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Controlled synthesis of $BaWO_4$ hierarchical nanostructures by exploiting oriented attachment in the solution of H_2O and C_2H_5OH

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Shape-controlled synthesis of $BaWO_4$ hierarchical nanostructures has been successfully achieved by exploiting oriented attachment in a mixture of water and ethanol. A controlled change in the volume ratio of C_2H_5OH and H_2O or the concentration of initial reagents has resulted in the synthesis of products of various morphologies, such as shuttle-like, ellipsoid-like, and flower-like ones. The obtained products are characterized by field emission scanning electron microscopy, high-resolution transmission electron microscopy, X-ray powder diffraction, and Fourier transform infrared spectroscopy. The altered nucleation and growth rates of primary particles that assembled to the final hierarchical nanostructures through oriented attachment are the main cause of the evolution of their morphologies. The room-temperature photoluminescent intensities of the products strongly depend on their morphology.

1. Introduction

Much effort has been devoted to the design of the hierarchical nanostructures because of their physicochemical properties and their potential applications in optics, electronics, magnetics, and

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biology [1,2]. Rational control of variables such as shape, phase, and size, is of importance in that they largely determine the properties of the hierarchical nanostructures [3,4]. Currently, the oriented attachment approach is one of the most frequently used research methods in nanotechnology [5–7] because most hierarchical nanostructures are formed by oriented attachment of their primary particles [5,8,9]. Much effort has been devoted to the synthesis of hierarchical nanostructures such as 2D rice-like PbS [5], ellipsoid-like, leaf-like, and butterfly-like CuO [9–11], rice-like α-Fe_2O_3 [12], flower-like $CaMoO_4$, $SrMoO_4$, and ZnO [13,14]. However, the above-mentioned cases demand intricate steps, high temperature or surfactants as templates introduce impurities in the final products.

Synthesis of nanomaterials in an ethanol–water mixture is an ideal low-cost process [15–18]. Compared with the reactions in pure water, the nucleation rate increases [17], hence, rapidly forming early-stage primary nanoparticles and promoting their subsequent epitaxial attachment [15]. In addition, primary particles can form the final products in the direction of their growth habit in pure water by oriented attachment [15] for water has strong polarity in the mixture. Therefore, hierarchical nanostructures can be obtained in the C_2H_5OH–H_2O system.

Scheelite-type $BaWO_4$, an important optoelectronic material, has been intensely studied for its competence in luminescence [19] and its strong potential applications in nuclear-spin optical hole burning hosts [20], photocatalysts [21], stimulated Raman scattering [22], and all-solid-state lasers [23]. Therefore, the synthesis of $BaWO_4$ hierarchical nanostructures with improved application efficiency is a necessity. Various morphologies of $BaWO_4$ hierarchical nanostructures such as layer-like, sheaf-like, corn-like, double-taper-like, scissor-like, fasciculus-like, peanut-like, kernel-like, bow-knot-like, and peniform-like forms, have been successfully synthesized by some solution-phase routes [12,24–29]. However, little effort has been made in the synthesis of $BaWO_4$ hierarchical nanostructures in C_2H_5OH–H_2O mixtures.

In a previous study, shuttle-like $BaWO_4$ hierarchical nanostructures were synthesized in a C_2H_5OH–H_2O system. In the present work, a novel flower-like $BaWO_4$ hierarchical nanostructure was synthesized at room temperature using the same approach. Moreover, a detailed investigation of the nucleation, growth, and epitaxial attachment of the primary $BaWO_4$ nanoparticles in the C_2H_5OH–H_2O mixture was undertaken. The relation between the photoluminescence (PL) intensities and the morphologies of the different products was also studied.

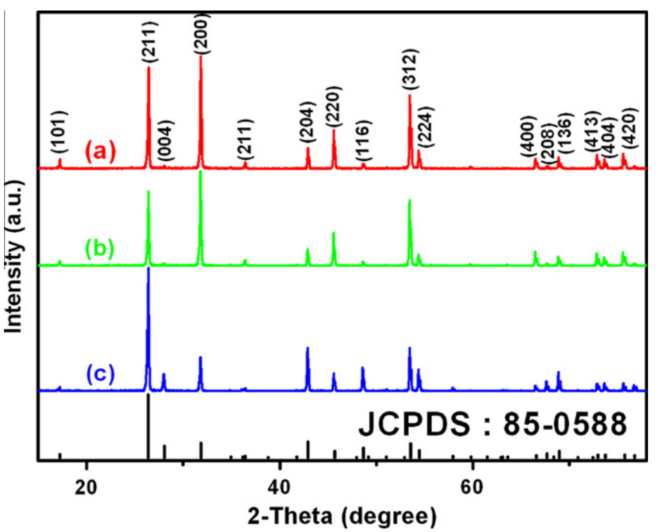

Fig. 1. XRD patterns of $BaWO_4$ nanostructures synthesized at three different initial concentrations (from (a) to (c): $C_{Ba^{2+}} = C_{WO_4^{2-}}$ is 12.5, 7.5, and 1.5 mM, respectively) and kept the volume ratio of C_2H_5OH to H_2O at 1:5.