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Microwave, sonochemical and combustion synthesized CuO nanostructures and their electrical and bactericidal properties

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ABSTRACT

Cetyltrimethylammonium bromide (CTAB)-assisted microwave synthesis of CuO provides nanoleaves and in the absence of CTAB the shape of CuO is irregular. Sonochemical synthesis of CuO using CTAB gives nanodiscs whereas irregularly shaped flake-like structure is obtained without CTAB. Combustion synthesized CuO is highly porous with innumerable large holes. CTAB does not provide any structure in combustion synthesis. Transmission electron micrographs (TEM) display the constituent nanoparticles of microwave and sonochemically synthesized CuO. The powder X-ray diffractogram (XRD) shows the sample obtained by sonochemical method in the absence of CTAB as a mixture of monoclinic CuO, cubic Cu_2O, and orthorhombic $Cu(OH)_2$. But the rest of the samples are pure CuO in monoclinic phase. The selected area electron diffractograms (SAED) of the microwave and sonochemically synthesized samples, in the presence as well as in the absence of CTAB, confirm the monoclinic phase of CuO and indicates the presence of amorphous CuO in traces. All the samples are characteristic of Fourier Transform infrared (FT-IR) Cu–O stretching frequencies. The method of synthesis and also the morphology influence the electrical properties as well as the bactericidal activity of CuO.

1. Introduction

Nanomaterials have attracted much attention in recent years because of their outstanding properties and potential applications, exhibited neither by small molecular system nor by larger particulate matter. NanoCuO is a *p*-type narrow band gap semiconductor with excellent electrochemical [1–5], catalytic [6], photocatalytic [7,8], and antibacterial [9–12] properties. It is inexpensive, nontoxic and easily produced. Because of these characteristics nanocrystalline CuO is widely used in many fields like magnetic storage media, solar energy transformation, electronics, sensor, lithium storage, supercapacitor, and catalysis [1–12]. Recently, the secondary architectures composed of nanostructured building blocks have attracted significant interest in material synthesis and device fabrications. This is because micro-/nanostructured semiconductors display wide applications due to the strong relationship between their geometry and their function [12,13]. Tailored organization of the primary building block units into ordered structures represents another challenge for nanomaterial self-assembly that are highly required for newly emerging applications. The great diversity of applications of nanocrystalline CuO needs distinct morphological structures [12,13]. Surfactants play an important role in synthesizing nanomaterials of different morphologies. They are employed to control the size, shape, and agglomeration of particles. They are likely to be adsorbed on the specific crystal planes and thus cause an anisotropic growth of the crystal structure. Addition of surfactant lowers the surface tension of the reaction solution, which facilitates nucleation and allows its easier spreading. Cetyltrimethylammonium bromide (CTAB) is a cationic surfactant and is widely used in the synthesis of inorganic materials with controlled shape and size. Surfactant molecule with a hydrophilic head and a hydrophobic tail forms reverse micelle in the reaction solution. Hydrocarbonic tail length and reverse micelles-formation control the growth and the distance between the particles and hence the agglomeration.

CuO (i) nanobats [14], (ii) nanorod arrays (by seed-mediation) [15], (iii) nanowire bundles [16], (iv) oval-plate-like, sphere-like, bundle-like, and plate-like nanostructures [13], (v) nanorods and rectangular nanoflakes [17], (vi) nanoboats, nanoplates, and nanoellipsoids (using polyethylene glycol, PEG) [18], (vii) nanoleaves (employing PEG) [19], (viii) nanowires, nanoneedles, and nanoflowers (using different polymeric surfactants with various alcohols as solvent) [20], (ix) hard and hollow nanospheres [7], (x) flower-like nanostructures [21], and (xi) flowers and hard spheres made of nanosheets [4] have been synthesized hydrothermally. Solvothermal syntheses of CuO nanoparticles [22], nanorods [5], and hierarchical microspheres made of nanosheets [23] are also reported. In situ crystallization has resulted in leaf-like nanostructured CuO [24]. Microwave synthesis has yielded CuO nanoplates, nanoflowers, nanorocks, nanotowers [25], and archetypal

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sandwitch-structure [2]. CuO nanoflowers made of nanopetals and nanosheets [8] and nanorods [11] have been synthesized by solution combustion method. CuO (i) nanoparticles [9], (ii) nanorods [26], (ii) nanoleaves [27], (iii) nanowires, nanosheets, nanobundles [28], (iv) nanocubes and nanosheets using CTAB [29], (v) petal-like three dimensional nanostructure through self-assembly [30], (vi) hedgehog-like spheres made of nanoparticles [31], (vii) hierarchical microspheres made of nanosheets [12], and (viii) microspheres composed of nanoparticles [32] have been obtained by chemical synthesis. While CuO nanospheres [33], nanorods, nanobelts, and nanospindles have been synthesized by precipitation method without employing any surfactant [34] PEG-assisted precipitation synthesis of CuO nanorods has also been reported [35]. Sequential dissolution–precipitation process provides CuO nanourchins [1]. Calcination of oxalate precursor yields sphere-like CuO nanostructure [3]. Synthesis of plate-like and flower-like CuO nanostructures by successive ionic layer adsorption and reaction is also reported [36]. Synthesis of CuO by reverse microemulsion method provides hierarchical 3D nanostructures [37]. CuO nanorods [38], hexagonal-shaped CuO nanoparticles [39], and cauliflowers-like CuO made of nanoparticles [40] have been obtained by electrochemical method. Sol–gel synthesis has also yielded nanoflakes and nanoparticles of CuO [10]. Syntheses of CuO nanowhiskers, nanoribbons, nanowires, nanorods, nanocrystals, and nanoparticles from different precursors have been listed by Anandan and Yang [41].

Bacterial contamination and growth in water are potential health hazards demanding disinfection. Now, the use of inorganic antimicrobial agents, compared to the organics, has attracted interest due to their improved safety and stability and ceramics with inherent bactericidal activity are convenient to use as they are insoluble and easily recoverable. Recently, the antibacterial activities of ZnO [42] and Ag_2O nanosemiconductors [43] have been shown to be size- and shape-dependent, respectively. Although many workers have synthesized CuO of different morphologies using different techniques there is no report on the electrical and bactericidal properties of CuO of different nanostructures and hence the present study. CuO of different morphologies have now been synthesized by microwave, sonication and combustion methods using CTAB; regular structure is not obtained in the absence of CTAB.

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade. Copper nitrate (Merck), sodium hydroxide (Merck), hexamine (Himedia), MacConkey agar (Himedia) and nutrient broth (SRL) were used as supplied. Cetyltrimethylammonium bromide (Himedia) was recrystallized from ethanol. Distilled deionized water was used throughout the study.

2.2. Microwave synthesis

The microwave-assisted synthesis was made in an LG 2150 W domestic microwave oven at a working frequency of 2.45 GHz. The oven was operated in cyclic mode. CTAB (0.092 g) was added to 100 mL of 10 mM copper nitrate solution under sonication. This was followed by 50 mL of 1.0 M NaOH and 100 mL of 10 mM hexamine to precipitate copper hydroxide. The contents were microwave-irradiated for 2 h in the oven with proper cutoff time for every 15 min. The crystals were allowed to settle overnight, separated, washed with distilled water followed by ethanol and dried. CuO with leaf-like microstructure was obtained on calcination at 180 °C for 2 h and 600 °C for another 2 h in a muffle furnace fitted with a PID temperature controller and the heating rate was 10 °C min^{-1}. Nanocrystalline CuO has also been synthesized following the same procedure but without adding CTAB.

2.3. Sonochemical synthesis

To 100 mL of 10 mM copper nitrate solution 0.092 g of CTAB was added under sonication. This was followed by 50 mL of 1.0 M NaOH and 100 mL of 10 mM hexamine to precipitate copper ions as copper hydroxide. The precipitate was sonicated for 2 h, allowed to settle overnight and washed with double distilled water and finally with ethanol. The nanodiscs of CuO were obtained on calcination at 180 °C for 2 h and at 600 °C for another 2 h in a PID temperature controlled muffle furnace with the heating rate set at 10 °C min^{-1}. A similar procedure was followed but without the addition of CTAB to obtain CuO of irregular shape.

2.4. Combustion synthesis

CTAB (0.092 g) and copper nitrate (0.315 g) were dissolved in 10 mL of 0.05 M glycine solution and was heated in a silica crucible of 25 mL capacity. After a few minutes, combustion with explosion occurred to yield nanocrystalline CuO. The experiment was repeated but without the addition of CTAB to get nanoCuO.

2.5. Characterization

The powder X-ray diffractograms (XRD) of the synthesized oxides were recorded with a Rich. Siefert model 3000 X-ray diffractometer employing Cu Kα radiation of wavelength 1.5406 Å in a 2θ range of 20–70°. A JEOL JSM-5610 scanning electron microscope (SEM) equipped with BE detector was employed to determine the morphologies of the samples. The samples were placed on an adhesive carbon slice supported on copper stubs and coated with 10 nm-thick gold dust using a JEOL JFC-1600 auto fine coater, prior to measurement. The energy dispersive X-ray (EDX) spectra were recorded with a JEOL JSM-5610 SEM equipped with EDX. The transmission electron micrograph (TEM) images of the samples were obtained with a JEOL 200 CX electron microscope operated at 200 kV; the specimen were crushed and deposited onto TEM Ni grids provided with holey carbon membrane. The solid state impedance spectra (IS) of the oxides, at room temperature in air over the frequency range of 0.1 MHz to 1 Hz, were obtained using a CH Instrument Electrochemical Analyzer 604C. The samples were pelletized using a hydrolytic press and the disk area of the pellets was 0.5024 cm^2. While the thicknesses of CTAB-assisted and unassisted microwave synthesized CuO pellets were 1.45 and 1.55 mm, those of sonochemically synthesized CuO in the presence and absence of CTAB were 1.50 and 1.10 mm; the thickness of the commercial Sigma–Aldrich CuO pellet was 1.37 mm.

2.6. Bactericidal study

Nutrient broth (13 g) was dissolved in distilled water (1 L) and sterilized in an autoclave at 121 °C to obtain a nutrient broth culture medium of pH 7.4. MacConkey agar (55 g) was dissolved in boiling distilled water (1 L), sterilized in an autoclave at 121 °C and poured into Petri dish to get MacConkey agar plates. *Escherichia coli* was inoculated in a nutrient broth (10 mL) and incubated for 24 h at 37 °C. The cultured bacteria were separated by centrifugation at 3500 rpm (5 min), washed twice with an autoclaved NaCl (0.9%) solution and suspended in 50 mL of an autoclaved NaCl (0.9%) solution. The *E. coli* colony forming units (CFU) were counted after serial dilution of the bacterial solution with autoclaved NaCl (0.9%) solution to get about 150 colonies on the Petri dish. The diluted *E. coli* (10 μL) was streaked on the MacConkey agar plate employing a loop and incubated at 37 °C for 24 h. The CFU was counted by a viable count method. The synthesized CuO nanoparticles (20 mg) were added to *E. coli* solution (60 mL) and shaken well continuously without any direct illumination. A finite volume of *E. coli* solution was removed from the nanoparticles after a specified time, diluted stepwise and enumerated as stated already.

3. Results and discussion

3.1. Nanostructures

The SEM images of CuO synthesized by microwave, sonochemical, and combustion methods in the presence as well as in the absence of CTAB are displayed in Fig. 1. The insets are at different magnifications. The SEM image of commercial CuO nanopowder is also shown in Fig. 1. The CuO synthesized by microwave method in the absence of CTAB is of irregular shape. On the other hand, in the presence of CTAB microwave synthesis yields CuO nanoleaves. The images show the thickness of the leaves in nanodimensions. In the absence of CTAB sonochemically synthesized CuO lacks any regular shape. They appear to be irregularly shaped flakes highly agglomerated. But the presence of CTAB during sonochemical synthesis leads to formation of CuO nanodiscs. The images indicate the thickness of the discs in nanoscale. These results clearly show that CTAB provides ordered structure to the synthesized CuO during crystal formation. Further, the shape given by the surfactant depends on the method of synthesis. Combustion synthesis of CuO