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Effect of Surfactant on the Structural and Optical Properties of CuO Nanoparticles

Physics

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ABSTRACT

Copper oxide nanomaterials are of interest on account of their potential uses in many technological fields. In this study, CuO nanoparticles capped with Polyvinyl Pyrrolidone (PVP) are synthesized by sol-gel method. The structural, optical and thermal properties of the prepared samples are characterized by X-ray diffractometer, Scanning Electron Microscope, Particle Size Analyzer, UV-Visible spectrometer, Fourier Transform Infrared Spectrometer and Thermo Gravimetric Analyzer. XRD pattern indicates the formation of monoclinic structure. The average size of the particle was calculated using Scherrer's formula. FT-IR measurements show the presence of O-H stretching vibrations along with C=O, C-H, C-O in various regions. The presence of Cu-O bond was also observed in this technique. SEM micrograph confirmed the effect of surfactant on the structure and morphology of CuO nanoparticles. The particle size was measured using Particle Size Analyzer. UV-Vis absorbance spectra of the synthesized nanoparticles show an increase in the band gap which indicates the decrease in the size of the CuO nanoparticles. Thermal properties of CuO capped with PVP are studied using TG-DTA analysis.

Introduction

The interest in nanomaterials has increased in recent years because of their unique physical and chemical properties (1). The experimental conditions used in the preparation of these materials play an important role in the particle size of the product. For this reason, a great variety of experimental methods have been used in the production of nanoparticles, such as the sol–gel technique (2–5), techniques that use liquid ammonia as solvent (6) and others. Sol–gel techniques are among the simplest ones and are much utilized nowadays (7–9). Copper Oxide (CuO) nanoparticles are also an important inorganic semiconductor with the direct bandgap value of 1.2eV (8). This material has a great potential for different technological applications such as gas sensors, magnetic phase transitions, catalysts, and superconductors (10-12). Recently, various methods have been developed for obtaining CuO nanoparticles, including alcohothermal route (13), in which large amounts of organic solvents are used in the preparation process (14). A great interest in metallic oxide nanocomposites has also emerged because of the possibility of modelling the properties of these materials for different applications, such as catalysis, photocatalysis, sensors, and novel optoelectronic (15). Copper nanoparticles have been obtained directly by low-energy ion implantation (16) however; the size of the particles generated is considerably large (17).

In this work, nanoparticles have been prepared through a relatively simple sol–gel method with water as a solvent. Quick precipitation, combustion, and calcination have been combined in only two steps. Thermal analysis, microscopic and spectroscopic methods have been used for product characterization.

2. Experimental details

CuO nanoparticles are synthesized by sol-gel method using Copper Chloride ($CuCl_2H_2O$), sodium hydroxide, de-ionized water, and Polyvinyl Pyrrolidone etc. Copper chloride ($CuCl_2H_2O$), and NaOH are used without purification. The synthesis reaction was carried out in the aqueous medium and the solution of 2g Copper Chloride and 2g Polyvinyl Pyrrolidone

$(C_6H_9NO)_n$ are prepared individually in 200ml de-ionized water. First the solution was stirred very well for 25-30min at room temperature, next 50ml of NaOH solution was added drop by drop to the above solution. Immediately flocculation of nanoparticles occurred. To remove the last trace of adhered impurities the particles were washed thrice using de-ionized water. The washed particles were dried at 100^0C in hot air oven for 12hrs. The prepared sample was sintered at 400°C for 6hrs and then powdered using mortar.

3. Results and Discussion

3.1 X-Ray Analysis

Powder X-ray diffraction study was carried out on the prepared CuO nanoparticles. This nanoparticles retained its monoclinic structure with lattice parameters; $a = 4.689Å$, $b = 3.24Å$, $c = 5.130Å$, $\beta = 9.570Å$ and $\gamma = 81.12Å$. The crystalline CuO nanoparticles are confirmed by the powder X-ray diffraction study and diffraction peaks are indexed in Figure1. The crystal structure parameters obtained, show that all the diffraction peaks are indexed with lattice planes and compared to the JCPDS card no: 89-5899. The d-spacing values of the peaks very well matched with the reported values in the card. The grain size for different FWHM (β) values was calculated using Debye - Scherrer's equation (18).

$D = K\lambda / \beta \cos\theta$

where,

K is a Scherrer's constant which is about 0.9,

λ is the X-ray wavelength used which is 1.54060 Å while,

β is the Full Width Half Maximum(FWHM) of the diffraction angle.

The peaks are broad due to the nanosize effect. The average crystalline size of CuO nanoparticles capped Polyvinyl Pyrrolidone was found to be 31nm. The Table 1.shows the 2θ and FWHM values of the CuO nanoparticles.

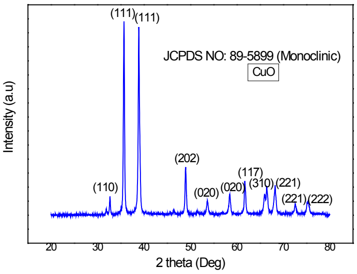

Figure 1. XRD pattern of CuO capped with PVP

Table 1. The 2θ and FWHM values of the CuO capped with PVP nanoparticles

2θ of the intense peak (deg)	(hkl) values	θ of the intense peak (deg)	FWHM of intense peak (β) radians	Size of the crystal in nm
36.00	(111)	18.0	0.00466	29.7
38.70	(200)	19.3	0.00420	29.2
49.12	(202)	24.5	0.00380	35.9

3.2 SEM Analysis

Scanning Electron Microscopic study of the sample was carried out to estimate the surface morphology of the sample. Thin films of the sample were prepared on a carbon coated copper grid by just dropping a very small amount of the sample on the grid, extra solution was removed using a blotting paper and then the film on the SEM grid are allowed to dry by putting it under a mercury lamp for 5min.

By changing the surfactants the morphology also changes. The SEM images of CuO capped with PVP in different magnifications are shown in Figures 2 (a) and 2(b). The CuO capped with PVP sample have morphology of irregular shape with random structure and minimal agglomeration (19).

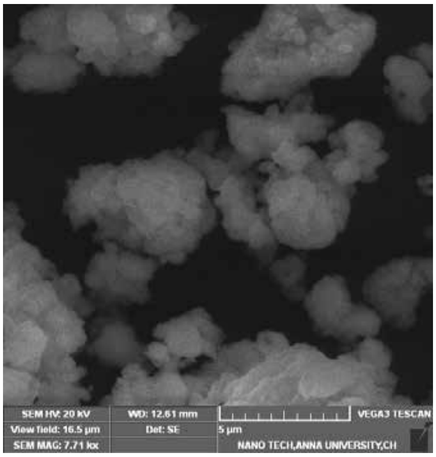

Figure 2(a) SEM image of CuO nanoparticles capped with PVP

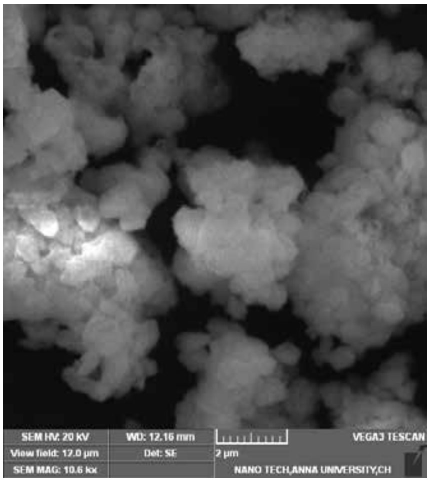

Figure 2(b) SEM image of CuO nanoparticles capped with PVP

3.3 Particle Size Analysis

The Particle Size Analysis spectrum was recorded using Malvern spectrometer. First the sample was dissolved in 5ml of de-ionized water, sonication for about 30min and then analyzed. After analyzing, it was found that the particle size of CuO capped with PVP was around 30nm. The Figure 3 shows the particle size of CuO nanoparticles using effective surfactant. This is in good agreement with the XRD result.

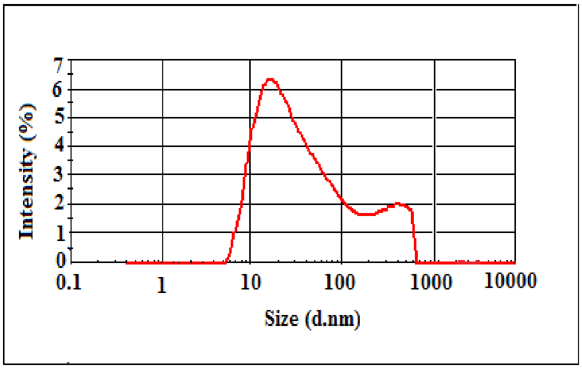

Figure 3. Particle Size distribution of CuO capped with PVP

3.4 UV-Visible Spectral Analysis

The optical absorption behavior and band gap of CuO nanoparticles capped with Polyvinyl Pyrrolidone as surfactant was studied by means of UV-Visible spectrometer. For recording UV-Visible absorption spectra, CuO nanoparticles capped with surfactant were dispersed well in 3ml of distilled water. The electronic absorption spectrum of CuO nanoparticles capped PVP in solid phase were recorded between 200 to 700nm using UV-Visible spectrometer. In the present study the absorption peak observed at 202nm in CuO capped with PVP was shown in Figure 4. The absorption spectrum of the sample was strongly blue shifted when compared with the bulk CuO at (1.2 eV). This blue shift of the band gap takes place because of the quantum confinement effect of the particles (20). UV always shows the quantum confinement size effect of the particles. When the size of the particle increases, band gap energy decreases and also absorption onset shifts to longer wavelength. The band gap refers to the energy difference between valence band and conduction band. The minimum energy required for the transition of electron from valence band to conduction band is known as band gap energy. The formula for band gap is given by

$$E = \frac{hc}{\lambda} \text{ eV}$$

where
h is a Planck's constant,
c is the speed of light,
λ is the cut off wavelength.

From these results, the band gap energy of CuO nanoparticles capped with PVP was found to be 6.1eV (21). Table 1.6 shows the calculated band gap energy of CuO nanoparticles.

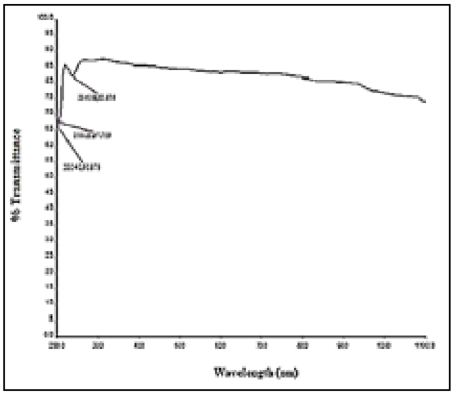

Figure 5. UV-Visible spectra of CuO nanoparticles capped with PVP

Table 2. Band gap energy of the CuO nanoparticles

Samples	λ cut-off Wavelength (nm)	Band Gap Energy (eV)
Bulk CuO	1033	1.2
CuO capped with PVP	202	6.1

3.5 FT-IR Study

FT-IR is a technique used to obtain information regarding chemical bonding in a material. The band positions and number of absorption peaks are depending on crystalline structure, chemical composition and also on morphology. In the FT-IR spectrum, there is a broad absorption peak in the range 3855, 3448, 3340 and 3793 cm^{-1}. The normal stretching vibration of O-H group indicates the existence of water absorbed in the surface of nanoparticle (22). The presence of this band can be clearly attributed to the adsorption of same atmospheric water during FT-IR measurements.

In Figure 5, there is a sharp absorption peak at 1117 and 1226cm^{-1} attributed to C=O stretching (23). The absorption peaks appeared at about 3448, 3340 and 1614cm^{-1} is due to the stretching and deformation of adsorbed water molecule. In this spectrum, it shoulders around 595, 513 and 476cm^{-1} conforming the stretching vibration of Copper Oxide. The peaks near 2000cm^{-1} are due to overtones and combination bands of the lower wave number of the substance involved in the experiment (24).

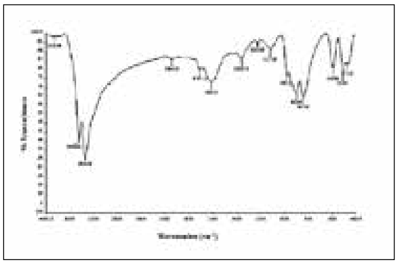

Figure 5. FT-IR spectrum of CuO nanoparticles capped with PVP

3.6 TG-DTA Analysis

The Figure 6 shows the TG-DTA curve of CuO nanoparticles capped with PVP recorded in the temperature range 0°C to 1000°C. This weight loss is mainly due to vaporization of water content in the sample. The DTA curve shows two endothermic peaks one at 261°C and the other at 339°C. From TG analysis the total weight loss calculated is 73.5%. The TGA results suggested that this compound is thermally more stable above 900°C and it has negligible weight loss when compared to bulk sample of CuO. From 139°C to 379°C, the weight loss of water molecule is 19.7%. From 437°C to 758°C the weight loss is 49.6% which may be due to organic loss (25).

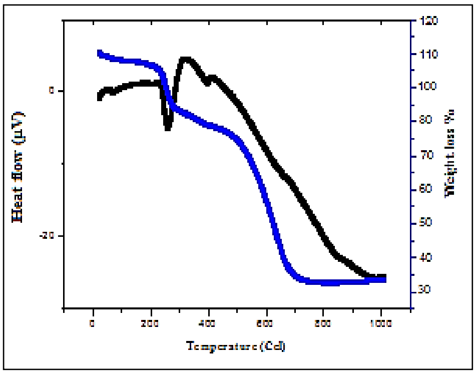

Figure 6. TG-DTA of CuO Nanoparticles capped PVP.

4. Conclusion

The CuO nanoparticles capped with PVP surfactant were successfully synthesized by sol-gel method in an air atmosphere without any high cost instrument. The formation of nanoparticles depends on the surfactant, because the surfactant Polyvinyl Pyrrolidone (PVP) helps to bind the surface of synthesized nanoparticles, thus acting as particle stabilizer and tuning the nucleation and growth of the particle to achieve a higher degree of uniformity. It is used to restrict the size of the particle and also avoid the agglomeration of nanoparticles.

XRD pattern confirms the monoclinic structure of Copper Oxide nanoparticles and the average crystalline size is found to be 31nm. SEM photograph shows good homogeneous distribution of CuO nanoparticles. The particle size of the CuO nanoparticles is around 30nm using PSA studies. FTIR studies also confirm the presence of functional group. The band gap of CuO nanoparticles is determined to be 6.1eV using UV- visible spectral analysis. TG-DTA analysis shows that the thermal weight loss is very low.

Thus it is concluded that the role of the surfactant in this work is not only to reduce the particle size but also to reduce the surface defect resulting in enhanced optical properties. Hence from the overall point of view, the CuO nanoparticles capped with PVP reduces the particle size to a greater extent with increase in the band gap when compared to bulk CuO nanoparticle.

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