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Full Length Article

Strong blue emission from zinc hydroxide carbonate nanosheets

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ABSTRACT

Zinc hydroxide carbonate (ZHC) is a typical layered salt composed of zinc hydroxide layers separated with carbonate ions and water molecules. Studies of morphology control and the constitution of functional ZHC material with intercalated ions has been widely developed. Also, ZnO can be easily obtained by anneal treatment of ZHC, and the porous structure as synthesized had great potential in gas sensors, photocatalysts and dye-sensitized solar cells. However, the optical of ZHC have rarely been investigated. In our research, a strong blue emission of ZHC is reported. The effect of growth time, annealing treatment and modification of surfactants on blue emission have been systematically studied. Combined with information of interior effect of OH groups, crystal structure and electronegativity of surfactants, a possible emission mechanism of ZHC has been proposed.

1. Introduction

Zinc hydroxide carbonate (ZHC) is a typical layered salt composed of zinc hydroxide layers separated with carbonate ions and water molecules [1]. It is usually obtained by the reaction of zinc salts with ammonia-releasing reagents, e.g. urea, under supercritical conditions [2–4]. ZHC is regarded as a promising material for many applications [5–7]. For example, because of the weak force between the zinc hydroxide layers, ZHC can be intercalated with different anions by ion-exchange, and used for separating isomers in a mixture [8]. On the other hand, the intercalated ions can confer different characteristics to the matrices thus leading to a functional material for optical, electrical and magnetic applications [5–7]. Moreover, the hydrophobic surface of ZHC endows it with a good anti-corrosion property [9].

Thus far, studies of ZHC have been focused on the morphology control (such as microspheres, nanosheets, or nanoflowers) [4,10]. and its application in surface modification of metal substrates [2]. Particularly, it was found that ZHC could transform facilely into zinc oxide by calcinations. [11–13], which retained the shape of ZHC precursor and owned a porous structure [14]. Accordingly, many attempts have been made to utilize the transformed ZnO nanostructures in gas sensors [10], photocatalysts [15,16], and dye-sensitized solar cells (DSSCs) [14,17]. However, the optical of ZHC have rarely been investigated. In our research, it is found that ZHC has a strong blue emission with a PL peak at 450 nm. In order to explore the blue emission origin in ZHC, the effect of growth time, annealing treatment, precursor species and modification of surfactants on blue emission have been investigated. Based on these knowledge, A possible emission mechanism of ZHC has been proposed.

2. Experimental

Growth of ZHC was carried out by using a hydrothermal method in a Teflon-lined autoclave, where the substrate was immersed slantways into an aqueous solution of 0.1 M zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 1.5 M urea in 35 ml distilled water. The autoclave was sealed, heated at 80 °C for certain hours, and then cooled in air. Afterwards, the substrate was taken out of the solution, rinsed with distilled water and dried at 90 °C for subsequent characterizations. For contrast experiment, $ZnSO_4$, $ZnCl_2$ and $Zn(CH_3COOH)_2$ with the same concentration were used instead of $Zn(NO_3)_2$ to reveal the effect of Zinc precursors. 0.1 M/l surfactants such as PVP, CTAB, AOT and SDBS were added separately into the synthetic process with other parameters unchanged for exploration of surfactants.

The X-ray diffraction (XRD) for crystal structure was carried out in Bruker D8 advance diffractometer. The morphology was observed by using a Hitach-S4800 scanning electron microscopy (SEM) with an energy-dispersive X-ray spectroscopy (EDS) unit. Transmission electron microscopic (TEM) observation was performed in a FEI Technai G2 F20 microscope with a field-emission gun operating at 200 kV. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured by a Hitachi F4500 fluorescence spectrometer. Time resolved photoluminescence analyses were performed with an Edinburgh FLS920

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fluorescence spectrometer at room temperature. The optical and fluorescent images were taken by using an Olympus BX51 fluorescence microscope. A Perkin-Elmer 7 analyzer was employed to make thermogravimetric analysis (TGA) measurement at a heating rate of 10 °C/min in nitrogen. X-ray photoelectron spectroscopy (XPS) studies were conducted on Perkin-Elmer PHI 1600 ESCA system with a monochromatic Mg Kα X-ray source ($h\nu = 1486.6$ eV) and a charge neutralizer.

3. Results

The top-view SEM image in Fig. 1a shows that the product consist of uniform nanosheets grow vertically on the substrate of FTO, and are about 10μm from the side view. XRD result in Fig. 1b reveal that all diffraction peaks agree well with $Zn_4(CO_3)(OH)_6.H_2O$ (JCPDS card no 11-0287). When observed with fluorescence microscope, strong blue emission can be seen with eye from the whole ZHC products. PL spectra showed that the emission peak is located at 450 nm, while the optimal excitation wavelength was located at 250 nm (Fig. 1c). To further understand the origin of the blue emission, we investigate its decay kinetics. As shown in Fig. 1d, the decay profile is fitted with two decay components of 50.98 ns (0.98%) and 677.81 ns (99.02%), which gives an average decay time of 671.6 ns. Such a long decay time suggests a defect-related emission rather than an intrinsic interband emission which usually shows an ultra-short decay life (several nanoseconds) [18,19]. Based on the above decay kinetics analysis, we exclude the possibility of emission from organics. The XPS measurement of ZHC shown in Fig. S1 showed that only Zn, O, and C exist in the product and no obvious impurity is detected.

3.1. The effect of growth time on optical property of ZHC

For further understanding of the blue emission in ZHC, we first investigate on the growth process and related emission property of ZHC

As revealed in Fig. 2, when the reaction time is below 4 h, no macroscopic product is formed. At reaction time of 1 h (Fig. 2a), SEM observation showed that primary ZHC nanostructure consisted by different numbers of nanosheets grow on the substrate of FTO sparsely. With the increasing reaction time, the growth and new nucleation of the nanosheets lead to the formation of nanoflowers. (Fig. 2b and c). When the reaction time is prolonged to 5 h (Fig. 2d), a thin white film constituted by well-formed nanoflowers came into being, but there are still some space between individual nanoflowers.

After further growth of the nanoflowers to 6 h, the profile of flower disappeared, and only uniform planes can be seen (Fig. 2e). The cross section image show clearly that the planes have a thickness of 10 μm (inset of Fig. 2e). At reaction time of 7 h, when nanosheets collide with each other and resistance will finally lead to the cease of the growth of nanosheets (Fig. 2f). New nucleation will go on the top of the as-formed compact film, and through the same growth habit, a second ZHC film with similar thickness formed on top of the first film (inset of Fig. 2f).

We measured the UV and PL spectra of samples obtained at 5 h, 6 h, and 7 h as shown in Fig. 3. All ZHC samples at different reaction times showed an obvious absorbance peak at wavelength of 230 nm. The corresponding PL spectrum in Fig. 3b exhibits a blue emission band centered at 450 nm. When reaction time increase from 5 h to 6 h, the emission strength showed a little enhancement, further prolongation of reaction time had no

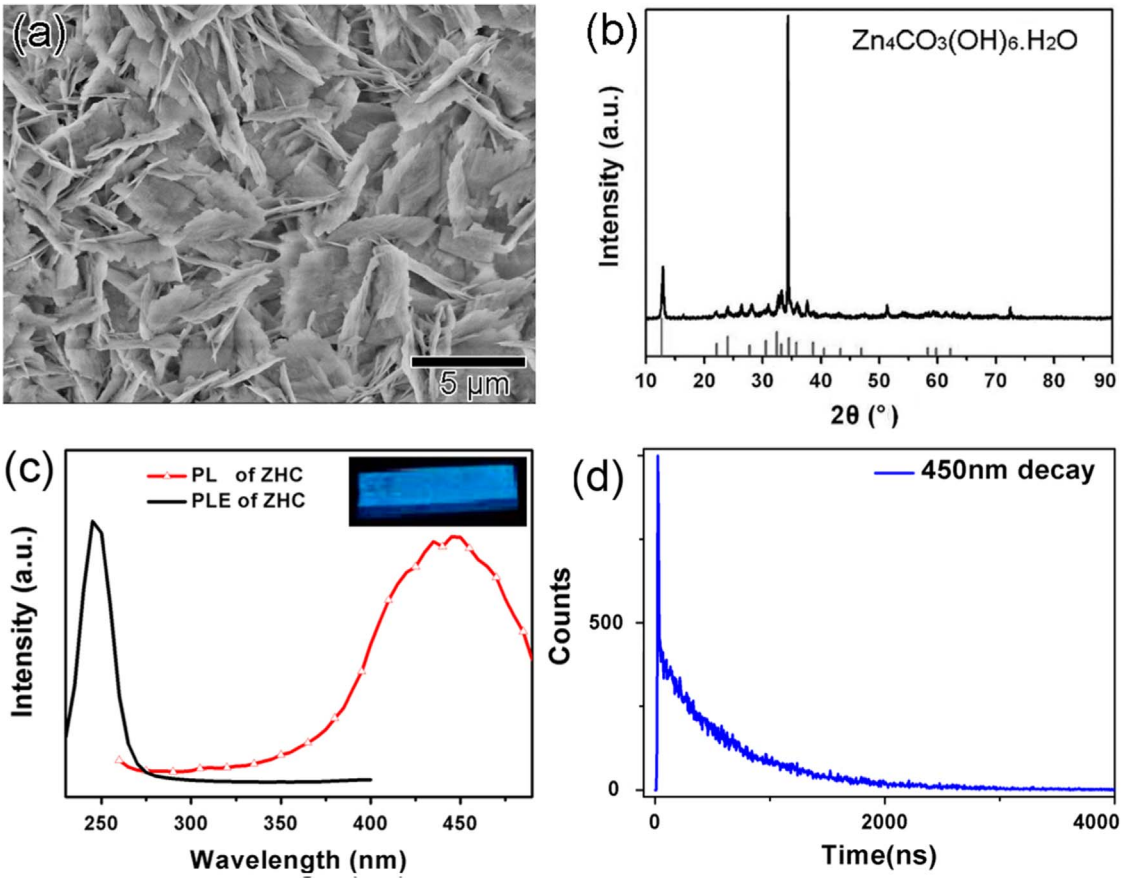

Fig. 1 (a). SEM image (b) XRD profile (c) PL and PLE spectra and (d) decay profile at PL wavelength of 450 nm of ZHC nanosheets; the inset of (c) show the fluorescence microscope image of obtained ZHC on FTO.