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Quantum size effects in CuO nanoparticles

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Size effects in cupric oxide nanocrystals, synthesized using a novel electrochemical route, having average diameters of about 4 and 6 nm, are probed by x-ray photoelectron spectroscopy. Cu—O bond ionicity was found to increase with reduction in nanocrystallite size. Formation of pure CuO phase was confirmed from x-ray diffraction, infrared spectrophotometry and photoelectron spectroscopy. This report also disproves the earlier conjecture that nanometer sized CuO phase is unstable below 25 nm.

I. INTRODUCTION

Nanocrystallites or quantum dots, provide a unique opportunity to observe the evolving electronic structure of materials growing from molecules to bulk. The investigations on size dependent electronic structure,[1–4] have revealed several interesting properties, including discretization of electron energy levels, concentration of oscillator strength, highly polarizable excited states, increased electron-electron correlation etc. Quantum size effects have been mainly studied in II-VI semiconductors, and relatively less studied in oxides.[5] Here, we report studies on the electronic structure of CuO nanoparticles, synthesized by a novel electrochemical route.

Copper oxide is a covalent semiconductor, having a band gap between 1.21 and 1.5 eV.[6–9] The optical properties of this transition-metal oxide are complicated by the strong electron correlation, which exists in this narrow-band semiconductor. Optical techniques are the most common techniques to study the quantum size effects. In spite of the great capability of x-ray photoelectron spectroscopy (XPS), to probe the electronic structure of solids, at present, XPS is rather under utilized in investigations of quantum dots. We have emphasized x-ray photoelectron spectroscopic studies, to examine the size-induced effects.

Apart from the routine use of XPS for chemical analysis, only some XPS studies[10–12] on quantum dots have indicated an increase in the binding energy of core levels, with size reduction. The use of XPS to determine size of quantum dots has also been demonstrated.[13,14]

As a matter of fact, very little is known about nanoparticles of transition metal oxides, with the exception of CoO, TiO_2, and NiO, which are useful for catalytic purposes.[15–20] Orel *et al.*[21] have reported structural studies of CuO nanoparticulate films using x-ray diffraction, scanning electron microscopy and infrared spectroscopy. Recently, CuO nanoparticles have been studied by XPS.[22,23] They have observed an increase in the amount of Cu^{1+} with decrease in size of the divalent copper oxide nanoparticles. Studies on CuO nanoparticles,[24,25] have been reported by Palkar and Ayyub. They have synthesized a series of oxide nanoparticles[25] using chemical routes. They observed that small sized, (diameter less than 25 nm) CuO nanoparticles were not stable;[24] cubic and more ionic Cu_2O was formed, in smaller size regime. They also proposed that the ionic character of a solid, tends to increase with reduction in particle size. An increase in ionicity, with decrease in size, has also been observed by them for other oxide nanoparticles.

Here, we report studies on CuO nanoparticles, in a much smaller size regime. A novel electrochemical method, has been established, for synthesis of CuO nanoparticles. This method yields small size distributed nanoparticles. Moreover, electrochemical route has a viability for commercial production of nanoparticles. This fact is significant from the view point of application of CuO in catalysis. Small sized, stable CuO nanocrystals were obtained. X-ray diffraction, x-ray photoelectron spectroscopic and infra red spectrophotometric investigations, clearly show CuO formation. Interestingly, photoelectron spectroscopic analysis indicates an increase in bond ionicity, with decreasing cluster size. Thus the present investigations, quantitatively support the hypothesis proposed by Palkar *et al.*,[24] but at much lower sizes. The present investigations indicate that, the stability of the nanoparticles is not only a function of size, but is also governed by the ligands, passivating the nanoparticles.

II. EXPERIMENT

Cupric oxide nanoparticles have been obtained using an electrochemical route, originally proposed by Reetz and Helbig,[26] for metallic nanoparticles. Modifications in the electrochemical route, can give rise to oxide nanoparticles,[5] having a narrow-size distribution. The electrochemical route

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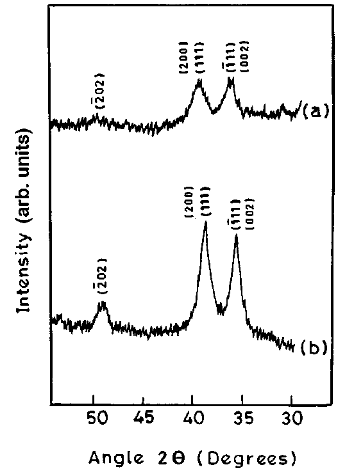

FIG. 1. X-ray diffraction patterns of CuO nanocrystals exhibiting monoclinic phase. Average diameter determined using Scherrer formula for (a) CuO-I and (b) CuO-II nanocrystals were 3.5±0.5 and 6.5±0.5 nm, respectively.

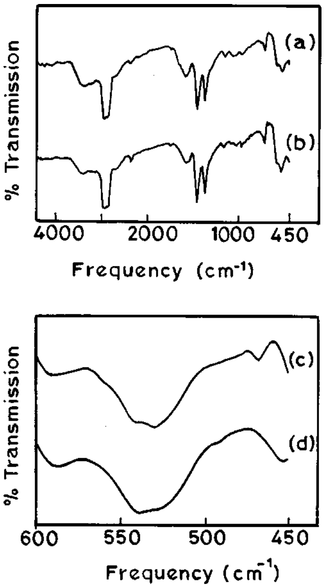

FIG. 2. Fourier transform infrared spectra of CuO-I and CuO-II nanocrystals. (a) and (b) reveal the absence of Cu_2O phase. (c) and (d) show the various CuO vibrational modes, at about 468, 529 and 590 cm^{-1}. (a) and (c) refer to CuO-I while (b) and (d) refer to CuO-II.

can be briefly explained as follows. Cu electrode was used as a sacrificial anode. The electrochemical bath comprised of tetraoctylammonium bromide (TOAB) in acetonitrile and tetrahydrofuran, in the ratio 4:1. Platinum was used as the cathode. The capping agent, TOAB also served as an electrolyte. Electrolysis under constant current mode was run in oxygen atmosphere for a few hours. The cupric oxide nanoparticles settle down as a black precipitate, which can be separated out by centrifugation. A free flowing powder of cupric oxide nanoparticles can thus be obtained.

Size estimation and structural studies of the nanoparticles, were carried out by x-ray diffraction (XRD), as well as transmission electron microscopy (TEM). XRD measurements were performed using a Philips PW 1840 powder x-ray diffractometer, with Cu $K_\alpha(\lambda = 1.54\ \text{Å})$ as the incident radiation. TEM was carried out using a JEOL TEM 2000 FX instrument, operated at 160 kV. The CuO nanoparticles were dispersed onto a carbon-coated copper grid for TEM analysis.

Fourier transform infrared (FTIR) spectra of the quantum dots were taken at room temperature, using a Perkin Elmer 1600 series FTIR spectrophotometer. The samples were embedded in the host media nujol, and scanned from 4000 to 450 cm^{-1}.

X-ray photoelectron spectroscopic studies were carried out using a VSW spectrometer, employing Al $K_\alpha(h\nu = 1486.6\ \text{eV})$ as the incident radiation source. Nanoparticles were dispersed onto graphite, in order to avoid charging effects. The spectrometer was operated at the resolution of about 1 eV. Au $4f_{7/2}$ line was used to determine the Fermi level, while C 1*s* served as an internal standard.

III. RESULTS AND DISCUSSION

Stable CuO nanoparticles having size as small as 4 nm, have been successfully synthesized, using a novel electrochemical route. Figure 1 shows x-ray diffraction patterns of CuO nanoparticles (having two different average diameters). Experimentally obtained interplanar distances for CuO nanoparticles, match well with standard diffraction data, as well as with that for high purity powder. Nominal size as estimated from Scherrer formula, is about 3.5±0.5 nm [Fig. 1(a)] and 6.5±0.5 nm [Fig. 1(b)] henceforth referred as CuO-I and CuO-II respectively. CuO-I showed about 1% lattice contraction, as compared to bulk CuO.

The average particle diameters, as determined from TEM, were found to be approximately 4.0±0.5 and 6.0±0.5 nm for CuO-I and CuO-II quantum dots, respectively. Particle diameters are thus in fairly good agreement with those estimated from XRD results. Selected area diffraction patterns show various diffraction rings of monoclinic CuO. Interplanar distances were consistent with the standard values for monoclinic CuO. Moreover, size distribution of these electrochemically synthesized CuO quantum dots is also significantly narrow.

Group theoretical calculations and experiments,[27–32] suggest that the six IR bands of CuO are located at about 147 (Bu), 161 (Au), 321 (Au), 478 (Au), 530 (Bu), and 590 (Bu) cm^{-1}. Reported values by different authors vary slightly, due to variation in sample type, temperature and also due to broadness of the spectrum.

Figure 2 exhibits the FTIR transmission spectra of CuO-I and CuO-II quantum dots, at room temperature. For CuO-I quantum dots, three main vibrational modes are observed at 468 (Au), 529 (Bu), and 590 (Bu) cm^{-1}. For CuO-II quantum dots, the broad peaks are centered at about 454 (Au), 526 (Bu), and 587 (Bu) cm^{-1}. The weak feature located at about 540 cm^{-1} in both spectra, is due to the capping agent TOAB. The high frequency mode at about 590 cm^{-1} is reported[28] to be a Cu—O stretching along the [$\bar{1}01$] direction and the mode at about 530 cm^{-1} is reported to be due to Cu—O stretching along [101]. Moreover, modes[33] due to Cu_2O are not seen (infrared active modes of Cu_2O, appear at 610 and 147 cm^{-1}). This goes to prove that the quantum

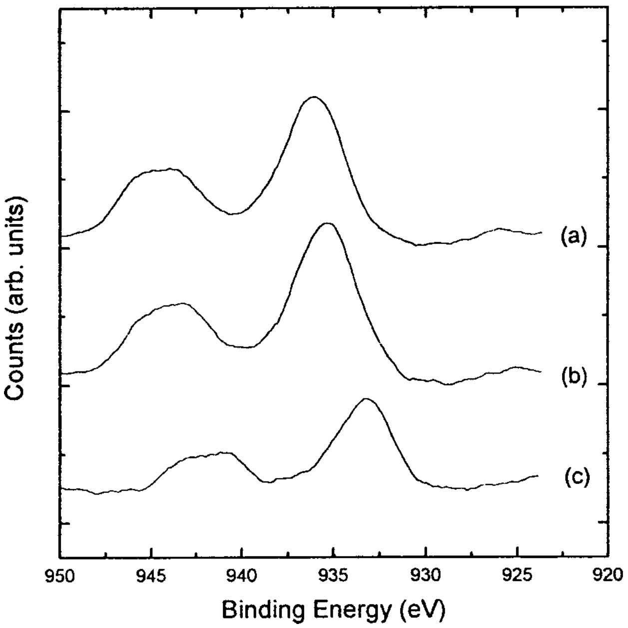

FIG. 3. X-ray photoelectron spectroscopic Cu 2p 3/2 level of (a) CuO-I (b) CuO-II and (c) CuO bulk powder. Spectra reveal main peak along with the satellite feature located at higher binding energy by about 8 eV.

dots comprise of purely CuO phase, without any trace of Cu_2O being present.

XPS is a powerful technique for studies of transition metal compounds having localized valence d orbitals. In CuO, copper exists in the divalent state having mainly d^9 character.[34–39] In a photoelectron emission process, as a consequence of creation of a core hole, electronic charge gets transferred from the surrounding to the core hole as it is energetically favorable. This situation causes the main peak (having lower binding energy) with $d^{10}L^{-1}$ character (L stands for ligand; in CuO, O 2p orbital) to be associated with a satellite having d^9 character. As the main peak has a component due to electron transfer from the valence band, it changes its energy as well as shape, with valence electronic structure. This is precisely also the reason why XPS core level spectra are broad in CuO. The energy and intensity of the main peak is predominantly determined by ligand, while satellite peak is rather insensitive to the chemical environment.

Laan *et al.*[34] have observed an increase in the intensity of satellite and main peak ratio I_s/I_m and decrease in the energy difference E_s with increasing ionicity of the ligand in copper halides ($CuBr_2$, $CuCl_2$, and CuF_2). The charge transfer satellites observed in copper divalent compounds have been studied formulating a molecular orbital model. This model has been successfully used[34] to understand the correlation between optical band gap and ligand electronegativity of Cu dihalides. In the last decade, this formulation has been applied[37] to copper oxide. Similar effects have also been observed in high T_c YBCO compound. In $YBa_2Cu_3O_{7-x}$, as x increases from 0.1 to 0.5, the satellite intensity decreases, with a concomitant increase in the satellite to main peak separation, thereby indicating a decrease in the average electronegativity of the ligands relative to the Cu atoms. Thus, change in oxygen stoichiometry, leads to variation in bond ionicity.

TABLE I. Experimentally obtained parameters for CuO nanoparticles. Size is determined from TEM measurements. I_s/I_m represents the intensity ratio of satellite to main peak, while E_s gives the energy separation between Cu $2p_{3/2}$ satellite and main peak.

Sample	Size nm	I_s/I_m	E_s
CuO-I	4.0	0.51	8.14
CuO-II	6.0	0.49	8.20
CuO	~25	0.43	8.35

XPS survey scans did not show any impurity in the quantum dots. Figure 3 shows Cu $2p$ XPS level for CuO quantum dots. In general, XPS core lines are broader for CuO quantum dots. Large number of atoms residing on the surfaces of quantum dots, lead to wider peaks [larger full width at half maximum (FWHM)]. Moreover, core line broadening can also be due to adsorbed oxygen and surface capping by TOAB.

Soriano *et al.*[19,20] have studied size effects on the electronic structure of NiO and CoO nanoparticles. Small sized nanoparticles show point defects on the surface, which act as adsorption sites for oxygen and water vapor. Photoemission spectra of the defective clusters are broad due to the presence of adsorbed species.

It may also be noted that nanoparticles are not as uniform as well-prepared single crystals. A subtle increase in binding energy has been observed in the main Cu $2p_{3/2}$ line, with decrease in size. The existence of strong satellite features for Cu $2p$ rules out the possibility of presence of Cu_2O phase. This is also corroborated by IR measurements. In the present case of CuO nanoparticles, I_s/I_m ratio for Cu $2p_{3/2}$, Cu $2p_{1/2}$ as well as $L_3M_{45}M_{45}$ Auger peaks was found to increase systematically with decreasing cluster size. Along with the systematic variation in I_s/I_m of Cu $2p_{3/2}$, a small decrease in energy separation between the main peak and satellite has also been observed (Table I). Although the variation in I_s/I_m and E_s is subtle, we have observed it repeatedly in several samples. This effect is similar to that observed when one goes from Br to Cl to F ions for Cu dihalides. The charge transfer energy and hence the Cu—O bond ionicity increases with size reduction.

The effect of lattice contraction/surface lattice expansion, on the electron energy levels of quantum particles has been addressed by Rama Krishna *et al.*[4] as well as by Ayyub *et al.*[25] It has been proposed that particle size reduction causes anisotropic lattice expansion. In covalent solids, therefore, the system becomes increasingly ionic with decreasing size. Subsequently, covalency generated by directionality is lost; thereby the crystal assumes a comparatively higher symmetry. In contrast to this, we have observed lattice contraction in nanoparticles. Consequently, the increase in charge transfer energy, or ionicity is not due to structural changes in the size regime studied here.

A decrease in size invariably leads to sharpening of the energy bands. We attribute the increased bond ionicity in CuO nanoclusters to dimension driven reduction in coordination number and narrowing of the electron energy levels.

Very high surface to volume ratio of nanoparticles make them highly reactive, hence surface passivation, or preparation and studies within ultrahigh vacuum (UHV) is neces sary. In the present investigations, CuO nanoparticles have been synthesized chemically and are encapsulated in a cage of large organic molecules, in order to control the particle size and avoid coagulation. These nanoparticles cannot be cleaned in UHV by usual methods. CuO nanoparticles hence show nonstoichiometry. We have found Cu/O ratio in CuO nanoparticles to be 0.23 and 0.16 for CuO-I and CuO-II, respectively. The nonstoichiometry could be due to adsorbed oxygen on CuO nanoparticles. Relatively broad XPS core levels also indicate the presence of adsorbed oxygen as discussed earlier.

We have never observed x-ray induced reduction of Cu^{2+} to Cu^{1+} valence as seen by Chusuei *et al.*[22] On the other hand, intensity of characteristic charge transfer satellites of Cu^{2+} valence increases with size reduction. This may be a consequence of using a chemical passivating agent, which prevents photon induced degradation of the bonds in these quantum dots.

To summarize, stable quantum dots of cupric oxide, having low-size distribution were synthesized at room temperature, using a novel, yet simple electrochemical synthesis route. This method gives a high yield of sample, without any undesired side products, allowing easy isolation of the quantum dots from the solution. We have obtained cupric oxide quantum dots of two different sizes. The crystal structure of CuO nanoparticles is the same as that of bulk CuO, though some amount of lattice contraction could be seen for quantum dots in the size regime of 4.0 nm. No size driven transition to a higher symmetry structure is seen, as reported in previous cases. XPS studies reveal an increase in bond ionicity with size reduction in CuO.

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