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Strategies for Scale-up and Yield Improvement in the Synthesis of CuO Nanoparticles

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ABSTRACT

The present work reports on the scale up of synthesis of CuO nanoparticles from two different precursors: Copper (II) nitrate and copper (II) acetate. This is in realization of the importance of scale-up procedures for synthesis of nanoparticles with an ultimate aim to extend the application of nanoparticles for large-scale industrial applications. Our results show that the reaction batch volume can be scaled up to 5000 mL at a yield of 42 g per batch, without loss of morphological and crystallographic features. While using copper (II) acetate as precursor, higher yield and control of particle size can be achieved through re-use of spent precursor solution.

Key words: CuO, scaleup, nanoparticles, synthesis

INTRODUCTION

Heat dissipation is one of the major industrial problems. Thermal and nuclear power plants, air conditioning systems, rocket launching vehicles, etc., are a few examples, where the safety depends on heat transfer. Nanomaterials possess characteristics such as high surface reactivity, higher specific surface area that make them suitable for several applications. Cupric oxide is one of the most widely used metal oxide nanoparticle. Its applications are in preparation of nanofluids, sensing, catalysis etc. (Xuan and Li, 2000; Dung *et al.*, 2013). Several methods are available for preparation of cupric oxide nanoparticles. These include sol-gel, hydrothermal and precipitation methods.

In some applications, nanomaterials are required in large quantities. One of such applications is the preparation of nanofluids. In order to prepare 1 L of CuO-water nanofluid with 2 vol% of nanoparticles, about 120 g of cupric oxide nanoparticles are required. Hence it is necessary to scale up the synthesis of cupric oxide nanoparticles to large batch volumes, so as to obtain relatively higher yield in terms of mass of cupric oxide nanoparticles. Also, it is desired to re-use the excess precursor repeatedly to reduce the consumption of precursor and hence reduce the cost of synthesis. The present work derives motivation from the fact that CuO nanoparticles have been successfully dispersed in a variety of coolants like water, propylene glycol, Therminol-55[®], etc. (Priya *et al.*, 2012; Anandan and Rajan, 2012; Naresh *et al.*, 2012; Das *et al.*, 2003) and hence the scale up of its preparation has immense potential for large-scale application.

The present study reports: (a) The scale up of synthesis of CuO nanoparticles using cupric nitrate as the precursor, (b) The re-use of spent precursor to improve the yield of CuO nanoparticles from cupric acetate precursor. The influence of batch volume on the yield and morphology of as-synthesized nanoparticles are reported here and is one of the rare attempts of its kind.

MATERIALS AND METHODS

Copper (II) acetate monohydrate, copper (II) nitrate trihydrate, sodium hydroxide and glacial acetic acid were procured from Merck, India. These chemicals were of laboratory grade and were used as received.

Preparation of cupric oxide nanoparticles from copper (II) nitrate: The first step in the preparation of cupric oxide nanoparticles from copper (II) nitrate is the preparation of cupric hydroxide. For this purpose, aqueous solutions of 0.1 M copper (II) nitrate and 0.5 M sodium hydroxide were mixed, by drop-wise addition of NaOH until pH changed to 12. The solid particles were obtained after filtration and drying and then subjected to optional calcination at 250°C. Magnetic stirrer was used for small volumes, while overhead mechanical stirrer was used for large volumes.

Preparation of cupric oxide nanoparticles from copper (II) acetate: The nanoparticles of cupric oxide were synthesized from acetate precursor following the procedure reported in the literature (Zhu *et al.*, 2011). In nutshell, a strong solution of NaOH (8 M) was added drop-wise to a boiling mixture of copper (II) acetate monohydrate and glacial acetic acid (Zhu *et al.*, 2011). The solid product was obtained by filtering the contents of the reaction vessel after cooling the same. During the synthesis of cupric oxide nanoparticles from acetate precursor, the conversion of precursor is incomplete. Hence, the filtrate containing unreacted acetate, obtained after recovering the nanoparticles was used as the precursor to increase the conversion and improve the yield. The filtrate was re-used twice, leading to reaction in three stages, viz., (i) Reaction with fresh copper (II) acetate, (ii) Reaction with spent copper (II) acetate obtained at the end of first cycle and (iii) Reaction with spend copper (II) acetate obtained at the end of second cycle.

Characterization: The as-synthesized powders were characterized to ascertain their chemical identity and morphology. A field emission scanning electron microscope (JSM 6701F, JEOL, Japan) was used to image the samples at an acceleration voltage of 3 kV. The powder diffraction patterns of samples were recorded using a X-ray diffractometer (D8 Focus, Bruker, Germany).

RESULTS

Yield of particles: The powder X-ray diffractogram of nanoparticles synthesized using copper (II) nitrate and copper (II) acetate precursors are shown in Fig. 1a and Fig. 1b, respectively. The yield of particles obtained using copper (II) nitrate as the precursor is shown in Table 1 as a function of reaction volume. The yields obtained using copper (II) acetate precursor in different batch volumes, with and without reusing the spent precursor solution are shown in Table 2.

Table 1: Yield of nanoparticles as a function of batch volume. The precursor is copper (II) nitrate

Batch volume (mL)	Yield (g)	Reaction time (h)
100	10.24	4.0
200	10.38	4.0
500	30.49	8.5
1000	80.07	8.5
2000	16.5	9.0
5000	42.0	9.0

Table 2: Yield of nanoparticles as a function of batch volume, the precursor is copper (II) acetate with and without re-use of spent precursor solution

Batch volume (mL)	Yield (g)	Remarks
600	2.5	No reuse of spent precursor
600	4.9	Re-use of spent precursor twice (3 reaction steps)
1000	4.5	No reuse of spent precursor
1000	16.0	Re-use of spent precursor twice (3 reaction steps)

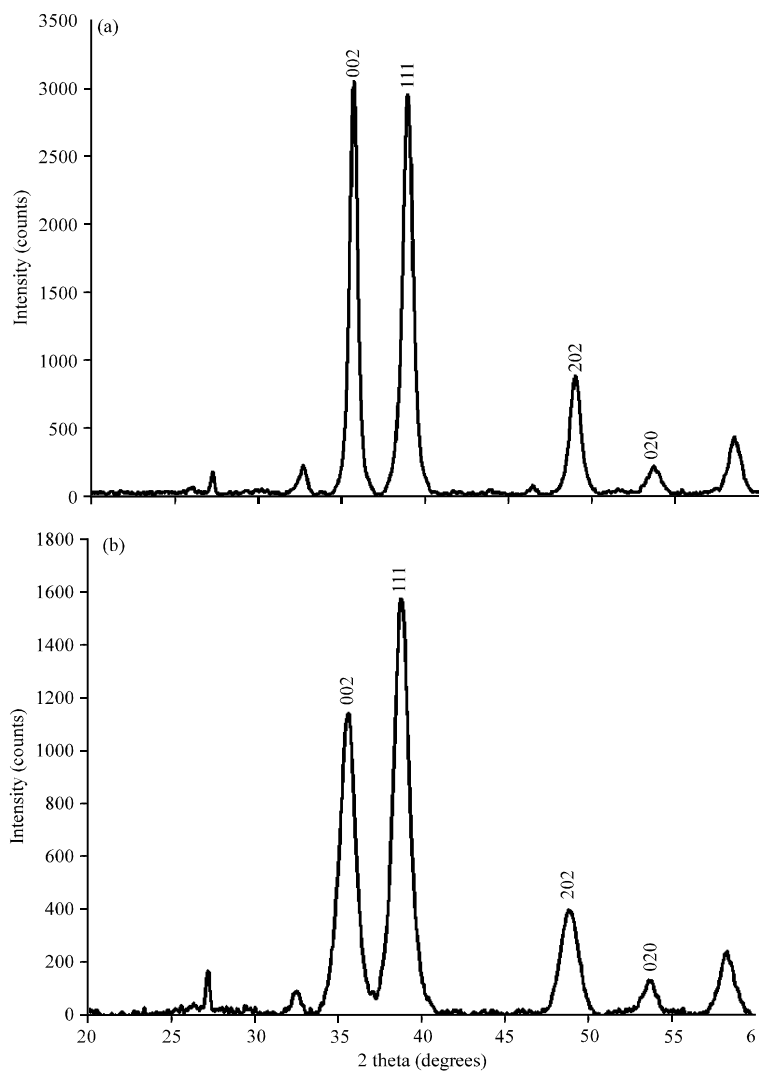


Fig. 1(a-b): X-ray diffractogram of CuO nanoparticles synthesized, (a) Copper nitrate precursor, (b) Copper acetate precursors

Morphology as a function of scale up: Figure 2 and 3 show the scanning electron micrographs of particles obtained from different scales (batch volumes) of synthesis using copper (II) nitrate as the precursor, at two different levels of magnification (10000 and 50000). The influence of scale-up on the morphology of CuO nanoparticles obtained from copper (II) acetate precursor is shown in Fig. 4. The morphology of particles obtained from re-using the spent copper (II) acetate solution is

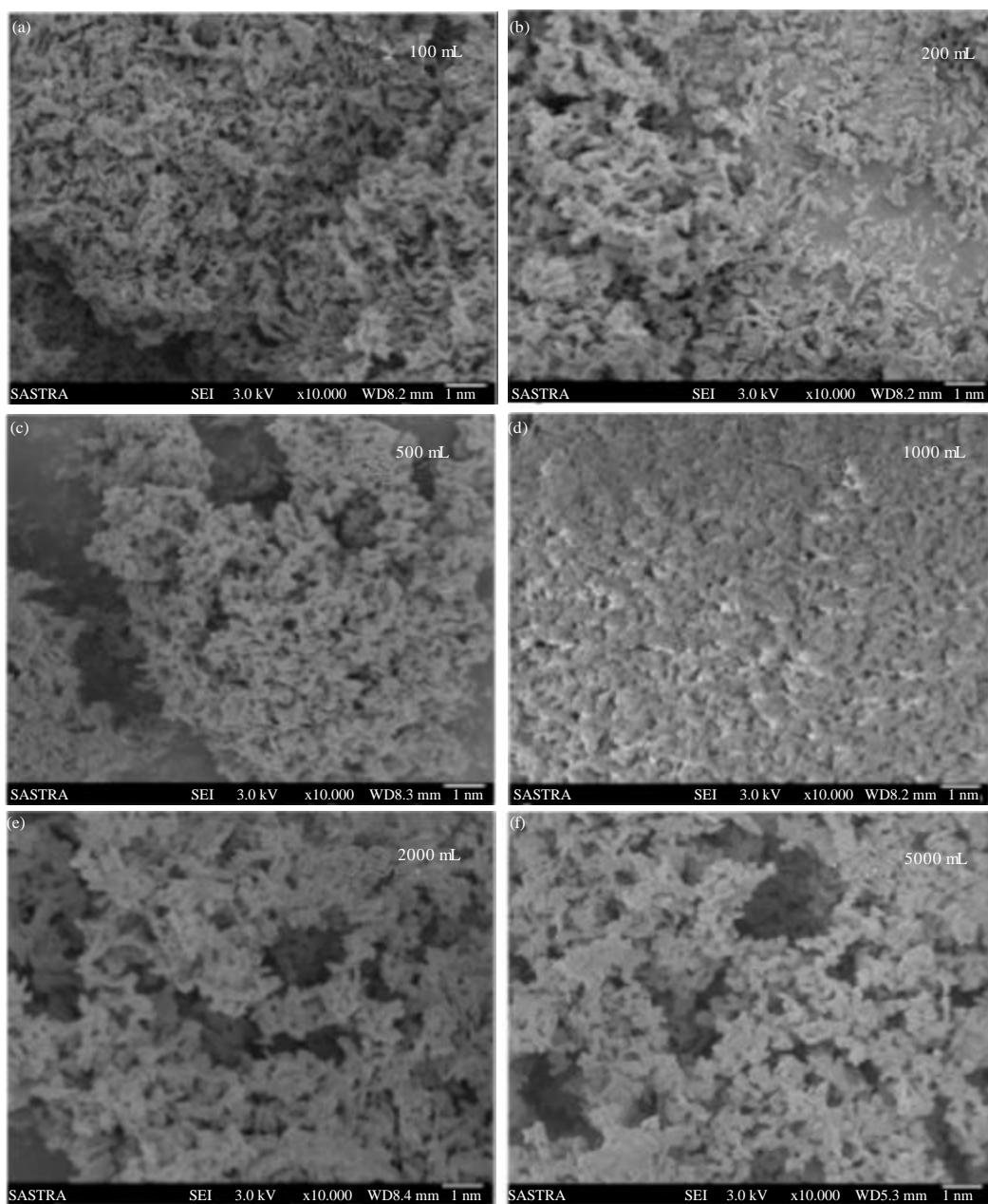


Fig. 2(a-f): Scanning electron micrographs of CuO particles obtained from different batch volumes at the magnification of 10,000, the precursor is copper (II) nitrate, (a) 100 mL, (b) 200 mL, (c) 500 mL, (d) 1000 mL, (e) 2000 mL and (f) 5000 mL

shown in Fig. 5 for the batch volume of 600 mL. Figure 6 shows the morphology of particles prepared with a batch volume of 1000 mL, using the fresh copper (II) acetate precursor, spent precursor from first stage and the spent precursor from second stage.

DISCUSSION

The powder X-ray diffractogram of the synthesized powders shown in Fig. 1 confirms chemical identity as cupric oxide (JCPDS card No. 89-5895). The crystalline phase did not change

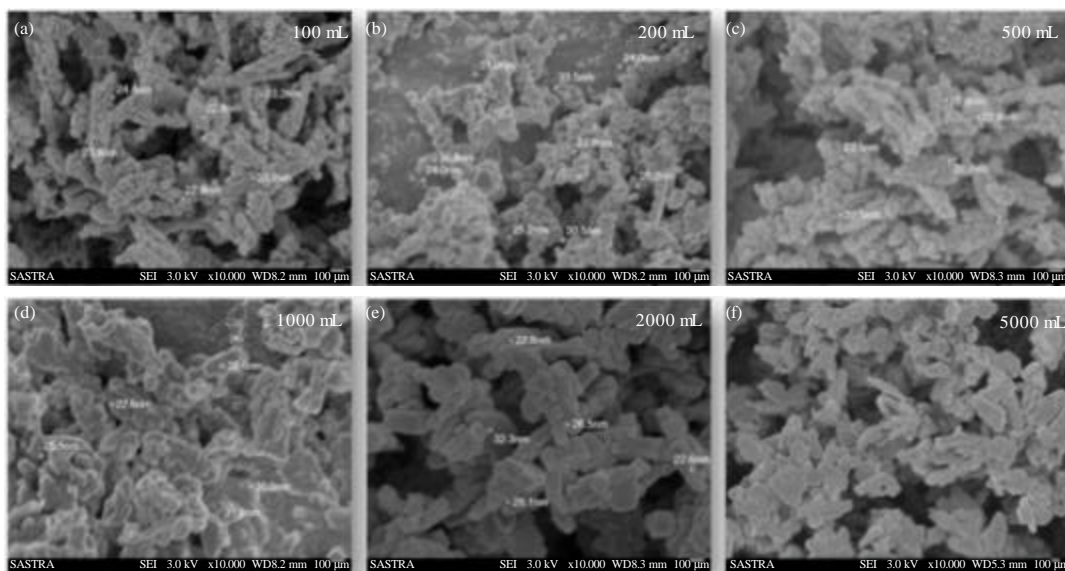


Fig. 3(a-f): Scanning electron micrographs of CuO particles obtained from different batch volumes (a) 100, (b) 200, (c) 500, (d) 1000, (e) 2000 and (f) 5000 mL at the magnification of 50,000, the precursor is copper (II) nitrate

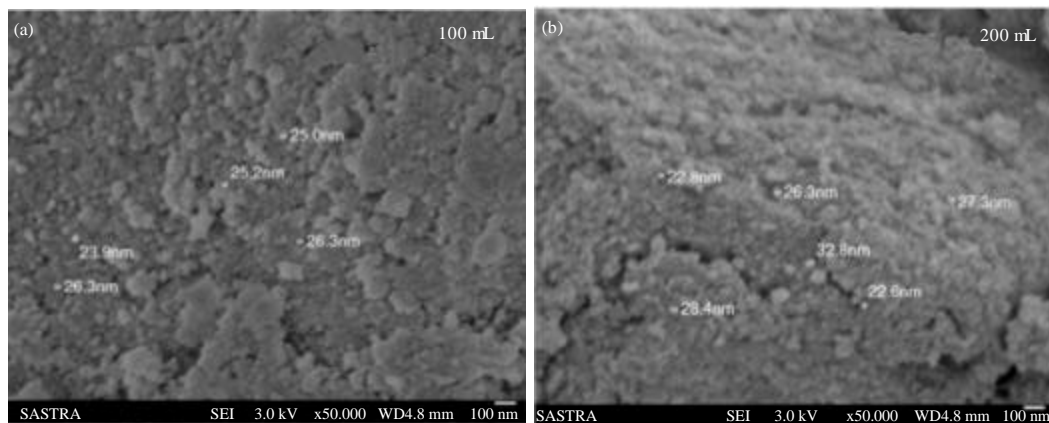


Fig. 4(a-b): Scanning electron micrographs of CuO particles obtained from different batch volumes, (a) 100 and (b) 200 mL using copper acetate precursor

due to change of precursor. The crystallite sizes of CuO obtained using copper (II) acetate (3-stage reaction) and copper (II) nitrate precursors are 8.1 and 15.3 nm, respectively, indicating the presence of nanocrystallites. The yield of CuO nanoparticles (Table 1) using copper (II) nitrate precursor increases linearly, indicating that the same stoichiometry is maintained at all scales. However, the reaction time is reduced at higher scales probably due to better contact between the reactants achieved by mechanical stirring. As far as the variation of yield of nanoparticles from copper (II) acetate precursor is concerned, it is nearly linear when reaction was carried out without re-use of spent precursor. However, the scale up of synthesis carried out in 3-stages involving two stages of re-use of spent precursor, is non-linear with higher yields obtained at 1000 mL capacity compared to that at 600 mL capacity. This shows that the yield at 600 mL capacity can be further improved.

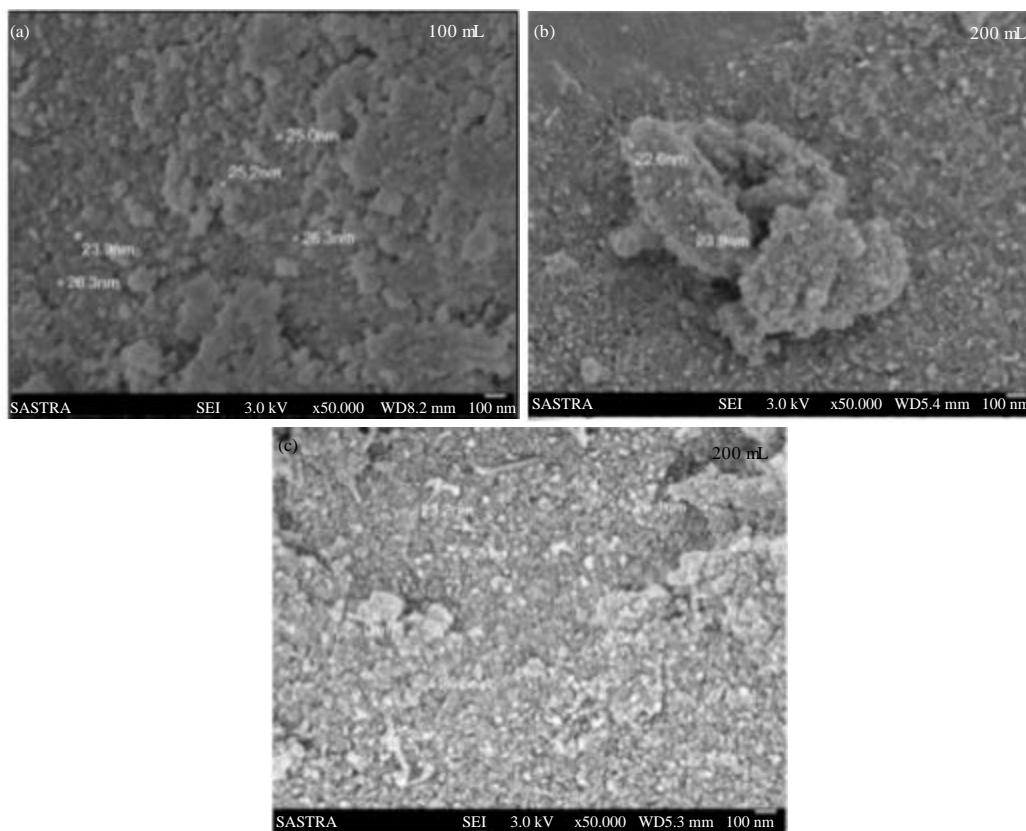


Fig. 5(a-c): Scanning electron micrographs of CuO particles obtained using (a) Fresh copper acetate, (b) Spent copper acetate from first stage and (c) Spent copper acetate from second stage, the batch volume was 600 mL

From Table 1 and 2, one may observe that the yield of nanoparticles for the same batch volume is higher while using copper (II) nitrate as the precursor, as against copper (II) acetate used in single state only. When the yield of multi-stage reaction for copper (II) acetate precursor is compared with the yield obtained from copper (II) nitrate precursor, the former is higher. This highlights the value addition in terms of increased yield that can be realized with the re-use of spent precursor.

It may be observed from Fig. 2 and 3 that the morphology of particles do not vary significantly with batch size. This indicates that the morphology control has been achieved even during the scale up from 100-5000 mL. This is essential for reliable scale-up leading to mass production of nanoparticles. The scale up of synthesis using copper (II) acetate precursor from batch volume of 600-1000 mL yielded nanoparticles with no significant dependence of morphology on reaction scale. While comparing the morphology of nanoparticles prepared using spent precursor and fresh precursor solutions, it is clear that better size control is achieved with spent precursor leading to particles of smaller sizes. This is also evident from the low crystallite size obtained (8 nm) while carrying out reaction with spent acetate. The low crystallite size may be attributed to the lower concentration of precursor in the spent solution, which limits the kinetics of conversion from acetate to oxide. It is well known that at lower reactant concentrations better size control can be achieved during synthesis.

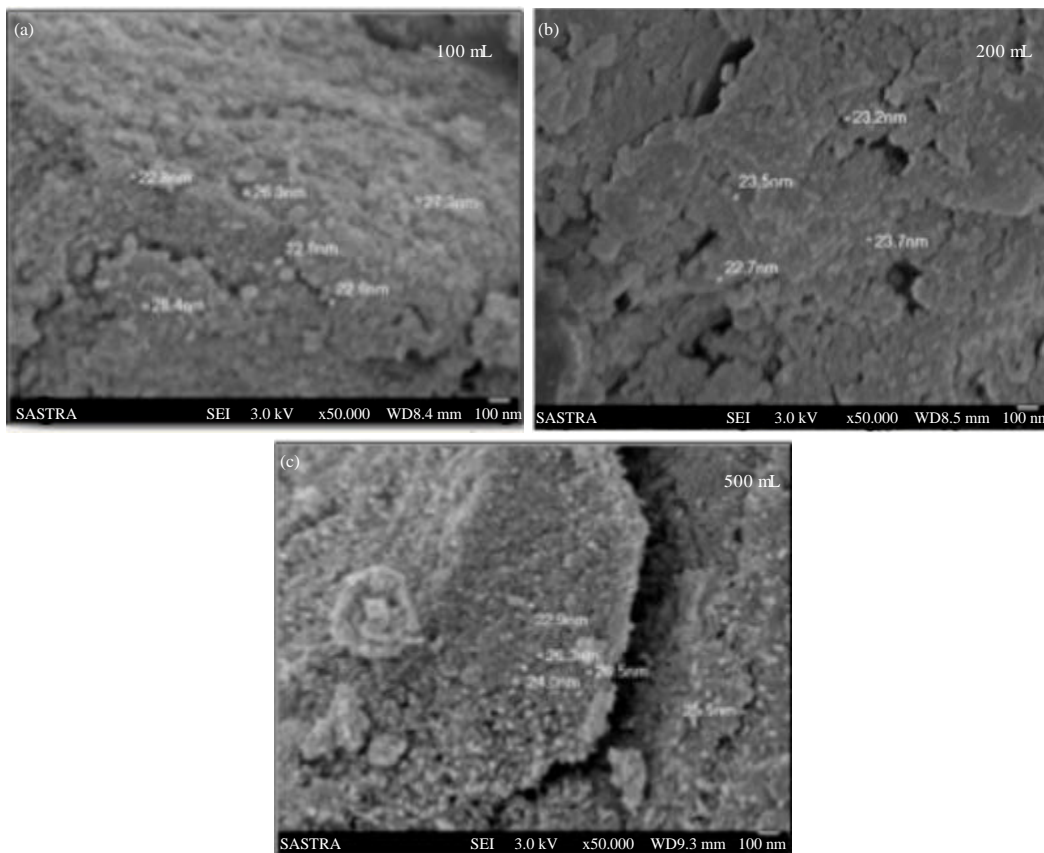


Fig. 6(a-c): Scanning electron micrographs of CuO particles obtained using: (a) Fresh copper acetate, (b) Spent copper acetate from first stage and (c) Spent copper acetate from second stage, the batch volume was 1000 mL

For applications involving catalysis, adsorption, photocatalytic degradation, thermal management, etc., smaller particles are preferred owing to their higher surface to volume ratio and higher specific surface area. Particles interact with liquid or fluid through their surfaces. Hence, higher particle surface area promotes interaction between fluid and particles (Rajan *et al.*, 2006, 2007a, b; 2008a, b), reaping the benefits of nanoparticles.

CONCLUSION

The synthesis of CuO nanoparticles has been successfully scaled up to yield 42 g of nanoparticles in a single batch of 5 L capacity with a residence time of 9 h, using copper (II) nitrate as the precursor. The morphology of nanoparticles was similar at various scales of synthesis. The yield of CuO nanoparticles from copper (II) acetate precursor can be improved by re-using the spent precursor repeatedly. Our results show that nearly 100 and 350% increase in yield can be obtained at batch sizes of 600 and 1000 mL, while re-using the spent precursor twice. In nutshell, synthesis can be carried out with the same precursor solution thrice, thereby improving the yield.

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