J. Mater. Environ. Sci. 4 (5) (2013) 792-797
ISSN : 2028-2508
CODEN: JMESCN

Copper(II)-Oxide Nanostructures: Synthesis, Characterizations and their Applications–Review

Mohammed Suleiman[1*], Muath Mousa[1], Amjad Hussein[2], Belkheir Hammouti[3], Taibi B. Hadda[4], Ismail Warad[1*]

[1]*Department of Chemistry, AN-Najah National University, Nablus, State of Palestine*
[2]*Medical Laboratory Sciences Department, AN-Najah National University, Nablus, State of Palestine*
[3]*LCAE-URAC18, Faculty of Sciences, University Mohammed Premier, Oujda-60000, Morocco.*
[4]*LCM, Faculty of Sciences, University Mohammed Premier, Oujda-60000, Morocco.*

Received 27 Apr 2013, Revised 16 May 2013, Accepted 16 May 2013
* Corresponding author. E mail: i.kh.warad@gmail.com

Abstract
Several successfully methods to prepare Copper(II)-oxide (Cu=O) nanostructures with different sizes and shapes and their applied in different man daily life applications were investigated in this study. This paper discusses different Cu=O nanostructures synthesis methods and their characterization as well as their applications. The pulsed wire explosion method of synthesis was discussed in detail.

Keywords: Copper(II)-oxide nanostructures (CO-NPs), TEM, SEM, XRD.

Introduction

Nanotechnology is an intensive branch of science that interesting in the materials among the size of 1-100 nm with different shapes of spherical nanoparticles, nanorods, nanoribbons, nanobelts and nanoplatelets [1,2]. The unique physical and chemical properties are due to its high surface-to-volume ratio comparing with micro or bulk-sized [1,2]. The nanomaterials can be obtained with different methods such as solid−liquid discharge process [3], novel quick-precipitation [4] and direct thermal decomposition [5] methods. Nanomaterials are now become available and useful in all the man daily life applications such as in: medicine, solar cells, water purification, pharmaceutical and catalysts [6].

Copper(ll)-oxide nanoparticles (CuO-NPs) belongs to monoclinic structure system. It has wide different applications according to the physical and chemical properties, such as superconductivity, photovoltaic properties, relatively stable, low cost and the antimicrobial activity [7].

Applications of CuO-NPs nowadays are very important for antioxidant [8], antibacterial [9], thermal conductivity [10], catalytic [2], battery [11] and solar cells applications [12]. CuO-NPs have been prepared with different sizes and shapes *via* several methods such as sonochemical [1, 13], alcohothermal synthesis[14-17], direct thermal decomposition [5], electrochemical methods [18-20], colloid-thermal synthesis process [21], and microwave radiation [22].

1. Preparation methods

Cu=O nanostructures with different sizes and shapes morphology were obtained by sonochemical method using copper(II) acetate as precursors, urea and sodium hydroxide as reducing agent and polyvinylpyrrolidone (PVP) as stabilizing polymer, followed by irradiation using high-intensityultrasound [1]. Monoclinic phase CuO-NPs were obtained with quasi-spherical microarchitectures and long-straw like structures when using urea and sodium hydroxide, respectively [1].

Other common method that used to prepare CuO-NPs is wet chemical precipitation method [23]. CuO nano-rods with the width range of 5-15 nm can prepared using copper nitrate [$Cu(NO_3)_2.3H_2O$] as precursor and water-ethanol mixture solvent and NaOH as reducing agent at 77-82 ºC. The study showed that the breadth increased with increases Cu ions concentrations [24].

Direct thermal decomposition method is other method to prepare CuO NPs. CuO NPs via Direct thermal decomposition method were prepared by adding Na_2CO_3 solution to $CuSO_4$ solution to precipitate $Cu_4(SO_4)(OH)_6$ followed by calcination at 750˚C to produce spherical CuO-NPs [5].

CuO-NPs were successfully prepared by microwave irradiation method. The 4 nm sized CuO-NPs were obtained by microwave irradiation method using copper(II)-bis-acetate as a starting material, NaOH as reducing agent and ethanol as solvent. High purity and regular shaped CuO-NPs were obtained by this method [22].

Solution plasma method can be used to synthesis CuO-NPs in a good yield [25]. The advantage of such method is that it needs no complicated equipment and the size and shape of CuO NPs can be easily controlled. CuO-NPs were prepared by using copper wire as a cathode and the electrolytes was K_2CO_3or citrate buffer (pH: 4.8) with the voltages of 105 to 130 V. The CuO-NPs have flower-like shape with size less than 100 nm. Size of CuO-NPs decreases with decreasing K_2CO_3 electrolyte concentration, spherical and porous spherical CuO-NPs were obtained when the applied voltages are 105 and 130 V, respectively [25].

Novel method was used to synthesis CuO nano-rods is pulsed wire explosion method. A schematic draw of the system that was used in this method is shown in Fig. 1, where Cu coil with wire diameter of 0.2 mm was installed in the top of the system and the wire was fed between two electrodes that connected with high voltage power source into500 ml deionized water and the wire touching two high voltage extension bars. 10^4–10^5 V, 10^{10} A/m^2 voltage and electric current, respectively, were applied on the electrodes. After 5 s the Cu wire were exploded to form CuO NPs. Different deionized water temperatures of 1, 10,15, 25, 30, 35, 40, 50, and 60 ºCwere used to obtain different nanoparticles sizes and shapes. The results showed that CuO NPs have spherical shapes at low temperatures (1-30 ºC) with diameter size about of 10-20 nm, while spindly shape at 60 ºC with width about 40-80 nm and 650 nm in length [26].

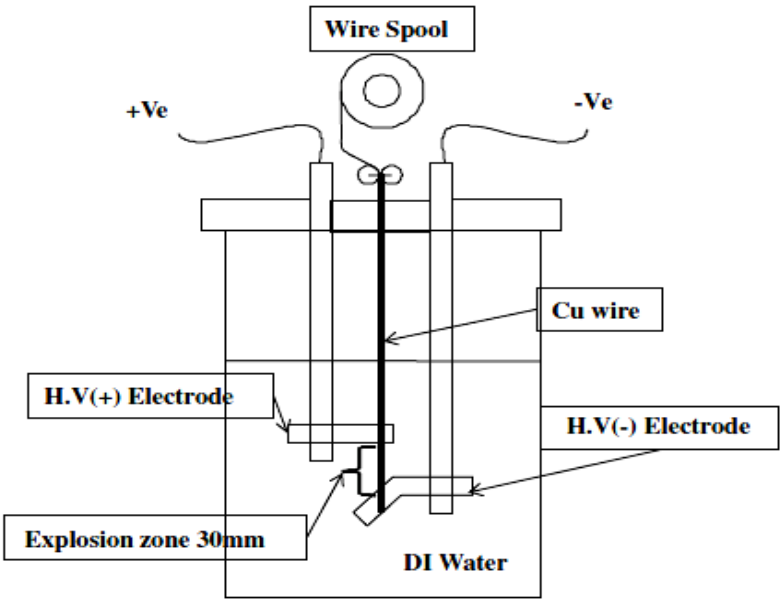

Fig. 1: Schematic pulsed wire explosion system used in is pulsed wire explosion technique [26].

Sol-gel method was investigated to prepare CuO Nps [27], they are good possibility to control the sizes of the obtained CuO NPs ranging from 10-40 nm. The nanoparticles focused on surface of sol-gel thin films and then calcination in air to 300 °C for different time periods, the physical properties of the nanoparticles depending here on several synthetic parameters [28].

2. Characterization of CuO NPs

Many techniques were used to investigate the size and shapes such as: transmission electron microscopy (TEM), scanning electron microscope (SEM) and X-ray diffraction (XRD).

As mentioned earlier, CuO-NPs with the morphology ofquasi-spherical micro-architectures and long-straw like were prepared. The obtained nanostructures results using TEM technique are shown in Fig. 2.

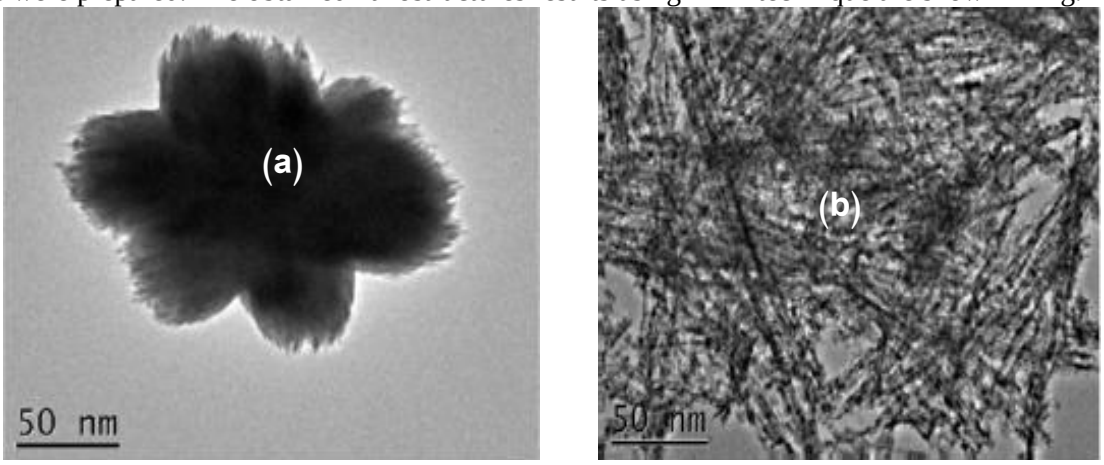

Fig.2. High resolution TEM images of different CuO nanostructures. (a) quasi-spherical microarchitectures and (b) long-straw like [1].

The effect of different synthesis parameters on the morphology of CuO nanostructures were studied. SEM technique was used to investigate the reaction time effect on the morphology of CuO nanostructures. Fig. 3 shows the morphology changes with the change of the reaction time. The needle-like changes to fiber-like and then to a more platelet-like aggregate with increasing the reaction time was observed [5].

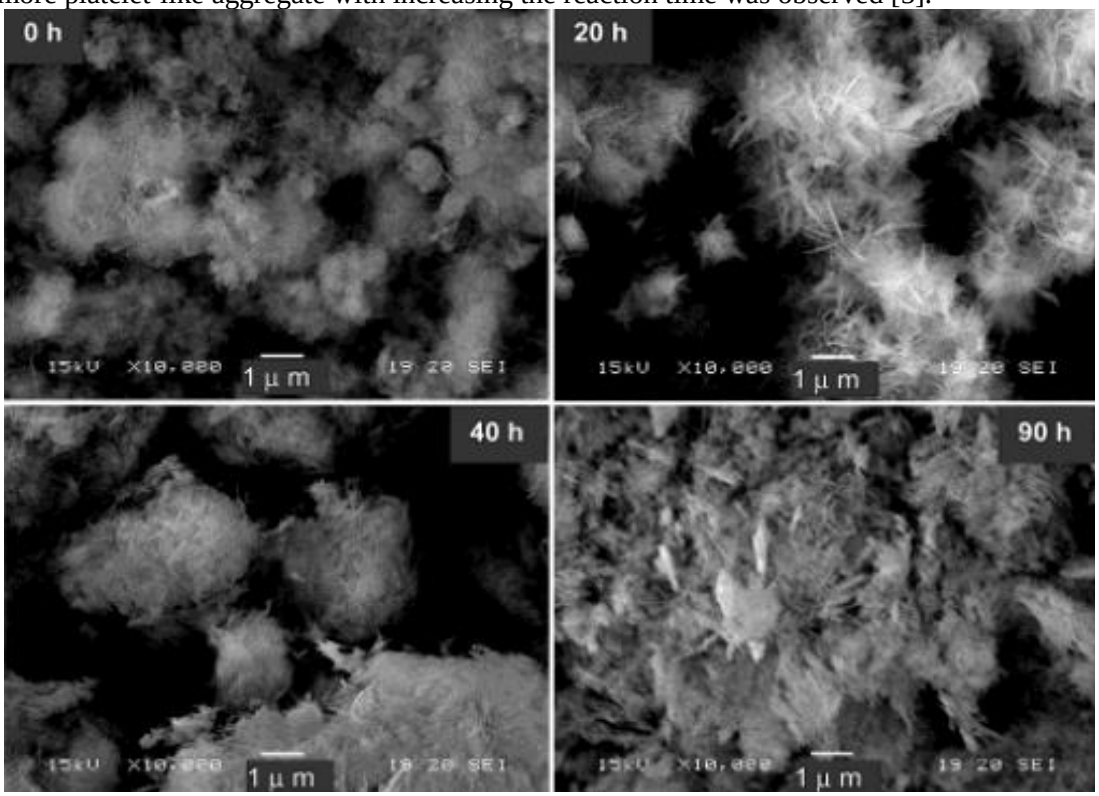

Fig. 3. SEM images of CuO nanostructures that changes from needle-like changes to fiber-like and then to a more platelet-like structure with changing the aging time of 0, 20, 40 and 90 h [5].

Monoclinic CuO-NPs were determined using XRD technique. Other use of XRD technique is to evaluate the particle size using Scherrer equation:

$$D = K\lambda / (B\cos\theta)$$

Where D is the mean size of crystallites (nm), K is crystallite shape factor a good approximation is 0.9, λ is x-ray wavelength, *B* is full width at half the maximum (FWHM) in radians of the X-ray diffraction peak and θ is the Bragg angle [29].

Different CuO nanostructures sizes were obtained using wet chemical precipitation method. By applying Debye–Scherrer equation to the obtained XRD pattern of the CuO-NPs, the average nanoparticles size was found to be 20 nm. Fig. 4 shows the obtained XRD pattern [6].

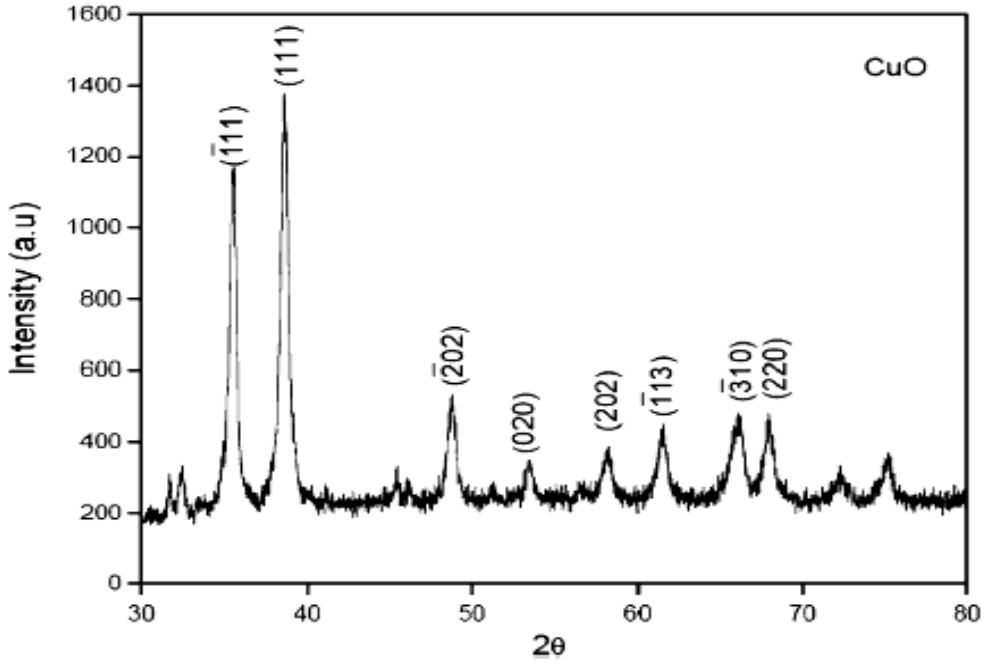

Fig. 4. XRD pattern of CuO nanoparticles.

3. Application

The antioxidant activity and antibacterial activity of CuO-NPs were studied. The antioxidant activity of CuO-NPs were measured using 2,2-diphenyl-1-picrylhydrazyl DPPH method, where DPPH used as radical source. While the antibacterial activity of CuO NPs were tested against *P. aeruginosaBS3, Bacilluscirculens BP2, Eschericia coli and Staphylococcus aureus.* The results showed that CuO-NPs havewell free radical scavenging activity up to 85%, also has good antibacterial activity against *E. col* and *P. aeruginosa* [8].

The activity of CuO-NPs with size of 20-40 nm against *E. coli* using a spread plate method were evaluated. *E. coli* inhibition rate of 14.9% and 45.4% were observed at 2 and 10 mg/L after 2 h contact time [9]. CuO-NPs also have an applications in heat transfer, solar energy and catalysis. CuO nano-fluids have thermal conductivity of 12.4% in the comparison with deionized water [6]. The catalytic reactivity of different CuO nanocrystallites shapes for the oxidation of CO were studied. The shapes were used of CuO are nanoparticles, nanobelts and nanoplatelets. The nanoplatelets show more reducible than other shapes where it converts CO to CO_2 at 77 °C and 134 ºC, followed by nanobelts and nanoparticles that convert CO at 90 ºC and 194 ºC, respectively [2]. Also CuO NPs were used as catalysis in the formation of C-N, C-O and C-S via cross coupling reaction. Cross-coupling of N, O and S nucleophiles with aryl using CuO NPs have the advantages of simple

and high efficiency method under free ligand conditions, while the CuO NPs catalyst are recyclable and can produce high yield of the product [10].

Because CuO-NPs have narrow band gab of 1.2 eV, it uses in solar cells applications. CuO-NPs that prepared by solvothermal method using $CuCl_2.2H_2O$ salt as starting material and oleic acid as solvent followed by calcination of CuO powders at 300 ºC and 400 ºC, were used in solar cells applications. The particle size of CuO that calcined at 400 ºC is smaller than those calcined at 300 ºC. The advantages of this method are no need to surfactant and complex capping agent. The CuO-NPs solar cell efficiency were studied.It was found that CuO-NPs calcined at 400 ºC have solar cell efficiency of 0.863% more than that calined at 300 ºC [11].
Widely used application of CuO-NPs is gas sensing, according to its excellent sensing performance toward different types of gases. CuO-NPs with cloud-like morphology have high sensitivity to detect CO gas [30-32]. CuO nano-rods exhibit high response to ethanol and ethyl-acetategases, where the length of CuO nano-rodsis 45-80 nm and 10-20 nm in width [33]. Furthermore, other study on the gases response of CuO nanostructures was on formaldehyde and ethanol. CuO nanoribbons show excellent sensing performance to the tested gases [34].

Nowadays, many devices type need to rechargeable batteries such as laptops and cell phones, where Li-ion batteries one of the most common battery types [35]. The Li-ion batteries performance when the anode materials for battery was CuO/ graphene nanocomposite were measured [35]. Other study shows that CuO/ grapheme nanocomposite can be used as anode material for Li-ion batteries and the results show high storage performance. CuO nanomaterials were used as anode material according to its low cost, environmentally friendly and its safety. While CuO/graphene nanocompositehas the advantages of excellent cyclic stability, high rate capability and large storage capacity. However, this result consents with previous results [35].

Conclusions

Copper(II)-oxide nanoparticles can be synthesized through different ways, the sizes and shapes of desired nanostructures materials can be controlled by limited number of synthetic factors such as: method, solvents, surfactants, starting precursors and temperature. TEM was the best physical technique to determine the particle size of CuO nanoparticles. Pulsed wire explosion classified as fast and regular size control preparation method.

Acknowledgements-The authors would like to thank AN-Najah National University for the research facilities.

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