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Facile preparation photocatalytically active CuO plate-like nanoparticles from brochantite

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ABSTRACT

The dendrite-like brochantite $Cu_4[SO_4](OH)_6$ microstructures were obtained by facile and cost effective precipitation method for preparation plate-like CuO nanostructures. The thermal stability and morphology of precursor investigated by XRD, TG-DTA and SEM methods. To estimate the thermal stability of precursor the series of brochantite annealing were carried out. According to XRD data above 400 °C CuO is the only product of decomposition of brochantite. XRD, AFM, SEM, UV–vis spectroscopy were employed to characterize the product of brochantite calcination. The CuO is composed of plate-like nanoparticles with a length up to hundreds nanometers and thickness about 30 nm. The investigation of photocatalytic activity shows high activity even in the absence of H_2O_2.

1. Introduction

Nanostructured cupric oxide (CuO) is one of the extensively investigated transition metal oxides because of its impotent functional properties of p-type semiconductor, low cost, abundant resources [1]. CuO nanostructures are promising materials for various applications including materials for solar cells [2], biosensors [3], photodetectors [4], gas sensors [5], photocatalysis [6–9] et al. It is known that important physical and chemical properties of the nanocrystals are strongly dependent on their sizes, shapes and type of structures. Therefore the employment of controlled synthesis of nanostructured material is crucial in the obtaining of materials with predetermined properties. Currently obtained micro- and nanostructures of CuO with different morphology such as nanowires [10], nanorods [11], nanospheres [12], nanowalls [13], nanoribbons [14] and others. Various methods have been suggested to preparation such nanostructures including thermal oxidation [15], electro-deposition [16], hydrothermal treatment [17], quick precipitation [18], sol–gel synthesis [19].

It has been shown that a perspective method of producing metal oxide nanoparticles is the thermal conversion of the precursors. The advantages of this method are the lack of labor-intensive operations of washing and filtration of the final products and high purity product powders. Feature of this method is that the obtained cupric oxide often retains morphological features of calcined precursors [20]. The application of the layered hydroxyl salts as precursors makes it possible to expect the formation of cupric oxide particles with unique morphology. $Cu(OH)_2$ have been used as a precursor for the preparation various forms of CuO nanoparticles [21,22]. The nanorod bundles [23] and sisal-like [24] $Cu(OH)_2$ were obtained by the reaction of the $Cu_2(OH)_3Cl$ precursor with NaOH. CuO interconnected nanosheets were obtained by hydrothermal treatment of $Cu(OH)_2$ nanorod bundles and cupric oxide with a well-preserved morphological feature of the sisal-like $Cu(OH)_2$ precursor was formed through thermal treatment. The $Cu_2(OH)_3NO_3$ were converted to CuO porous nanoribbons [25]. The $Cu_2(OH)_2CO_3$ have been used for preparation CuO peanut-shaped nanoribbons [26] and hierarchical sphere-like structures [27].

In this work dendrite-like brochantite $Cu_4[SO_4](OH)_6$ microstructures were obtained by facile and cost effective precipitation method. The thermal stability and phase transition $Cu_4[SO_4](OH)_6$ precursor was investigated for preparation plate-like CuO nanostructures. The photocatalytic activity of CuO nanostructures for degradation of methyl orange under visible light irradiation was carried out.

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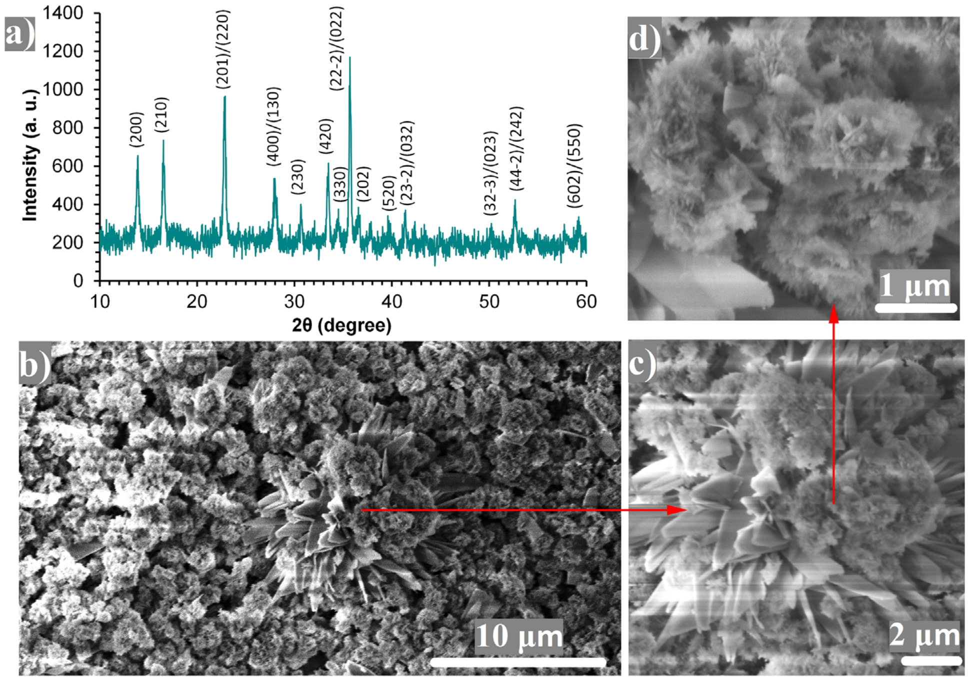

Fig. 1. (a) XRD pattern, (b) low-, (c) and (d) high-magnification SEM images of brochantite.

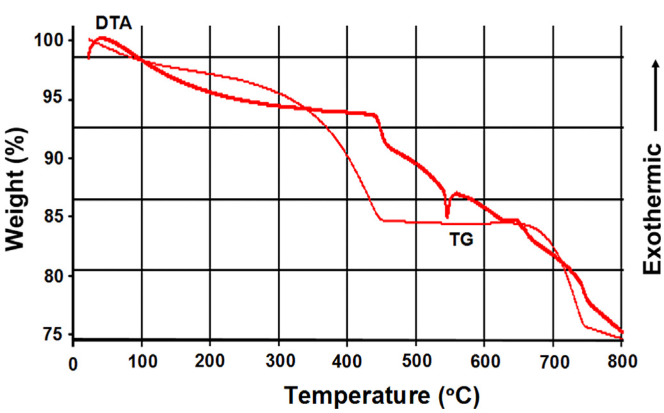

Fig. 2. TG-DTA curves of the brochantite precursor.

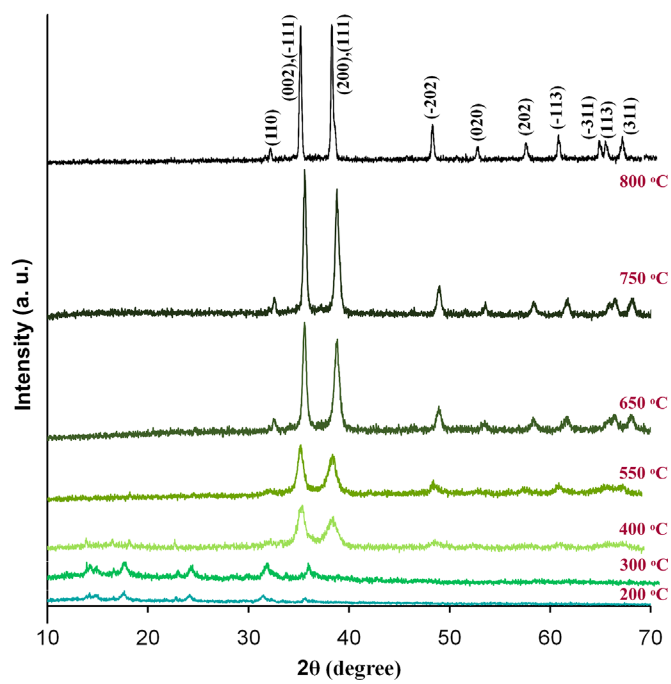

Fig. 3. XRD patterns of the products of brochantite calcination.

2. Experimental

2.1. Materials

Copper (II) sulfate 5-hydrate ($CuSO_4 \cdot 5H_2O$), sodium carbonate (Na_2CO_3) and methyl orange (MO) used in the present study were of analytical reagent grade. All aqueous solutions were prepared using distilled water.

2.2. Synthesis

The dendrite-like microstructures $Cu_4(OH)_6SO_4$ were prepared by simple precipitation method. According to [28,29] pure brochantite formed at 60 °C from $CuSO_4 \cdot 5H_2O$ and Na_2CO_3 solutions at pH 8.0. The 50 ml of sodium carbonate 0.5 M solution was heated to 60 °C and slowly with vigorous stirring 75 ml of copper (II) sulfate 0.5 M solution was added. The obtained green precipitate filtered and washed hot distilled water. The precursor dried at 80 °C for 2 h.

To investigate the optimal conditions for obtaining of copper oxide nanoparticles and the precursor thermal stability the series calcination for 2 h in the temperature range from 200–800 °C were carried out.

2.3. Characterization

The precursor and products of calcination were characterized by means of powder X-ray diffraction (XRD, ARL'Xtra, filtered Cu Kα radiation, $\lambda = 1.5406$ Å), the thermogravimetric-differential thermal analysis (TG-DTA, Elmer Perkin Diamond DTA, in 10 °C min^{-1}, in air atmosphere, from 25 to 800 °C). The morphology were investigated by atomic force microscopy (AFM, Phywe) and scanning electron microscopy (SEM, Tescan Mira).