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Preparation and luminescent properties of GdOF:Ce, Tb nanoparticles and their transparent PMMA nanocomposites

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ABSTRACT

GdOF:Ce, Tb nanoparticles and their poly (methyl methacrylate) (PMMA) nanocomposites have been successfully prepared by a thermolysis route and thermal polymerization of methyl methacrylate (MMA) monomer, respectively. The obtained nanoparticles and nanocomposites are characterized by XRD, EDS, TEM, FTIR, TGA, UV–Vis and PL spectrum. The as-synthesized transparent GdOF:Ce, Tb/PMMA nanocomposites exhibit green photoluminescence under the irradiation of 254 nm UV lamp due to the incorporation of luminescent GdOF:Ce, Tb nanoparticles into the PMMA matrix. The present route would provide a general strategy to prepare other functional nanocomposites.

1. Introduction

Nanocomposites combining both the properties of inorganic and organic materials have attracted much attention for their various applications in many fields owing to their tunable optical, electrical, thermal and mechanical properties. Luminescent nanomaterials doped with lanthanide ions have been extensively investigated due to their potential applications in a lot of new technologies, such as LED [1] and solar inverter [2,3]. Fluoride oxides are important host materials for luminescent lanthanide ions. For examples, Eu^{3+}-doped LaOF, GdOF and YOF have been obtained [4,5]. Among the lanthanide ions-doped fluoride oxides, GdOF:Ce, Tb nanoparticles with high quantum efficiency, thermal stability, excellent performance and a sharp and strong emission around 545 nm, are employed as the green emitting phosphor for fluorescent lamp. Yan's group has reported the preparation of GdOF:Ce, Tb nanoparticles by thermolysis of lanthanide trifluoroacetate precursors ($Ln(CF_3COO)_3$) in oleic acid/oleylamine [6]. On the other hand, among the broad variety of available polymers, poly (methyl methacrylate) (PMMA) is the most popular and extensively-utilized one because of its excellent transparent and processing properties. It is not only used in aviation signal light and construction, but also as a nontoxic matrix in dentures, medical machines, larynx lights and lenses, etc. Researchers have been incorporating nanoparticles into bulk PMMA or its thin film to improve the properties of materials [7–19], such as conductivity, photoconductivity, fluorescent and magnetic properties. Luminescent rare earth-doped fluoride nanoparticles have also been reported for application in the scintillators [20–22]. Gadolinium is a naturally occurring element which has two isotopes with very high thermal neutron absorption cross-sections. These cross-sections are significantly higher than nearly every other isotope, which makes gadolinium an ideal neutron absorption material for neutron scintillators [23]. It is very promising for GdOF:Ce, Tb nanoparticles to be used in the scintillators if they are embedded into the polymer matrix, such as PMMA, with a relatively high concentration and at the same time remain the transparency of the nanocomposites. To the best of our knowledge, very few reports on the study of bulk PMMA nanocomposites are available. No reports have appeared concerning the integration of luminescent GdOF:Ce, Tb nanoparticles into PMMA matrix. In this paper, we synthesized the monodisperse GdOF:Ce, Tb nanoparticles by using a thermolysis process and obtained their bulk PMMA nanocomposites via a thermal polymerization. The obtained transparent PMMA nanocomposites emit green photoluminescence under the irradiation of 254 nm UV lamp.

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2. Materials and methods

2.1. Materials

Oleic acid (OA), oleylamine (OM), methyl methacrylate (MMA), initiator 2,2′-azobisisobutyronitrile (AIBN), ligand bis(2-(methacryloyloxy)-ethyl) phosphate (BMEP, $C_{12}H_{19}O_8P$), absolute ethanol, and hexane were purchased from Sigma–Aldrich and used as received. $Gd(CF_3COO)_3$, $Tb(CF_3COO)_3$, and $Ce(CF_3COO)_3$ (lanthanide trifluoroacetate precursors ($Ln(CF_3COO)_3$)) were prepared from the corresponding lanthanide oxides and trifluoroacetic acid according to the Ref. [24].

2.2. Preparation of GdOF:Ce, Tb nanoparticles

The synthetic route is similar to the described in the Refs. [6,25,26] with modification. In a typical procedure: a given amount of $Gd(CF_3COO)_3$ (0.40 mmol), $Ce(CF_3COO)_3$ (0.45 mmol) and $Tb(CF_3COO)_3$ (0.15 mmol) were added into 40 mmol mixture of OA and OM (molar ratio of OA:OM is 5:3) in a three-necked flask at room temperature. Then the slurry was heated to 125 °C and maintained for 25 min to remove water and oxygen with vigorous magnetic stirring under vacuum in a temperature controlled electromantle, and thus to form an optically transparent solution. The solution was then heated to a temperature of 320 °C and kept for 50 min under an argon atmosphere. On cooling to room temperature, the nanoparticles were precipitated by adding an excess amount of ethanol into the reacted solution, then the obtained nanoparticles were dried. The as-synthesized nanoparticles were easily redispersed in hexane for characterization. For preparation of only Tb^{3+} ions-doped GdOF nanoparticles, OM molecules were used as the surfactants and other synthetic conditions were kept the same.

2.3. Exchange of the ligands on the surface of nanoparticles

To avoid nanoparticles aggregation during thermal polymerization, bis (2-(methacryloyloxy)-ethyl) phosphate (abbreviated as BMEP) was used to exchange the ligands on the surface of nanoparticles. In a typical procedure: 0.1 g of OA and OM-capped nanoparticles were dispersed in 10 ml of toluene solution of BMEP (0.1 g). The resulting mixture was stirred overnight. The BMEP-capped nanoparticles was precipitated by ethanol, separated by centrifuge, washed with ethanol and dried in vacuum, respectively. The TGA curve of GdOF:Ce, Tb nanoparticles after ligands exchange shows about 50 wt% of capping molecules (Fig. 4B).

2.4. Preparation of bulk GdOF:Ce, Tb/PMMA nanocomposites

The bulk GdOF:Ce, Tb/PMMA nanocomposites with different content of inorganic phase (0, 0.32, 0.50, 1.0, 1.5 wt%) were prepared by in situ bulk polymerization of MMA monomer. The polymerization was conducted in a glass tube as follows: appropriate amount of GdOF:Ce, Tb nanodisk with 10–15 nm of average diameter and 4 nm of thickness were dispersed in 1.0 g of methyl methacrylate (MMA) by shaking and sonication, then 0.006 g of AIBN (0.6% by weight of MMA) was added to the above transparent dispersion and the pre-polymerization was carried out at 75 °C for 10 min in an oil bath. Then the mixture was cured at 50 °C for 22 h in another oil bath, and finally a series of transparent bulk GdOF:Ce, Tb/PMMA nanocomposites were thus obtained.

2.5. Characterization

XRD was carried out with a Panalytical X'Pert Pro Powder Diffractometer using Cu Ka radiation ($\lambda = 0.15405$ nm, an accelerating voltage of 40 kV, scan range 10–80°, scan step 0.02°). TEM was conducted on a Philips CM120 transmission electron microscope operated at 120 kV. FTIR spectrum was obtained by using JASCO FT/IR-420 spectrometer. TGA was performed on a Perkin–Elmer Thermal Analysis Pyris Diamond TG/DTA instrument, the sample was heated from room temperature to 800 °C with a rate of 5 °C/min in air (flow velocity of 40 cc/min). Fluorescence spectrums were measured with a PTI QuantaMaster 30 spectrofluorometer. UV–Vis transmittance of the nanocomposites was acquired by using a Shimadzu UV-1700 spectrophotometer.

3. Results and discussion

3.1. Crystal structure, phase composition, morphologies, photoluminescence, surface composition and thermal stability of nanoparticles

The crystal structure and phase composition of the nanoparticles were characterized by using X-ray diffraction (XRD) technique. Fig. 1 shows the XRD patterns of the as-formed Ce^{3+} and or Tb^{3+} doped GdOF nanoparticles and the standard data for GdOF as well. The well resolved four peaks between 10° and 70° correspond to (111), (200), (220), and (311) crystal planes of cubic GdOF (JCPDS card NO 50-569). No other crystalline side products can be identified. The peaks in the XRD patterns of each sample show light relative movement because there is little difference in the diameter size between Ce and Tb atom.

The morphologies of the as-prepared nanoparticles were investigated by using transmission electron micrographs (TEM). Representative TEM of the GdOF:Ce, Tb nanoparticles are shown in Fig. 2. When OA and OM molecules were used as the surfactants, an overview images (Fig. 2a and c) illustrates that the sample entirely consists of numerous monodisperse GdOF:Ce, Tb nanoparticles. At a high magnification TEM (Fig. 2b and d), it can be seen that the nanoparticles have disk-like morphology, some of them are standing and others are lying. The average diameter and thickness of nanodisk are 10–15 and 4 nm, respectively. When only OM molecules were used as the surfactant in the starting materials, the product still was composed of a large number of monodisperse nanoparticles (Fig. 2e and g), but at a high magnification (Fig. 2f and h), it can be seen that the nanoparticles have a spherical or polyhedral morphology, and the average size of the product is less than 10 nm and the Ce^{3+} and Tb^{3+} co-doped GdOF nanoparticles have a smaller size of 4 nm (Fig. 2g and h), which is very similar to those reported in Ref. [6], but with a smaller grain size. The size of nanoparticles is so small that the Rayleigh scattering is nearly neglected when they are incorporated into the polymer matrix.

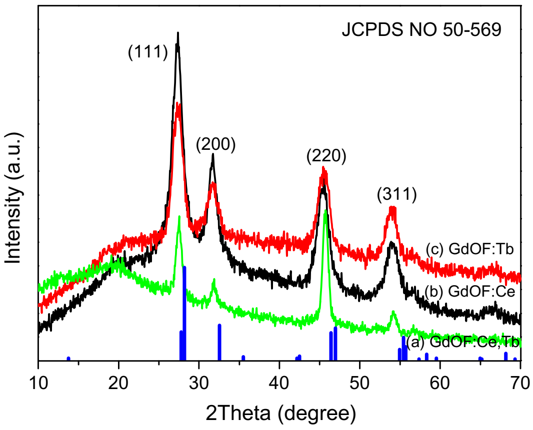

Fig. 1. XRD patterns of the Ce^{3+} and or Tb^{3+} doped GdOF nanoparticles.