Observation of confinement effects through liner and nonlinear absorption spectroscopy in cuprous oxide

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Abstract. Cuprous oxide nano clusters, micro cubes and micro particles were successfully synthesized by reducing copper (II) salt with ascorbic acid in the presence of sodium hydroxide via a co-precipitation method. The X-ray diffraction studies revealed the formation of pure single phase cubic. Raman spectrum shows the inevitable presence of CuO on the surface of the Cu$_2$O powders which may have an impact on the stability of the phase. Transmission electron microscopy (TEM) data revealed that the morphology evolves from nanoclusters to micro cubes and micro particles by increasing the concentration of NaOH. Linear optical measurements show that the absorption peak maximum shifts towards red with changing morphology from nano clusters to micro cubes and micro particles. The nonlinear optical properties were studied using open aperture Z-scan technique with 532 nm, 6 ns laser pulses. Samples exhibited saturable as well as reverse saturable absorption. The results show that the transition from SA to RSA is ascribed to excited-state absorption (ESA) induced by two-photon absorption (TPA) process. Due to confinement effects (enhanced band gap) we observed enhanced nonlinear absorption coefficient ($\beta_{eff}$) in the case of nano-clusters compared to their micro-cubes and micro-particles.

1. Introduction
The past few years have witnessed an increasing trend toward micro- and nano structures of Cu$_2$O with well-controllable size and shapes. Controlling is being pursued with great interest in current material synthesis and device fabrication. Two crystalline forms of copper oxides are cupric oxide (CuO) and cuprous oxide (Cu$_2$O). Cuprous oxide having simple and highly symmetric cuprite structure (space group O$_h$) with six atoms in the unit cell. Cu$_2$O is low cost, with low toxicity and the natural abundance of its source materials and important inorganic p-type semiconductors with a direct band gap of 2.17 eV. It is believed to be a promising application in multiple technical fields including, solar cells, electrocatalytic, electrode material for lithium ion batteries, dilute magnetic semiconductor (DMS) and bio and gas sensors. Tuning the band gap and influencing the physical, chemical and electronic properties of the semiconductors are possible by the use of changing particle size from nano to even submicron scale or doping with transition metal ions [1-3] leading to properties that are different from those of their bulky counterparts, makes them candidates for various important applications in the field of material research. Cu$_2$O with different morphologies have been prepared by many methods, such as electrochemical, sonochemical, microwave irradiation, solution phase, sol–gel, etc. Chemical coprecipitation is simple and easy method to prepare Cu$_2$O with different morphologies. Some of the studies on Cu$_2$O show that Cu$_2$O phase was stabilized by a controlled oxidation and the formation of a thin protecting film of CuO [4].
Intense research is currently being pursued in the field of new nonlinear optical material preparation, with high optical nonlinearities [5] and fast response time is gaining interest both from the research as well as industrial point of view. To find the nonlinear optical parameters such as nonlinear absorption (NLA), we utilized the standard Z-scan technique, which is a simple single beam nonlinear transmission experiment [6].

The present work is focused on the cost-effective synthesis and characterization of its linear and nonlinear optical absorption of Cu$_2$O with different morphologies at nano second excitation.

2. Experimental Section

2.1 Synthesis

Cu$_2$O with different morphologies were prepared by simple chemical co-precipitation method. By reducing copper (II) salt with ascorbic acid in the presence of sodium hydroxide. In the typical synthesis, CuSO$_4$. 5H$_2$O (2.5g) was dissolved in milli Q water (20ml). Then NaOH (0.8g, 0.5 molL$^{-1}$) was dissolved in 40 ml milli Q water and added to the 20 mL aqueous solution of CuSO$_4$ by constant stirring. A clear blue Cu(OH)$_2$ precipitate appeared immediately. Then 0.88 g ascorbic acid dissolved in 50 mL milli Q water was added drop wise to the above solution with vigorous stirring at room temperature. After 60 minutes of stirring, the precipitate particles were isolated from the solution by centrifugation at 2000 rpm for 15 min. The product was washed by milli Q water and absolute ethanol through multiple cycles of centrifugation and redispersion. The final product was dried at 80 °C for 7 hours. Cu$_2$O powders with different morphologies prepared by simply changing the concentration NaOH with similar procedure (0.75, and 1.5 M). The sample codes of the Cu$_2$O powders obtained by varying the concentration of NaOH as 0.5, 0.75, and 1.5 M are referred as Cu$_2$O-I, Cu$_2$O-II, and Cu$_2$O-III, throughout this script.

2.2 Instruments

X-ray powder diffraction (XRD) patterns of the as prepared powders were recorded by using Inel -C120 X-ray diffractometer, which is equipped with a curved position sensitive detector and data was collected using Co-Kα radiation of wavelength 0.17889 nm. Raman spectra of as-synthesized solid powders were recorded using Horiba Jobin Yvon LabRam HR high resolution micro-Raman spectrograph with 514 nm of Argon ion laser as the excitation source. UV–Visible spectroscopy analysis was carried out on a JASCO UV-Visible absorption spectrophotometer. The morphology and the particle sizes of as prepared powder samples were measured with TECNAI G$^2$ FEI F12 model TEM. For TEM measurement, the samples were deposited on carbon coated copper grids. Second harmonic from the Nd:YAG laser with 6 ns (Spectra-Physics INDI-40) pulse duration and 10 Hz repetition rate was used as the excitation sources for nonlinear absorption (NLA) measurements.

3. Results and Discussion

Fig. 1 shows XRD pattern of as synthesized Cu$_2$O powders, all of the peaks match well with Bragg reflections of the standard cubic cuprite structure and is compatible with the literature standard value (standard JCPDF file no. 05-0667). One can observe that increasing the concentration of NaOH from 0.5 to 1.5 M, Bragg reflections (peaks) narrowing indicates particle size increase. The average crystallite size of Cu$_2$O-I (0.5M), was calculated using the (111) diffraction peak as reference according to the line-broadening method using the Scherrer’s formula. The average crystallite size was found to be around 20 nm.

TEM samples were prepared by placing a drop of an iso-propanol dispersion of Cu$_2$O powders on carbon coated copper grid was used for particle morphology and as shown inset of Fig. 1 Cu$_2$O-I particle size varies from 15-20 nm and agglomerated with 100 to 150nm size. Cu$_2$O-II powder are cubic in nature and it size varies from 100-150nm. Cu$_2$O-III powders are in micron size. OH$^-$ ions affect the stability of Cu$_2$O with different morphologies [7].
The Raman spectrum of as synthesized powders is shown in Fig. 2(a). The peaks at 218, 620 cm\(^{-1}\) are assigned to Cu\(_2\)O phase, whereas the peak at 280 cm\(^{-1}\) belongs to CuO phase [8]. Linear optical absorption spectra of as prepared Cu\(_2\)O powders of different morphologies were recorded by dispersing them in iso-propanol by ultrasonication for 15 minutes and as shown in Fig. 2(b). From UV-Vis absorption spectra, the optical band gaps of Cu\(_2\)O-I, Cu\(_2\)O-II, and Cu\(_2\)O-III are calculated as 2.6, 2.3 and 2.1 eV respectively. Cu\(_2\)O-I, Cu\(_2\)O-II optical band gap shifts towards higher energy compared to the bulk Cu\(_2\)O band gap at 2.1 eV. This can be ascribed to the quantum confinement effect.

Fig. 3 shows open aperture Z-scan traces of Cu\(_2\)O powder (3X10\(^{-4}\) M) in iso-propanol. All samples show SA to RSA behaviour. Since 532nm excitation falls in the absorption region, all samples show SA behaviour first (at lower intensities) and then due to strong excited state absorption (ESA), the RSA behaviour dominates at higher intensities or nearer to the focal point. During ESA, the nonlinear process dominates taking the first excited electron in the lower conduction band region to the higher excited conduction band states through a second photon. Such a process is referred to as free-carrier or excited-state absorption.

Switchover from SA to RSA on increase of the input intensity has been observed in various materials under different pulse excitation. In order to model [9] this type of behavior of RSA within SA, the observed experimental data is fitted with the following equation that combines the saturation behavior with saturation intensity of \(I_S\) and the effective excited state absorption (\(\beta_{eff}\)) coefficients that included both the excited state absorption and two photon absorption (TPA)

\[
\alpha(I) = \frac{\alpha_0}{I} + \beta_{eff} \frac{I}{I_S} \tag{1}
\]

Here, the first term describes the saturable absorption and the second term describes reverse saturable absorption including possible direct two photon absorption (\(\beta\)). \(\alpha_0\) is the linear absorption coefficient at 532nm and is derived from the absorption spectrum. \(I\) and \(I_S\) are laser intensity at each position in the Z-scan and saturation intensity, respectively. In this case, the propagation of the laser beam through the medium can be given by

\[
\frac{dl}{dz} = -\alpha(I)I \tag{2}
\]
where \( \alpha(I) \) is the total nonlinear absorption coefficient and \( z \) is the propagation distance in the medium. In Fig. 3 solid lines show theoretical fit to the experimental data using above equations, where \( \beta \) and \( I_S \) have been used as fitting parameters to match the valley and peak, respectively, in the experimental data. We can find that the theoretical simulations are in good agreement with the experimental results. One can observe that \( \beta_{\text{eff}} \) values are higher for nano-clusters and micro-cubes compared to their micro-particles.

![Figure 3](image-url)

**Figure 3.** Open aperture Z-scan curves of (a) Cu$_2$O-I (b) Cu$_2$O-II (c) Cu$_2$O-III (open circles, open triangles and open squares are experimental curves and solid line theoretically generated curves.)

4. Conclusions
We observed a strong dependence of the band gap with the change in the particle size inferred from the XRD line shapes, and TEM data. We also observed a strong variation in the effective nonlinear absorption coefficient with change in the particle size. Effective nonlinear absorption coefficient (\( \beta_{\text{eff}} \)) values in the case nanoclusters are higher compare to the micro-particles.

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