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The self-assembly mechanism of $CaWO_4$@$CaWO_4$:Dy^{3+} core/shell microspheres via a simple surfactant-free hydrothermal route

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ABSTRACT

In this work, we reported the fabrication and characterization of $CaWO_4$@$CaWO_4$:Dy^{3+} core/shell microspheres via a facile hydrothermal method without organic surfactant. The samples were characterized by XRD, SEM, EDS and photoluminescence. These core/shell microspheres were constructed by nanoparticles through a self-assembly way without any organic surfactant or template. The solid and hollow microspheres prepared through positive and reverse precipitation respectively were used as the precursor. The reduction of the surface energy and high temperature in the hydrothermal process provided the kinetics and thermodynamics motion of the self-assembly course respectively. The direct doped $CaWO_4$:Dy^{3+} and $CaWO_4$@$CaWO_4$:Dy^{3+} (core–shell) microspheres show characteristic emission of Dy^{3+}. The luminescent intensity of the core/shell phosphor was enhanced with respect to the direct doped one of the same doping concentration. The possible mechanism was also proposed.

1. Introduction

The fabrication of complex three-dimensional hierarchical structures self-assembled by nanoscale building blocks are of significant interest in materials. Among them, core/shell structures have a wide range of applications in photoluminescence, sensing and catalysis due to the variable interior structure, surface functionality and strong correlation existing among core–shell [1–4]. For the fabrication of core/shell structure materials, most of these studies use epitaxial growth to get these unique structure [2,3], or concentrated on the organic additives (e.g., coordinate agent, structure-directing agent or template [1,4]) to the conducted the crystal growth. Little intension was paid to self-assembly and its important role in the crystal growth process [5].

$CaWO_4$ is one of the most important compounds for its self-activated intriguing luminescent properties and used as host materials for rare earth doped phosphor. Recently, fascinating $CaWO_4$ nano/microstructures with various morphologies, including nanocrystals [6], microspheres [7], hollow microspheres [8] and core–shell structure [4] have been successfully fabricated. Moreover, the formation of the morphologies or structures of these studies was attributed to the template effects of organic surfactants. The role of self-assembly and its mechanism have drawn little attention. Hydrothermal is a common solution-based method to prepare a wide range of micro/nanostructures having diverse shape and sizes [9,10]. Herein, we reported a novel template-free and surfactant-free facile hydrothermal method to synthesis the core/shell $CaWO_4$@$CaWO_4$:Dy^{3+} microspheres. Dy^{3+} ions were used as a probe to test the proposed self-assembly mechanism and the morphologies, structure, and self-assembly mechanism of these core/shell structure are investigated.

2. Experimental

$Ca(NO_3)_2 \cdot 4H_2O$ (AR), $Na_2WO_4 \cdot 2H_2O$ (AR) and $Dy(NO_3)_3 \cdot 4H_2O$ (4 N) were used as starting materials. The core/shell structure was prepared by three steps. Step 1, stoichiometric weighted $Na_2WO_4 \cdot 2H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ were dissolved in deionized water separately with stirring. Then, Na_2WO_4 solution was dropped into $Ca(NO_3)_2$ solution slowly under continuous stirring, i.e. in a positive precipitation route. Step 2, as same as step 1, except for this time $Dy(NO_3)_3$ was dissolved with $Ca(NO_3)_2$ together and this solution was dropped into Na_2WO_4 solution, i.e. in a reverse precipitation route. Step 3, the suspension prepared in step 1 and step 2 were transferred together into a Teflon-lined stainless steel autoclave and maintained at 180 °C for 12 h. In the precipitation process of step 1 and 2, white precipitate was immediately

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observed. Some of these precipitate was preserved and separated, washed and dried together with the final products. Part of the samples was kept for further characterization: XRD, SEM and photoluminescence, while the other part was embed in epoxy resin and fine polished in order to observe its inside structures. Different doping concentration $CaWO_4$:Dy^{3+} phosphors were also synthesized via the same hydrothermal route for compare.

The powder X-ray diffraction data were acquired in the range of $10° < 2\theta < 80°$ by a diffractometer (XRD-7000, Shimadzu Limited) with Cu$K\alpha$ radiation. The morphology and particle size of the powders were characterized by scanning electron microscopy (JEOL, Model JSM-6700F). Photoluminescence spectra were measured by F920 Fluorescence Spectrophotometer (Edinburgh Instruments) at room temperature.

3. Result and discussion

The X-ray powder diffraction patterns of undoped $CaWO_4$, $CaWO_4$ doped with different Dy^{3+} concentrations and $CaWO_4$@$CaWO_4$:0.10Dy^{3+} core/shell structure are showed in Fig. 1a. All XRD patterns match well with the standard PDF card (no. 41-1431) without any impurity. Based on the half-height width of (101), (112), (200) and (204) peaks, the mean crystallite sizes for all samples were calculated to be 50, 46, 43, 36, 18 and 22 nm using the Scherrer formula. It can be seen that with increasing doping concentration, the crystallite size decreased gradually. This suggests that the doping of Dy^{3+} will lead to an inhibition of grain growth. The difference of ionic radius between Dy^{3+} (1.167 Å for CN=8) and Ca^{2+} (1.12 Å for CN=8) results in the breaking of crystal long-range order, thereby hinders the crystal

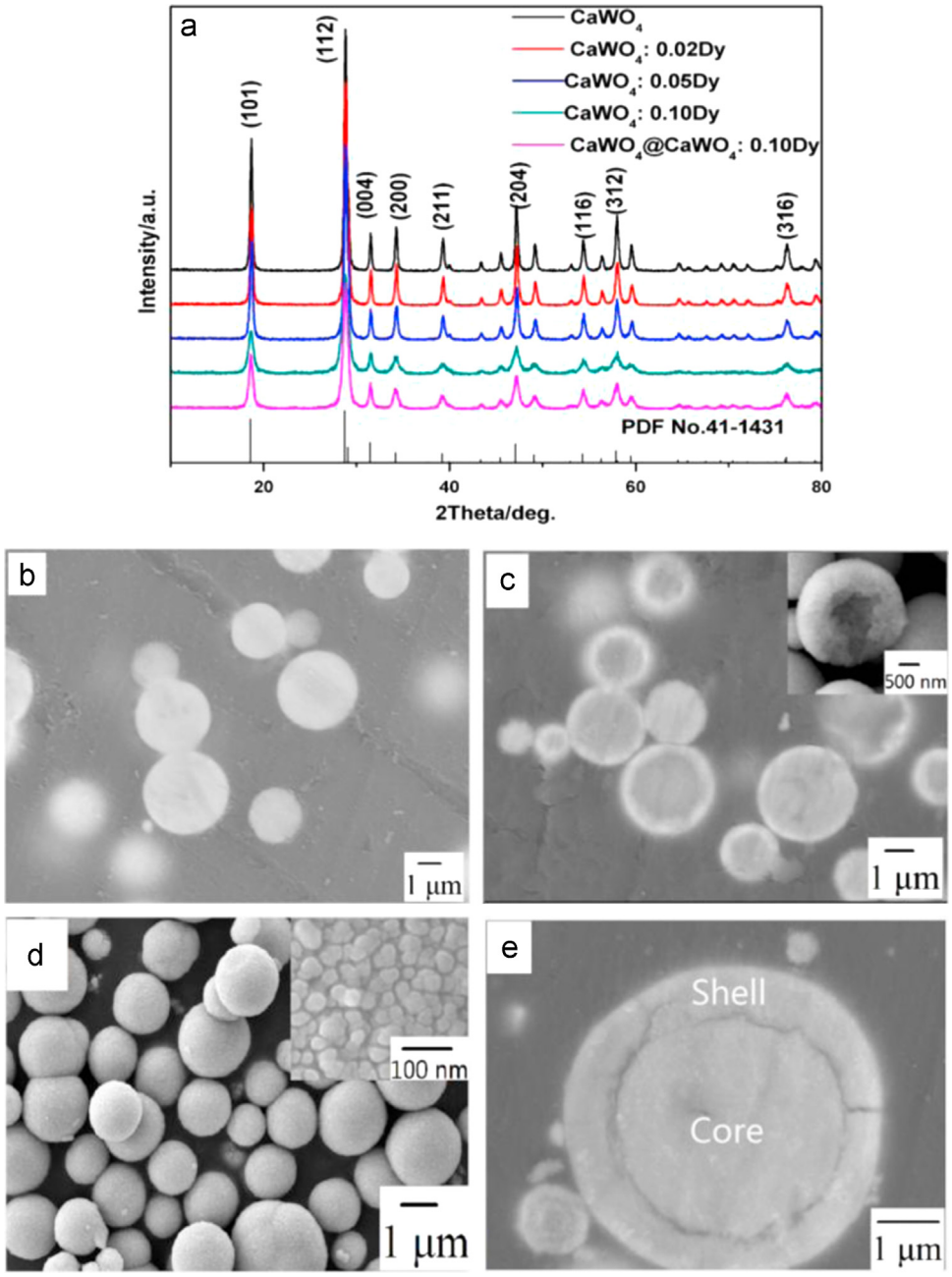

Fig. 1. (a) XRD patterns; cross section SEM images of (b) solid microsphere; (c) hollow microsphere (e) core/shell microsphere; (d) distribution of core/shell microsphere.