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Properties of Au/Copper oxide nanocomposite prepared by green laser irradiation of the mixture of individual suspensions

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ABSTRACT

The fundamental wavelength of a Q-switched pulsed Nd:YAG laser was employed to produce Au and copper oxide nanoparticles via pulsed laser ablation method in water. Different volumetric ratio of nanoparticles were mixed and irradiated by the second harmonic pulses of the Nd:YAG laser to prepare Au/Copper oxide nanocomposite. The experimental investigation was dedicated to study the properties of Au/Copper oxide nanocomposite as a function of volumetric ratio of Au nanoparticles and copper oxide nanoparticles. Nanocomposites of Au and copper oxide were found almost spherical in shape. Adhesion of spherical nanostructure in Au/Copper oxide nanocomposites was decreased with increasing the concentration of Au nanoparticles. Crystalline phase of the Au/Copper oxide nanocomposites differs with the change in the volumetric ratio of Au and copper oxide nanoparticles. The intensity of surface plasmon resonance of Au nanoparticles was decreased after irradiation. Au/Copper oxide nanocomposites suspensions have emissions in the visible range. Results reveal that green laser irradiation of nanoparticle suspensions is an appropriate method to synthesize Au based nanocomposites with controlled composition and size.

1. Introduction

Numerous studies have been focused on the synthesis of metal oxide nanoparticles and composition of them with other components due to their unique optical, electrical and catalytic properties. The novel properties of these nanomaterials and nanocomposites yield more application of them in diverse areas such as photonics, nanoelectronics, biosensor, biomedical and spectroscopy [1–3]. Among the different metal oxide, CuO nanoparticles have received more consideration and there have been huge researches devoted to its fabrication, properties, application and combination with other components. Copper oxide nanoparticles have been widely used in catalysts, energy storage, lithium batteries, solar energy conversion, chemical and biological sensing and high temperature superconductivity, as well as for light emitters, biomedicals, personal care and health care [1,4–10]. Giannousi et al. [11] showed that CuO nanoparticles could reduce viability of tumor cells. Also, copper oxide is used in consumer products such as pillow cases and socks due to its cosmetic and antimicrobial properties [12].

In recent years, nanocomposites of metal and semiconductor oxide components have attracted much interest because of their large application in nano/biomaterials, and optoelectronics fields [13]. The Cu-CuO nanocomposites along with the presence of H_2O_2 cause excellent degradation of methylene blue under UV irradiation [2]. The use of Ag-CuO materials in low-voltage switches because of their lower materials transfer characteristic is reported [14]. Among the nanocomposites the Au/CuO nanocomposites have been regarded as an important material. The use of CuO-supported Au catalyst for benzyl alcohol oxidation has been shown [15]. Pal et al. reported the flower like Au-CuO nanocomposite upsurges higher surface enhanced Raman scattering activity than individual components (Au or Cu_2O or CuO) [1]. Au-CuO composite can be used as a novel type of radar absorber material. Because Au-CuO composite with two components and two different dielectric constants, leading to a wider frequency band for absorption [16].

Different approaches have been utilized to fabricate nanoparticles such as wet chemical methods, thermal oxidation, thermal evaporation, thermal decomposition, electrospinning, chemical vapor deposition, microwave or ultrasonic assisted

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method and laser ablation in liquid [1,10,12,17–19]. Pulsed laser ablation of metal target in liquid phase is a chemical free method which has been used to prepare noble metals, semiconductors, alloys and oxide nanoparticles in liquid such as CdSe, TiO_2, CuO and ZnO [20,21]. Cost-effective, environmental friendly and high purity product with no impurities and harmful compositions make this technique as a prominent one [22–27].

In this experimental research, Au and copper oxide nanoparticles suspensions were produced individually by laser ablation method and then synthesis of Au/Copper oxide nanocomposites suspensions was achieved by green laser irradiation of the mixture of Au and copper oxide nanoparticles suspensions. Researchers have prepared nanocomposites through different methods [13,28]. By applying the green laser irradiation at the mixture suspensions, since the Au nanoparticles had a strong plasmonic absorption band close the wavelength of the laser irradiation, Au nanoparticles were heated and melted to form nanocomposite with copper oxide nanoparticles nearby. The aim of this work is investigation of the effect of the volumetric ratio of Au and copper oxide nanoparticles suspensions on the structural and optical properties of Au/Copper oxide nanocomposite.

2. Experimental

Au/Copper oxide nanocomposite suspensions were prepared through a sequential two-step process, laser ablation and laser irradiation.

2.1. Synthesis of gold nanoparticles and copper oxide nanoparticles

Copper oxide nanoparticles and Au nanoparticles were produced individually by pulsed laser ablation of a Cu plate (99.9%) and Au plate (99.9%) in distilled water environment respectively. Before the ablation process gold and copper targets were cleaned ultrasonically in acetone, ethanol and deionized water separately. After proper cleaning, the gold target was located in a beaker containing of distilled water. Height of distilled water on the gold target was 8 mm. The gold target was ablated using a Nd:YAG laser source with wavelength of 1064 nm. Output of laser was focused on the surface of gold target using an 80 mm focal length convex lens. The pulse-repetition rate, laser fluence and laser pulses were 5 Hz, 1.5 J/cm^2 and 5000 respectively. The copper oxide nanoparticles were synthesized in the same experimental condition of producing gold nanoparticles.

2.2. Synthesis of Au/Copper oxide nanocomposite

For preparation of Au/Copper oxide nanocomposite, Au nanoparticle suspension was mixed with copper oxide nanoparticle suspension at the volume ratio of 1/2 (sample 1), 1/1 (sample 2), 3/2 (sample 3) and 2/1 (sample 4). In other words, 25, 37, 45, and 50 ml of Au nanoparticles suspension was mixes with 50, 37, 30, and 25 ml of copper oxide nanoparticles suspension respectively. These samples were irradiated with 5000 pulses of the second harmonic of Nd:YAG laser operating at 532 nm. The laser fluence and pulse repetition rate were 1 J/cm^2 and 10 Hz respectively.

Pictures of Au nanoparticles, copper oxide nanoparticles and Au/Copper oxide nanocomposite suspensions are presented in Fig. 1. It was observed that the color of Au nanoparticles and copper oxide nanoparticles suspensions produced by laser ablation in water medium were dark red and dark green respectively. As can be seen the color of the irradiated mixture of Au nanoparticles and copper oxide nanoparticles suspensions with increasing the volumetric ratio of Au nanoparticles suspension was changed from dark green to dark red.

2.3. Characterization

Different diagnostics were applied to characterize the properties of nanoparticles and nanocomposite. The optical properties of the Au nanoparticles, copper oxide nanoparticles suspensions and Au/Copper oxide nanocomposite were examined at room temperature by Varian Cary-500 spectrophotometer in the range of 200–1100 nm. The crystalline structure of the dried suspensions on silicon substrates was obtained by a STOE-XRD diffractometer using Cu-K_α radiation at $\lambda = 1.54060$ °A. Transmission Electron Microscopy (TEM, Zeiss- EM10C- 80 kV) was employed to examine samples which prepared by deposition a drop of the concentrated suspension on a grid. The morphology images of dried suspensions on silicon substrates were also taken by Scanning Electron Microscopy (SEM, KYKY- EM 3200). The photoluminescence (PL) characterization was collected by (Cary Eclips) spectrophotometer using a Xe lamp as the light source at room temperature.

3. Results and discussion

3.1. Absorption spectra

The UV–Vis–NIR absorption spectra of samples before and after the green laser irradiation are shown in Fig. 2. The absorption spectra of samples were recorded with distilled water as the baseline reference in 1 cm thickness quartz cell. The absorption peak due to the surface plasmon resonance (SPR) of gold nanoparticles in samples before and after the green laser irradiation was occurred around the 533 nm and 546 nm respectively. In addition, the absorption peak due to the exitonic oscillations of CuO nanoparticles was occurred in UV range. Another broad peak at about 690 nm is due to exitonic oscillations of Cu_2O nanoparticles, which was disappeared after the green laser irradiation of mixtures. Au nanoparticles in samples were heated by applying green laser irradiation due to the absorption of Au nanoparticles close to green laser irradiation wavelength, and therefore Au nanoparticles melted to form composite with CuO nanoparticles nearby. Absorption spectra show that after green laser irradiation, the intensity of absorption peaks of Au nanoparticles was decreased and these peaks were red shifted. Decreasing the intensity of SPR peak after the green laser irradiation is due to the reduction of number of Au nanoparticles in samples because of formation of Au/Copper oxide nanocomposite.

The UV–Vis–NIR absorption spectra of Au/Copper oxide nanocomposites, Au nanoparticles and copper oxide nanoparticles are presented in Fig. 3. According to the absorption spectrum of Au nanoparticles suspension two peaks were occurred in the ultraviolet region around 263 nm and in the visible region around 525 nm due to the interband transition and SPR oscillations in Au nanoparticles, respectively [13,29]. The absorption peak of CuO nanoparticles suspension was observed in the ultraviolet region at 222 nm. The salient feature in the present nanoparticles prepared from Cu metal in water environment by pulsed laser ablation is that the surface plasmon band of Cu nanoparticles near 580 nm was not observed. In former work we produced Cu nanoparticles in acetone and the absorption peak was occurred at 576–581 nm which was due to the surface plasmonic resonance wavelength of Cu nanoparticles [30]. Im et al. reported that the colloidal nanoparticles prepared from Cu target by laser ablation in water were initially oxidized to Cu_2O from its surface and then further to CuO. The absence of Cu colloid absorption peak near 580 nm is due to the partially oxidized copper oxides through the route $Cu \rightarrow Cu_2O \rightarrow CuO$ [31]. This result shows that the Cu nanoparticles suspensions prepared in water environment are very unstable and highly reactive. Of course this reaction can be control by using the