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Room-temperature solid-state synthesis and fluorescence performance of 8-hydroxyquinoline-based nanomaterial complexes with different morphology

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ABSTRACT

Three main-chain 8-hydroxyquinoline-based metallocomplexes (aluminium(III) tri-(8-hydroxyquinoline) (AlQ_3), cadmium (II) bis-(8-hydroxyquinoline) monohydrate ($CdQ_2{\cdot}H_2O$), and magnesium(II) bis-(8-hydroxyquinoline) tetrahydrate ($MgQ_2{\cdot}4H_2O$)) nanomaterials were prepared by room-temperature solid-state reaction technique. The results of X-ray diffraction (XRD), elemental analyses (EA), fourier transform infrared (FTIR) spectroscopy and thermogravimetric/differential scanning calorimetry (TG/DSC) analysis demonstrated that the chemical composition of the products were AlQ_3, $CdQ_2{\cdot}H_2O$, and $MgQ_2{\cdot}4H_2O$, respectively. The field emission scanning electron microscopy (FESEM) images and the transmission electron microscopy (TEM) images showed the morphology of AlQ_3 nanoshuttles, $CdQ_2{\cdot}H_2O$ nanorods, and $MgQ_2{\cdot}4H_2O$ nanosheets, respectively. The UV–vis absorption spectra indicated that they existed charge transfer from the metal to the ligand (MLCT bands). The photoluminescence (PL) spectra revealed that three products displayed efficient and intense photoluminescence in yellow-green, deep-green and blue-green emissions region in the state of solid powder. PL intensity was weaker at different degree in chloroform, dimethylformamide, acetone and acetonitrile solutions, which attribute to solvate effect. The fluorescence quantum yields indicated that this metal complex materials can possibly act as functional composites to be used in optoelectronic devices, such as organic light-emitting diodes and fluorescent sensor.

1. Introduction

In the past few years, multi-dimension nanomaterials including sheets, tubes, rods, and belts have attracted extensive investigations, owing to their unique prospective applications in nanoscale devices. Most of researches have focused on inorganic materials [1,2]. Recently, metal organic complex (MOC) nanomaterials have attracted tremendous interests for application in functional nanoscale optoelectronic devices. The crystallinity and molecular arrangement of MOC nanomaterials have a great influence on the performance of these devices [3–5]. There were some reports on MOC nanoparticles prepared by various methods, such as reprecipitation, microemulsion and thermal evaporation [6,7]. But multi-dimensional MOC nanomaterials have been paid much less attention. Therefore, the development of a facile and mild approach for the fabrication of multi-dimensional MOC nanostructures is desired for the synthesis and application of nanomaterials.

Since the first efficient low-voltage-driven organic light-emitting diodes (OLEDs) based on aluminium tris(8-hydroxyquinoline) (AlQ_3) were reported by Tang and VanSlyke [8], AlQ_3 has become a important prototypical electron transport and emitting material for OLED devices because of its excellent stability and electroluminescence properties. From then on, 8-hydroxyquinolinemetal complex nanomaterials were studied extensively from various practical angles due to their distinctive characteristics originating from their small size, shape anisotropy, unique structures, and novel properties, which make them promising candidates for various devices, such as fluorescent sensor and metal ion detector [9–16]. The mainly synthetic strategies are divided into three categories, which include vapor phase growth, solution phase growth, and self-assembly growth [17–20]. However, to the best of our knowledge, the control of the uniformity of the products is always the bottleneck for most of the existing strategies for preparing multi-dimensional MOC nanomaterials.

Room-temperature solid-state synthesis is a facile and feasible method for preparing nanomaterials, and has achieved some success in fabricating inorganic materials [21–24], which due to one-step synthesis, low consumption, environmental protection, low cost, and so on. Herein, this method was developed to fabricate metallorganic nanomaterials, which will open up a new approach for our research. Some 8-hydroxyquinolinemetal complex nanomaterials have been synthesized,

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and the fluorescence properties were also investigated in detail.

2. Experimental section

2.1. Materials

All the reagents in this work, including aluminium chloride, cadmiumacetate, magnesium acetate, sodium hydroxide, 8-hydroxyquinoline (HQ), N,N-dimethylformam (DMF), chloroform, acetone, and acetonitrile were of analytical reagent grade, and were used without further purification.

2.2. Synthesis

2.2.1. AlQ_3

Solid aluminium chloride, sodium hydroxide and HQ with a molar ratio (1:3:3) were apart weighed and ground in an agate mortar for about 5 min to ensure the evenness of starting materials. Firstly sodium hydroxide was added into aluminium acetate and ground for about 5 min. Due to moisture absorption of sodium hydroxide, it was used immediately once it was weighed. Then HQ was added into the mixture and ground until an hour. Finally, the mixture was washed with distilled water and ethanol for a certain time respectively to remove starting materials. The product was naturally dried in air, then AlQ_3 nanocomplex was successfully obtained.

2.2.2. $CdQ_2{\cdot}H_2O$ and $MgQ_2{\cdot}4H_2O$

Solid cadmium acetate or magnesium acetate, and HQ with a different ligand-to-metal molar ratio (L/M = 2 depending on the metal center) were apart weighed and ground in an agate mortar for about 5 min to ensure the evenness of starting materials, then mixed. They produced ethanoic acid. The mixture was ground for an hour. Finally, the mixture was washed with distilled water and ethanol for a certain time to remove the starting materials. The product was naturally dried in air, then $CdQ_2{\cdot}H_2O$ and $MgQ_2{\cdot}4H_2O$ nanocomplexes were successfully obtained.

2.3. Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 advance X-ray diffractometer using Cu-Kα radiation (1.5418 Å), in which the X-ray tube was operated at 40 kV and 40 mA, a scanning rate of 0.1°/s was applied to record the patterns in the 2θ range of 5–80°. Thermal analysis (TG/DSC) were performed with NETZSCH STA 449 F3 Jupiter thermogravimetric analyzer (Germany) in nitrogen atmosphere at a heating rate of 20 °C/min from room temperature to 900 °C. The elemental analyses were made on FLASH EA 1112 Series NCHS–O analyzer. The Fourier transform infrared spectrum (FTIR) was recorded using Perkin Elmer spectrophotometer in the range of 400–4000 cm^{-1}. The size and morphology of the products were studied by S-4800 field emission scanning electron microscopy. The TEM images were measured on a Hitachi H-600 transmission electron microscopy. The UV–visible absorption spectra were performed with HITACHI U-3900H spectrophotometer. The steady-state fluorescence spectra were obtained on a Hitachi F-4500 (Tokyo, Japan) spectrofluorometer with a quartz cell and a high-pressure xenon lamp as the light source. The fluorescence measurements were done by excitation at the absorption maximum. The fluorescence quantum yields were measured on Fluorolog®−3 (HORIBA Jobin Yvon Inc) spectrofluorometer, on which Quanta-4 F-3029 Integrating Sphere (HORIBA Jobin Yvon Inc) was installed. All the counting progress of Abs error and relative error is automatically performed by the work station of Quanta-4 F-3029. The particular counting progress was shown in the supporting information of this paper.

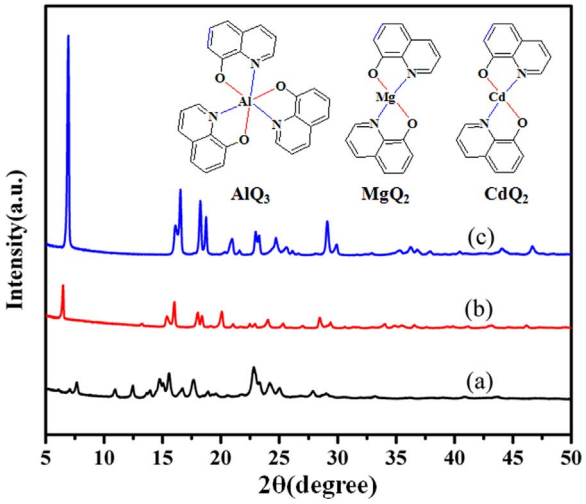

Fig. 1. XRD patterns of solid powder: (a) AlQ_3, (b) $CdQ_2{\cdot}H_2O$ and (c) $MgQ_2{\cdot}4H_2O$.

3. Results and discussion

XRD experiment was performed to investigate the structure of the AlQ_3 in Fig. 1(a). All the peaks in the pattern can confirm that the product was consisted of pure AlQ_3. It was found that all the peaks in the XRD pattern of the product could be indexed well by the simulated pattern of α-phase AlQ_3 obtained by Masciochi and co-workers (CCDC Ref. code: QATMON01) [25]. Furthermore, the pattern of the product was distinctively different from those simulated value from other known AlQ_3 phases, such as the β, γ and δ phases. Therefore, the XRD pattern supported that AlQ_3 had the α-phase structure. Besides, Fig. 1(b) showed the XRD pattern of the synthesized $CdQ_2{\cdot}H_2O$. The X-ray peaks were indexed, the peaks at 2θ= 8.5 and 9.2° in the XRD pattern of the synthesized $CdQ_2{\cdot}H_2O$ were strong, which indicated that the synthesized $CdQ_2{\cdot}H_2O$ had a good crystallinity. We can also find that all peaks of the obtained $CdQ_2{\cdot}H_2O$ in Fig. 1(b) were in agreement with those reported in literature [20], which indicated that the synthesized product was $CdQ_2{\cdot}H_2O$. In addition, it was obtained in Fig. 1(c) that all the diffraction peaks were sharper than Fig. 1(a) and Fig. 1(b), which showed it had better crystallinity. Besides, it was identical with the previous report for $MgQ_2{\cdot}4H_2O$ [26]. The organic element analysis results are shown in Table 1. The measured values are in agreement with the theoretical values for AlQ_3, $CdQ_2{\cdot}H_2O$ and $MgQ_2{\cdot}4H_2O$. The chemical structure of the as-synthesized nanomaterials (AlQ_3, $CdQ_2{\cdot}H_2O$ and $MgQ_2{\cdot}4H_2O$) was shown in the inset of Fig. 1.

The thermal properties of the products were measured by thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses in Fig. 2. From the three TGA curses, it suggested that the three complexes have the different mass loss from the room temperature to 900 °C, indicating the composition change for three complexes. In TG curves, there is no loss of water of crystallization, and it is decomposed into aluminium oxide in the range of 300–530 °C for AlQ_3, however, there are the loss of one water molecule and four water molecules in the range of 30–360 °C, and they are decomposed into cadmium oxide and

Table 1
The data of elemental analysis for the three as-synthesized complexes.

	C% Measured value (Theoretical value)	H%Measured value (Theoretical value)	O%Measured value (Theoretical value)	N%Measured value (Theoretical value)
AlQ_3	69.83 (70.58)	3.91 (3.95)	10.20 (10.45)	9.08 (9.15)
$CdQ_2{\cdot}H_2O$	51.70 (51.63)	3.26 (3.37)	11.72 (11.46)	6.75 (6.69)
$MgQ_2{\cdot}4H_2O$	55.82 (56.20)	5.11 (5.24)	23.62 (24.96)	7.53 (7.28)