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OPTICAL CHARACTERIZATIONS OF COPPER OXIDE NANOMATERIAL

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Abstract: Copper oxide nanomaterial is synthesized by pulsed laser ablation of copper plate in aqueous medium of cetyltrimethyl ammonium bromide using 1064 nm of nanosecond pulsed Nd:YAG laser. The synthesized nanomaterial is characterized by UV-VIS absorption, X-ray diffraction (XRD) and photoluminescence (PL) spectroscopic techniques. XRD characterization confirms the formation of copper oxide nanomaterial. The absorption and PL characterization shows that the synthesized nanomaterial has wide band gap. Mechanisms of nanoparticles synthesis and PL are also discussed.

1. INTRODUCTION

Metal oxides nanoparticles (NPs) have shown their great interest in field of sensing, optoelectronics, catalysis, solar cells and so on due to their unique physical and chemical properties differing from the bulk [1]. Among all the metal oxides, copper oxide nanomaterials have attracted more attention due to its unique properties. Cu_2O (cuprous oxide) and CuO (cupric oxide) are two important oxide compounds of copper. Cuprous-oxide is mostly p-type, direct band gap, II-VI semiconductor with band gap of ~2 eV and cupric-oxide has a monoclinic crystal structure and presents p- type semiconductor behavior with a indirect band gap of 1.21 – 1.51 eV. Copper oxide nanomaterials may have the advantage of a lower surface potential barrier than that of the metals, which affects electron field emission properties. Copper-oxide is considered as a potential field emitter, an efficient catalytic agent, as well as a good gas sensing material. It also plays an important role in the optoelectronics and solar cell [2, 3].

The synthesis of copper oxide NPs with controllable sizes, shapes and surface properties is vital for exploring copper based catalysis. Many methods have been reported for the synthesis of copper based nanomaterials like; sol-gel, flame spray, vapor-phase reaction, aqueous precipitation, template method, electrochemical route, sacrificial anode technique, laser ablation in vacuum etc [4-6]. Laser ablation in liquid medium is simplest and versatile technique for production of oxide nanomaterials [7, 8] and offers chemical contamination free NPs.

There are very few reports in the literatures on synthesis of copper/ copper oxide quantum dots/ NPs by a physical method and their modified properties. This report describes the findings of an investigation on the synthesis of copper oxide NPs with controlled size in liquid medium containing cationic surfactant CTAB. The synthesized colloidal NPs have been characterized by using UV- visible absorption spectroscopy, X-ray diffraction (XRD), and photoluminescence (PL) spectroscopic techniques.

2. EXPERIMENTAL

The high purity Cu plate, placed on the bottom of glass vessel containing 20 ml aqueous solution of 2mM CTAB, is irradiated with focused output of 1064 nm from nanosecond pulsed Nd:YAG laser (Spectra Physics Inc. USA) operating at 40mJ/pulse energy, for 30 minutes. This ablation of copper plate in liquid medium results in formation of a light green colored colloidal solution. Thus obtained colloidal solution of NPs is employed for optical and structural characterizations.

The UV-VIS absorption spectrum of as synthesized colloidal solution of NPs has been recorded by using Perkin Elmer Lambda 35 double beam spectrophotometer. The powder XRD pattern of NPs, dried at 60ºC, is recorded with Rikagu, D-Max X-ray diffractometer using 1.5405 $\mathring{A}$ Cu K_α line. For recording PL spectrum of colloidal NPs, 514.5 nm line of Ar^+ laser (Spectra Physics Inc., USA) is used as excitation source and emission spectrum is recorded on computer controlled 0.5 M triple grating spectrometer with R928 PMT as detector.

3. RESULTS & DISCUSSIONS

UV-visible absorption spectrum of as synthesized colloidal solution of NPs produced by pulsed laser ablation of copper in aqueous medium of 2mM concentration of cationic surfactant CTAB has been recorded in the entire visible to near IR region is illustrated in Fig.1. The spectrum has two peaks, one of the peak is centered at 260nm while the other one at 650nm. The peak centered at 260 nm is due to the Cu_2O shell layer of the $Cu@Cu_2O$ (Copper core @ copper oxide shell nanoparticles) while that of peak around 650 nm correspond to the conversion of some upper shell layers of the Cu_2O into more thermodynamically stable CuO layers.

Higher symmetry of Cu^{+} causes more stability of Cu_2O nanoparticles as compared to CuO in smaller size ranges (2-7 nm), while CuO is more stable in larger sized ranges (8-100 nm) due to low symmetry of Cu^{++} complexes. Therefore, CuO nanoparticles are usually found on the surface of Cu_2O nanoparticles. Cupric oxide readily forms on the NPs surface and

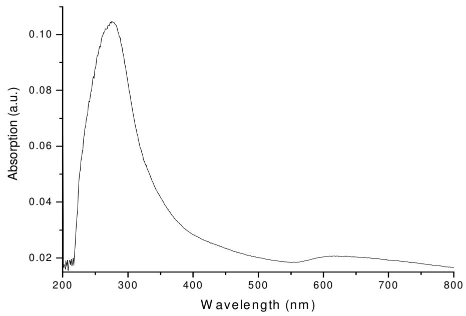

Figure 2: UV-VIS absorption spectrum of as synthesized colloidal NPs

suggest that there should be an energy barrier to its synthesis in smaller sizes. It is possible that for smaller nanoparticles, the barrier becomes excessive and condition for the synthesis of pure Cu_2O nanoparticles is favorable. Therefore Cu_2O may actually metastable and conversion to CuO, the thermodynamically stable oxide is kinetically hindered for small size ranges.

The optical band gap of the produced NPs is calculated using the Tauc's relation

$$\alpha h\nu = (h\nu - E_g)^n \text{……………………} (1)$$

where hν is the incident photon energy, n is the exponent that determines the type of electronic transition causing the absorption and can take the values 1/2 and 2 depending whether transition is direct or indirect respectively. Figure 2 shows $(\alpha h\nu)^2$ versus hν plot of absorption spectrum of colloidal

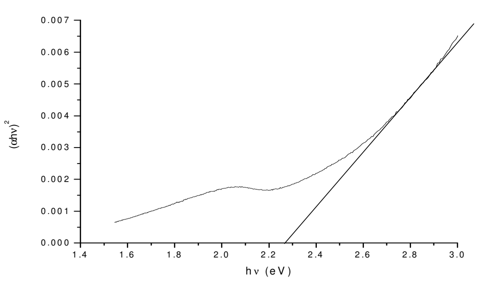

Figure 4: Tauc plot for as synthesized NPs

solution of NPs. The best linear relationship is obtained by plotting $(\alpha h\nu)^2$ against hν indicating that the optical band gap of these colloidal NPs is due to a direct allowed transition. The value of the band gap is determined from the intercept of the straight line at α = 0, which is found to be 2.26eV.

XRD pattern of the as synthesizes nanopowder dried at 60ºC is illustrated in fig. 3. XRD pattern reveals

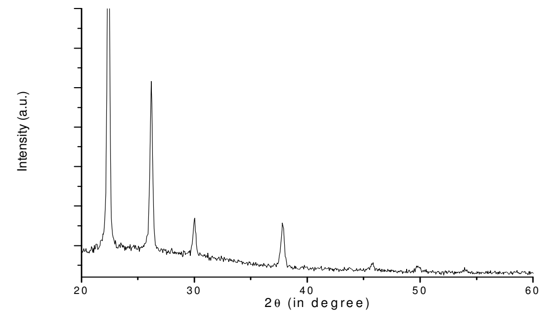

Figure 1: XRD spectrum of as synthesized NPs

intense and wide diffraction peaks at 2θ = 22.39º, 26.20º, 30.01° and 37.86°. Out of these peaks, there are three less intense peaks at 2θ = 45.73º, 49.80º and 53.93º also observed. The peak at 2θ = 30.01° corresponds to the (110) plane of Cu_2O, while peak at 2θ = 37.86° corresponds to (200) plane of CuO. XRD result is in good agreement with absorption result that Cu_2O and CuO both exist in the sample. The crystallite sizes can be estimated using Scherrer's formula

$$D = K\lambda / \beta\cos\theta \text{ …………………} (2)$$

where the constant K is taken to be 0.94, λ is the wavelength of X-ray used which is CuK_α radiation (λ = 1.5406 Å), and β the full width at half maximum of the diffraction peak corresponding to 2θ. Using equation (2), the crystallite sizes found to be in the range of 30-40nm.

Figure 4 shows smoothed and curve fitted photoluminescence spectrum of NPs. The spectrum shows a broad intense green luminescence having

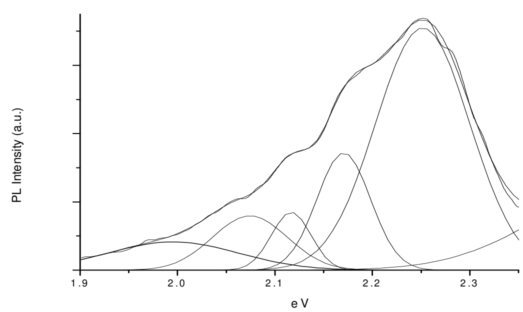

Figure 3: Smoothed and curve fitted PL spectrum of copper oxide NPs

five peaks at 2.25, 2.17, 2.12, 2.07, and 1.99 eV. This fluorescence arises due to band to band transition of copper-oxide and other defects inside the NPs. The luminescence peak corresponding to 2.25 eV is due to band to band transition of copper-oxide which is also supported by UV-visible absorption spectrum (band gap 2.26 eV). A transition from conduction band to acceptor level (above the valence band at 0.08 eV) takes place and correspond to a emission at 2.17 eV , while another transition from donor level (below the conduction band at 0.13 eV) to valence band and acceptor level with emitting fluorescence of energy 2.12 and 2.07 eV respectively. Out of these transitions, a transition from electron trapping level (below the conduction band at 0.25 eV) to valence band take place with a fluorescence of energy 2.0 eV through a non-radiative transition from conduction band to electron trap level. Balamurugan et al. [9] have reported defect level at 0.08 is due to copper ion vacancies in copper oxide. Jung et al. [10] had also reported the PL spectrum at ~ 2.26 eV from Cu_2O NPs embedded in a polyimide layer, due to interband transitions from the ground electronic sublevel to the ground heavy-hole sublevel ($E_1 - HH_1$) of the Cu_2O NPs.

The mechanism of the laser ablation can be explained in terms of the dynamic formation mechanism postulated by Singh and Gopal [11] which is as follows "A dense cloud of the metal atoms (plume) was accumulated in the closed vicinity of laser spot on the metal surface during the course of the ablation. These metal atoms supersonically expand against liquid media and form clusters of atoms/ molecules after cooling. These atoms/ molecules act as seed for the growth of the NPs. Termination of the growth of the particles and their stabilization in the colloidal solution is achieved by equilibrium between production of atoms by laser ablation and capping of clusters by surfactant molecules".

4. CONCLUSIONS:

Copper oxide NPs are synthesized successfully by pulsed laser ablation of copper plate in aqueous medium of 2mM CTAB. The flat SPR peak present in UV-visible absorption spectrum indicates the formation of copper oxide NPs, which is confirmed by XRD analysis also. The photoluminescence spectrum of nanoparticles shows a broad luminescence in green region which indicates that these nanoparticles can be applicable for fabrication of photonic devices such as green LED's.

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