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An EDTA-assisted hydrothermal synthesis of $BiVO_4$ hollow microspheres and their evolution into nanocages

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Abstract

$BiVO_4$ hollow microspheres have been synthesized in the presence of ethylenediaminetetraacetic acid (EDTA) by a microwave hydrothermal method. The as-prepared hollow microspheres were composed of hundreds of nanorods. Increasing the amount of EDTA produced a new nanocage structure. The evolution process of $BiVO_4$ with different microstructures indicated that the amount of EDTA added played a crucial role in determining the shape of the samples. Additionally, it was found that the existence of EDTA was vital to mediate the crystal growth, and the hydrothermal time and temperature were key parameters in determining the $BiVO_4$ morphologies. A possible formation mechanism is proposed.

Keywords: A. Powders: Chemical preparation; $BiVO_4$; Microwave hydrothermal synthesis

1. Introduction

Bismuth vanadate ($BiVO_4$), a non-titania based photocatalyst, has attracted increasing attention due to its narrow band gap and effective photocatalytic activities for water splitting [1–3] and pollutant decomposing [4–8] under visible-light irradiation. Recently, interest in developing morphologically controllable synthesis of $BiVO_4$ microstructures has been aroused by the recent success in the fabrication of various morphologies, such as nanosheets [7], microtubes [9], dendrites [4,10], and pyramidal-shaped nanowire arrays [11]. As the material's properties hugely depend on its morphology [9,10,12–16], it is of great importance to develop methods for controllable synthesis of desired structures of $BiVO_4$. Until now, various methods have been utilized to prepare $BiVO_4$, among which an additive-assisted solution method has been widely accepted as the most cost-effective and convenient way to prepare some novel morphologies.

Ethylenediamine tetraacetic (EDTA), a chelating agent and surfactant, has been used to synthesize various $BiVO_4$ morphologies. Sun et al. [17] reported that nanoplate-stacked starlike $BiVO_4$ was prepared by a hydrothermal method, using water/ethanol mixture as the solvent and EDTA as a chelating agent. Neves et al. [18] reported that $BiVO_4$ microrectangles were grown on glass substrates via a chemical bath deposition method, in which Bi^{3+} could coordinate with EDTA to form complex [$Bi(EDTA)^-$], avoiding spontaneous precipitation. Therefore, EDTA has great influences on the formation of these unique morphologies.

Herein, hollow microspheres and nanocages self-assembled from $BiVO_4$ nanorods were successfully synthesized by a microwave hydrothermal method, in which EDTA was the chelating agent and assembly reagent. The key to the controllable synthesis was the use of EDTA to mediate the crystal growth, and the morphology evolution was investigated by tailoring the amount of EDTA added. Through time-dependent and temperature-dependent experiments, a possible growth mechanism for the $BiVO_4$ microspheres and nanocages was explored in detail.

2. Experimental

2.1. Preparation of $BiVO_4$ hollow microspheres

For the preparation of hollow spherical $BiVO_4$, a typical experiment was as follows: aqueous solutions of $Bi(NO_3)_3{\cdot}5H_2O$ (5 mmol) and NH_4VO_3 (5 mmol) in 1:1 molar

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ratio were mixed together to get the yellow suspensions. After being stirred for 30 min, and then left to stand, the supernatant was removed. Subsequently, 30 mL H_2O and 1.0 g EDTA were added into the above yellow precipitates and stirred with a magnetic bar for about 30 min. The microwave hydrothermal growth was carried out at 180 °C for 3 h in a 100 mL Teflon-lined autoclave. The equipment that we used to run is MDS-8 closed vessel microwave chemistry workstation. It is manufactured by Shanghai Sineo Microwave Chemistry Technology (China) Co., Ltd. and we mainly use it for microwave digestion. This workstation is suitable for supporting high-strength frame closed reaction vessel with 10 rotors. The temperature and pressure are controlled by high-precision resistance temperature sensor and piezoelectric crystal pressure sensor. After cooling down to room temperature, the samples were taken out and washed with de-ionized water and absolute ethanol several times, and then were dried in vacuum at 60 °C for 12 h.

To confirm the effect of the addition of EDTA on the formation of the structure of $BiVO_4$, the addition of EDTA was varied to 1.5 g and 2.0 g: these produced $BiVO_4$ nanocages. In addition, a comparative experiment without surfactant was also carried out. In order to reveal the formation process and the

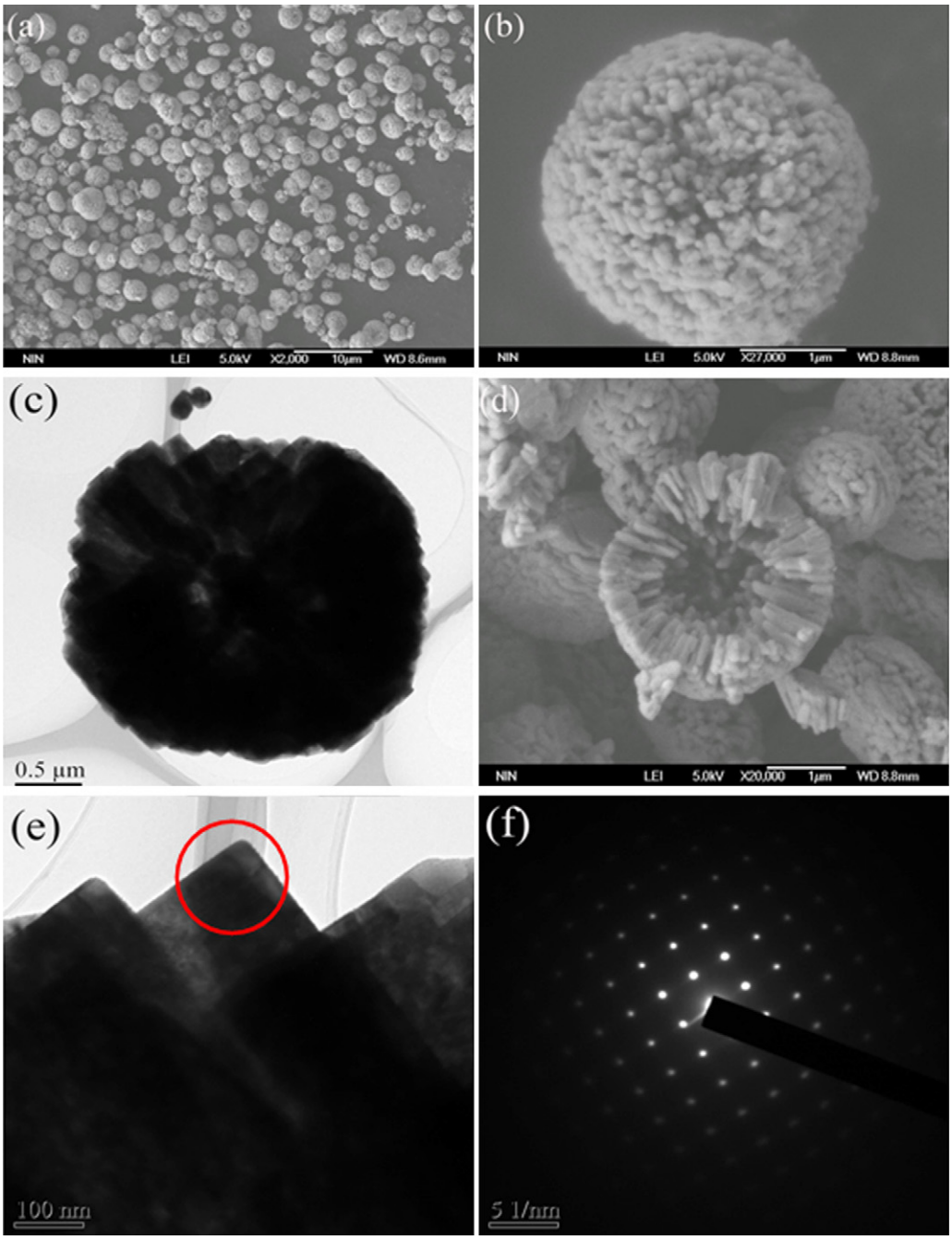

Fig. 1. FE-SEM images of $BiVO_4$ hollow microspheres obtained by the microwave hydrothermal treatment for 3 h at 180 °C with the addition of 1.0 g of EDTA: (a) low-magnification product morphology; (b) detailed view of an individual sphere; (c) high-magnification TEM image of an individual sphere; (d) one cracked sphere, showing the hollow interior structure; (e) HRTEM images of a hollow microsphere; (f) SAED pattern of the marked region.