Low-temperature hydrothermal synthesis of hierarchical flower-like CuB$_2$O$_4$ superstructures

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Received 21 November 2019; Received in revised form 30 January 2020; Accepted 22 March 2020

Abstract

We report for the first time the fabrication of hierarchical ordered superstructure CuB$_2$O$_4$ with flower-like morphology via a one-step, low temperature hydrothermal method. The tetragonal structure of CuB$_2$O$_4$ was determined by X-ray diffraction and high-resolution transmission electron microscopy. Optical measurements attested of the quality of the fabricated CuB$_2$O$_4$ and high temperature X-ray diffraction confirmed its thermal stability up to 600 °C. The oriented attachment growth and the hierarchical self-assembly of micrometer-sized platelets producing hierarchical superstructures with flower-like morphology are designed by pH of the hydrothermal solution. The excellent band gap, high thermal stability and hierarchical structure of the CuB$_2$O$_4$ are promising for the photovoltaic and photocatalytic applications.

Keywords: copper metaborate, hierarchical structure, flower-like morphology, hydrothermal method

I. Introduction

The ability to control and manipulate the geometrical parameters of materials (size and shape) is one of the challenging issues in materials science. The development of efficient synthetic routes to obtain well-defined morphologies is important task [1–4], as hierarchical superstructures could be a way to design the physical and chemical properties of a material.

Copper borate has been extensively studied for their magnetic properties [5,6] and especially for the applications in photocatalytic water splitting [7]. Recently, the gigantic direction dependent luminescence and the possibility of introducing crystal chirality by a weak magnetic field and the magnetic field found in the copper borate showed that this material is still actual for the development of the new applications [8,9].

To the best of our knowledge, the synthesis methods reported for CuB$_2$O$_4$ require high pressures and temperatures under thermal conditions [10–12], precipitation reaction in aqueous solution with modifying agent [13] or hydrothermal synthesis in alkaline solution [14]. So far, the morphologies of the copper borates obtained by different methods were ellipsoidal [13], round and rod-like in shape [14].

In this context, we revisited the CuB$_2$O$_4$ system using hydrothermal synthesis in acidic medium and thus the fabrication of the hierarchically ordered superstructure CuB$_2$O$_4$ with flower-like morphology is reported for the first time.

II. Experimental procedure

Copper precursor (Cu) and boron precursor (B$_2$O$_3$) were purchased from Sigma-Aldrich and used without any prior purification. In a typical synthesis process, the desired copper and boron precursors quantities were mixed in water and pH = 4 has been established using acetic acid. The molar ratio of metals Cu:B varied from 1:2 to 1:10. The obtained suspension was transferred into Teflon-line autoclave with a volume of 60 ml. The fill factors of the autoclave were in the range of 10 to 30%. The autoclave was cooled down to room temperature naturally. The precipitates were separated by the filtration using MN 640 de/diameter 125 mm filter paper, then washed with deionized water and dried at 80 °C for 1 h.
The structure of the products was determined by powder X-ray diffraction (XRD) PW 3040/60 X’Pert PRO using Cu-Kα radiation with λ = 1.5418 Å, in the range 2θ = 10–80°. The morphology of the CuB₂O₄ powder was observed using scanning electron microscopy (Inspect S, SEM/EDX) and transmission electron microscope (TEM, Titan G2 80-200). The TEM specimens were prepared by crushing powder samples under ethanol in an agate mortar and depositing the drops onto a holey carbon membrane supported by a copper grid. The d-spacing of the lattice was calculated using fast Fourier transform (FFT) image obtained by NIH’s ImageJ software. The topography and particle size of the samples were investigated by AFM (Model Nanosurf® EasyScan 2 Advanced Research). UV-visible diffuse reflectance spectra of the powdered samples were analysed by using a spectrophotometer (LAMBDA 950 UV/Vis/NIR Spectrophotometer, PerkinElmer, wavelength range up to 3300 nm). Micro Raman measurements were performed on Nanonics Raman module mounted on optical microscope (Olympus) using Raman excitation given by argon laser Stellar Pro Module with selected wavelength of 514 nm. Raman signal was detected using ANDOR SR 500i-A-R spectrometer equipped with CCD.

The electrochemical investigations were performed using a Voltalab potentiostat model PGZ 402, with VoltaMaster 4 (version 7.09) software. A single compartment three-electrode cell based on a platinum wire as counter electrode, Ag/AgCl/KCl sat. electrode coupled to a Luggin capillary as reference electrode and CuB₂O₄ thin film as working electrode (area 0.28 cm²) were used. The synthesized CuB₂O₄ powder was mixed with 5 wt.% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) solution and the obtained paste was coated on the FTO substrate using doctor-blade technique. All potentials were referenced to the standard hydrogen electrode (SHE). The capacitance of the interface was measured using 0.1 mol/l Na₂SO₄ aqueous solutions with pH = 7, in the potential range from −0.6 to −0.1 V with a 25 mV potential step at 1 kHz and AC potential amplitude of 20 mV. The thermal stability of the obtained CuB₂O₄ structures was studied by in situ XRD using a variable temperature chamber (Anton Paar HTK 2000 high temperature chamber). The diffraction patterns were recorded in 2θ angular range 10–80° using a heating rate of 10 °C/min.

III. Results and discussion

The following specific conditions: 1:2 molar ratio of Cu:B₂O₃, pH = 4, 250 °C and 48 h were used to obtain pure copper metaborate CuB₂O₄. In accordance with the Eh-pH diagram and pC-pH diagram for the system B−O−H and Cu−O−H, under acidic pH, hydroxo Cu(II) complexes and H₃BO³(aq) are thermodynamically favourable [15,16]. Thus, for certain temperature, pH, reaction time and molar ratio of Cu:B, the stability of Cu(OH)−₃ and B(OH)₃(aq) species is realized, the supersaturation is reached and CuB₂O₄ is obtained.

Figure 1 shows X-ray diffraction pattern of the CuB₂O₄ compound prepared by the hydrothermal method. All the diffraction peaks could be indexed as CuB₂O₄ with tetragonal structure (space group: I42d, JCPDS Nr. 01-070-2446).

Figure 2. SEM image of the CuB₂O₄ product (a) and a hierarchically ordered CuB₂O₄ superstructure with flower-like morphology (b)
Figure 3. TEM (a) and HR-TEM (b) images of CuB₂O₄ thin platelets and d-spacing calculated using FFT obtained by NIH’s ImageJ software (c)

Figure 4. AFM images of CuB₂O₄ thin platelets (a), enlarged AFM image of 2D micrometric square structures (b) and height distribution for 2D micrometric square structures extracted from the AFM image (c)

hierarchical structures, which are built by self-assembly of the thin platelets (Fig. 2b).

In addition, HR-TEM analysis of the thin platelets was used to determine the crystal lattice and to confirm CuB₂O₄ single phase identified by the XRD study. At first, the d-spacing of the CuB₂O₄ lattice was calculated using Fast Fourier transform (FFT) image obtained by NIH’s ImageJ software. In Fig. 3, the d-spacing of the lattice fringes calculated from FFT image (inset) was found to be 3.2 Å and 2.6 Å. These values are consistent with the standard PDF 01-070-2446 values of (301) crystal plane (i.e. 3.16 Å) and (112) crystal plane (i.e. 2.65 Å) of tetragonal CuB₂O₄ revealing to be perfectly single crystalline.

In order to study in-depth the growth of the copper borates in platelet-like morphology, AFM analysis was performed. AFM image (Fig. 4a) revealed that these thin platelets are built by self-assembly of 2D square structures with 1 µm side. Furthermore, the enlarged AFM image (Fig. 4b) highlights that 2D micrometric square structures are themselves built from the nanoparticles with the height distribution presented in Fig. 4c.

In order to further investigate the optical properties of the 3D flower-like CuB₂O₄ hierarchical structures, UV-visible charcterizations were performed. UV-visible absorption spectrum is shown in Fig. 5a. The CuB₂O₄ exhibits a band absorption edge at 315 nm and an intense absorption peak near 635 nm. The latter peak is associated with the d–d transition absorptions of Cu²⁺ [17].

The optical direct band gap of the CuB₂O₄ was estimated from the equation \((a hv)^2 = A(hv-Eg)\) where a, v, A and Eg are the absorption coefficient, the frequency of light, a constant and the band gap, respectively [18,19]. The optical band gap of the prepared CuB₂O₄ was estimated from the \((a hv)^2 \text{ vs. } hv\) plot to be 3.61 eV (Fig. 5b), which is higher than 3.29 eV reported in earlier studies [6]. The increase in the band gap energy could be explained by the reduction of the crystal-size, also highlighted by AFM analysis.

The Raman spectrum of the prepared CuB₂O₄ (Fig. 6) shows three bands at 298, 344 and 630 cm⁻¹. In accordance with earlier studies, the bands below 800 cm⁻¹ in copper borates are assigned to the bending vibrations of tetrahedral BO₄ groups and vibrations related to Cu–O bond [20].

The Mott-Schottky analysis of the CuB₂O₄ sample is presented in Fig. 7, where the linear part of the curve is extrapolated to \(1/C^2 = 0\) and the values of \(V_{fb}\) are estimated to be 0.505 V vs. SHE. The donor concentration \((N_D)\) was obtained by the Mott-Schottky equation [21]:

\[
\frac{1}{C^2} = \frac{2}{e \cdot \varepsilon_0 \cdot N_D \cdot A^2} \left( V - V_{fb} - \frac{k \cdot T}{e} \right) \tag{1}
\]

where \(C\) represents the capacitance of the space charge.
region, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon$ is the dielectric constant of the CuB$_2$O$_4$, $e$ is the electron charge, $A$ is the surface area of the semiconductor/electrolyte interface, $V$ is the electrode applied potential, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $N_D$ is the donor concentration and $V_{fb}$ is the flat-band potential of the semiconductor. The positive slope of the Mott-Schottky plot confirmed n-type conductivity of the CuB$_2$O$_4$.

According to the M-S relationship, the donor density value ($N_D$) of $9.68 \times 10^{18}$ cm$^{-3}$ was calculated from the slope of the linear region (Fig. 7), assuming that dielectric constant of the CuB$_2$O$_4$ is 6 in the following equation [21]:

$$N_D = \frac{2}{e \cdot \varepsilon \cdot \varepsilon_0} \left[ \frac{d(C^{-2})}{dV} \right]^{-1}$$  \hspace{1cm} (2)

*In situ* XRD patterns, presented in Fig. 8, show the phase evolution of the prepared CuB$_2$O$_4$ in the temperature range from 25 to 600°C in air. The thermal stability of the CuB$_2$O$_4$ compound in air was confirmed in the whole temperature range up to 600°C. In addition, no effect of temperature on the morphology was observed, i.e. the flower-like hierarchical superstructures show high stability even at 600°C (Fig. 9).
specific crystallographic planes. High temperature X-ray mal solution, as a way to minimize energy in the spe-
like morphology are designed by pH of the hydrother-
erarchical self-assembly of micrometer-sized platelets drothermal method. The results revealed that the hi-
like morphology via a one-step low temperature hy-
ronal solution, the di-
strong evidence of the
assembly of micrometer-size square structures based on the coalescence of nanoparticles as building blocks. In accordance with the model proposed by Ribeiro et al. [22], oriented attachment growth occurs by effective collisions between particles with the same orientation in order to minimize the surface energies. Hydrothermal medium provides a very high degree of freedom for rotation and translation motions of dispersed particles and the frequency of the ori-
entended collisions is high.

The formation of the thin platelets by the self-
assembly of micrometer-size square structures followed by their self-assembly in the hierarchical superstructures with the flower-like morphology is proposed as the formation mechanism of these copper borates. Owing to the acid hydrothermal solution, the difference of the surface energy between crystal planes leads to the prefer-
ential growth. But without a theoretical modelling of the surface energy corresponding to each crystal plane, an in-depth study of the formation mechanism is diffi-
cult.

IV. Conclusions

We report for the first time the fabrication of hier-
archically ordered superstructure CuB₂O₄ with flower-
like morphology via a one-step low temperature hy-
thermal method. The results revealed that the hi-
erarchical self-assembly of micrometer-sized platelets producing hierarchical superstructures with the flower-
like morphology are designed by pH of the hydrother-
mal solution, as a way to minimize energy in the spe-
cific crystallographic planes. High temperature X-ray diffraction analysis has revealed a high thermal stability of CuB₂O₄ up to 600 °C. The excellent band gap, high thermal stability and hierarchical structure of the CuB₂O₄ are promising for the photovoltaic and photocatalytic applications.

Acknowledgement: This work was supported by the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI under Grant project number PN-III-P2-2.1-PED-2016-0526, within PNCDI III.

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