. Fig. 8 shows the TEM images of gold nanorods taken from solution (a) at the start and (b) at the end of the experiment. Fig. 9 illustrates the normalized absorption spectra of the gold nanoparticles at different aspect ratios and different irradiation time courses. The figure shows that the rate of photodecomposition depends on the aspect ratio. As observed from the figure, a slight decreasing in the rate in case of nanosphere or with using the diode laser. When UV-light was used the results shown high increases in the pho-
todecomposition in linear way with increasing the aspect ratios \((L/d)\). The effect of the aspect ratio on the photodecomposition rate was calculated from the slope of different aspect ratios in Fig. 9. In case of the aspect ratio of 2.6 the photodecomposition rate was \(\sim 6 \times 10^{-5}\) absorbance s\(^{-1}\), while for 3.8 aspect ratio, the photodecomposition rate was \(\sim 2 \times 10^{-4}\) absorbance s\(^{-1}\). The relation between the photodecomposition rates s\(^{-1}\) versus the different aspect ratios illustrated in Fig. 10, and could be calculated according the following equation.

\[
R = C + B \times X = 5 \times 10^{-5} + 6.4e^{-6} \times X
\]  

where \(R\) is the rate of photodecomposition s\(^{-1}\). \(C\) is the intersection of the linear curve with the y axis, \(B\) is the slope of the linear curve and \(X\) is the aspect ratio.

The critical aspect ratio given by intersection of the linear curve with the x axis. The figure shows that at aspect ratio 2.3 \(\pm 0.1\) the nanorods may be difficult to decompose by UV–visible light. It also showed that, the rate of photodecomposition increases by \(\sim 5.3e^{-8}\) s\(^{-1}\) with increasing the \(L/d\) by 0.1. Fig. 11a shows the absorption spectra of gold nanoparticles prepared by laser ablation technique in distilled water. By UV-irradiation the nanoparticles as a function of time courses, 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 within ~600–850 nm. The broadening might be due to inhomogeneous in the size and shape distribution. The observed red shifts from $\lambda_{\text{max}} = 521$ nm to $\lambda_{\text{max}} = 540$ nm with the decreasing in the optical density of the absorption maximum can be ascribed to the increasing in the particle sizes of the aggregated gold nanoparticles. Fig. 11b showed the TEM of gold nanoparticles before (a) and after irradiation (b) where aggregation is clearly observed. It is worthwhile to maintain that the capping micelles prevent the spherical nanoparticles from aggregation during the irradiation time courses.

Acknowledgment

The author gratefully acknowledge the help of Prof. M.A. El-Sayed, the director of Laser Dynamics Lab. (LDL) at the School of Chemistry and Biochemistry, Georgia Institute of Technology for his many helpful discussions during the preparation of this manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matchemphys.2010.01.048.

References