

Copper Oxide Nanostructures; Syntheses and Characterization

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Abstract

Copper oxide (CuO) nanoparticles are synthesized by pulse laser ablation (Nd:YAG, $\lambda=1064\text{ nm}$) of copper (Cu) in pure water (DDDW). The synthesized nanomaterial is characterized with UV-Visible spectroscopy; atomic force microscopy AFM, in combination with FTIR. AFM image shows that the CuO are spherical in shape with average diameter 50 nm and FTIR spectrum confirm the formation of CuO nanoparticles. The UV-vis spectrum of the colloidal nanoparticles shows maximum absorbance around the UV region at $\sim 270\text{ nm}$ and in Vis region at $\sim 600\text{ nm}$, indicating the formation of CuO nanoparticles with a direct bandgap energy of $\sim 3.2\text{ eV}$.

Keywords: laser ablation, Nano particles, Cuonano-particles, nanoparticles.

Introduction

The oxides of transition metals are an important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics and catalysis [1-3]. CuO is a semiconducting compound with a narrow band gap and used for photoconductive and photothermal applications [4,5]. However, the reports on the preparation and characterization of nanocrystalline CuO are relatively few to some other transition metal oxides such as zinc oxide, titanium dioxide, tin dioxide and iron oxide. Some methods for the preparation of nanocrystalline CuO have been reported recently such as the sonochemical method [6], sol-gel technique [7], one-step solid state reaction method at room temperature [8], electrochemical method [9], thermal decomposition of precursors [10] and co-implantation of metal and oxygen ions [11] etc. Laser ablation in liquid media is a 'top down' approach for the synthesis of nanomaterials having desired shape, size and chemical composition and surfaces free from chemical contamination, which are essential for further functionalization of nanomaterials for biological and sensing applications. This technique is adopted by several workers [12-13] for the synthesis of colloidal solution of nanoparticles of different metals and semiconducting materials. Recently, copper-based nanomaterials are of great interest because of their optical, catalytical, mechanical and electrical properties, resulting in a wide range of applications in the field of

metallurgy, catalysis, nano and optoelectronics [14]. Cu₂O (cuprous oxide) and CuO (cupric oxide) are two important oxide compounds of copper and mostly behave like p-type semiconductor. Cuprous oxide is a II-VI semiconductor having direct bandgap of $\sim 2\text{ eV}$, while that of cupric oxide has a monoclinic crystal structure with a bandgap of $1.21-1.51\text{ eV}$ [15]. Copper oxide nanomaterials have lower surface potential barrier than metals, which affects their electron field emission properties, and therefore are highly application as electron sources in cathode ray tube and flat panel display [16].

Experimental

To produce the copper nanoparticles, a piece of copper metal (99.99%) placed at the bottom of glass vessel containing 3ml of double-distilled water was irradiated with the focused output of fundamental wavelength (1064 nm) of Nd : YAG laser operating at 50 mJ energy with a positive lens having a focal length of 110 mm , was utilized as an ablation source. The number of laser pulsed applied for the metal target 100 pulses and laser energy 50 mJ . Fig.(1) shows the experimental setup of PLAL system were light green colure colloidal solution was obtained after ablation as shows in Fig.(2). The UV-Visible absorption spectra of colloidal solution of nanoparticles so synthesized with double beam spectrophotometer CECIL, C. 4200 (France) with energy band gap E_g (eV). The average particle size and amount of

aggregation of NPs were characterized with atomic force microscope (AFM) AA300 scanning probe microscope Angstrom Advanced Inc. the recording FTIR spectrum, in the wave number region of $4000-400\text{ cm}^{-1}$.

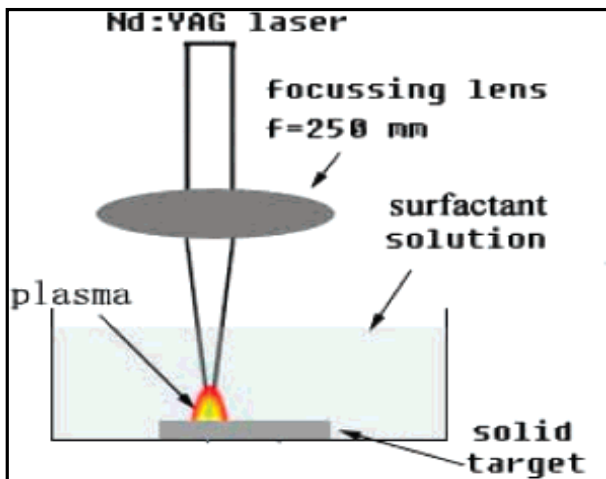


Fig. (1) Typical set-up for pulsed laser ablation in liquid media.



Fig. (2) Photograph of colloidal CuO NPS.

Results and discussion

The UV-Visible absorption spectrum of the as-synthesized solution of colloidal nanoparticles is recorded in the wavelength region of $200-900\text{ nm}$. It exhibits an intense peak center at $\sim 270\text{ nm}$ and another peak with low intensity at $\sim 600\text{ nm}$ as shown in Fig.(3). The peak at $\sim 270\text{ nm}$ is due to interband transition of copper electron from deep level of valence band while peak at $\sim 600\text{ nm}$ is due to interband transition of copper electron from upper level of valence band, agreement with reported previously (Curtis et.al)[16]. The optical bandgap of the synthesized

nanoparticles is calculated using the Tauc relation (Singh et al 2009b) $\alpha hv = (hv - E_g)^n$, where hv is the incident photon energy and n is the exponent that determines the type of electronic transition causing the absorption and can take the values $1/2$, $2/3$, 2 and $3/2$ [17]. The best linear relationship is obtained by plotting $(\alpha hv)^{1/n}$ against hv , indicating that the optical bandgap of these nanoparticles is due to a direct allowed transition. Tauc plot for as synthesized colloidal nanoparticles is shown in Fig.(4). The bandgap of as synthesized colloidal nanoparticles is determined from the intercept of the straight line at $\alpha = 0$, which is found to be 2.5 eV .

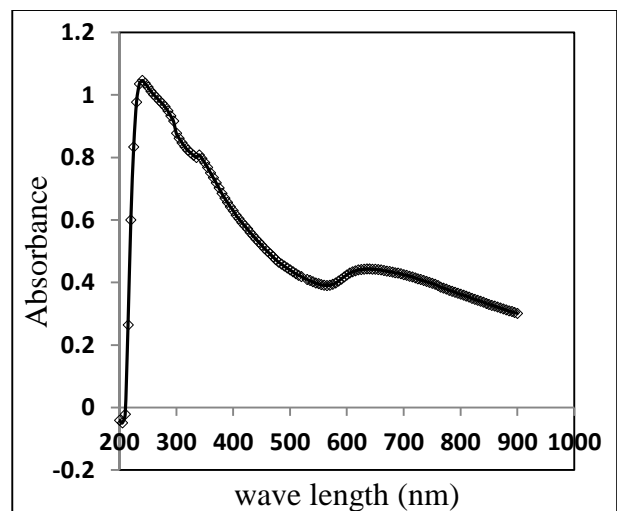


Fig. (3) UV-Visible absorption spectrum of as synthesized colloidal solution of CuO nanoparticles by laser ablation of copper in water.

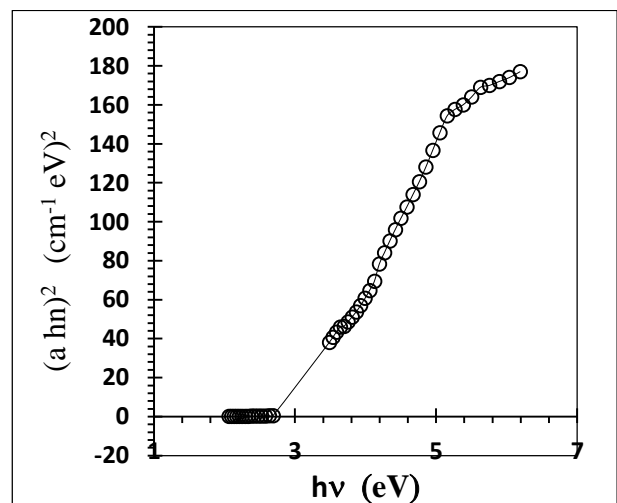


Fig. (4) Taucplot of UV Visible absorption data of as synthesized colloidal CuO

nanoparticles for the calculation of bandgap energy.

Fig. (6) shows the AFM images and the corresponding size distributions of the copper oxide nanoparticles. It's clear from figure that CuO nanoparticles are spherical in shape having average diameter of 51 nm are observed over the entire surface, as shown in the inset. The 3-dimensional (3D) AFM image of material nanoparticle in which the irregular and randomly distributed CuO nanoparticles pillars and voids over the entire surface can be seen with a maximum value of 6.83 nm exhibits morphology with a root-mean-square (RMS) roughness of 0.824 nm.

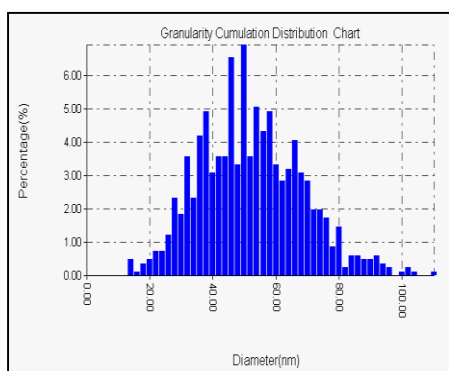
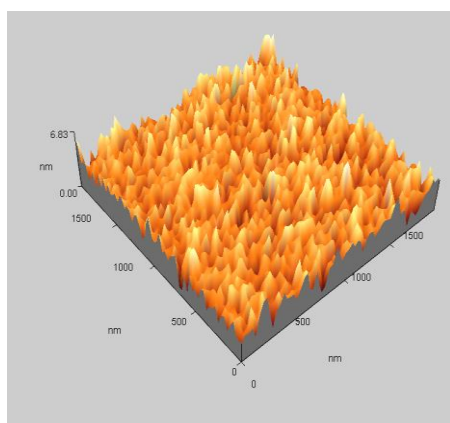
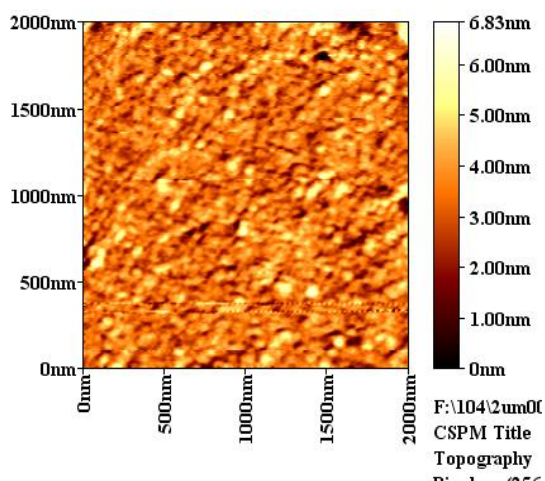


Fig.(6) AFM image of as prepared CuO nanoparticles.

The FTIR spectrum of CuO nanoparticles is shown in Fig.(7). An intense and wide peak centered at 3440 cm^{-1} is assigned as H-OH stretching. The peak centered 500 to 610 cm^{-1} corresponds to the vibrational mode of Cu-O in Cu_2O phase (Heltemes 1976) [18]. Therefore, one can conclude that the nanoparticles have cuprous oxide.

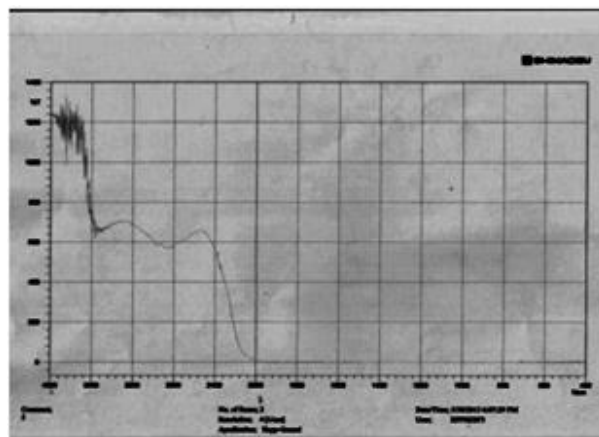


Fig.(7) FTIR spectra of the extracted CuO NPs.

Conclusion

In this study the film structure and the surface morphology of the deposits materials have been studied using atomic force microscopes (AFM). The UV-VIS spectrum of the colloidal nanoparticles shows maximum absorbance around the UV region at $\sim 270 \text{ nm}$ and in Vis region at $\sim 600 \text{ nm}$, indicating the formation of CuO nanoparticles with a direct bandgap energy of $\sim 3 \text{ eV}$. from the FTIR spectrum of CuO nanoparticles, the peak centered 500 to 610 cm^{-1} corresponds to the vibrational mode of Cu-O in Cu_2O phase with spherical in shape having average diameter of 51 nm.

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الخلاصة

جسيمات ثنائي اوكسيد النحاس CuO النانوية تم تحضيرها بواسطة تشيع معدن النحاس النقي بليزر النديميوم ياك النبضي ذو الطول الموجي 1064 nm داخل الماء المقطر. تم تشخيص الجسيمات المتولدة بواسطة مطياف المنطقة المرئية وفوق البنفسجية UV-Vis، مجهر القوى الذرية بالإضافة الى مطياف تحويلات فورير للأشعة تحت الحمراء FTIR. أظهرت صور المجهر الذري جسيمات اوكسيد النحاس النانوية ذات شكل كروي والتي اثبتت بواسطة قياس الـ FTIR. أطيف الامتصاص للعوالق النانوية تظهر قيمة أمتصاص عظمى في المنطقة فوق بنفسجية عند طول موجي 270 نانومتر وفي منطقة المرئية عند 600 نانومتر والتي تدل على توليد جسيمات CuO النانوية وبفجوة طاقة 3,2 إلكترون فولت.

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