

A simple microwave assists aqueous route to synthesis CuS nanoparticles and further aggregation to spherical shape

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Abstract The aggregation of CuS nanoparticles during synthesis by a hassle-free aqueous route under microwave irradiation gave remarkable spherical shape, utilizing $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ as the source of copper and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, as sulfur source; these materials were used without assistance of any surfactant or template. An X-ray powder diffraction pattern proved that the product is hexagonal CuS phase. The morphologies of the product were observed by scanning electron microscopy. Thermal behavior, different solid state, and chemical conversion in CuS with respect to temperature were studied by DSC/TGA, which confirmed the thermal oxidation of CuS and its conversion into CuO then to Cu_2O .

Keywords Microwave · Nanoparticles · Copper sulfide · Aggregation · Thermal oxidation · Spherical shape

Introduction

For the past few years, researchers have been showing extensive concentration on the study of the appropriate control over the size and shape of nanoparticles. Nanomaterials show illustrious and exceptional chemical, optical,

catalytic, magnetic, and electronic properties depending on the size of the nanoparticles (Shipway et al. 2000; Wong et al. 2002; Qingyi et al. 2002; Brust and Kiely 2002). Copper sulfide exist in various stoichiometric products including covellite (CuS), djurleite ($\text{Cu}_{1.95}\text{S}$), digenite (Cu_9S_5), anilite (Cu_7S_4), and chalcocite (Cu_2S) (Wuled Lenggoro et al. 1998). Copper sulfides are a predominantly attractive group of metal sulfides due to their use in widespread applications in fields such as semiconductors electrochemistry cells, IR detectors, sensors, and catalysts and solar energy conversion (Thongtem et al. 2007; Rodriguez et al. 2000; Chunyan et al. 2006; Kiely et al. 1998; Anuar et al. 2002; Nair and Nair 1989; Parkin 1996; Nascu et al. 1997). However, copper sulfide has multifarious crystal chemistry due to its capability to form a variety of stoichiometric copper sulfide compounds. Jumble phase copper sulfides are generally synthesized in many synthetic means (Yang and Xiang 2005; Zou et al. 2007; Tan et al. 2005; Zhu et al. 2007; Wang et al. 2007; Zhang et al. 2004; Nafees et al. 2011). Ni et al. (2004) reported the formation of CuS nanotubes using aqueous phase technique with different starting materials of diameter ranging from 350 to 1,000 nm. While we adopted an aqueous sol method to synthesize definite morphology of CuS nanomaterial with spherical structure of average diameter of 850 nm under microwave irradiation.

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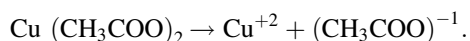
Experimental details

In our experiment, all chemicals were analytically pure and used without additional purification. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ was used as sulfur source, which provides the sulfur ion for the reaction and similarly $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ as copper sources, which provides the copper ion for the reaction. Solutions were prepared for copper and sulfur sources for

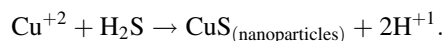
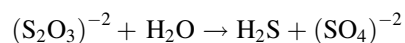
required molarities. Then, solution of copper source was added to solution of sulfur source drop wise under sturdy stirring condition. The mixed solution was then treated under microwave irradiation (2.45 GHz) at 160 and 320 W for 30 and 15 min by a domestic microwave oven. After the treatment of solution, CuS (black ppt) was formed which were collected, these CuS (black ppt) was washed by distilled water and ethanol several times and dried at 600 °C in air. Effects of experimental conditions on synthesis of CuS are given in Table 1.

Chemical reactions involve can be describe as

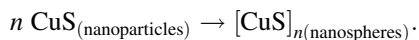
Copper source decompose into Cu^{+2} in their aqueous solution as



For copper source and sodium thiosulfate system the reactions can be written as



Now CuS nanoparticles aggregated to spherical shape



Microwave irradiation played a vital role in the aggregation process; to get an appropriate morphology of CuS, power of microwave and time of irradiation should be adopted carefully, erroneous combination of microwave power and time may knock down the required results.

Characterization of the product

Powder X-ray diffraction (XRD) data were recorded and collected on the XRD model MPD X'PERT PRO of PANalytical Company Ltd., Holland using Cu $K\alpha$ as characteristic radiation ($\lambda = 0.15418$ nm) with θ - θ configuration. The measurements were made in 2θ ranging from 20° to 70° . Analysis was mainly done by the software X'Pert HighScore of the same company. Scanning electron microscopy (SEM) images were taken on a scanning electron microscope (JEOL JSM-6480). Thermal oxidation,

Table 1 Experimental conditions for synthesis of CuS nanomaterials

Copper source	Sulfur source	Molar ratio	Microwave irradiation/time	Morphology
$\text{Cu}(\text{CH}_3\text{COO})_2$	$\text{Na}_2\text{S}_2\text{O}_3$	1:2	160 W and 15 min	Particles
$\text{Cu}(\text{CH}_3\text{COO})_2$	$\text{Na}_2\text{S}_2\text{O}_3$	1:2	160 W and 30 min	Spheres
$\text{Cu}(\text{CH}_3\text{COO})_2$	$\text{Na}_2\text{S}_2\text{O}_3$	1:2	320 W and 30 min	Random shapes

phase changes in copper sulfide, a differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA) were performed by SDT Q600 of TA Instrument in oxygen and argon environment.

Results and discussion

Figure 1 gives the XRD patterns for the products. Samples were well crystallized. All diffraction peaks can be indexed as the hexagonal CuS by comparison with data from JCPDS file no. 00-001-1281 with lattice constants $a = 3.8020$ Å, $b = 3.8020$ Å and $c = 16.4300$ Å, no characteristic peaks of any other impurity was observed. Crystallite size calculated by Scherrer formula is 15 nm.

Morphological characterization by SEM imaging shows the growth of CuS nanoparticle, their aggregation to form spherical shape. From Fig. 2a, b the aggregation of CuS nanoparticles into spheres can be seen, some non-aggregated particles are also identified from SEM; size of the spheres were calculated in the range of 794 nm to 1.47 μm from SEM images. Figure 3a, b shows the CuS nanoparticles of disorganized morphology due to haphazard aggregation.

Power and time for microwave irradiation played very significant role in aggregation process; we used microwave irradiation (2.45 GHz, 800 W) at 160 W (20 %) for 30 min by a domestic microwave oven for the formation of spherical morphology of CuS nanomaterial. Aggregation is assumed to be restricted only by the limited transportation of particles on to one another; hence, we could not get the exact morphology, just the non-aggregated nanoparticle when we apply microwave irradiation for less time (15 min) as shown in SEM images Fig. 4a, b. By increasing time or power of operating microwave oven aggregation kinetics could be increased and structure size will be changed; at low

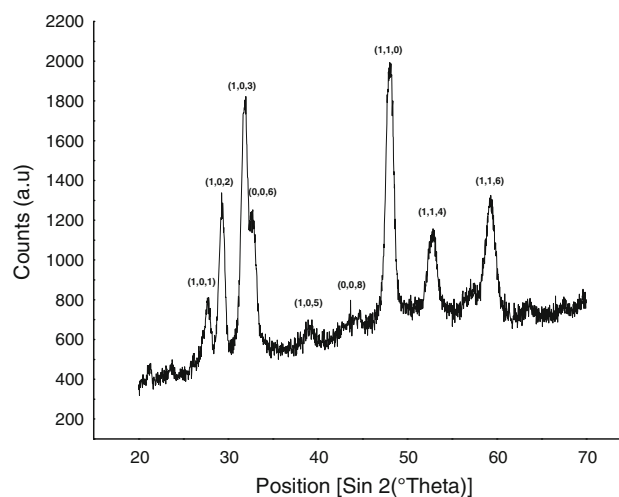


Fig. 1 XRD graph for CuS sub-micro spheres

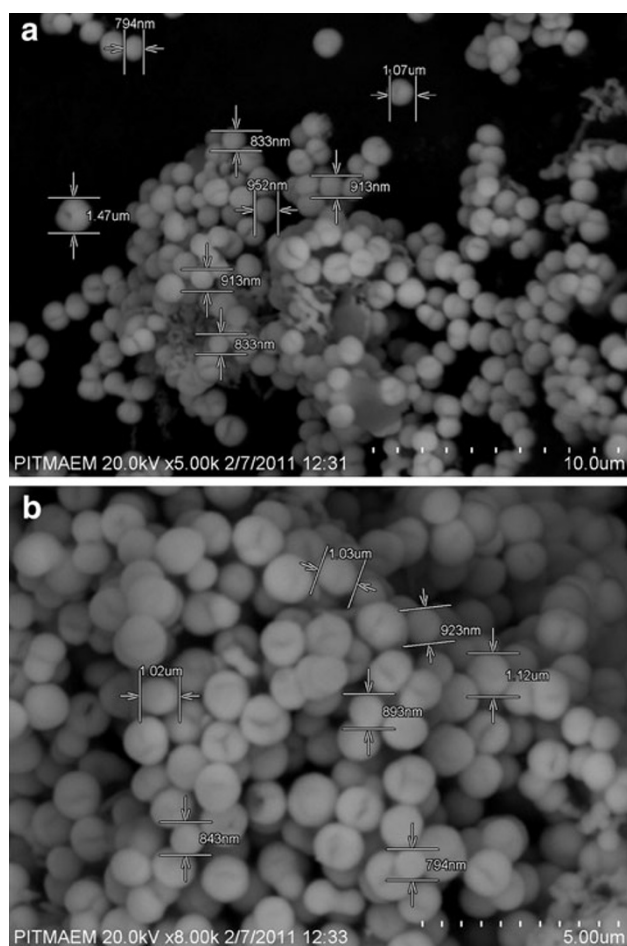


Fig. 2 a, b SEM for CuS sub-micro spheres synthesized by microwave irradiation (160 W and 30 min)

power microwave irradiation, nanoparticles aggregation would not start properly due to lesser number of collisions between CuS nanoparticles. In this situation when nanoparticles are not able to collide well with each other, time of irradiation cannot contribute greatly. On the other hand, when appropriate power of microwave irradiation is used, more time and high power make aggregation process fast, morphology of product can be changed. To get definite morphology of product, an apt combination is required.

Thermal behavior of CuS nanomaterials

It was well known that thermal decomposition of CuS in free air is a process of several steps, and depending on experimental circumstances (temperature, environment). In this process different copper sulfides ($\text{Cu}_{1.8}\text{S}$ and/or Cu_2S), copper oxides (Cu_2O and CuO), copper sulfates (Cu_2SO_4 , CuSO_4), copper oxy-sulfates ($\text{CuO}\cdot\text{CuSO}_4$) were formed (Godočková et al. 2006; Simonescu et al. 2007). The thermal stability and decomposition curves (DSC, TGA) of

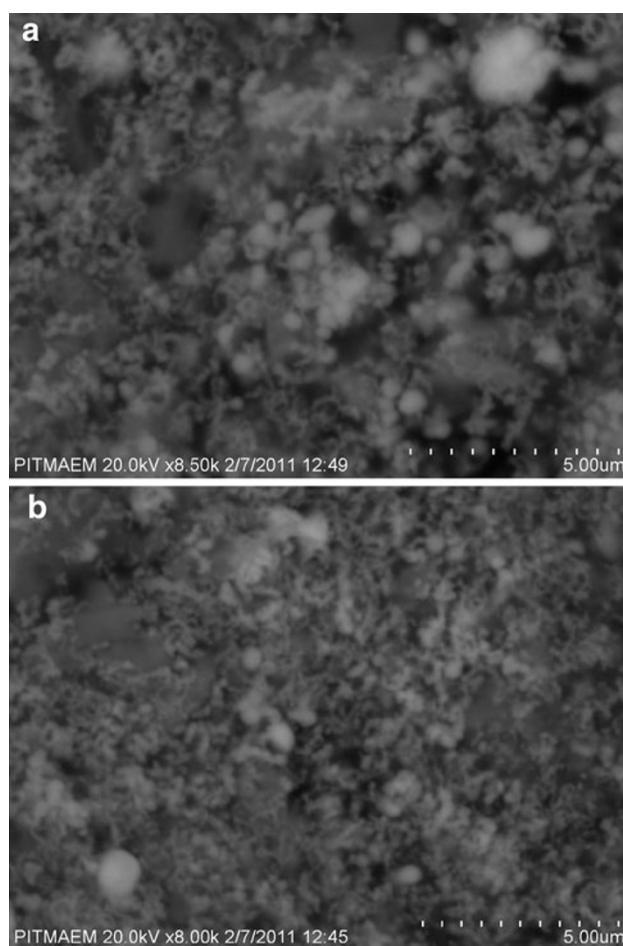


Fig. 3 a, b Non-aggregated CuS nano particles synthesized by microwave irradiation (320 W and 30 min)

the copper sulfides (CuS) nanospheres are depicted in (Fig. 5). We treated the sample prepared from room temperature to 1,175 °C in oxygen atmosphere at the ramp rate of 10 °C/min, TGA curve shows CuS nanospheres experienced a mass loss of 6.41 % between 250 and 300 °C, which is due to the fractional decomposition of CuS to Cu_2S . 40 % of total material (CuS) was converted to Cu_2S at that stage due to formation of sulfur dioxide. It was trailed by an increment of 61.5 % which corresponds to the conversion from CuS to CuSO_4 and Cu_2S to $\text{CuO}\cdot\text{CuSO}_4$; the experimental and theoretical values (61 %) have very close agreement. The oxidation reactions are exothermic in nature indicated by sharp peak in the DSC curve. Further, copper sulfate and copper oxy-sulfate were decomposed into CuO with a large mass loss (70.9 %) starting at 750 °C, the remaining mass was 84.01 % at that stage which is very close to theoretical one (83.25 %). The reaction was endothermic as shown by the DSC curve from 960 °C. There was another thermal conversion and TGA/DSC graph shows endothermic mass loss of 13.9 % which

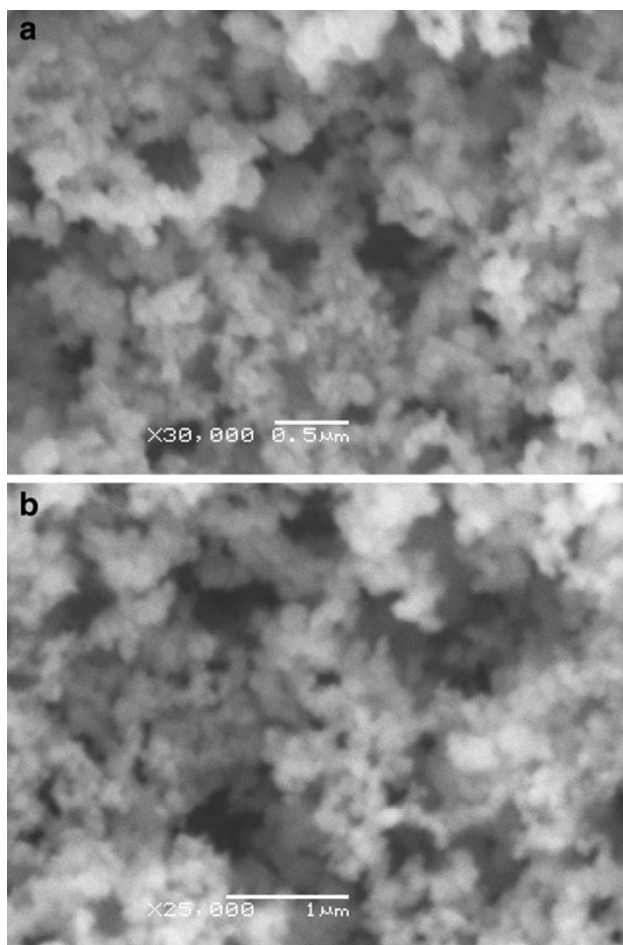


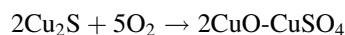
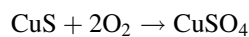
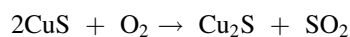
Fig. 4 a, b SEM for CuS nanoparticles synthesized by microwave irradiation (160 W and 15 min)

Table 2 Phase changes in CuS during DSC/TGA

Conversion	Temperature (°C)	Mass variation (%)
CuS → Cu ₂ S	250–300	–6.41
CuS → CuSO ₄	320–420	61.5
Cu ₂ S → CuO–CuSO ₄		
CuSO ₄ → CuO	750–810	–70.9
CuO → Cu ₂ O	950–1,010	–13.9

was caused by conversion of CuO to Cu₂O. Theoretical amount of residue should be 74.8 % but we got very close to a residual amount of 70.1 %. Different phase changes in CuS during DSC/TGA are discussed in Table 2.

The chemical equations involved during DSC/TGA can be described as:



When DSC/TGA of CuS nanospheres was done in inert atmosphere (argon flow, 100 ml/s), CuS nanospheres showed great stability under inert atmospheres, from 50 to 1,000 °C. There was only 0.7 % mass loss and no other characteristic transition in mass and heat flow was observed (Fig. 6).

It is clear from the DSC/TGA graph of CuS nanospheres that thermal oxidation of CuS produces CuO above 750 °C; to confirm the formation of CuO, we treated CuS nanomaterial at 800 °C for 1 h in open air atmosphere.

Fig. 5 DSC/TGA graph for CuS sub-micro spheres

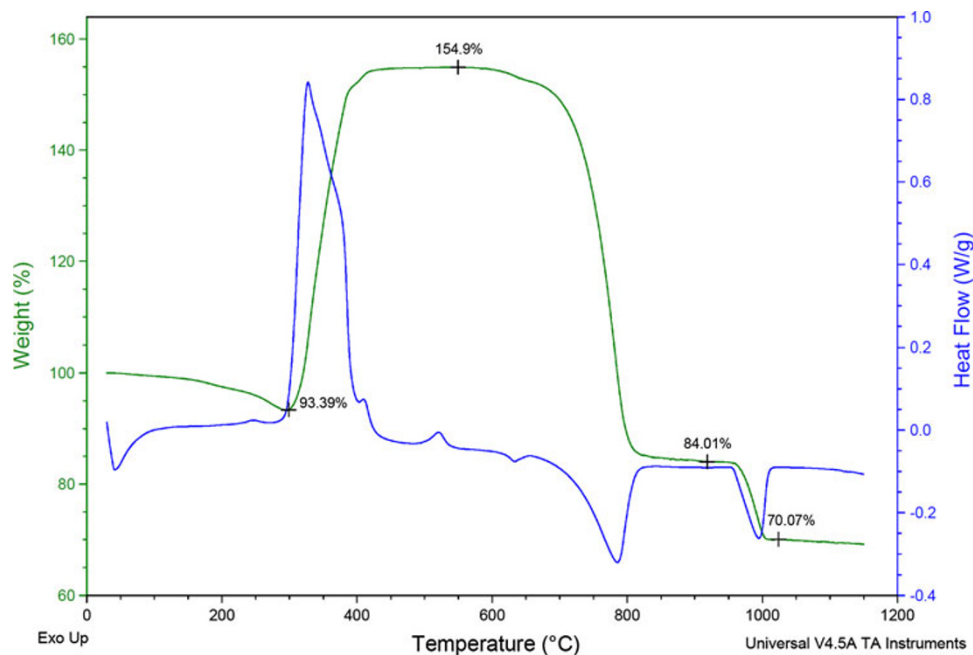


Fig. 6 DSC/TGA for CuS sub-micro spheres (argon atmosphere)

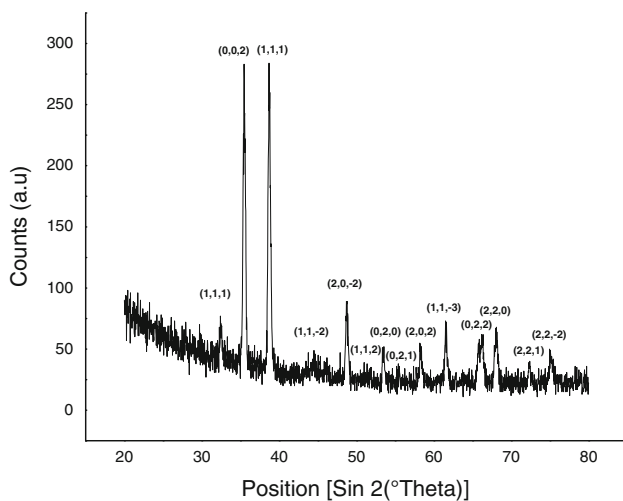
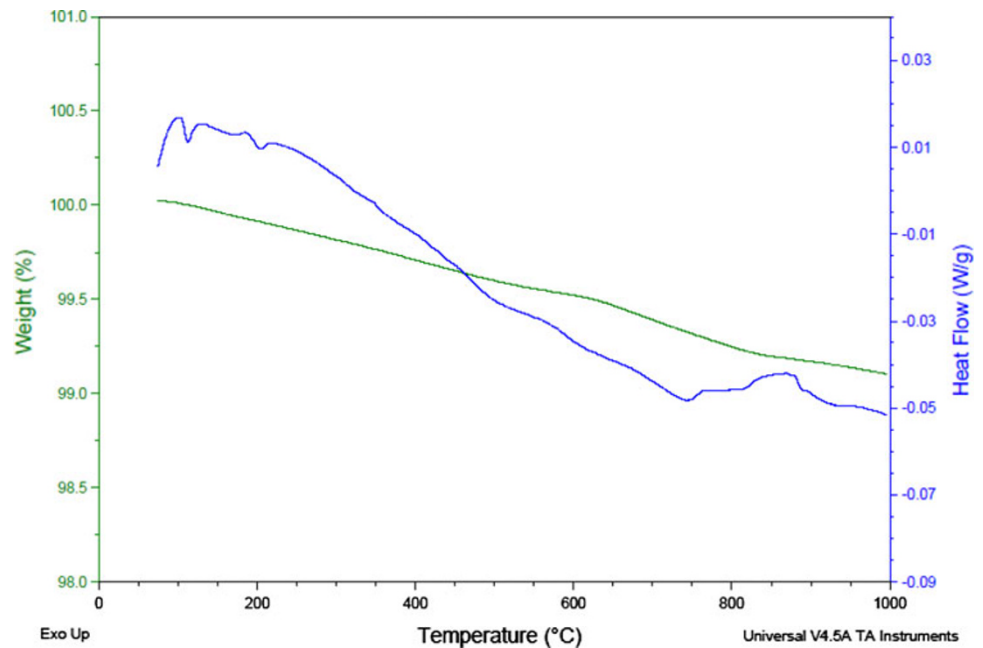


Fig. 7 XRD graph for CuO nanocrystals

The composition and phase purity of CuO nanocrystals were examined by powder XRD, which confirmed good crystallinity and peaks can be indexed to the monoclinic CuO (JCPDS card no. 00-48-1548) having cell parameters $a = 4.688 \text{ \AA}$ and $c = 5.132 \text{ \AA}$ (in Fig. 7). CuO was fabricated by thermal oxidation of CuS nanomaterial; Fig. 8a, b shows the SEM images of fabricated CuO nanocrystal with random morphology and wide size distribution.

Conclusion

CuS nanomaterial with spherical structures have been prepared in a simple aqueous sol system, employing Cu

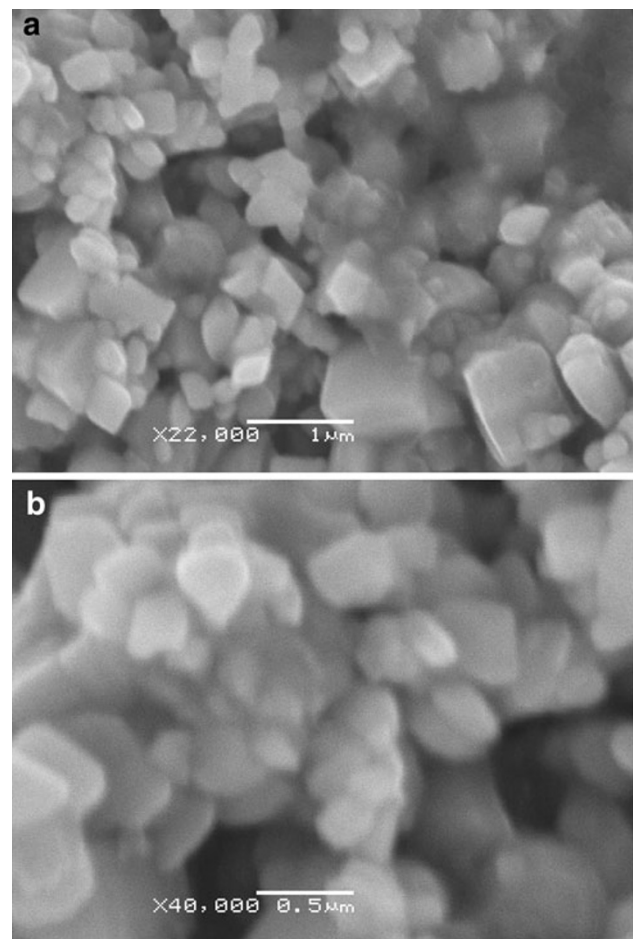


Fig. 8 a, b SEM for CuO nanocrystals fabricated by thermal decomposition of copper sulfide

(CH_3COO)- $2\text{H}_2\text{O}$ as copper sources and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ as sulfur ion source, under microwave irradiation. Experimental results showed that a great deal of spheres of average diameter of 900 nm was obtained; the thermal decomposition of copper sulfide (CuS) is complex in nature. The associated solid-state transformations and phase changes depend upon preparation of the sulfides. Thermal decomposition of CuS gives Cu_2S then converted to CuSO_4 which was decomposed into CuO. In inert atmosphere no phase change was observed, CuS nanomaterial showed great stability.

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