

Engineering plasmonic nanostructures with combining ultrasound and laser pulses

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ABSTRACT

The experimental conditions were investigated to fabricate Au nanorod (NRs) by pulsed laser ablation in water. This study revealed that it is possible to produce alternatively nanoparticles or nanorod at certain wavelengths depending on the laser. The values of the laser fluence for both wavelengths under the experimental conditions were chosen from several J/cm² to tens of J/cm². The optical extinction spectra of the colloids in the UV-Vis and IR regions were obtained to evaluate the structure of the dispersed Au phase. Scanning electron microscopy (SEM) was applied to visualize the size and morphology of the colloidal particles. Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded.

Keywords: Laser ablation, SEM, crystal sizes, Au nanorod

INTRODUCTION

Noble metal nanocrystals grab attention from a fundamental point of view and for

technological applications mainly due to the position of their surface plasmon resonance lying in the visible spectral range. The strong dependence of the optical, electronic,

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magnetic, and catalytic properties of the nanoparticles on their size [1] and their shape [2,3] provide opportunities of nanostructures for specific application by controlling the preparation conditions to produce nanoparticles with the desired size and shape. Spherical nanoparticles could be characterized by a single surface plasmon resonance (SPR) peak in their extinction spectrum. The appearances of two peaks arising from the transverse and longitudinal SPRs are observed at extended shapes such as spheroids or nanorods (NRs) [4,5]. The positions of these peaks in the extinction spectrum depend on the aspect ratio of the nanostructure considered [5]. The existence of aggregates or nanowires in the colloid influences the corresponding extinction spectrum in a specific way. One-dimensional nanostructures excite substantial interest regarding the fundamental properties of surface plasmon polaritons (SPPs) propagation in nanoscale structured matter [6]. On the other hand, they have potential applications in fields such as microelectronics, optoelectronics, nanoscale electronic devices and sensorics [7–9]. The gold nanorods exhibit excellent electric-conductivity, chemical and biocompatibility. Their properties depend on substances absorbed on the surface. In this study, we used the method of nanosecond laser ablation

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of a gold (Au) disc immersed in double distilled water to produce contamination-free nanorods network. The roles of the laser wavelengths and fluence were established. Some fundamental conditions specific for their formation were pointed out.

MATERIALS AND METHODS

The experimental setup employed for the fabrication of gold nanoparticles (NPs) and nanorods mentioned previously [10]. A detailed description of the materials and the preparation of the samples mentioned previously [11]. Briefly, a gold target in the form of a disc was placed on the bottom of a borosilicate vessel filled with double-distilled water. During the experiments, the vessel was rotated slowly at a constant speed and the water level above the surface of the target was fixed at 1cm. The second ($\lambda_{\text{SHG}} = 532 \text{ nm}$) and the third ($\lambda_{\text{THG}} = 1064 \text{ nm}$) harmonics of a Nd:YAG laser system were utilized to produce different Au colloids. The value of the laser fluence was varied in the range of a few J/cm^2 upto $50 \text{ J}/\text{cm}^2$. The lowest value was the ablation threshold, at which the characteristic values for the ablation process were observed. The highest value was determined by the onset of a spark discharge on the surface of the water due to optical break down in water. The diameter of the laser beam spot on the target surface when

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the second harmonic was used with increasing of the laser fluence from 0.5 mm (10 J/cm²) to 1 mm (50 J/cm²). The duration of the ablation process was from 10 to 30 min in all experiments. The SEM images obtained by JEOL JSM-6510LV/LGS. Both the NRs and NPs were further characterized by assessing their optical properties. The optical transmission spectra of the colloids were obtained by an Ocean Optics HR 4000 spectrophotometer in the range of 300–800 nm and FTIR spectrometer (Nexus, USA). The FTIR spectra were obtained in the wave number range from 400cm⁻¹ to 4000cm⁻¹. Ultrasonic irradiation was carried out using a standing wave sonication system (Kaijo 4021 type lot. no. 11EA00105, Oscillator 4611 type lot. no. 00102; frequency, 200 kHz; power, 200 W). The XRD diffraction pattern shows characteristic NRs diffraction maximum at 2 θ values. NRs characterized by XRD diffraction (D-5000 diffractometer, Siemens, Cu anode as the X-ray source, 25°C, 2 θ range 2–90 degree). Crystallite sizes were calculated using the Scherrer formula.

RESULTS

Three different approaches for fabrication of Au NRs by pulsed laser ablation of an Au target immersed in double-distilled water have been reported in the literature. The building of NRs is a result of the aging of

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already created NPs and is independent of the laser wavelength used for ablation [12]. The second approach was taken place in two steps [13,14]. In the first step, the Au NPs are prepared in pure water using the fundamental wavelength of a Nd:YAG laser (1064 nm). In the second step, the colloid thus prepared and mixed with an aqueous solution of sodium dodecyl sulfate (SDS) at prescribed gold nanoparticle and SDS concentrations is irradiated by a high-power pulsed laser emitting at 532 nm or 355 nm. The third approach consists informing Au NRs by laser ablation at 1064 nm and 532 nm or 355 nm of a gold metal disc in pure water without using any surfactant [15–17]. In the second and third approaches, using the wavelengths of 532 nm is of crucial importance in forming NRs. In this study, we set ourselves the task to elucidate the role of the laser and ultrasound fluence in forming the morphology of the nanostructures obtained by pulsed laser ablation of bulk Au material (disc) immersed in double-distilled water at the two wavelengths considered in fusion of ultrasonic generator. We described a novel one-pot ultrasonic_laser ablation fusion method to synthesize gold nanorods. We reported results on simultaneously in gold nanoparticles production. Gold plate in collide solution is placed into ultrasonic irradiation. The laser after passing lens in the

focal distance collides gold plate. As a result, ablation occur for gold particle through receiving exposure.

Figure 1 shows changes in the extinction spectra of the sample solution during ultrasonic irradiation under laser ablation. It can be seen that the extinction intensity gradually increases with irradiation time, and extinction peaks at around 510 and 880 nm are clearly observed. These peaks corresponded with the surface

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plasmon bands of gold nanorods. This result suggests that formation of the nanorods occurs. Since the formation of high temperature and pressure cavitation bubbles. Figure 2 shows SEM images of Au nanostructures fabricated at the above wavelength and four different time of the laser fluence, pulsed laser ablation by the laser fluence under ultrasound irradiation produce NRs.

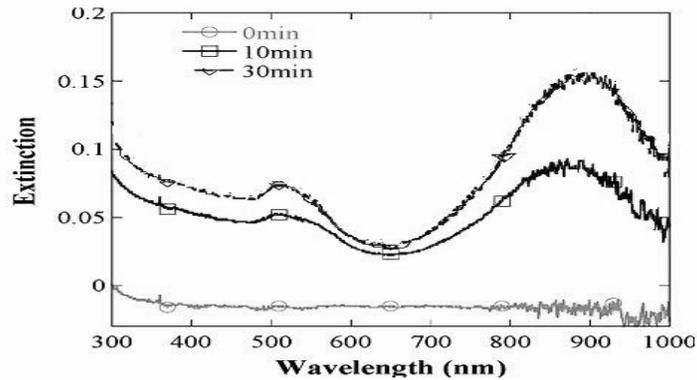


Figure 1. Changes in extinction spectra of sample solution of Au (I) during ultrasonic and laser irradiation.

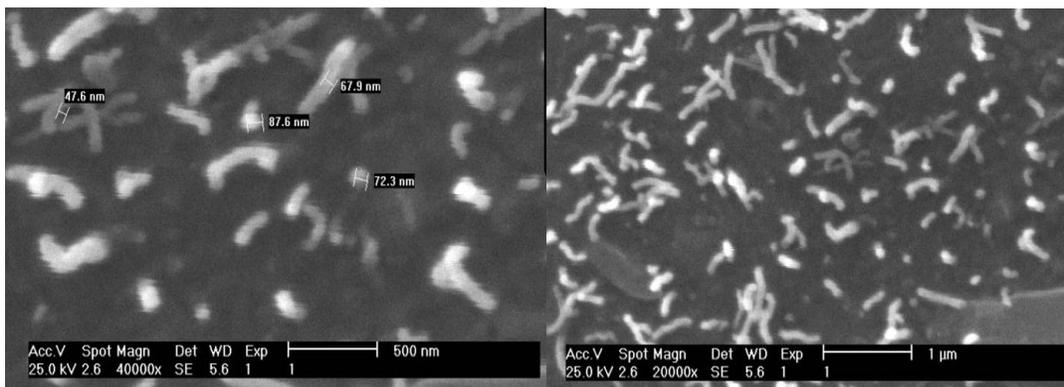


Figure 2. SEM micrographs of nanostructures.

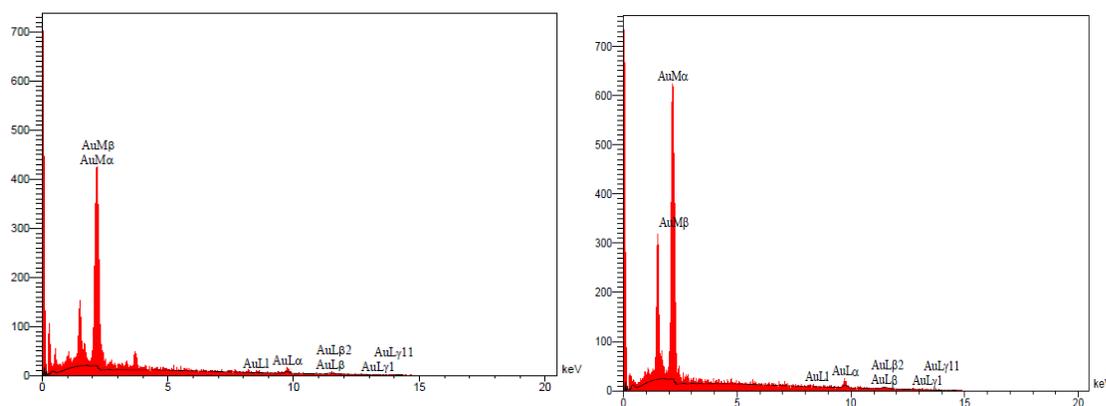


Figure 3. EDX images of gold nanoparticles fabricated by a Nd:YAG laser.

The XRD diffractogram in figure 3 shows characteristic NRs diffraction maximum at 2Θ values of 31.8, 34.5, 36.2, 47.6, 56.6, 62.9, 66.4, 67.9, 69.1, 72.6, and 76.9. Calculated crystallite size using the Scherrer equation is 50 nm. The XRD diffractogram shows characteristic NRs diffraction maximum at 2Θ values of 31.8, 34.5, 36.2, 47.6, 56.6, 62.9, 66.4, 67.9, 69.1, 72.6, and 76.9. Calculated crystallite size using the Scherrer equation is 50 nm. Compared to the XRD diffractogram of spherical NPs nanoparticles it shows higher intensity of (002) peak, indicating the preferential growth of rods along (002) direction (c-axis). The preferential growth in one direction is the consequence of the growth rate difference in various directions of the gold crystal. During hydrothermal synthesis the relative growth of

(0001) face is higher than that of other ones, leading to the formation of extended prismatic hexagonal Au crystals. The FTIR spectra of NRs were shown a characteristic absorption band between 420 and 510 cm^{-1} due to two transverse optical stretching modes of NRs. The NRs spectra were splitted into two maximum at 507 and 910 cm^{-1} .

CONCLUSION

This study was emphasized the important role of the self-absorption in creating NRs by pulsed laser ablation under sonication in water. It was shown that there exists an optimal interval of values of the laser fluence at the ablation laser wavelength. In conclusion, a one-pot laser ablation in fusion of ultrasound method was developed to synthesize gold nanorods. It was suggested

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that the ultrasound formation of gold seeds with an appropriate size for the formation of gold nanorods occurred under laser irradiation. The aspect ratio of the nanorods was governed by the initial nucleation step in the laser ablation formation of gold seeds. The method of pulsed laser ablation in fusion to ultrasound for producing contamination free gold NRs are suitable for medical and research aims.

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