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Preparation of luminescent layered zirconium phosphate nanocomposites by the layer-by-layer technique

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ABSTRACT

In the present work, photoactive cation N, N′-Dimenthyl-9, 9'-bisacridinium nitrate (BNMA) was assembled with exfoliated layered α-zirconium phosphate (α-ZrP) via an electrostatic layer-by-layer (LBL) assembly method. As a result, the luminescent films which were well-aligned and periodical had been successfully fabricated. Surprisingly, the lifetimes of $(BNMA/ZrP)_n$ were found to be prolonged by 16-fold for the first time, due to the isolation effect of inorganic nanosheets and hydrogen ion migration between the interlayers. Therefore, it is testified that α-ZrP can be used as the laminate and has remarkable influences on enhancing the lifetimes of chromophores. We expect that this new discovered effect can enable α-ZrP a kind of new potential material to develop novel light-emitting materials and optical devices.

1. Introduction

Layered materials present a broad prospect because of their unique stratified structure and excellent physicochemical properties. They could change the physical and chemical properties including electricity, optics and magnetics of materials at low temperatures [1–4]. Therefore, layered materials have a wide range of applications in heterogeneous catalysis [5,6], non-linear optics [7,8] and energy storage [9], *etc*.

When the interlayer spacing of the layered compound expands indefinitely, laminas will be separated. This kind of reaction is of great importance to layered compound. And as a separate dynamics tabular grains, each layer disperses into the solution to form colloidal solution. Compared with intercalation, this exfoliation approach may not consider the interlayer distance so that it is applicable for molecules of different size [10,11]. And it can be used to assemble a larger host molecules, producing new film materials and organic/inorganic hybrid materials [12]. Layer by layer self-assembly method [13,14] is one of the most important ways for preparing film materials. In recent years, lots of people prepared film materials with good performance by it. For example, Kim [15] prepared nanoscale carrier copolymer capsules of hydrophobic drugs by method of LBL. These capsules can be quickly decomposed and released under physiological conditions because hydrogen bonds are sensitive to acidic environment. Sum [16] assembled PDDA and sodium silicate by LBL on the substrate covered with silicon sphere and got super-hydrophobic materials after fluoridation.

As a kind of important layered compound, α-ZrP [17,18] is easy to prepare with good crystal form and chemical stability. The proton hydrogen in the hydroxyl of the interlamination is easy to be transmitted and, as a result, the laminate is negatively charged [19] (Fig. 1). Once the fluorescent material is placed in the interlayer of α-ZrP, the limited space and negative charge will definitely change the microenvironment of the chromophore. It can help reduce the collision probability between the fluorescent molecules so that it could reduce energy loss and improve the luminous efficiency of the fluorescent molecules [20]. The limited space between layers is helpful to control the orientation of chromophore which is also related to luminescent properties [21]. What's more, it is highly expected that the electronic microenvironment due to the proton transfer could play an important role of the effects on chromophore.

With their rapidly development, fluorescent film materials give rise to many possible applications in optical devices [22–24], chemical sensors [25,26], *etc*. This kind of materials have wide

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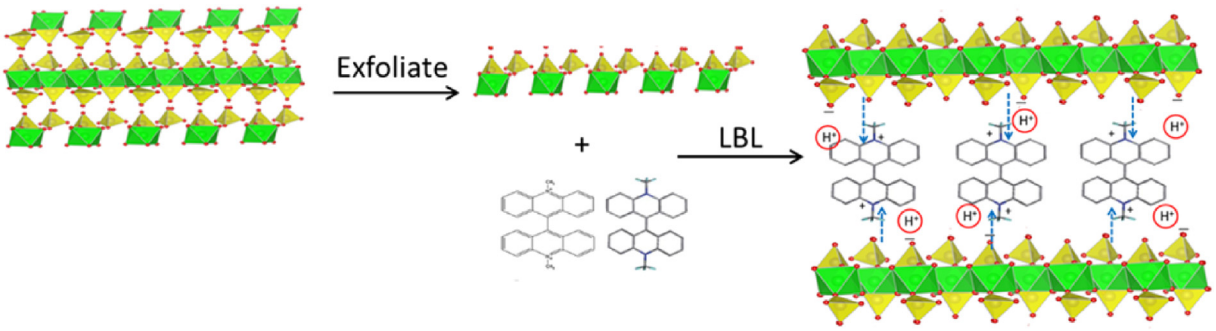

Fig. 1. Schematic of N, N′-Dimenthyl-9, 9'-bisacridinium nitrate (BNMA) in electronic microenvironment between α-ZrP layers.

prospects for their extensive sources, high luminescence quantum efficiency and being easily manufactured in a large scale [27]. But there are many disadvantages for fluorescent film materials. They have poor thermal stability, short service life and are prone to aging [28]. What's more, it is difficult to obtain the regular and order films in the traditional process so that the fluorescence efficiencies of the materials are always reduced. Recent years, our group reported for the first time that oppositely-charged nanosheets (constructed with exfoliated LDHs and MMT laminas) were expected to form a nanoscale capacitor providing an electronic microenvironment for chromophores [29,30], which can dramatically lengthen the lifetimes of chromophore. The results demonstrate that the specific laminates have remarkable effects on the as-fabricated fluorescent membrane materials. As a kind of important stratified material, we aim to explore whether α-ZrP which had the characteristic of proton transfer could be used to prepare a new type of fluorescent ultrathin film materials.

In this work, we prepared α-ZrP using direct precipitation method, and then layered α-ZrP was peeled into nano layers with stripping agent–propylamine. Layered α-ZrP with negative charge is assembled with the positively charged BNMA by electrostatic force using LBL technique. After that, the fluorescent properties are discussed in detail.

2. Experimental section

2.1. Synthesis of α-ZrP nanosheets

α-ZrP powder was prepared following procedures reported in previous paper [16]. 5.50 g $ZrOCl_2 \cdot 8H_2O$ was dissolved in 80 mL distilled H_2O. Then 5 mL 37% HCl, 5 mL 40% HF and 46 mL 85% H_3PO_4 was slowly and successively added into the resultant solution. The mixture was kept under stirring at room temperature for 4 days. After reaction, the mixture was centrifuged and washed with distilled water repeatedly until pH = 5. The solid powder was then dried at 60 °C.

The method of α-ZrP exfoliation was following the procedures described previously [31]. 1.5 g α-ZrP was dissolved in 125 mL distilled H_2O. Then 27 mL aqueous solution of propylamine (0.12 mol L^{-1}) was added to the solution. The mixture was kept under stirring at room temperature for 4 days and then centrifuged. The obtained supernatant was ZrP nanosheets.

2.2. Assembly of α-ZrP/BNMA multilayer films

The glass slides was immersed in acetone, ethyl alcohol and H_2SO_4/H_2O_2 (7/3 v/v) solution successively for ultrasonic cleaning. And it was washed by distilled water after each completed step.

The BNMA aqueous solution was obtained by dissolving 0.0176 g BNMA in 100 mL distilled water. To obtain each bilayer, the glass was firstly immersed in α-ZrP aqueous solution for 10 min. After being washed by distilled water for 1 min, the glass was dried with nitrogen. Then put the glass in BNMA aqueous solution for 10 min and washed it using the method mentioned above. The same procedure was repeated for different times to get the wanted multilayer films.

2.3. Characterization

X-ray diffraction (XRD) analyses were carried out using a Shimadzu XRD-6000 diffractometer with Lynxeye detector and monochromated Cu Kα radiation. Infrared Spectroscopy (IR) was recorded on a Spectrum 100 Fourier Transform Infrared Spectrometer. UV—visible spectroscopy (UV) was recorded on a TU-1901 Double beam UV—vis spectrophotometer with bromine-tungsten lamp and deuterium lamp. Fluorescence spectra were recorded on F-4600 Fluorospectrophotometer whose resolution ratio was 1.0 nm. Fluorescent lifetime was recorded by Edinburgh FSL-920 steady and transient time-resolved fluorescence spectrometer and the probe laser wavelength was 375 nm.

3. Results and discussion

The microstructure of zirconium phosphate materials was evaluated by the analysis of the XRD patterns of α-ZrP. The XRD pattern of α-ZrP (Fig. 2) shows diffraction peaks at 2θ = 11.7°, 19.76°

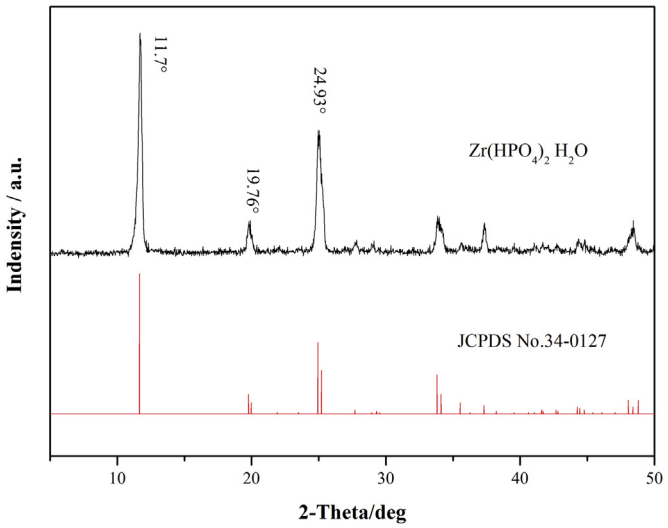

Fig. 2. XRD patterns of α-ZrP.