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## CTAB Assisted Oxidation of Copper Nanoparticles Synthesized by Pulsed Laser Ablation and It's Characterization

Raj Kumar Swarnkar <sup>(1)</sup>, S.C. Singh <sup>(1)</sup>, M. K. Singh <sup>(2)</sup> and R. Gopal <sup>(1)</sup>

(1) *Laser Spectroscopy & Nanomaterials Lab, Physics Department, University of Allahabad, Allahabad - 211002, INDIA.*

(2) *Department of Physics, M. N. National Institute of Technology, Allahabad-211004, INDIA.*

Copper oxide is considered as an efficient catalytic agent and also a good gas sensing material. Here, surfactant assisted copper oxide colloidal nanoparticles(NPs) is synthesized in 1 mM aqueous solution of CTAB by laser ablation using focused out put of 1064 nm of Nd: YAG laser. The synthesized colloidal NPs are characterized by using UV-VIS absorption, TEM, XRD, Raman and FTIR spectroscopic techniques. The synthesized copper oxide NPs are self assembled with average size lying in the range between 40-60 nm and crystalline in nature.

### Introduction :

Metal oxide nanoparticles have shown great attention due to their tunable optical, electronic, magnetic and catalytic properties [1]. In addition, a size dependent optical, electronic and vibrational property of the nanomaterials has also been observed in several semiconductors and oxides materials [2]. Copper oxide is an excellent nanoparticle system for investigating the size induced structural transformations and phase stability. Copper oxide has two phases i.e. cuprous oxide (Cu<sub>2</sub>O) and cupric oxide (CuO). The oxides of copper are p- type semiconductor and having direct band gap. Lin *et al.* [3] have reported copper oxide nanofibrils of 50 nm diameter exhibits high field emission current density therefore can be used as electron source in cathode ray tubes and flat panel displays. Copper oxide is considered as an efficient catalytic agent and also a good gas sensing material [4]. There are several methods reported to synthesize copper oxide nanoparticles like sol-gel, hydrothermal route, electrochemical [5-7] etc. Materials synthesized by these processes include significant amount of chemical contamination on the surface of synthesized nanomaterials, which limits their applications in optoelectronic and sensing device fabrications. Therefore, it is highly required to synthesize

nanomaterials having chemical contaminations free surfaces for the fabrication of surface phenomenon based devices and biological applications.

Lasers have open new doors in the processing of Nanomaterials and their characterization. Pulsed laser ablation process has several advantages over other conventional routes including (a) large number of available ablation parameters for controlling the size and shape of nanomaterials, (b) produced nanomaterials have inherent stoichiometry as their mother targets therefore, capability to produce nanomaterials of desired chemical composition and (c) ability of producing nanomaterials having surfaces free from chemical contamination. This technique is used by several workers to synthesized colloidal NPs of different metals and semiconductors [8, 9]. In the present study copper oxide nanoparticles are synthesized using laser ablation technique in aqueous solution of 1 mM of CTAB. The synthesized colloidal NPs are characterized by using UV-VIS absorption, TEM, XRD, Raman and FTIR spectroscopic techniques.

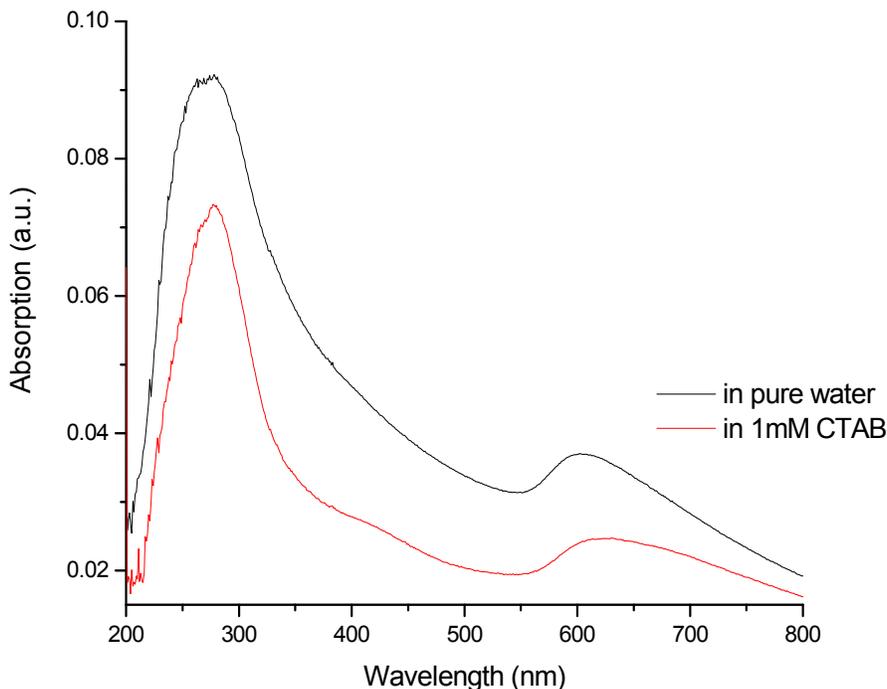


Fig.1: UV-VIS absorption spectra of as synthesized nanoparticles in pure water as well as in 1mM aqueous solution of CTAB.

### Experimental :

Copper oxide nanoparticles (NPs) is synthesized by pulsed laser ablation of high purity copper plate (99.99%) placed on the bottom of glass vessel containing 20 ml aqueous solution of 1 mM CTAB. It is irradiated with focused output of 1064 nm of Nd:YAG laser (Spectra Physics Inc. USA) operating at 40mJ/ pulse energy, 10 ns pulse duration and 10 Hz for 30 minutes. This results a light green colored colloidal solution. The

absorption spectrum of synthesized colloidal solution of NPs is recorded in the region 200-800 nm using Perkin Elmer double beam spectrophotometer Lambda 35.

TEM image of the NPs is recorded on Technai G20 – stwin electron microscope operating at 200kV. A drop from colloidal solution of NPs is placed onto a carbon coated copper grid and dried for TEM analysis. Few drops of sample are dried at 60°C on a glass slide to obtain a thick layer (~100µm). XRD pattern of this thick layer of sample is recorded with Rikagu, D-Max X-ray diffractometer using 1.5405 Å Cu K<sub>α</sub> line. Dried powder is dispersed into KBr discs and palletized at 10 ton pressure. Obtained pellet is suspended in the path of IR beam of Perkin Elmer RX-1 FTIR spectrometer, to record spectrum in the wave number region of 350 – 4000 cm<sup>-1</sup>. For recording Raman spectrum of synthesized colloidal NPs, 488 nm line of Ar<sup>+</sup> laser (Spectra Physics Inc., USA) is used as excitation source and spectrum is recorded with computer controlled 0.5 M triple grating monochromator (Acton Research Corp., USA) with R928 PMT as detector by using Spectra Sense software. Grams 32 software is used for spectral analysis and post processing.

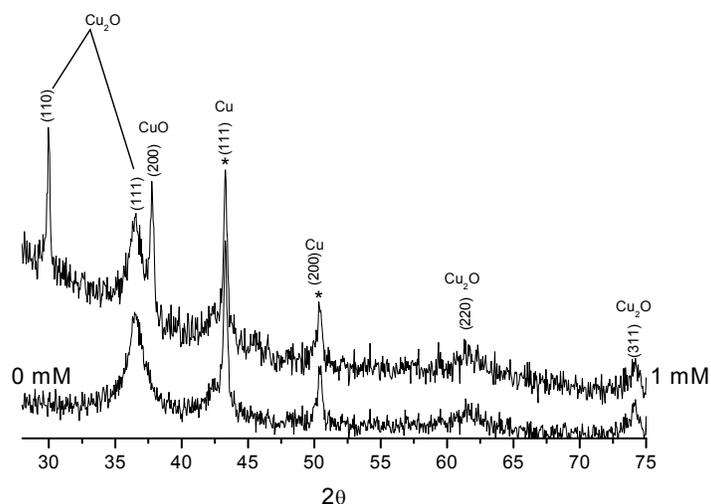


Fig. 2 : XRD spectra of as synthesized samples in 0 and 1mM CTAB

### Results and Discussions :

Fig.1 illustrates UV-VIS absorption spectra of as synthesized colloidal solution of NPs produced in the pure deionized water i.e. without any surfactant and 1mM concentration of cationic surfactant CTAB. The peak at 260 nm is due to inter band transition of core electrons of copper metal while that of peak around 640 nm correspond band edge transition of cuprous oxide [10]. As absorption spectra showed that with addition of CTAB the peak shifted towards red indicating more oxidation of copper nanoparticles take place, indicated that CTAB increases oxidation of copper.

XRD spectra of the NPs synthesized in pure deionized water and 1mM aqueous solution of CTAB at room temperature are illustrated in fig 3. The material synthesized in pure water have peaks at  $2\theta = 43.28^\circ$  and  $50.42^\circ$  correspond to diffraction from (111) and (200) planes of copper nanoparticles with cubical symmetry while peaks at  $2\theta = 36.53^\circ$ ,  $61.71^\circ$  and  $74.35^\circ$  correspond to (111), (220), and (311) plane of cubical  $\text{Cu}_2\text{O}$  Nanocrystals. With the addition of 1mM CTAB, additional peaks are observed at  $2\theta = 30.01^\circ$ , and  $37.86^\circ$ . Out of these peak at  $2\theta = 30.01^\circ$  corresponds to the (110) plane of  $\text{Cu}_2\text{O}$ , while peak at  $2\theta = 37.86^\circ$  corresponds to (200) plane of  $\text{CuO}$ . XRD result is in agreement with UV-VIS absorption result that with the addition of CTAB quantity of copper oxide nanoparticles increases.

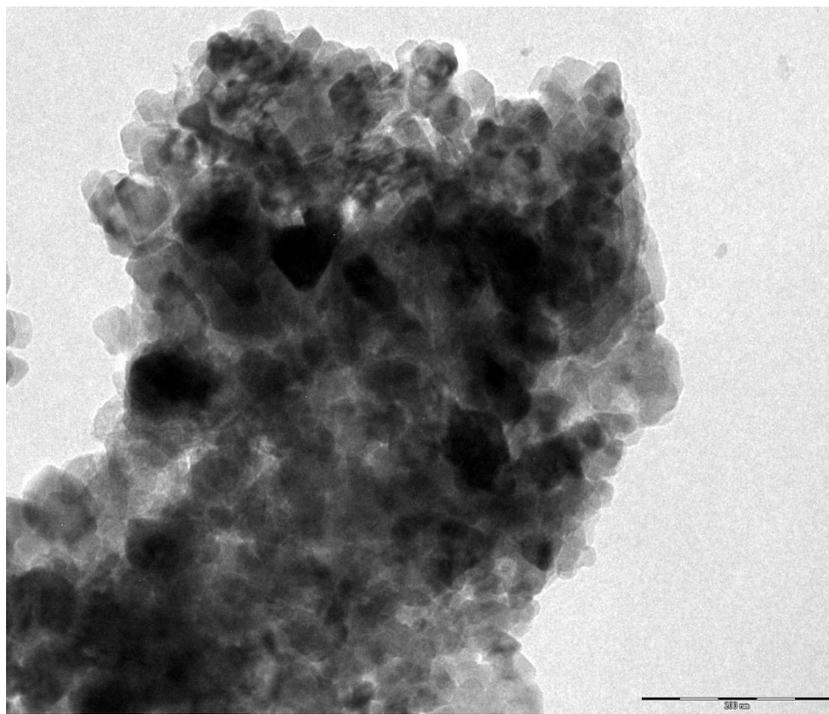


Fig. 3 : TEM image of as synthesized material in 1mM CTAB.

TEM image of the surfactant activated copper oxide NPs is shown in figure 2. It is evidenced from the TEM micrograph that synthesized NPs have size ranging from 40 - 60nm and get self assembled.

Raman spectrum of the NPs synthesized in 1mM CTAB is shown in fig 4. The strong peak at  $\sim 350\text{ cm}^{-1}$  is assigned to  $B_g$  symmetric mode vibration of  $\text{CuO}$ , while the broad peak  $\sim 650\text{ cm}^{-1}$  is due to sub- peaks of  $\text{Cu}_2\text{O}$  [12], agreeing well with XRD result.

FTIR spectra of the Nanopowder and pure CTAB powder are shown in figure 5. The Nanopowder has similar peaks in the region  $1000 - 4000\text{ cm}^{-1}$  as CTAB instead of intensity variation. But there is a broad peak in the region  $400-1000\text{ cm}^{-1}$  of FTIR spectrum of Nanopowder, due to resultant of different oxides of copper [13], confirms the

synthesis of copper oxide NPs, completely in agreement with the XRD as well as absorption results.

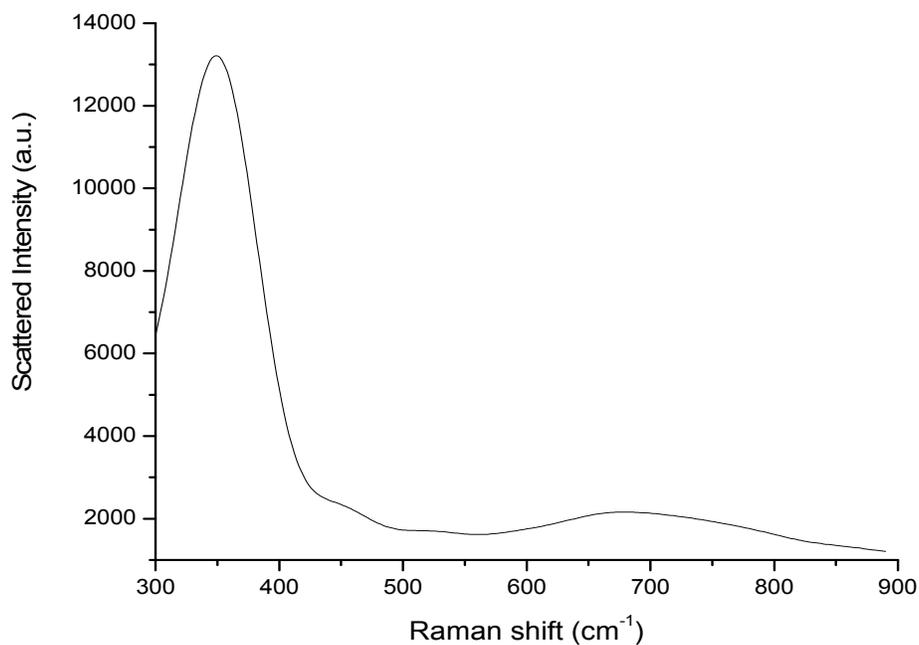


Fig. 4 : Raman spectrum of Copper oxide Nanoparticles synthesized in 1mM CTAB.

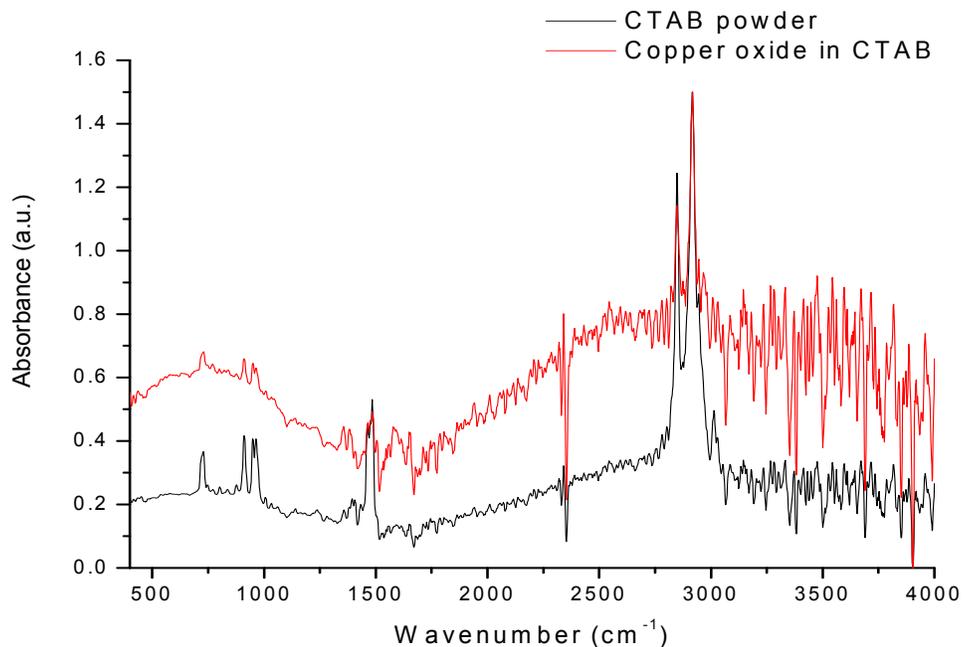
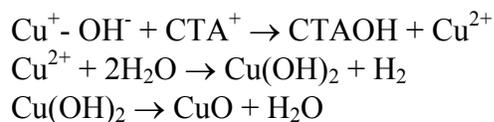
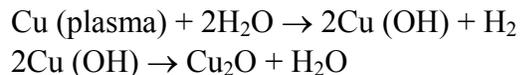


Fig. 5 : FTIR spectra of pure CTAB and copper oxide nanoparticles synthesized in CTAB.

The synthesis of Copper oxide nanoparticles by laser ablation in pure water and CTAB can take according to the following equation :



The mechanism of the nanoparticles formation by laser ablation in liquid media can be explained in terms of the dynamic formation mechanism [8] given as “A dense cloud of the metal atoms (plume) is 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 nanoparticles. 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”.

### Conclusions :

Surfactant activated copper oxide NPs has been synthesized using a physical approach pulsed laser ablation technique in aqueous media. NPs are self assembled having average size 40-60 nm. Formation of copper oxide is confirmed by XRD, Raman and FTIR spectrum which shows presence of cuprous and cupric oxide.

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### References :

1. S.C. Singh, R.K. Swarnkar and R. Gopal, *J. Nanosci. Nanotech.* 1 (2009) 9.
2. B. Balamurugan, B.R. Mehta and S.M. Shivprasad, *Appl. Phys. Lett.* 3176 (2001) 79.
3. H. Lin, C. Wang, H.C. Shih, J. Chen and C. Hsieh, *J. Appl. Phys.*, 5889 (2004) 95.
4. J.J. Zhang, J.F. Liu and Y.D. Li, *Chem. Mater.* 867 (2006) 18.
5. H. Zhang and Z. Cui, *Mater. Res. Bull.* 1583 (2008) 43.
6. K. Borgohain, J.B. Singh, M.V.R. Rao, T. Shripati, S. Mahamuni, *Phys. Rev. B*, 11093 (2000) 61.
7. J. Gong, L. Luo, S. Yu, H. Qian, L. Fei, *J. Mater. Chem.*, 101 (2006) 16.
8. S.C. Singh and R. Gopal, *J. Phys. Chem. C*, 2812 (2008) 112.

9. C.H. Liang, Y. Shimizu, T. Sasaki, N. Koshizaki, *Appl. Phys. A*, 819 (2005) 80.
10. D. Mott, J. Galkowoski, L. Wang, J. Luo, C. Zhong, *Langmuir*, 5740 (2007) 23.
11. B. Balamurugan, B.R. Mehta, *Thin Solid Films*, 90 (2001) 396.
12. J.H. Jung, T.W. Kim, M.S. Song, Y.H. Kim, K.H. Yoo, *J. Appl. Phys.*, 0937083 (2007) 101.
13. W. Hu, M. Matsumura, K. Furukawa and K. Torimitsu, *J. Phys. Chem. B*, 13116 (2004) 108.