Synthesis and characterization of Copper Oxide nanoparticles by solution evaporation method

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In recent years, copper oxide has attracted increasingly interests for both fundamental and practical reasons. Until now, many different methods such as co-precipitation, sol-gel processing, micro-emulsions, hydrothermal synthesis, solution evaporation method etc. have been developed for the preparation of copper oxide (CuO) nanostructures. In this work, the simplest and cost effective technique solution evaporation was used to synthesize the copper oxide (CuO) nano-powder. The crystallite size of copper oxide (CuO) nanoparticles can be controlled by annealing temperature and pH. In order to study the effect on crystallite size annealing temperature increases from (400-600°C) while pH increases from (8-12). The structural and surface morphology of CuO nano powder was characterized by X-ray diffraction (XRD) and Scanning electron microscope (SEM). XRD analysis revealed that the CuO nanoparticles had monoclinic structure and average crystallite size increases with increasing annealing temperature and pH. SEM micrograph shows spherical and rounded particles with increasing annealing temperature and flower like structure appear with increasing pH.

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1. Introduction

Nanoparticles research is gaining increasing interest due to their unique properties, such as increased electrical conductivity, toughness and ductility, increased hardness and strength of metals and alloys, luminescent efficiency of semiconductors, formability of ceramics. In recent years, there has been increasing interest in the synthesis of metal nano-and micromaterials because of their special physical and chemical properties and potential applications [1]. Currently, many nanoparticles are synthesised from noble metals such as gold and silver, in spite of their high cost. However, copper is a promising alternative material due to its high conductivity and lower cost. Metal oxides represent the most diverse class of materials with properties covering almost all aspects of materials science and physics.

Copper oxide nanoparticles are of special interest because of their efficiency as nanofluids in heat transfer applications. Copper oxide (CuO) is one of potential p-type semiconductors and gains considerable attentions due to its excellent optical, electrical, physical, and magnetic properties. CuO with narrow band gap of 1.2 eV is extensively used in various applications such as catalysis [2], solar energy conversion [3], gas sensor [4] and field emission [5]. However, these novel properties can be improved by synthesis in CuO nanostructures that shown excellent performance comparing to bulk counterpart. It has been reported that 4% addition of CuO improves the thermal conductivity of water by 20% [6].

Different nanostructures of CuO are synthesized in form of nanowire, nanorod, nano-needle, nano-flower and nanoparticle. In the past decades, various methods have been proposed to produce CuO nanoparticles with different sizes and shapes such as alcohothermal [7] sonochemical [8], electrospinnig [9], combustion [10], hydrothermal [11], solvothermal [12]. However, these methods usually require high temperature, multiple steps and sophisticated equipment. On the contrary, Wet chemical processes such as soft chemical method [13], sol–gel method [14] and homogeneous precipitation method [15] are cost-effective and scalable and have been used in the synthesis of a wide variety of CuO nanostructures. The solution evaporation method in particular has been successfully used to design different structures of CuO. Solution evaporation method (soft chemical method) [13] shows some advantages.(i) Nanometer- size nanoparticles at ambient temperature (ii) The reaction is carried out under moderate condition (iii) Nanoparticles obtained with different morphologies by adjusting the reaction condition (temperature) (iv) good controllability (v) Economical and cost effective method [16].

The solution-based growth approach is a facile way which attracts considerable interest in industries because of low energy and temperature, inexpensive and cost-effective approach for large scale production and good yield. In order to controlled synthesis of collected nano structures, many new-born efforts have been directed to the morphological and structural control of primary building blocks. Many experimental parameters, such as reaction temperature, annealing temperature and chemical agent can be utilized to control the morphology and microstructure of nano crystals. In addition, the pH value also has a meaningful effect on the morphology and dimensionality control.

In annealing, atoms migrate in the crystal lattice and the number of dislocations decreases, leading to the change in ductility and hardness. In the cases of copper, steel, silver, and brass, this process is performed by heating the material (generally until glowing) for a while and then slowly letting it cool to room temperature in still air. Copper, silver and brass can be cooled slowly in air, or quickly by quenching in water, unlike ferrous metals, such as steel, which must be cooled slowly to anneal. In this fashion, the metal is softened and prepared for further work such as shaping, stamping, or forming.

pH is the significant parameter which influences the structural morphology of the particle as well as the size of particles. Crystallite size increases by increasing pH. The reduction of Gibb's free energy is the driving force for both nucleation and growth. The hydroxyl ion concentration plays an important role for morphology and size. After nucleation the hydroxyl ions excess in solution is adsorbed on the polar face of growing particles.

In the present work, pure nanocrystalline copper oxide has been synthesized in powder form at low temperature in short time (1hour) without using any surfactant. The nano-powder will be calcined in air at 400°C-600°C for 1 hour and with addition of NaOH vary pH (8 - 12).Finally, in order to reveal the effect of annealing temperature and pH on CuO nanostructure the structural and morphological properties have been characterized by XRD(X-ray diffraction) and SEM(Scanning electron microscopy).

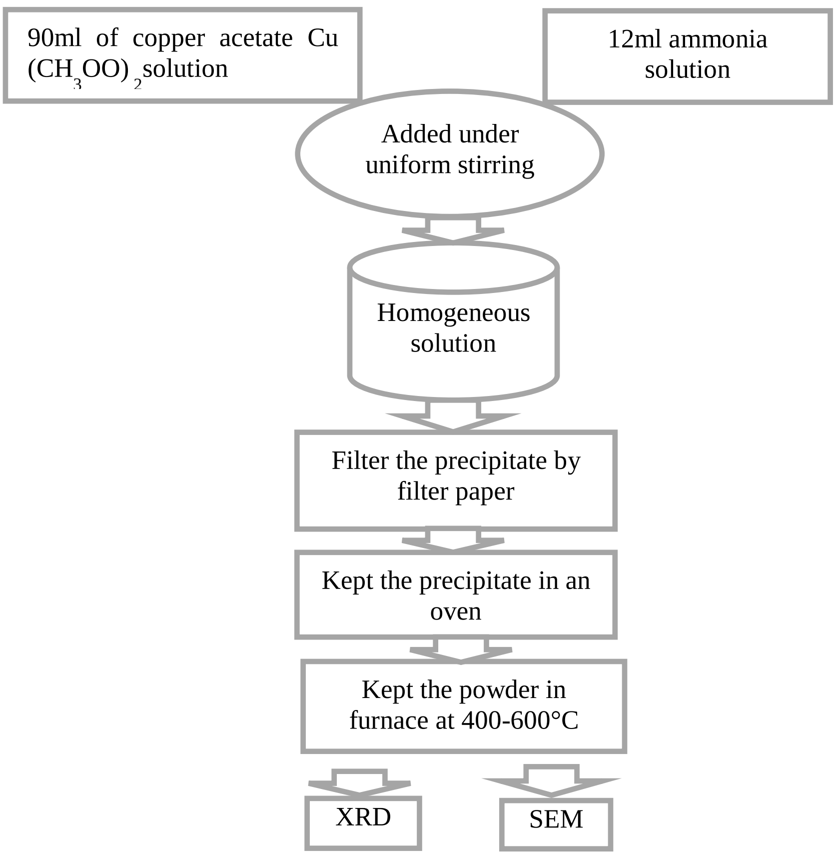
2. Experimental procedure

2.1. Synthesis method of Copper Oxide (CuO) nanoparticles

Copper oxide nanoparticles will be prepared by solution evaporation technique. Aqueous solution of copper acetate Cu $(CH_3COO)_2$ and ammonia solution were taken in a 250mL beaker. The solution was heated with continuous stirring for 1 hour. And to control the pH (8, 10, 12) NaOH (0.25M, 0.50M and 1M) was added in to the solution drop-wise. During the reaction, a black powder was formed. The solution was filtered and washed with water many times to remove the impurities and then dried at 80°C in an oven. The synthesized copper oxide nanoparticles were annealed in air at 400^oC-600^oC for 1 hour inside a muffle furnace. The colour of copper oxide nanoparticles appeared black before and after annealing temperature. The following reactions occurred to synthesize the CuO nano-particles.

$$Cu\,(CH_3COO)_2(aq.) + 4NH_3\,(aq.) \rightarrow$$
$$\rightarrow Cu\,(NH_3)_4^{2+}\,(aq.) + 2CH_3COO\,(aq.)$$
$$Cu\,(NH_3)_4^{2} \rightarrow (aq.)\,Cu^{2+} + 4NH_3(g)$$
$$Cu^{2+} + [O] \rightarrow CuO\ (black)$$

2.2. Flow chart



3. Results and discussion

3.1. X-ray diffraction (XRD)

Fig.1 shows the XRD pattern of CuO nanoparticles formed at 400°C, 500°C, and 600°C. At 400°C the XRD pattern of CuO nanoparticles illustrates the development of 6 diffraction peaks. All the peaks in diffraction pattern shows monoclinic structure of CuO, and the peaks compared with JCPDF card no. [89-5895] and miller indices are identified. Diffraction peaks of calcined samples observed at 2θ values are 35.031°, 38.446°, 48.496°, 58.223°, 61.426°, 66.696° which are related to CuO (002), CuO (111),CuO (202^-), CuO (202),CuO (113^-) and CuO (310) phases respectively. The XRD pattern of CuO indicates that peak intensity is different for every plane. The crystallite size of CuO nanoparticles was calculated by using the Scherrer formula,

$$D = 0.9\ \lambda / \beta \cos\theta \quad (1)$$

Where λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the peaks at the diffracting angle θ. Crystallite size of three peaks (002,111,202) of maximum intensity calculated by the Scherrer formula was found to be 6.3 nm. Whereas, Wongpisutpaisan et al., 2011 [8] calculated the average particle size from 50-70nm synthesized by sonochemical method. Mayekar et al., 2014[17]reported that the average grain size calculated by using Debye -Scherrer formula is approximately 52.09nm which are prepared by chemical route. It indicates that calculated results by solution evaporation method are more precise than sonochemical method.

In order to demonstrate the effect of annealing temperature on CuO nanoparticles, samples were annealed at 500°C and 600°C. Fig. 1 shows the XRD pattern of CuO nanoparticles at different annealing temperatures. It is clear from these results that the crystallinity of peaks increases with annealing temperature [18]. Simultaneously, the peaks become narrow as the annealing temperature increases resulting in the increase of crystallite size. Table 1 shows variation of crystallite size increases from 6.3 to 8.7 nm with increase in annealing temperature from 400^{o}C to 600^{o}C.As we increase the temperature the collision of the particles increases to its maximum value and the particles coalesces with one another because of atomic diffusion [18] due to which crystallite size increases. In earlier work Joshua et al., 2014 [19] reported that average particle size of copper oxide nanoparticle is 28.22nm which are synthesized by wet chemical method. In recent work Gopalakrishnan et al., 2014[20] prepared copper oxide nanoparticles of 15nm by solvothermal technique. Fernandez et al., 2012[21] reported that the average size of the particle observed is found to be between 13.92 nm and 22.08 nm which are synthesized by Hydrothermal synthesis technique.

Fig. 1 shows the XRD pattern of CuO nanoparticles formed at 8, 10 and 12pH at constant annealing temperature 400°C. All the peaks in diffraction pattern shows monoclinic structure of CuO, and the peaks compared with JCPDF card no. [89-5895] and miller indices are identified. At 8 pH diffraction peaks of calcined samples observed at 2θ values are 32.688°, 35.288°, 38.466° ,48.506°, 53.953°, 58.207°, 61.884°, 66.129°, 68.157° which are related to CuO (110), CuO (002), CuO (111), CuO (202^-), CuO (113^-), CuO (311^-), CuO (220) phases respectively. Crystallite size of three peaks (002,111,202) of maximum intensity calculated by the Scherrer formula was found to be 4.14 nm. It is clear from these results that the intensity of crystalline peaks increases with increasing pH, which indicating the improvement in the samples crystallinity. Simultaneously, the peaks become narrow as the pH increases resulting in the increase of crystallite size. Table 1 shows that crystallite size increase from 4.14 to 10nm with pH increases from (8-12pH), which is due to increase in the molar concentration of NaOH consequently OH ion concentration increases, the reaction kinetics and growth of the nanostructures take place in different ways. The faster and slower reaction kinetics is accountable for the formation of different nanostructures [22]. Fig. 2&3 shows variation trend of CuO nanoparticle crystallite size at different annealing temperatures and pH.

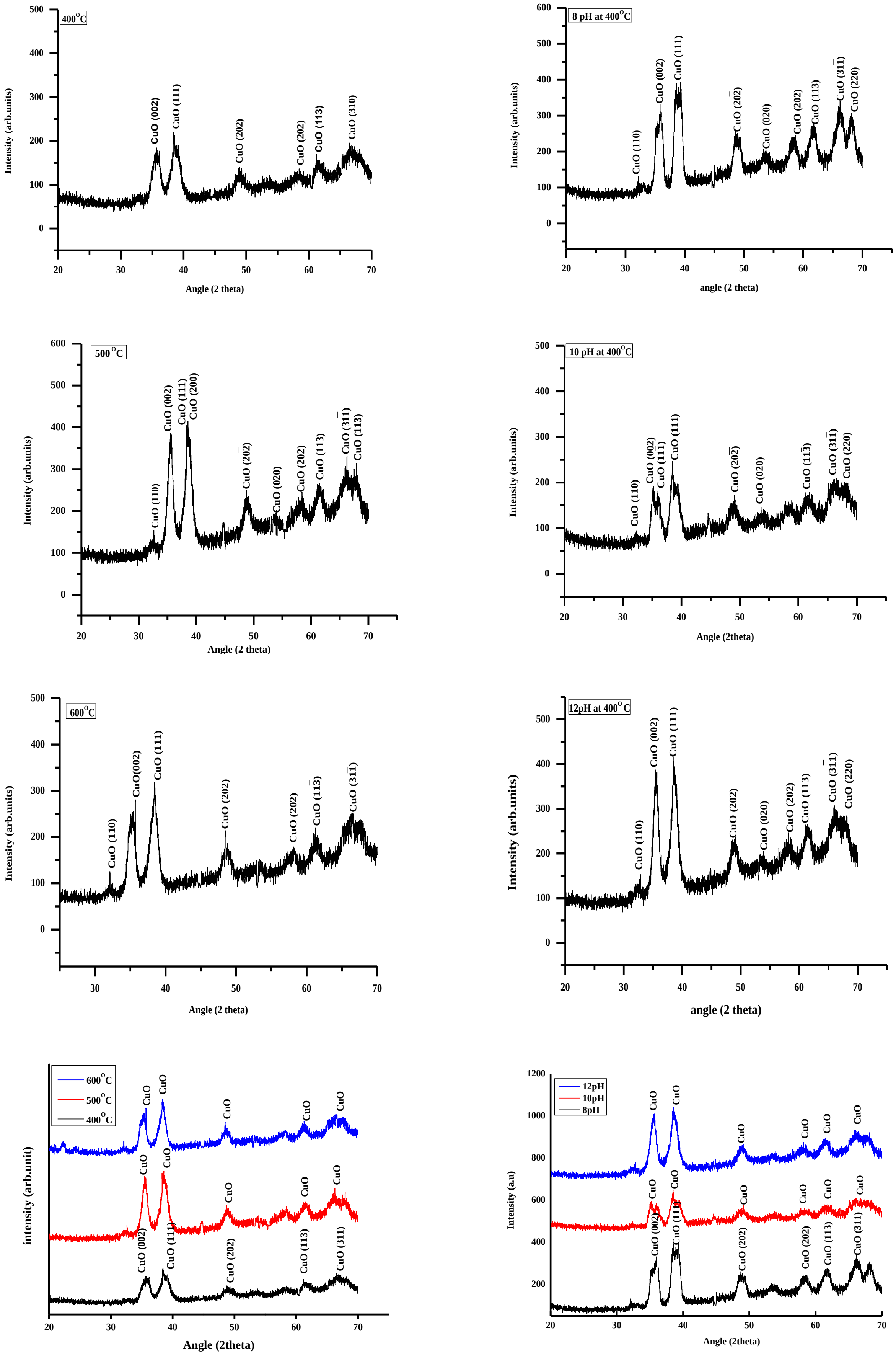


Fig. 1. XRD of CuO nanoparticles annealed at 400°C, 500°C and 600°C annealing temperature and at different pH (8,10 and 12).

Table 1. Average crystallite size of copper oxide (CuO) nanoparticles synthesized at different annealing temperatures and pH

Sr. No.	Temperature (°C)	Average Crystallite size(nm)	pH	Average Crystallite size(nm)
1	400	6.3	8	4.14
2	500	7.3	10	7.5
3	600	8.7	12	10

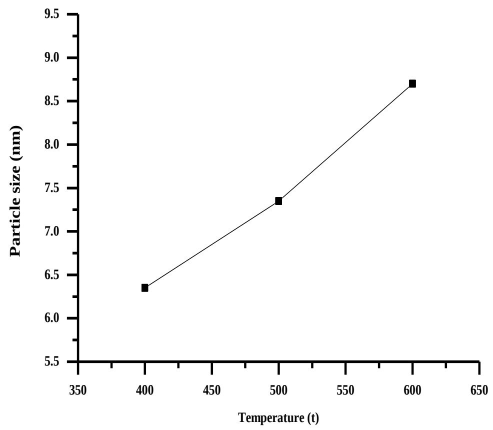


Fig. 2. Variation of CuO nanoparticle size at different annealing temperatures

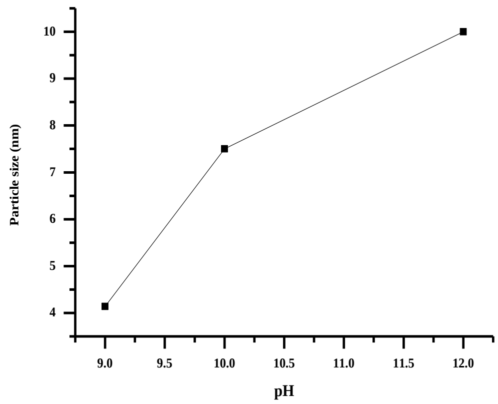


Fig. 3. Variation of CuO nanoparticles size at different pH

3.2. Scanning electron microscope Analysis

Fig. 4 illustrates the SEM images of copper oxide (CuO) nanoparticles synthesized at different annealing temperatures 400°C, 500°C and 600°C. Actually SEM image contain the three kinds of particles namely: Cluster of the spherical particles, bigger particles, rounded particles. Each cluster consists of several particles showing different shape and dimension. Some bigger and smaller particles are overlapped. It is also clear from the figure that the particles are distributed over the whole scanned area.

Careful investigation reveals that at 400°C the average size of the particles is 600 nm. At 500°C the average size of the nanoparticles is 700nm. At 600°C the SEM image shows the formation of much bigger particles of different shape and size as compared to 400 and 500°C. The average size of the particles is 800nm. It means that the shape, size and distribution of the microstructure strongly depend on the annealing temperature. The grain size of copper nanoparticles is also calculated. The nanoparticles are almost spherical in shape and crystalline in nature. The calculated grain size at 400°C, 500°C and 600°C is 200nm, 208nm and 163 nm respectively.

Fig. 4 shows SEM micrograph at 8,10 and 12 pH respectively at 400, 500 and 600°C annealing temperature, copper oxide nanoparticles appear like flower structure and image confirmed that synthesized materials are porous. The shape of flower likes nanoparticles might be appeared due to change in pH of synthesized materials.

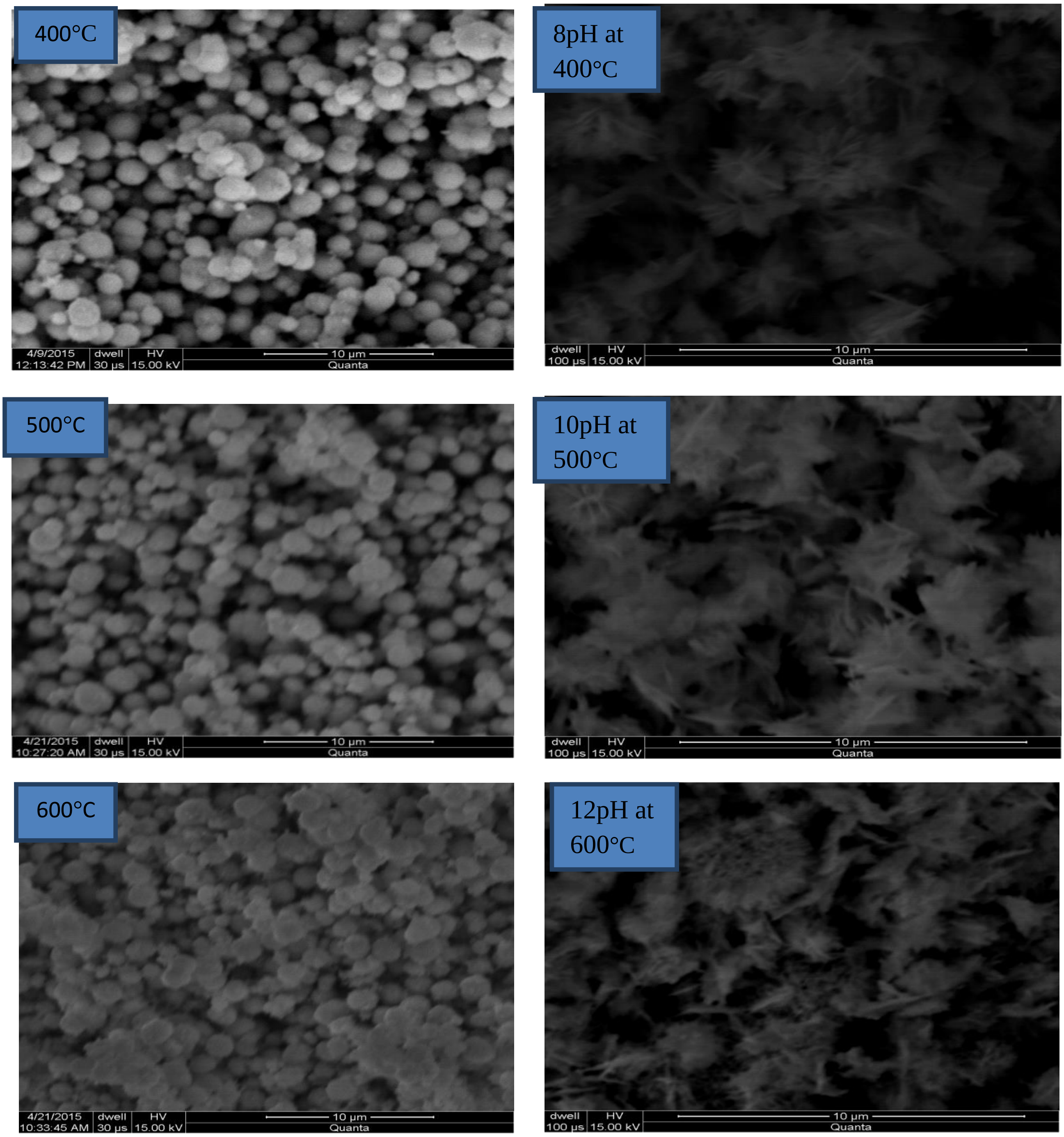


Fig. 4. SEM images of CuO nanoparticles synthesized at 400, 500 and 600°C annealing temperature and at 8, 9 and 12pH

4. Conclusion

CuO nanoparticles were synthesized using solution evaporation method. The XRD analysis demonstrates that the nanoparticles have the monoclinic structure and the crystallite size increases from 6.3 to 8.7nm with annealing temperature (400to 600°C) due to atomic diffusion and with increase in pH from (8 to 12), crystallite size increases from 4nm to 10nm due to the fact that the concentration of OH- can significantly affect the nucleation and growth behaviours (such as the number of nuclei and the concentration of “growth units”) of the nano crystals. The SEM analysis reveals the formation of nanoparticles of different shape and size at different annealing temperatures and flower shape particles appear with increasing pH. These nanoparticles of various shape and size are linked to one another resulting in the formation of complex nanostructure. The complex nanostructure image is spread over the whole scanned area.

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