



Short Communication

A novel sonochemical synthesis of antlerite nanorods



Elad Segal, Ilana Perelshtein, Aharon Gedanken*

Department of Chemistry, Institute of Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan 52900, Israel

ARTICLE INFO

Article history:

Received 10 February 2014

Received in revised form 7 July 2014

Accepted 23 July 2014

Available online 31 July 2014

Keywords:

Antlerite

Nanorods

Minerals

Sonochemistry

ABSTRACT

Antlerite – $\text{Cu}_3(\text{OH})_4\text{SO}_4$ was prepared, for the first time, by the sonochemical method from an aqueous solution of CuSO_4 , without any additives. The source of OH^- is a result of protonation of SO_4^{2-} forming HSO_4^- and OH^- . The extreme local conditions inside the cavity that are developed during the bubble collapse (pressure is above 1000 atm and the temperature is higher than 5000 K) lead to the formation of the crystalline mineral. A suggested mechanism for the mineral formation is proposed. Due to the collapse of the bubbles, the distances between the opposite charge Cu^{2+} and SO_4^{2-} ions is shortened and a crystallization process is initiated. In addition, the reaction is a one-step process with short irradiation time of less than 30 min. The chemo-physical analysis of the sonochemically obtained product has revealed the presence of single phase antlerite nanorods.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Previous reports on the sonochemical reduction of metallic ions by ultrasound have been presented and discussed. These reports include the sonochemical reductions of metallic ions that were carried out without a reducing agent. For example, the reduction of Ag^+ in an aqueous solution of AgNO_3 and the deposition of metallic silver upon silica sub-micron spheres by ultrasonic method under argon atmosphere was reported [1]. Fabrication of Pt NPs (nanoparticles) with no stabilizer or capping agent, by reducing Pt^{IV} to Pt^0 in pure water under Ar atmosphere, in a 2-step process [2] was reported. In the case of copper the sonochemical reduction of Cu^{2+} from CuSO_4 and CuCl_2 as starting compounds, has led to the formation of Copper hydride (CuH) [3]. Needless to point out that many examples of the sonochemical reduction of metallic ions in the presence of a reducing agent have been published [4–9]. The sonochemical reduction of metallic ions is of great interest because it is considered a cheap technique which yields small NPs of the corresponding metal. In the absence of a reducing agent the reaction occurs as a result of the collapse of the cavitation bubbles, leading to the homolytical cleavage of water into H^\cdot and OH^\cdot radicals [10–12]. It is clear that the number of metals that can be reduced just by radicals formed from the dissociation of water is limited to those having a highly positive standard reduction potential.

Hasin [3] has reported on the sonochemical synthesis of CuH when the reaction was conducted under argon. In the current paper, we report on the same reaction employing the same reactant, CuSO_4 as described in Ref. [3] and obtained $\text{Cu}_3(\text{OH})_4\text{SO}_4$. The main difference between the work of Hasin and ours, is that we have performed the reaction under air and as a result a different product, the mineral antlerite ($\text{Cu}_3(\text{OH})_4\text{SO}_4$) was synthesized. This mineral is well known – and was synthesized previously in a few different ways. Koga and co-workers [13] have shown a large-scale microwave-assisted hydrothermal method for the synthesis of micron-size needle-like ($\text{Cu}_3(\text{OH})_4\text{SO}_4$). Another research [14] has demonstrated the use of urea and carbonate for the precipitation of antlerite. Vilminot et al. [15] has prepared antlerite in a long process of six days, under 170 °C with NaOH as the hydroxide source. The main disadvantages of the available techniques for the synthesis of antlerite are either long processes or the involvement of special chemicals added as a source of hydroxide. The current article introduces a new preparation technique, i.e. the sonochemical method. The current manuscript reports on a one-step process conducted under ultrasonic waves to produce the mineral antlerite from CuSO_4 aqueous solution in a non-inert atmosphere within less than 30 min. Nanorods of up to ~150 nm width and 1.5 μm in length were prepared and characterized by common materials science techniques.

Herein we report on applying ultrasonic waves on a solution of inorganic salt under air. When ultrasonic irradiation is applied to an aqueous solution of an inorganic salt, the acoustic bubbles that are being formed during the process adsorb the ions of the salt on their surface [16,17]. When the bubbles collapse, extreme local (inside the cavity) conditions of pressure (above 1000 atm) and

* Corresponding author.

E-mail address: gedanken@mail.biu.ac.il (A. Gedanken).URL: <http://www.ch.biu.ac.il/gedanken> (A. Gedanken).

high temperature (higher than 5000 K) occur next to the ions [11]. So unlike sonochemical reaction of volatile materials that happen inside the collapsing bubble, in our case the reaction takes place on the surface of the collapsing bubble.

2. Experimental section

2.1. Materials, equipment, and experimental methods

Analytically pure grade of chemicals were used as received without any further purification. Typically, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in deionized water [DDW] to obtain a 0.5 M aqueous solution. The dissolution of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was done by stirring the solution magnetically for 15 min at room temperature until a transparent bluish solution was obtained. Then, 50 ml of the solution was poured into a 100 ml beaker. The ultrasonic treatment was done by immersing the high-intensity Ti horn (20 kHz, 750 W, 1.3 cm horn diameter) with 2X booster into the reaction vessel, the reaction time varied from 10 to 25 min. The reaction was carried out without external cooling, and the temperature inside the beaker was $\sim 60^\circ\text{C}$. The efficiency of the sonicator remained constant during the sonication at 25%, meaning amplitude of 25% out of the maximum sonotrode vibration. After 25 min a bluish-green precipitate was noticed at the bottom of the beaker, the solution was allowed to cool down to room temperature under ambient conditions (the reaction temperature was $\sim 60^\circ\text{C}$ at the end of the sonication) and the desired product was collected by centrifugation, washed twice repeatedly with DDW and dried under vacuum at room temperature.

Good reproducibility was obtained for all of the 5 repeated experiments, under the same conditions.

In the experiment that probed the possibility of obtaining a higher yield, the reaction conditions were kept as described above and urea was added until a pH of 4 was measured.

3. Characterization

The structural characterization of the product as the mineral antlerite was done by XRD with $\text{Cu } K\alpha = 1.541 \text{ \AA}$ radiation, using a Bruker D8 diffractometer. The imaging and morphology of the mineral was studied by a high resolution transmission electron microscope (HR-TEM, JEOL JEM 2100 instrument), and in addition to by an environmental scanning electron microscope (ESEM)

employing the FEI QUANTA 200F device. Elemental analysis characterization was made by Energy-dispersive X-ray analysis (EDAX) attached to the ESEM instrument, and selected area electron diffraction (SAED) crystallographic analysis was also collected by the HR-TEM device.

The Cu^{2+} ions concentration was characterized by elemental analysis using an inductively coupled plasma (ICP) spectrometer (Ultima 2, Jobin Yvon Horiba). Classic calibration method with standard solutions was used in order to analyze the elements mentioned above.

4. Results and discussion

The product obtained from the sonochemical reaction was characterized by XRD (Fig. 1). The diffraction peaks observed from the pattern of the product are assigned to the orthorhombic structure of antlerite (PDF 01-84-2037), and its main peaks are depicted in Fig. 1. The product can be assigned to highly pure antlerite due to the absence of other impurity peaks. It is important to emphasize that the diffraction peaks of metallic Cu or CuSO_4 compound were not detected in the XRD diffraction pattern of the product.

The morphology and elemental characterization of the obtained product was made by ESEM (Fig. 2). The image depicts that the product was formed having a needle-like morphology. The length of the needles varies between 0.5 and 1.5 μm and the width ranges between 80 and 150 nm. In order to confirm the formation of antlerite, elemental analysis using Energy-dispersive X-ray analysis (EDAX) were performed. The results indicate the following composition of atoms: Cu ($31.3\% \pm 1.5$), S ($11.9\% \pm 1.9$), O ($56.8\% \pm 1.8$), these values are given in $A_i(\%)$. The measurements determine a 2.64 as the Cu:S molar ratio which is close to the expected Cu:S = 3:1 molar ratio according to the antlerite formula. In any case it is very different from the 1:1 Cu:S molar ratio of the starting material or from other well-known compound Cu_2S , and the less known Cu_3S_2 compounds.

The structural nature of the synthesized particles was also confirmed by HR-TEM measurements. The HR-TEM images were taken at low (Fig. 3A) and at high (Fig. 3B) magnifications, and similarly to the SEM results depict a nanorods structure. The needle-like structure size ranges up to $\sim 150 \text{ nm}$ width and up to 1.5 μm length. The crystalline nature of the particles was studied by measuring the electron diffraction of the selected area (Fig. 3C). The highly crystalline nature of the nanorods is evident from the SAED

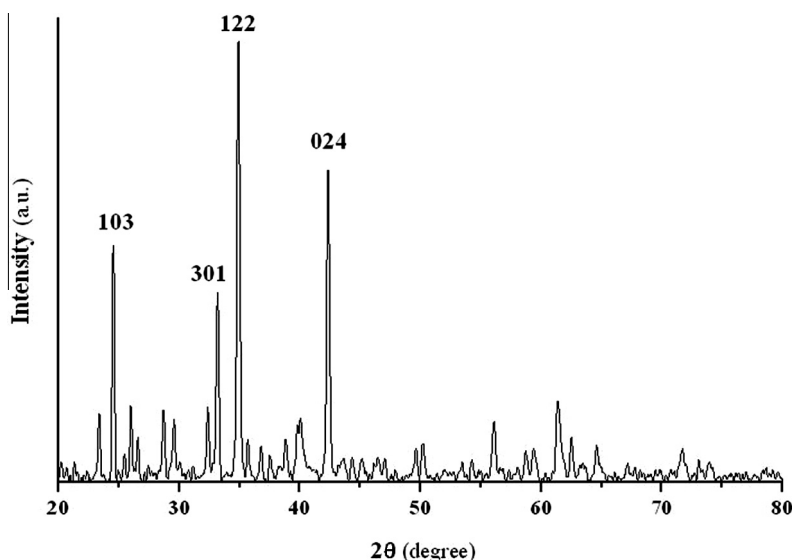


Fig. 1. XRD pattern of $\text{Cu}_3(\text{OH})_4\text{SO}_4$ particles.

Download English Version:

<https://daneshyari.com/en/article/1269613>

Download Persian Version:

<https://daneshyari.com/article/1269613>

[Daneshyari.com](https://daneshyari.com)