Synthesis of Cuprous Oxide (Cu₂O) Nanoparticles – a Review

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Cuprous Oxide (Cu₂O) a semiconductor material oxide; with unique optoelectronic properties; gains significant importance for its synthesis in view of its various technological and industrial applications. A few liquid phase methods for the synthesis of Cu₂O nanoparticles are reviewed on the basis of materials, methodology, synthesis conditions and key findings. A comparative study of these methods is also performed following criteria of repeatability, safety, cost, time span and simplicity. Contextual to the above mentioned criteria, three liquid phase synthesis techniques were shortlisted and actually experimented (as reported) to synthesize the Cu₂O nanoparticles. This was done to investigate the effectiveness, repeatability and stability of the synthesized Cu₂O product as a function of ageing time. The synthesized Cu₂O using all these techniques are prone to be unstable and undergo the rapid phase change to CuO phase which was ascertained from the shift of absorbance peak in UV-VIS spectra. The results have highlighted the urgent need to develop a facile, economical, scalable and safe method to synthesize stable Cu₂O nanoparticles at room temperature.

Keywords: Ageing, Cuprous oxide, Nanoparticles, Nanosynthesis, Phase stability.

1. INTRODUCTION

The Cuprous Oxide (Cu₂O) is semiconductor metal which is nontoxic, low cost and has abundant source materials. Cu₂O has gained a renewed interest for various technological applications owing to its optoelectronic properties. It is a well-known p-type semiconductor with theoretical direct band gap of 2.2 eV [1-6] which allows fabrication of high efficiency solar cells (theoretical efficiency ~ 18 %) [7]. Moreover, the prospective application areas of Cu₂O also includes chemical industry [8], biosensors [9] Lithium ion batteries [10] photo catalysis [11], photoluminescence [12], optoelectronic and gas sensors [13, 14].

Literature reports several methods for the synthesis of Cu₂O nanoparticles/thin films/structures such as: thermal oxidation [15], potentiostatic deposition [16], activated reactive evaporation [17], spray pyrolysis [18], laser ablation [19], microemulsion [20], sono-chemical [21], microwave [22], liquid phase synthesis [23-27]. The summary of synthesis method, conditions, temperature, particle size, key findings in context with the above mentioned methods is provided in the Table 1.

This shows that usually liquid chemistry techniques are preferred for synthesis of Cu₂O nanoparticles and nanostructures. Moreover, we decided to stick with the methods reported by Gau et. al., Bai et. al. Huang is low cost, simple to execute, less time consuming. Hence, the synthesis of Cu₂O nano-particles was actually carried out using these techniques by following the exact procedure as reported. Furthermore these methods were investigated in view of their a) repeatability for Cu₂O nanoparticle synthesis and b) the phase stability of Cu₂O over aging period.

2. EXPERIMENTAL

2.1 Materials and Synthesis Methods

We successfully synthesized cuprous oxide nanoparticles by following [A] Gau [25], [B] Bai [26] and [C] Huang [27] methods exactly by following their synthesis procedure as reported in the literature and prepared four different Cu₂O samples namely A, B, C and D. Out of which as A, B and C samples corresponds to methods [A], [B] and [C] respectively. However, it was observed that the method [C] of Huang et. al. was found to give very low yield of Cu₂O powder. Therefore, the Huang's method was scaled up to get large yield of Cu₂O nanoparticles by following the procedure in method [C] but increasing the precursor concentration proportionately to obtain the sample D. The methods [A], [B] and [C] are explained briefly as given below. All the reagents used in above mentioned methods were of AR grade, were purchased from Loba Chemie Pvt. Ltd. Mumbai, Maharashtra, India and were used without any further purification.

Method [A]

In this method, copper sulphate pentahydrate (0.01 M/ml), L-ascorbic acid (0.1 M/ml), polyethylene glycol (PEG, MW 600) (0.05 M/ml) and sodium hydroxide (0.5 M/ml) were used as reagents. Typically, 4 ml solution of copper sulphate pentahydrate was first mixed with 1 ml of PEG solution and into the resulting solution sodium hydroxide (3 ml) and L-ascorbic acid (1ml) solutions were simultaneously added. On stirring the resulting solution for 5 minutes it was left undisturbed under nitrogen for 30 minutes to complete the reaction to give yellow-orange color solution of Cu₂O nanoparticles. It was later centrifuged twice at 6000 rpm for 30 minutes by dispersing in distilled water in a centrifuge machine (Make: Remi PR 24, Vasai,

Table 1 - Comparative analysis of different techniques used for synthesis of Cu_2O nanostructures

S. N.	Method	Materials	Temp./ Pressure	Particles/Thin films/wires	Grain size/Morphology	Remarks about the method	Ref.
1	Thermal Oxidation	Oxidation of copper foil, in the Furnace	1040 °C – 1050 °C	Thin films	Crystallite Size Un-annealed /Annealed: 0.66 μm / 0.83 μm	High temp, high energy requirement, needs temp. and pressure control, high cost	15
2	Potentiostatic deposition (Reduction)	Alkaline cupric lactate solution on polycarbonate membrane	Room temp.	Nanowires	Diameter ~100 nm length ~16 μm,	Issues with scalability, control of pH (7-10) is must, demands proper temperature control	16
3	Activated reactive evaporation technique	Cu evaporation in the presence of a reactive O_2 plasma	150-200 °C	Nano-crystalline Thin films	Nanometer Size Grain morphology – Spherical	High temperature and voltage is required, high cost, needs precise control and monitoring	17
4	Spray pyrolysis	Copper nitrate in ethanol / ethanol + water solvent as precursor	450 °C	Nanoparticles	With ethanol ~ 50 to 80 nm, solid spherical, without ethanol ~100 nm hollow spherical	High temperature, high cost, precise control over temperature is mandatory	18
5	Laser ablation (Nd:YAG pulsed laser)	Copper target in PVP aqueous solution.	1 hr. High temp. Pulsed laser ablation	Nanoparticles	Polycrystalline Grain size ~29 nm	High power, temp. and pressure, high cost, precise control, handling safety is the key issue.	19
6	Micro emulsion	Copper (I) acetate with chelating agents (*n*-propylamine / benzylamine)	Room temp.	Nanoparticles / thin film	Polycrystalline nanoparticles Size – 3 to 6 nm. Thin films grain size 24 nm	Stoichiometry control is crucial, benzylamine / cyclohexane are costly, flammable, severe eye irritant, eco-hazardous,	20
7	Sono-chemical (acoustic cavitation)	Copper (II) acetate with 1% v/v aniline – water as solvent	Local heating at high temp. & pressure	Nanoparticles	Nanocrystalline	High infrastructure cost, requirement of specific instrument, external energy source is required	21
8	Microwave radiation (power 800 W frequency 2.45 GHz)	Copper acetate and benzyl alcohol solution, rapid synthesis	High temp.	Nanoparticles	Polycrystalline average grain size – 38 nm	Benzyl alcohol is hazardous, safety issues, practically difficult to scale up, high cost	22
9	Pathological	Copper Sulfate, Benedict reagent, Glucose	Boiling	Nanoparticles	Size – 25-123 nm Hexagonal – but unclear morphology	Low cost liquid phase synthesis, annealing leads to phase change from Cu_2O to CuO	23
10	Oxidative etching method	Copper Sulfate, PVP, Sodium citrate, sodium carbonate, glucose	Room temp. and 80 °C	Nanoparticles	Size – 700 nm Truncated octahedral with hollow interior – edge length 300 nm	Low cost liquid phase synthesis, Requires drying for 16 days, vacuum drying required, time consuming process	24
11	Simple Solution synthesis	Copper Sulfate, PEG, Ascorbic acid, and NaOH	Room temp.	Nanoparticles	Size – 25-200 nm Nano-cubes	Low cost liquid phase synthesis,centrifugation required, nitrogen environment needed	25
12	Colloidal Chemistry Approach	Cupric Acetate, PVP, Ascorbic acid, and NaOH	4 °C to 90 °C	Nanoparticles, Size – 0.1 μm-1.7 μm, Nano-cubes, spheres, polyhedron, truncated cubes, octahedron, spicule, dandelion		Low cost liquid phase synthesis,centrifugation and vigorous stirring required	26
13	Redox reaction synthesis	Copper Chloride, NaoH, SDS, Hydroxyl amine	Room temp.	Nanoparticles, Size: 40 nm-420 nm, Nano-cubes, spheres, octahedra, rhombic dodecahedra, truncated rhombic dodecahedra, hexapod		Low cost liquid phase, SDS and Hydroxyl amine are hazardous, low throughput	27

Thane, Maharashtra) to remove excess PEG. The as pre-pared colloidal dispersion of Cu_2O nanoparticles used for further characterization.

Method [B]

At first 0.25 mmol (0.05 g) of cupric acetate and (0.005 mmol) of polyvinylpyrrolidone (PVP K30, MW 10,000) were dissolved in 100 ml of distilled water. In this solution then 20 ml aqueous solution of 5 mmol (0.2 g) sodium hydroxide was at room temperature under vigorous stirring to obtain a blue suspension. In this blue suspension 15 ml aqueous solution of ascorbic acid 0.75 mmol (0.132 g) was then drop wise added at a rate of 3 drops/second under vigorous stirring for 30 minutes to form reddish suspension. The reddish suspension was later centrifuged at 4000 rpm for 15 min. The obtained product was washed with distilled water three times to obtain Cu_2O nanoparticles in colloidal dispersion form which was labelled as sample B before used for further characterization.

Method [C]

Initially, 0.1 ml (0.1M) copper chloride was mixed with 9.55 ml of double distilled water to which 0.20 ml of 1 M of sodium hydroxide solution was added while stir-ring at room temperature. This resulted in to bluish solution to which 0.087 g of sodium dodecyl sulphate (SDS) was further added while stirring. Finally, 0.15 ml of 0.2 M hydroxylamine solution was quickly added while shaking and the resulted solution was left for ageing for 2 hrs. In the end, centrifugation at 5000 rpm with subsequent washing in distilled water leads to Cu_2O sample C. An additional sample D was prepared with 10 times more precursor concentrations following the method [C] to obtain the large throughput.

2.2 Characterization

All the Cu_2O samples prepared by above methods were dispersed in double distilled water (colloidal solu-tions) and maintained in separate bottles for further characterization. The Cu_2O synthesis was confirmed on the basis of absorbance spectra measurements done using UV-VIS spectroscopy (Shimatzu 1650PC spectro-photometer). The characteristic absorbance peak for Cu_2O is generally observed in the neighborhood of $\lambda = 490$ nm. The phase stability study was also per-formed by monitoring the UV-VIS absorbance character-istics as a function of ageing period.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows UV-VIS spectra for A, B, C and D samples of Cu_2O nanoparticles. UV-VIS spectra for A, B, C and D samples shows the characteristic absorption peak at $\lambda = 502$ nm, 484 nm, 462.5 nm and 494 nm respectively. The absorption peak is due to plasma resonance excitation of copper atoms on the surface of nanoparticles. Reports shows that the characteristic absorbance peak for Cu_2O is generally observed in the neighborhood of $\lambda = 490$ nm [22, 25, 28]. The blue shift observed in the characteristic absorption peak at $\lambda = 462.5$ nm of sample C and $\lambda = 484$ nm of sample B may be attributed to the decrease in the particle size. The bandgap measurement was done by using the

formula $E_g = hc/\lambda$ where h is the Planck's constant, c is the speed of light and λ is the wavelength for the characteris-tic absorption peak. The direct band gap (E_g) values were observed to be increased from 2.47 eV, 2.51 eV, 2.56 eV and 2.68 eV for A, D, B and C samples respectively. These E_g values are higher than the theoretical direct bandgap (2.137 eV – bulk Cu_2O) mainly due to nano size which leads to quantum confinement effect [1-6].
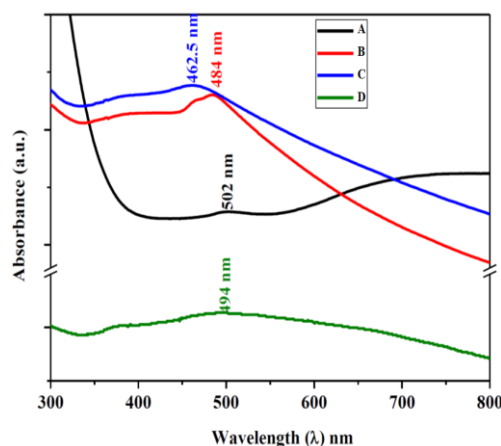

Fig. 1 – UV-VIS spectra of A, B, C, D samples
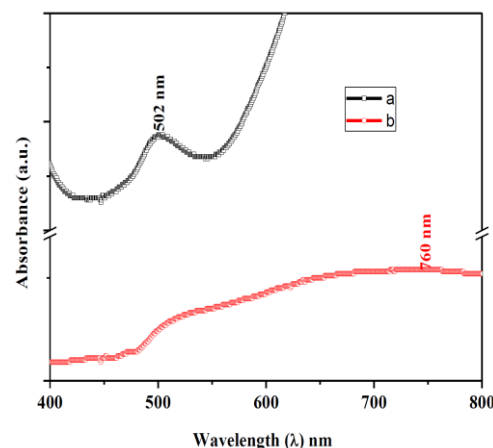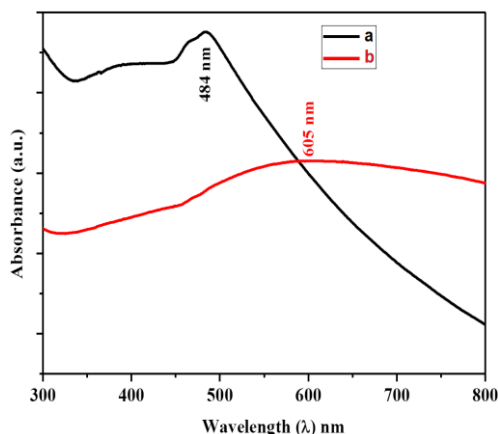

Fig. 2 – UV-VIS spectra of sample A: (a) as synthesized and (b) after 10 days

After synthesis experiments it was observed that Cu_2O phase was not quite stable and showed ageing with time for all the samples. Thus, the phase stability of as synthesized samples A, B, C, D was investigated over an ageing period by recording the UV-VIS absorb-ance spectra.

Fig. 2 shows the measured UV-VIS spectra over the spectral range of λ: 400 nm-800 nm for sample A: (a) as synthesized (b) after 10 days. Plot (a) shows the presence of characteristic absorption peak around $\lambda = 502$ nm thereby affirming the formation of Cu_2O nanoparticles. However, after ageing period of 10 days it was observed that the Cu_2O characteristic absorbance peak was com-pletely vanished and rather a broad absorption peak around $\lambda = 760$ nm emerged corresponding to formation of CuO phase as seen from the Fig. 2 plot (b). Thus the phase transition from Cu_2O to CuO for sample A has occurred within ageing time 10 days [29].

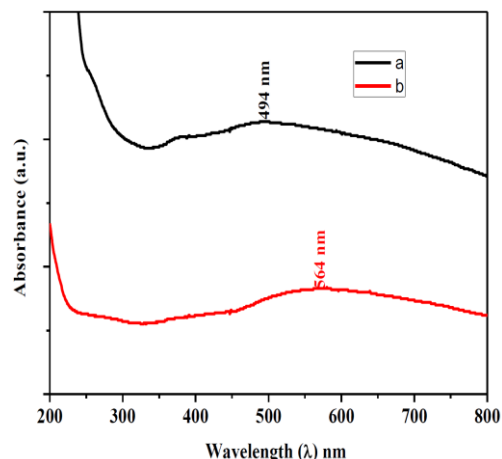**Fig. 3** – UV-VIS spectra of sample B: (a) as synthesized and (b) after 7 days

Fig. 3 depicts the recorded UV-VIS spectra over the spectral range of λ: 300 nm-800 nm for sample B: (a) as synthesized (b) after 7 days. The UV-VIS spectra for as synthesized sample Fig. 3 (a) indicates the formation of Cu_2O nanoparticles exhibiting the characteristic absorption peak around $\lambda = 484$ nm. However, the UV-VIS measurements over the ageing period of 7 days as shown in Fig. 3 (b) shows annihilation of absorption peak for Cu_2O and presence of fairly broad absorption peak around $\lambda = 605$ nm after corresponding to CuO phase [29]. This means that the sample B is rapidly degraded from to Cu_2O nanoparticle phase to CuO phase within 7 days.

Fig. 4 exemplifies the UV-VIS spectra over the spectral range of λ: 300 nm-800 nm for sample C (a) as synthesized and (b) after 12 days. Fig. 4 (a) shows the presence of characteristic absorption peak at $\lambda = 462.5$ nm [30] ascertaining the formation of Cu_2O nanoparticles. However, Fig. 4 (b) clearly demonstrates the presence of mixed phase of Cu_2O and CuO with less intense absorption peak around $\lambda = 528$ nm (Cu_2O phase) [22] and a broader peak at $\lambda = 641$ nm (CuO phase) respectively [29]. Furthermore, after 12 days for extended ageing time no substantial change was observed in UV-VIS absorbance spectra when comparison was done with Fig. 4 (b). This shows that in method C the conversion of Cu_2O to CuO is a slow process, moreover Fig. 3 shows that even the peak corresponding to Cu_2O for sample C has underwent the red shift from 462.5 to 528 nm due to ageing effect. This red shift may be attributed to agglomeration of Cu_2O nanoparticles over ageing period contributing to increased particle size.
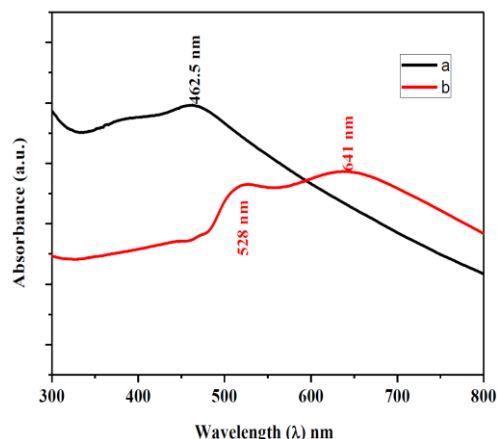
Fig. 4 – UV-VIS spectra of sample C: (a) as synthesized and (b) after 12 days

Fig. 5 describes the UV-VIS spectra of sample D: (a) as synthesized (b) after 15 days. Fig. 5 (a) shows the presence of characteristic absorption peak at $\lambda = 494$ nm thereby has confirmed the formation of Cu_2O nanoparticle. However, in Fig. 5 (b) shows the characteristic peak of Cu_2O diminished and rather presence of a broad absorption peak around $\lambda = 564$ nm (CuO phase) after ageing period of 15 days [29].

Fig. 5 – UV-VIS spectra of sample D: (a) as synthesized (b) after 15 days

The summary of phase stability study performed for A,B,C,D sample is represented in the Table 2. This means that although short listed methods demonstrate successful synthesis of Cu_2O nanoparticles yet their phase stability over ageing time forms a critical issue.

Table 2 – The summary of phase stability study performed for A, B, C, D samples

Method	Sample code	Absorption peak position (λ) in nm (reported)	Absorption peak position (λ) in nm (just synthesized (observed for Cu_2O phase)	Ageing period in days	Absorption peak position (λ) in nm (after ageing) (observed for CuO phase)	Ref.
[A]	A	500	502	10	760	25
[B]	B	484	484	07	605	26
[C]	C	490	462.5	12	641	27
[C]	D	–	494	15	564	27

4. CONCLUSIONS

Simple, low cost, liquid phase methods (three methods) for synthesis of Cu_2O nanoparticles at room temperature are reviewed and reworked in view of their ability to repeatedly synthesize the stable nano Cu_2O colloids. The methods lead to successful synthesis of Cu_2O nanoparticles; however the synthesized Cu_2O colloidal suspensions were found to be unstable and underwent a phase change to a more stable CuO phase. The results indicate the inability of reviewed methods to synthesize stable Cu_2O nanocolloids. Thus, this demands for a simple, room temperature method for the synthesis of Cu_2O nanoparticles which would stable for longer ageing period.

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