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Biosynthesis of colloidal copper hydroxide nanowires using *Pistachio* leaf extract

Akl M. Awwad[1*], Borhan Albiss[2]

[1]*Royal Scientific Society, El Hassan Science City, Amman, Jordan*
[2]*Department of Physics, Jordan University of Science and Technology, Irbid, Jordan*

[*]Corresponding author. Tel: (+962 6) 5344701; E-mail: akl.awwad@yahoo.com

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ABSTRACT

Copper hydroxide nanowires were synthesized from copper chloride dihydrate and sodium hydroxide in the presence of Pistachio leaf extract at room temperature. The results of scanning electron microscopy (SEM) exhibited that the copper hydroxide $Cu(OH)_2$ are nanowires in shape and having an average diameter of ca. 10 nm and lengths of up to 500 nm . The Fourier transfor infrared spectroscopy (FT-IR) results examined the bioactive functional groups , which acts as dispersing, binding and capping agent for the copper hydroxide nanowires. X-ray diffraction (XRD) spectra confirmed the copper hydroxide nanoparticles crystalline in nature. The current research introduces a new, simple, and rapid route for the in – laboratory synthesis of copper hydroxide nanowires. This facile and green approach may provide a useful tool to large scale synthesis other copper nanoparticles that have potential biotechnology. Copyright © 2015 VBRI Press.

Keywords: Biosynthesis; copper hydroxide nanowires; *Pistachio* leaf extract; characterization.

Akl M. Awwad is a professor and senior scientist at Royal Scientific Society, El Hassan Science City, Amman, Jordan. He received his Ph.D. degree from the department of pure and applied chemistry, Strathclyde University, Glasgow, U.K. His main research interests are mainly green synthesis of metal and metal oxide nanoparticles, and their antimicrobial activity.

Borhan Albiss is a professor at the physics department, Jordan University of Science and Technology, Irbid, Jordan. He received his Ph.D. from the physics department at the Middle East Technical University, Ankara, Turkey. His research interests are mainly: biomedical and sensing applications of nanostructured devices, functional materials, nanocomposites, magnetism and scanning probe microscopy.

Introduction

Synthesis of copper hydroxide ($Cu(OH)_2$), copper oxides (CuO, Cu_2O), and copper (Cu) nanoparticles attracted increased attention due to reliable low cost, specific size, well-defined morphologies and wide range of potential applications. Copper hydroxide particles is used as broad spectrum foliar fungicide on fruits and vegetables, in the manufacturing of rayon, good precursors for the synthesis of copper oxides (Cu_2O and CuO), in kill mold in paints, and in ceramics as colorant. Various methods for synthesis of copper hydroxide oxide (CuHNPs) nanoparticles have been achieved via various routes, including aqueous-organic interface method **[1, 2]**, chemical co-precipitation method **[3, 4]**, a two-step template approach **[5],** wet chemical route **[6, 7],** anion exchange method **[8]**, controlling the pH of an aqueous copper ions solution with weak bases **[9]**, solvothermal method with surfactants **[10]**, and an electrochemical method **[11, 12].** Pistachio trees grow up to 10 meters tall and having deciduous pinnate leaves 10-20 centimeters long. The trees are separate male and female.

The present study was designed with a novel, rapid, clean, non-toxic, and environmentally acceptable green route for the production of copper hydroxide nanowires (CuHNPs) by co-precipitation method using copper chloride and sodium hydroxide in the presence of Pistachio leaf extract *via* a single step reaction at room temperature.

Experimental

Materials

Cupric chloride dihydrate ($CuCl_2.2H_2O$) and sodium hydroxide (NaOH, 99%) were purchased from Sigma-Aldrich and used as received without further purifications.

Deionized distilled water was used for all aqueous preparations.

Preparation of plant leaf extract

Pistachio leaves (P.L.) were collected from *Pistachio* trees planted at the campus of Royal Scientific Society, El Hassan Science City, Jordan. Leaves were washed several times with distilled water to remove dust particles and then sun dried to remove the residual moisture. *Pistachio leaf* extract was prepared by placing 10 g of dried fine cut in 500 ml glass beaker along with 400 ml of sterile distilled water. The mixture was then boiled for 5 minutes and then the mixture was cooled to room temperature and filtered with Whatman No. 1 filter paper before centrifuging at 1200 rpm for 2 minutes to remove biomaterials. The extract was stored at room temperature in order to be used for further experiments.

Synthesis of copper hydroxide nanowires

In a typical reaction, precise amount of cupric chloride dihydrate ($CuCl_2.2H_2O$) was dissolved in 100 ml deionized water under magnetic stirring at room temperature. After obtaining a homogenous blue solution, 1-10 ml of aqueous solution of pistachio leaf extract was added drop by drop, the blue color changed to green color, leaving the mixture under stirring for 5 minutes. Afterwards, 0.1M sodium hydroxide solution is added to the mixture drop by drop, the green color started changing to blue suspended particles with continuous stirring for 10 minutes. The suspended blue particles were purified by dispersing in sterile distilled water and centrifugation three times. Afterwards, the blue particles were washed with ethanol and dried for FT-IR, XRD and SEM analysis (**Scheme 1**).

Scheme 1. Schematic representation for synthesis copper hydroxide nanowires.

Characterization techniques

Scanning electron microscopy (SEM) analysis of synthesized copper hydroxide nanoparticles was done using a Quanta FEI 450 SEM machine. Powder X-ray diffraction was performed using a X-ray diffractometer, Shimadzu, XRD-6000 with CuKα radiation λ = 1.5405 Å over a wide range of Bragg angles ($20^o \leq 2\theta \leq 80^o$). Fourier transform infrared spectroscopic measurements were done using Shimadzu, IR-Prestige-21 spectrophotometer.

Results and discussion

The XRD pattern of the synthesized copper hydroxide nanoparticles are shown in **Fig. 1.** XRD studies reveal that copper hydroxide particles are nano-sized and crystalline. The fine particle nature of the sample is reflected in the X-ray line broadening. The position and relative intensity of the diffraction peaks match well with the standard XRD data for copper hydroxide (JCPDS file No. 35-0505). The 2θ peaks 16. 56°, 23.64°, 33.98°, 35.78°, 37.98°, 39.56°, 53.06°, 54.10°, 62.86°, 63.52°, 67.26° and 72.38°are corresponding to planes of copperhydroxide at 020, 021, 002, 111, 041, 130, 132, 061, 113, 200, 221 and 240 respectively. The assigned peaks at 2θ = 31.22°, 43.04° and 45.8°denoted by (*) are thought to be related to crystalline and amorphous organic phase. The X-ray diffraction results clearly show that the copper hydroxide nanoparticles formed by our green method using *pistachio* leaf extract are crystalline in nature. The average crystallite size of the synthesized copper hydroxide nanoparticles calculated using Debye-Scherrer equation **[13-15]:**

$$D = K\lambda/\beta\cos\theta$$

where, D is the crystallite size of copper hydroxide nanoparticles, λ represents wavelength of x-ray source 0.1541 nm) used in XRD, β is the full width at half maximum of the diffraction peak, K is the Scherrer constant with value from 0.9 to 1 and θ is the Bragg angle. 2θ = 23.64°; β = 0.8668x 3.14/180 = 0.01512; D = 0.9 x 0.1541/ 0.00314 x cos 11.82 = 9.37 nm.

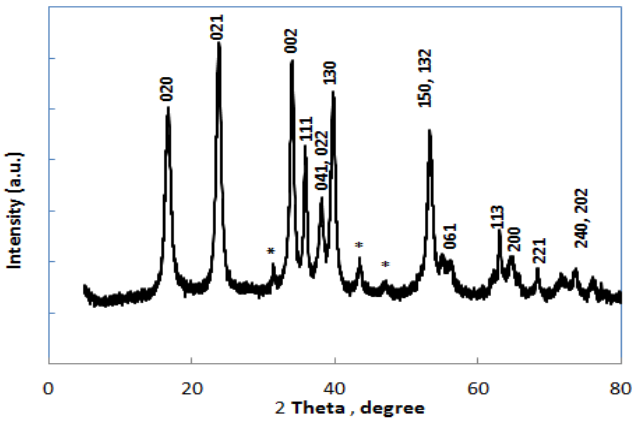

Fig. 1. XRD pattern of the synthesized copper hydroxide nanowires.

Particle size analysis was performed for the copper hydroxide nanoparticles synthesized using different concentration of pistachio leaf extract. The result indicates that the average particle size of the synthesized copper hydroxide nanoparticles is highly influenced by the concentration of leaf extract. Increasing leaf extract concentration in the reaction mixture decreases the particle size. The similar trend was observed in SEM analysis. The smallest particle size was found to be 5 nm, which was

obtained using the leaf extract to copper chloride solution ratio of 1: 4.

The FT-IR spectrum of the synthesized copper hydroxide nanowires (CuHNPs) using Pistachio leaf extract is shown in the **Fig. 2**. FT-IR spectrum for CuHNPs indicated the existence of surface hydroxyls and coordinated Pistachio leaf extract molecules on $Cu(OH)_2$. The strong peak at 3568 cm^{-1} corresponding to the free O-H group and the peak at 3368 $cm^{-1}$is due to the hydrogen bonded O-H group. The peaks at 3302 and 3368 cm^{-1} indicated the existence of *Pistachio* leaf extract molecules in the synthesized copper hydroxide nanoparticles. The band at 1010 cm^{-1} corresponds to the C-O stretching vibration coordinating to copper metal cations, which shifts about 12 cm^{-1} to lower wavenumbers compared to the FT-IR spectrum of pure Pistachio leaf extract, **Fig. 3** suggesting the formation of hydrogen bonds between Pistachio leaf extract molecules and the copper components. The absorption bands at 2812 and 2912 cm^{-1} are attributed to the alkyl chains of the Pistachio leaf extract. The peaks at 3302 cm^{-1} and 1620 cm^{-1} are due to the hydrogen bonded hydroxyl groups and bending mode of the hydroxyl group of water. The peak at 1404 cm^{-1} indicates Cu-OH bond. The peak at 1010 cm^{-1} indicates the Cu-OH vibrations. The peaks appeared at 413cm^{-1}-929 $cm^{-1}$are due to the Cu-O-H bond. These differences indicate that the Pistachio leaf extract act as dispersing and capping agent for as-synthesized copper hydroxide nanoparticles.

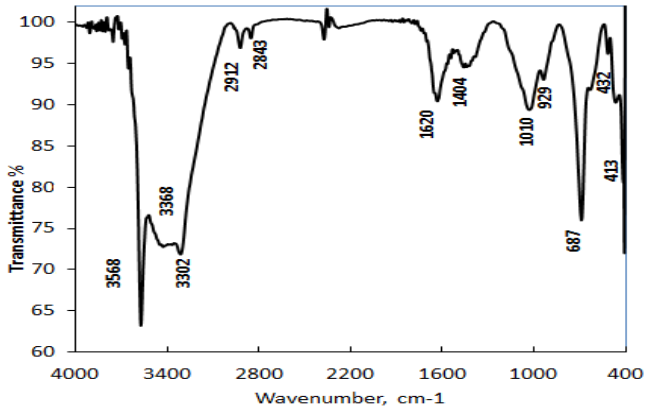

Fig. 2. FT-IR spectra of synthesized copper hydroxide nanowires.

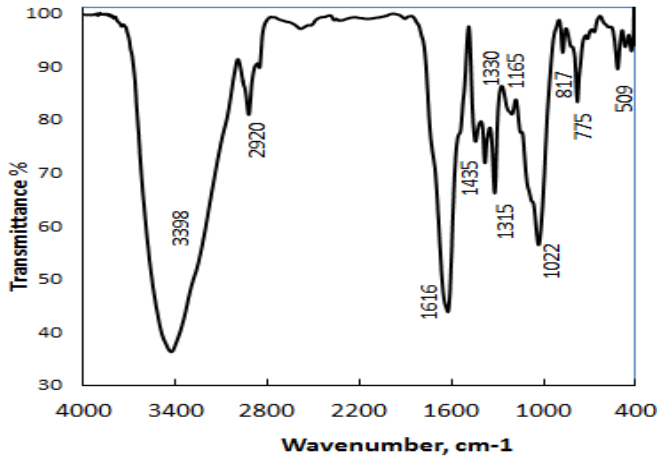

Fig. 3. FT-IR spectra of *Pistachio* leaf extract.

The SEM images of copper hydroxide nanoparticles are shown in **Fig. 4** shows typical dark field SEM images of the as-prepared $Cu(OH)_2$ nanostructures at different magnifications. It can be seen that the sample consists entirely of nanowires with an average length of 250 nm and diameter of 10 nm, and it appears that the nanowires tend to assemble into nanowire bundles and each bundle consists of several nanowires with random orientations. The bright field SEM images, **Fig. 5** suggest that the 1D nanostructures exhibit relatively uniform nanowire width 10nm, which is consistent with a cylindrical wire like morphology. However, few round ends nanoribbon-like morphology of width 30 nm and length 250 are formed from the self- assembled nanowires. A comparison between the bright-field image and a corresponding dark-field SEM image shows that the sample is quite pure and there are no impurity phases which may come from the carbon coated copper grid used for the SEM sample characterization. Knowing that $Cu(OH)_2$ can be transformed into CuO due to heating from the electron beam, the electron dosage was kept low to minimize the sample heating. However, no visible change in the SEM images indicating the high stability of $Cu(OH)_2$ in vacuum and under the electron beam.

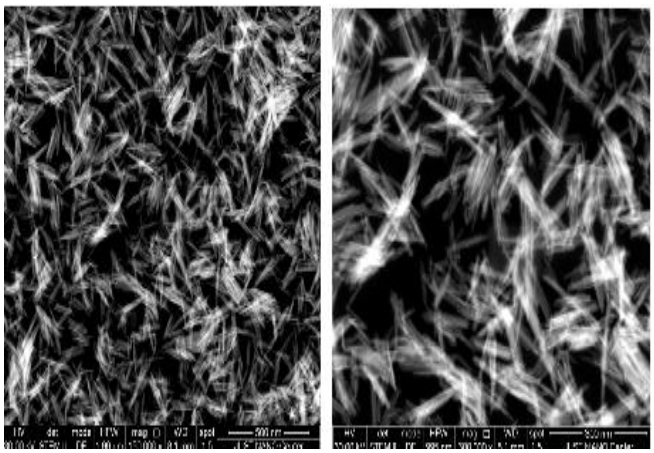

Fig. 4. SEM dark field image of the synthesized copper hydroxide nanowires.

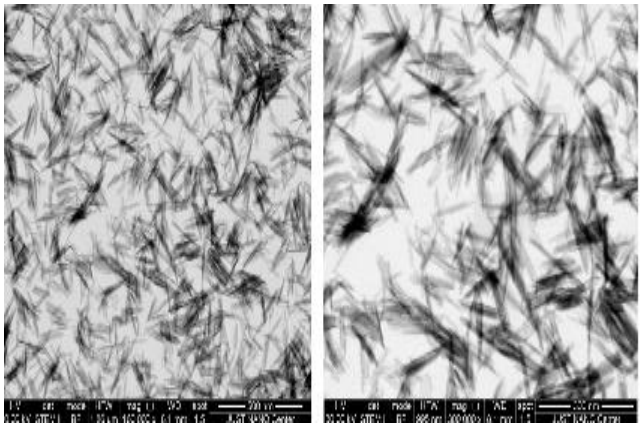

Fig. 5. SEM bright field image of the synthesized copper hydroxide nanowires.

Conclusion

A new and simple synthesis approach has been successfully developed to synthesize copper hydroxide $Cu(OH)_2$ nanowires from copper chloride dhhydrate, $CuCl_2.2H_2O$ and sodium hydroxide, NaOH in the presence of Pistachio leaf extract at room temperature. XRD analyses suggest that the average particles size is in the nano range 9 nm. The SEM images reveal that copper hydroxide nanoparticles well crystallized nanowires with an average diameter of 10 nm and lengths of up 500 nm. The Pistachio leaf extract was observed to serve as binding, dispersible and capping agent. Highly crystalline copper hydroxide nanowires were synthesized using environmentally friendly agents requiring one step of reaction. The method in the present study offers several important advantageous features. First, the synthesis method is economical and environmentally friendly, because it involves inexpensive and non-toxic materials. Second, size-controlled magnesium hydroxide nanowires are produced easily by different amounts of *Pistachio* leaf extract and third scale up the process.

Acknowledgements

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