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Sonochemical shape control of copper hydroxysulfates

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ABSTRACT

Shape control of inorganic nanoparticles generally requires the use of surfactants or ligands to passivate certain crystallographic planes. Additive free shape control methods utilize the differences in the growth rates of crystallographic planes. We combined this approach with the sonochemical method to synthesize copper hydroxysulfate (Brochantite) with morphologies ranging from flowers, to bricks, belts and needles. Sodium peroxydisulfate, which was used as the sulfate and hydroxide source, was decomposed thermally and/or sonically under various pH and temperature conditions. The relative release rates of the sulfate and hydroxide anions determined the final form of the crystals. This technique yielded products even at acidic pH, marking a distinction from the literature reactions, which start with stoichiometric amounts of sulfate and hydroxide anions and yield only a single crystal morphology.

1. Introduction

There has been a growing interest towards the ultrasound assisted reactions due to the peculiar conditions they possess. It has been shown that the ultrasonic field can induce cavitations in the liquid [1,2]. These cavitations survive through couple of cycles of the sonic field and collapse in several nanoseconds leading to extreme temperature (>1000 K) and pressure (>100 atm) conditions [3–7]. These extreme conditions, albeit short lived, can induce chemical changes through radicals, which form in the epicenter of the collapse. While only volatile species can exist at the center of the collapse, solutes with low vapor pressures experience still high temperatures (>500 K) at the interfacial region. Radicals from these kinds of solutes have been observed at relatively high precursor concentrations [8]. Since radicals form during the cavity collapse rather than thermal activation, it is possible to run radical reactions at relatively low temperatures (by using a cold bath) and obtain novel products, which differ from the products of thermal reactions. In addition to the radical production, ultrasound mixes the contents of the solution violently and substantially decreases the effects of charge layers and the diffusion control on the reaction kinetics.

Inorganic nanomaterials with desired sizes and shapes have attracted both technological and fundamental interest for shape dependent properties and possible wide range applications [9–11]. Wet chemistry is one of the promising methods for the synthesis of nanoparticles with different shapes. This approach employs hard or soft templates or utilizes the anisotropic crystal structure of solid materials without using templates [12–14]. However, these reactions can be typically slow and may even require a couple of days to a couple of weeks before the product is obtained. Sonochemical method, on the other hand, is a quick alternative which has been utilized for the synthesis of nanoparticles of metal oxides [15,16], chalcogenides [17,18] and noble metals [19]. Recently, shape control of nanomaterials produced under ultrasonic field has been demonstrated with ZnO [20,21] and gold nanoparticles [22]. While ultrasonic reactions may still employ surfactants to passivate certain crystallographic planes [21], in our study, we demonstrate shape control under ultrasonic field, without the use of surfactants, by affecting the growth kinetics of the crystals under different conditions.

Copper hydroxysulfates are corrosion products of copper surfaces exposed to natural conditions [23]. Synthetic crystals, namely Antlerite $Cu_3(OH)_4SO_4$ and Brochantite $Cu_4(OH)_6SO_4$ are typically synthesized by the stoichiometric mixtures of sulfates and hydroxides [24,25] at moderate temperatures. Hydrothermal conditions (120–200 °C) have also been utilized for these stoichiometric mixtures from several days to several weeks for growing large crystals [26–28]. Alternative routes such as homogenous precipitation from solution by urea hydrolysis [29] and precipitation from a mixture of sulfate and carbonate solutions [30] as well as the traditional methods typically yield only the needle-shaped morphology. Copper hydroxysulfate particles have recently drawn attention due to their magnetic properties and structures [26–28,31]. These salts are composed of polymerized edge sharing polyhedra forming double chains. It is the orientation of (Cu^{2+}) spins in these chains and the coupling in and in-between the planes, which makes these compounds interesting [27].

Copper ions and complexes have been used for centuries as antibacterial, antifungal agents in different applications such as

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Table 1
Summary of reaction conditions and product morphologies for sonochemically/thermally synthesized Brochantite.

Sample #	Initial pH	Reaction Temperature (°C)	Final pH	% Yield	Crystal Morphology
1	5.59	5	4.56	3.5	Brick
2	5.55	25	4.98	8.2	Brick
3	5.55	60	4.09	16.5	Flower
4	5.54	80	3.91	11.8	Lumps
5	6.51	5	6.23	59.0	Lumps
6	6.50	25	5.59	66.0	Lumps
7	6.50	60	5.11	68.4	Needle
8	6.50	80	4.99	77.8	Needle
9	7.50	5	7.25	87.3	Belt-Needle
10	7.52	25	6.45	82.5	Belt
11	7.50	60	5.19	73.1	Needle
12	7.51	80	4.96	51.9	Needle
13	8.50	5	6.67	68.8	CuO-Lumps
14	8.51	25	6.03	55.3	CuO-Lumps
15	8.50	60	5.54	46.9	CuO-Lumps
16	8.50	80	5.21	60.3	CuO-Lumps
Initial pH = 5.60 Reaction temp. = 80 °C		Time	pH	Yield	Form
		2 hours	4.37	12.2	Lumps
		4 hours	4.30	15.9	Lumps
		6 hours	4.13	16.7	Lumps
		8 hours	4.15	17.7	Lumps

medicine, agriculture, water treatment, etc [32–34]. Bordeaux mixture (mixture of copper sulfate, lime and water) has been used as fungicide over the world in agriculture since 1880s [33]. Standard Bordeaux mixture contains brochantite, antlerite, posnjakite [35] and lately brochantite itself was proposed as fungicide [36]. Recent studies show that the antibacterial activities depend on the size as well as the shape of the particles in cuprous oxide and silver [37–39].

In this paper, we present the ultrasound assisted facile method for the synthesis of Brochantite yielding micron-size crystals with various morphologies in only 1 h at 5–80 °C. We have utilized the ultrasonic field to decompose peroxydisulfate anion in the presence of copper acetate salt under various pH and temperature conditions. Unlike the traditional hydrothermal method described above, we demonstrated that the hydroxysulfate minerals can be formed even at acidic pH of 5 from these precursors.

It has been known that the thermal degradation of copper hydroxysulfates yields copper oxides [24,25,27,40,41]. Copper oxides have been used as catalysts for various applications. Controlling the morphology of copper oxide is highly important since the catalytic activity typically depends on the morphology [42]. However, the morphology of copper oxides obtained by the thermal decomposition of Brochantite was only recently investigated [30]. In this study, only a single morphology, needle type, was observed since authors synthesized Brochantite by the traditional methods. This limitation can be overcome by the various morphologies of Brochantite synthesized in our study.

2. Experimental section

The reactions took place in a custom glass sonication cell fitted with a water jacket for temperature control. The solution can be purged with gas prior to and during the sonication. A Bandelin HD 3200 model 20 kHz ultrasonic probe with 13 mm $TiAl_6V_4$ alloy tip was used. The average intensity was on the order of 50 W/cm^2. Copper acetate monohydrate and sodium peroxydisulfate were from Merck and were used as received (>99%).

In a typical run, 0.749 g (3.752 mmol) copper salt and 0.446 g (1.874 mmol) sodium peroxydisulfate were dissolved in 50 mL deionized water (18.2 MΩ cm^{-1}). The solution was placed in the sonication vessel and purged for 30 min with nitrogen gas to remove dissolved oxygen. The natural pH of this solution was around 5.5. Ammonia was used to adjust the initial pH of solutions to 6.5, 7.5 and 8.5. The temperature of the solution was adjusted to 5, 25, 60 and 80 °C with a circulating chiller. The solution was sonicated for 60 min. Then, the products from the reaction were separated by centrifuging, and washed several times with deionized water and dried in oven at 80 °C. In separate set of experiments, time evolution of products was observed by running the reactions for shorter and longer periods. The thermally activated control reactions were carried out at 80 °C in temperature-controlled vessels.

The OH· radical yields were compared by the fluorescence spectroscopy using terephthalic acid as the marker. In a typical procedure, aqueous solution containing 2 mM terephthalic acid (Alfa Aesar, %98+), 1 mM sodium peroxydisulfate and 4 mM sodium acetate (Merck, %99 anhydrous) was prepared. The pH of the solution was adjusted with ammonia and/or acetic acid. The experimental procedure was the same as above except copper ions were not present in solution. Reaction times were limited to 30 min. The reactions were run at pH 5.5, 6.5 and 7.5 at 25 °C, and at pH 7.5 at 80 °C under ultrasound irradiation. For comparison, thermal decomposition of peroxydisulfate was tested at pH 5.5 and at 80 °C. Cavitation induced OH· radical production in pH 5.5 water was also tested at 25 and 80 °C. A Horiba Fluoromax-3 spectrometer was used for fluorescence experiments. 2-Hydroxyterephthalic acid was excited at 315 nm and the emission between 350 and 550 nm were collected. The reported spectra are corrected for the excitation intensity and dilution factors.

The electron microscopy studies were carried out in a Zeiss Evo 40 SEM furnished with a LaB_6 electron source. The crystals were cast on aluminum stubs from alcohol suspensions and were not coated for analysis. The powder X-ray diffraction measurements were performed using a HUBER-G670 diffractometer utilizing a Germanium monochromator and Cu Kα radiation (λ = 1.5406 Å). The thermal analyses were performed using a SII Seiko SSC/5200 thermal analysis instrument with TG/DTA 220 module under argon flow. The samples were heated up to 1050 °C at a rate of 5 °C/min in Al_2O_3 holders. The optical emission measurements for concentration determination were carried out with a Spectro Genesis inductively coupled plasma optical emission (ICP-OES) spectrometer using solutions of products dissolved in hot nitric acid. Standard stock solution of Cu^{2+} was prepared by dissolving the appropriate amount of $Cu(NO_3)_2{\cdot}3H_2O$ in 3% nitric acid solution. Standard solution of sulfur was prepared from sulfuric acid solution. In each case, a 5-point calibration curve was used to cover the concentration range of interest.