

Surfactant Assisted Synthesis of Cuprous Oxide (Cu₂O) Nanoparticles via Solvothermal Process

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Abstract Cuprous oxide (Cu₂O) nanoparticles have been synthesized by facile solvothermal scheme. The reduction of copper sulphate pentahydrate (CuSO₄·5H₂O) was carried out with D-glucose as a reductant, in the presence of organic additive polyvinyl pyrrolidone (PVP K-30). The synthesized Cu₂O nanoparticles have been characterized by UV-Vis Spectroscopy, Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) Spectroscopy. The SEM images showed that the morphology of the Cu₂O nanostructures was highly uniform and growth was controlled. The nanoparticles were found to be single crystalline and monodispersed in octahedral shapes. Such type of morphology has not been reported yet using PVP K-30 as surfactant. XRD peaks confirmed the single crystalline phases of Cu₂O nanoparticles. The growth of the monodispersed single crystals has been explained on the basis of diffusion mechanism. The grain size of the nanoparticles was found to be in the range of 34- 45 nm. UV-visible absorptions spectra showed that the bandgap transition is around 635 nm (~ 2.0 eV). FTIR transmission peak at 623 cm⁻¹ confirmed Cu(I)-O vibrations, which is very well consistent with the reported value.

Keywords: cuprous oxide (Cu₂O), nanocrystals, solvothermal synthesis, semiconducting materials

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1. Introduction

The study of nanoscience and nanotechnology have advanced greatly in recent years and a large amount of research has focused in determining the properties and potential functions of nanomaterials [1,2,3] Nanomaterials show numerous exceptional and valuable properties which can be applied in the areas of life science, biology and medicine research [4,5,6,7,8].

Metal oxide nanoparticles are resourceful materials with many scientific and industrial applications. Synthesis of high quality metal oxide nanoparticles with respect to chemical purity, phase selectivity, crystallinity, and homogeneity in particle size with controlled state of agglomeration in a cost effective procedure is still a challenge [9]. Among various metal nanoparticles, copper (Cu) and copper oxide (Cu₂O) nanoparticles have attracted considerable attention because copper is one of the most important in modern technologies and is readily available [10]. Copper oxide (CuO) nanoparticles are important due to their applications as antimicrobials and in gas sensors, batteries, high temperature superconductors, solar energy conversion tools and so on [11,12,13,14]. Human beings

have been using copper (Cu) and Cu complexes for various purposes for centuries, such as water purifiers, algacides, fungicides, and as antibacterial and antifouling agents [15].

Cuprous oxide (Cu₂O) is an important metal oxide p-type semiconductor [16,17,18] with a direct bandgap of 2.2 eV, which makes it a promising material for the conversion of solar energy into electrical or chemical energy [19,20]. Recently, Cu₂O has been reported to act as a stable catalyst for water splitting under visible light irradiation (≤ 600 nm) [21,22,23]. In the past few years, numerous Cu₂O nanostructures, including nanoplates [24], nanocubes [25], octahedra [26], spherical particles [27], nanoboxes [28], and nanowires [29] have been synthesized. The detailed structural analysis of cuprous oxides has been performed on these nanostructures. However, the growth mechanism, which is important for the controlled synthesis of Cu₂O nanostructures, still needs a detailed investigation.

Cu₂O belongs to the space group *Pn3m* and the unit cell contains two copper and four oxygen ions. These are arranged with oxygen atoms in a body centered cubic lattice surrounded tetrahedrally by copper ions. This arrangement is different from that of CuO in which four

oxygen atoms surround the copper ion with square planar geometry. Therefore, these two close copper oxides show quite distinct XRD spectra and also differ in stability.

For the synthesis of Cu₂O nanoparticles, many efficient approaches have been carried out as; sono-chemical preparation, alkoxide-based preparation, microwave irradiation, precipitation pyrolysis and thermal decomposition [30, 31]. Here, we report a solvothermal route to prepare Cu₂O nanoparticles by the reduction of CuSO₄.5H₂O with D-glucose as a reductant in the presence of organic additive Polyvinylpyrrolidone also called Povidone (PVP K-30) as modifier at different reaction time and temperature. Since organic molecules even in tiny quantity can alter inorganic microstructures, indicating a very powerful tool for developing novel materials. So PVP K-30 played an important role in the formation of Cu₂O nanostructures.

2. Experimental

2.1. Materials and Synthesis

The materials used to synthesize cuprous oxide (Cu₂O) nanoparticles include:

- Copper sulphate pentahydrate (CuSO₄.5H₂O)
- Sodium hydroxide (NaOH)
- D-glucose and
- Polyvinylpyrrolidone (PVP K-30).

Cuprous oxide was synthesized by the reaction of CuSO₄.5H₂O, NaOH and D-glucose in the presence of organic modifier polyvinylpyrrolidone (PVP K-30). In a

typical method, 35.0 mL of distilled water was mixed with 2.0 m mol of CuSO₄.5H₂O and 2.0 g of PVP K-30 and then stirred vigorously until it dissolved completely. Then 8.0 m mol of NaOH was mixed with 1.0 m mol of D-glucose into the solution. The final solution was then kept in an autoclave at 50°C for 60 minutes. Then autoclave was allowed to cool down gradually at room temperature. Finally, the reddish precipitates of Cu₂O associated with PVP K-30 particles were obtained. The associated PVP K-30 particles were eliminated by washing the final product first with distilled water several times and then with ethanol in ultrasonic bath. In the last, the final product was dried at 60°C in an oven for 3 hours. The same synthesis procedure was repeated to prepare several samples for a set of different autoclave temperatures. The detail of the samples prepared at different temperatures with all other experimental parameters same is summarized in Table 1.

2.2. Characterization

The prepared samples were characterized by UV-Vis spectrometer (Perkin-Elmer Lambda-950), Scanning Electron Microscope (Jeol JSM-6510 LV), X-ray diffraction (Bruker AXS D8 FOCUS Diffractometer) using Cu K α ($\lambda=1.54056\text{\AA}$) radiation and Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer Spectrum 100 Series). The specimens for SEM were prepared by dissolving the synthesized solid product in an absolute ethanol and immersing them in an ultrasonic bath for 15 min. A few drops of the suspension were used to make grids for SEM study.

Table 1. Summary of the samples prepared at different reaction temperatures

Samples	CuSO ₄ .5H ₂ O (m. mol.)	Distilled water (mL)	PVP K-30 (g)	NaOH (m. mol.)	D-glucose (m. mol.)	Temperature (°C)	Time (minutes)
A	2	35	2	8	1	50	60
B	2	35	2	8	1	60	60
B ₁	2	35	2	8	1	65	60
C	2	35	2	8	1	70	60
C ₁	2	35	2	8	1	80	60

3. Results and Discussions

Solvothermal route, a promising method for the synthesis of transition metal oxide nanostructures, has been employed to synthesize cuprous oxide (Cu₂O) nanostructures. Using this method, highly uniform and morphologically controlled Cu₂O nanoparticles were obtained at different synthesis temperatures.

The overall chemical reaction occurring in an autoclave can be written as given in equations (1-3), where, the Cu²⁺ ions first are reduced to Cu⁺ by D-glucose [32]. When D-glucose powder is added to the Cu²⁺ salt system, the D-glucose powder first contacts with organic additives and then reaches the pool. Thus, Cu²⁺ ions are reduced to Cu⁺ by D-glucose. If there are sufficient OH⁻ ions in the pool, then the main reaction tendency of equation (3) becomes dominant. However, if quantity of OH⁻ ions is limited in the pool, then the reaction of Cu⁺ occurs partly along with the equations (1) and (2). [33]

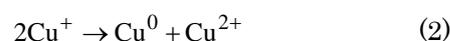


Figure 1 shows SEM images of as-synthesized Cu₂O nanomaterial samples. These are synthesized at different reaction temperatures. All these images showed that Cu₂O nanoparticles were highly uniform and stable. They all had well-defined profile having octahedral shape. The nanoparticles were single crystalline and XRD spectra confirmed the crystallinity nature of the nanoparticles. The evidence of single crystal Cu₂O nanoparticles was also confirmed by FTIR spectra. These nanoparticles were monodispersed and their size was varying in the range 400 nm to 600 nm. As we see from Figure 1, the average particle size was found to be 45 nm for sample-A prepared at temperature of 50°C, while the particle size reduced to 34 nm for sample C₁ synthesized at 80°C. Thus increase in temperature decreased the size of nanoparticles. This behavior was also in good agreement with the work of K. Karthik et al. [34], which reported that the increase in reaction temperature decreased the size of the nanoparticles.

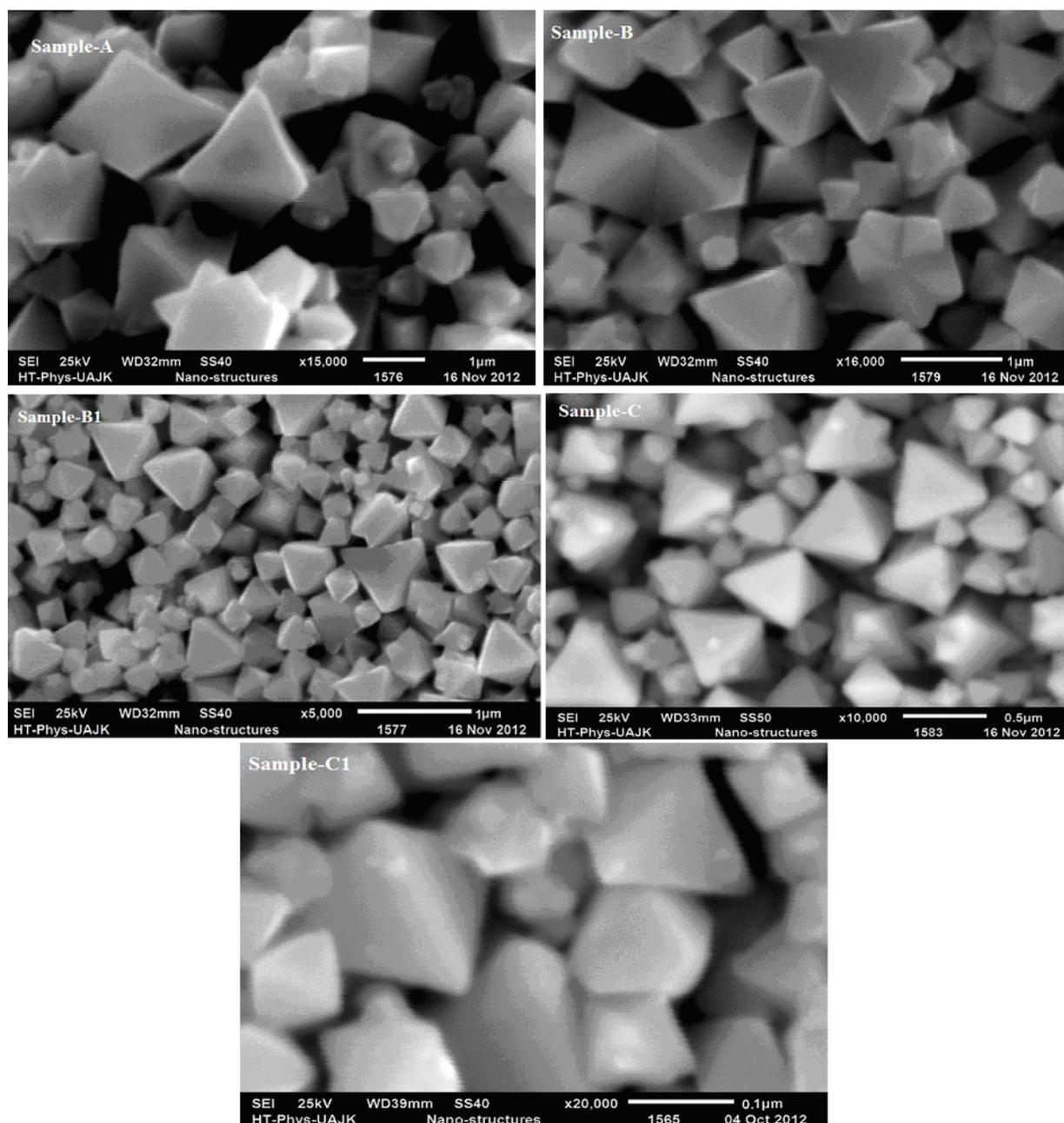


Figure 1. SEM images for sample-A, sample-B, sample-B₁, sample-C and sample-C₁ prepared at different reaction temperatures

These results are summarized in Table 2. It is quite clear from Table 2 that the reaction temperature has a substantial influence on the size of the Cu₂O nanoparticles. That is, with the increase in temperature, the particle size decreased. Thus, we conclude that the higher synthesis temperature would result in smaller particle size. It is worth mentioning that the morphology of the samples was

not changed significantly with the rise in temperature except the size of nanoparticles. It is noteworthy that reaction temperature has a considerable influence on the size of the particles. This type of morphology has not been reported by using PVP K-30 as a surfactant. The growth of these nanocrystals has been explained on the basis of diffusion mechanism.

Table 2. Morphology and size of Cu₂O nanoparticles prepared at different temperatures

Cu ₂ O Samples	Temperature (°C)	Reaction time (min)	Morphology	Particle Size (nm)
A	50	60	Octahedral	45
B	60	60	Octahedral	42
B ₁	65	30	Octahedral	40
C	70	60	Octahedral	38
C ₁	80	60	Octahedral	34

The synthesis temperature was also plotted against the Cu₂O nanoparticles size as shown in Figure 2. It is evident

from the graph that as the temperature goes to higher value, the size of nanoparticle moved to smaller value.

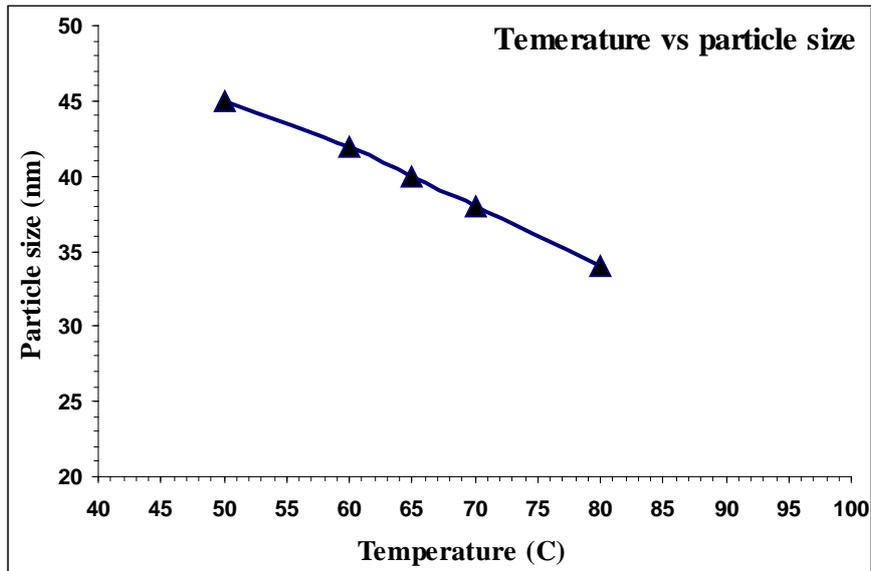


Figure 2. Synthesis temperature versus Cu₂O nanoparticles size

The XRD patterns of all samples have been shown in Figure 3. All the peaks of the pattern were labeled and indexed to a cubic phase of Cu₂O (JCPDS 5-669). The sharp peaks at 2θ values of 29.68° , 36.68° , 42.6° , 61.76° , 73.98° and 77.8° corresponded to (110), (111), (200), (220), (311), and (222) phases of crystalline Cu₂O respectively and no obvious peaks of impurity were detected in the XRD pattern. That indicates the formation of single crystalline phases of Cu₂O nanoparticles through

the presented solvothermal process. The formation of these monodispersed single crystalline nanoparticles can be attributed to the diffusion mechanism. In this mechanism, monodispersed precipitation is controlled kinetically, resulting in a short nucleation burst, only once a critical super-saturation of particle forming species is reached. The nucleation stage is then followed by diffusion of constituent complexes onto these primary particles [33].

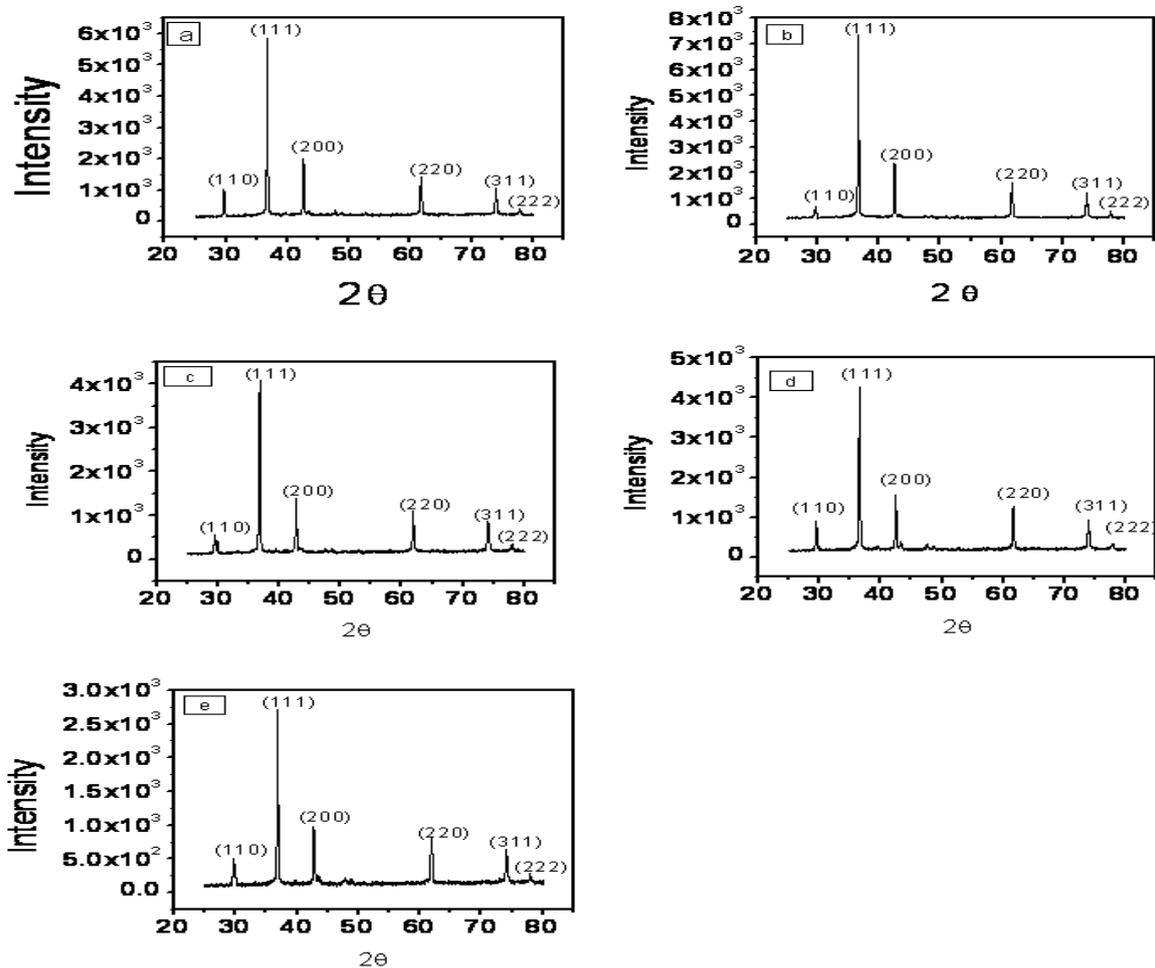


Figure 3. XRD patterns of (a) sample-A, (b) sample-B, (c) sample-B₁, (d) sample-C and (e) sample-C₁

The broadness of the peak (111) which is highest peak, has been used to calculate crystallite size of Cu_2O nanoparticles using Debye-Scherrer formula ($D = k\lambda/\beta\cos\theta$), where D is the average crystalline grain size, k is the Scherrer's constant related to the shape of the crystals, λ is the wavelength (1.540 \AA) of the X-ray, θ is the diffraction angle, and β is the full width at half-maximum. The average size of these nanoparticles was found to be in the range of 34 nm-45 nm. The lattice constants calculated for samples A, B, B₁, C, and C₁ were found to be 4.21 \AA , 4.22 \AA , 4.24 \AA , 4.25 \AA and 4.26 \AA ,

respectively. This is comparable with the reported data (4.42 \AA).

UV-visible absorption spectra of Cu_2O nanostructures were obtained by UV/vis spectrometer in the wavelength range of 300 nm to 850 nm as shown in Figure 4. The UV-vis absorption measurements have been carried out to resolve the excitonic or interband transitions of Cu_2O nanostructures. UV-vis absorption spectra (Figure 4) of the Cu_2O nanostructures dispersed in ethanol solution showed broad absorption peaks with center at about 635 nm.

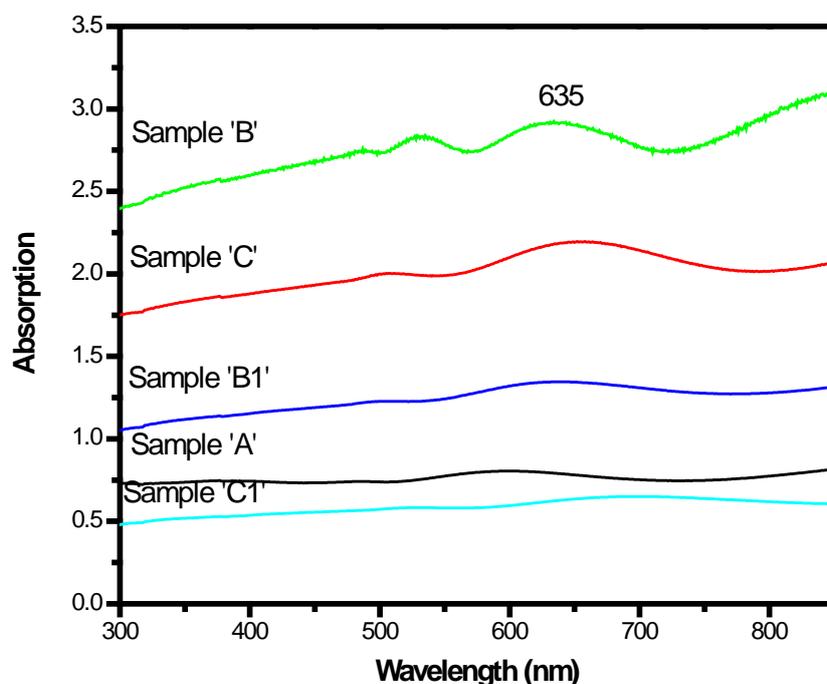


Figure 4. UV-Vis absorption spectra of samples A, B, B₁, C and C₁

The bandgap of the sample-A was computed from the UV-visible absorption spectrum shown in Figure 4 and it come out to be 2.07 eV, which was comparable to the reported value for the bulk Cu_2O ($E_g = 2.17 \text{ eV}$) [35]. Similarly for the other samples, B, B₁, C, and C₁, the values of the bandgap were found to be 1.96 eV, 1.94 eV, 1.90 eV, and 1.87 eV, respectively. This showed that, the

bandgap decreased as the temperature was increased and the wavelength shifts towards the higher value. The slight decrease in the bandgap was due to the fact that the crystal lattice expanded and the interatomic bonds weakened with the rise in temperature. Weaker bond means a lesser amount of amount of energy is needed to break a bond and get an electron in the conduction band.

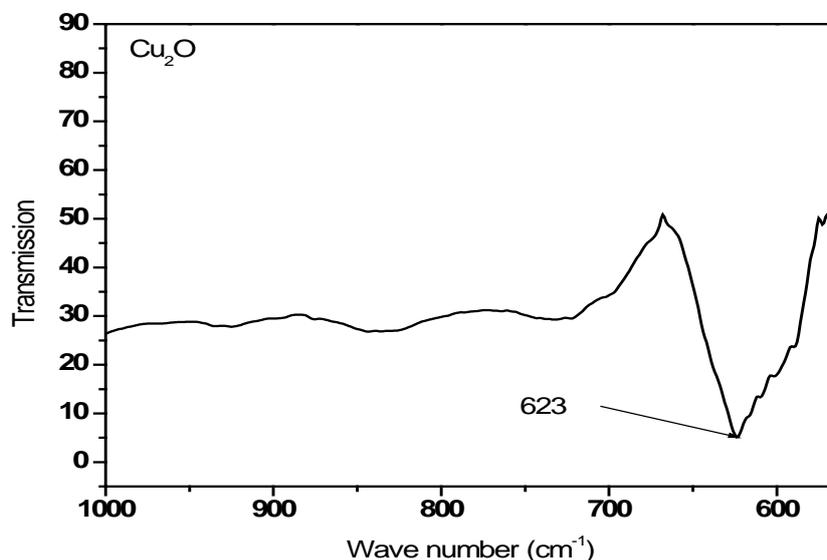


Figure 5. FTIR spectra of Cu_2O nanostructures

The synthesized Cu₂O nanostructures were further characterized by Fourier-transform infrared (FTIR) spectroscopy. This spectroscopy has long been utilized as a powerful tool to provide supplementary information on the nature of synthesized materials [36,37]. The FTIR spectrum of the synthesized Cu₂O in the wave number range 565-1000 cm⁻¹ is shown in Figure 5. The spectrum displayed a transmission peak at around 623 cm⁻¹, which can be attributed to the Cu(I)-O vibrations. This was well consistent with that of Cu₂O reported value [38,39]. The spectrum also excludes the presence of any cupric oxide (CuO) impurity, since CuO always exhibits three obvious transmission peaks at around 588, 534 and 480 cm⁻¹, which can be assigned to the vibrations of Cu (II)-O bonds.

4. Conclusions

In summary, monodispersed, stable and morphologically controlled Cu₂O nanoparticles have been synthesized successfully in the presence of an organic additive (PVP K-30) as modifier by solvothermal route. This reliable method gave a high yield of nanostructures and narrow size distributions. With this approach, we have synthesized Cu₂O nanoparticles in octahedral shapes. Growth of these nanoparticles was attributed to diffusion mechanism. It is important to mention that with PVP K-30 as modifier, these types of nanostructures have not yet been reported. The diameter of nanoparticles was found to be decreasing with rise in synthesis temperature. The Cu₂O nanostructure diameter could be tuned from 45 nm to 34 nm by controlling the synthesis temperature. From structural analysis we concluded that the Cu₂O had a highly stabilized single crystalline phase. UV-Vis absorptions spectra revealed the dependence of bandgap on synthesis temperature and it was found that the bandgap was slightly changed with changing crystallite size. As the temperature was increased, the bandgap value decreased and the bandgap transition was around 635 nm. FTIR transmission peak at 623 cm⁻¹ confirmed Cu(I)-O vibrations.

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