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Fabrication of novel $La_2O_2CN_2$ one-dimensional nanostructures via facile electrospinning combined with cyanamidation technique

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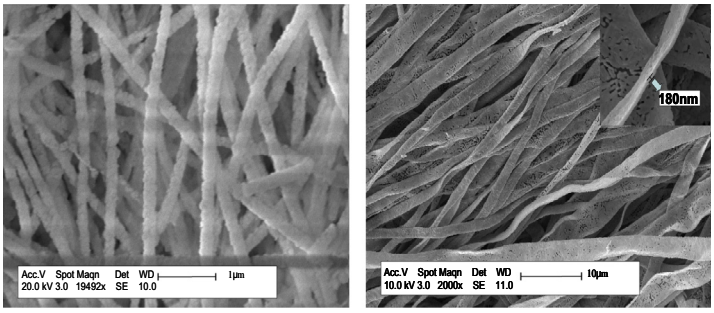
HIGHLIGHTS

- For the first time, $La_2O_2CN_2$ nanofibers and nanobelts were successfully prepared.
- Photocatalytic performance of $La_2O_2CN_2$ nanofibers and nanobelts was firstly studied.
- Electrospinning combined with cyanamidation technique was firstly adopted.
- Formation mechanisms of $La_2O_2CN_2$ nanofibers and nanobelts were advanced.

GRAPHICAL ABSTRACT

For the first time, $La_2O_2CN_2$ nanofibers and nanobelts were successfully prepared via cyanamidation of La_2O_3 respective nanostructures employing NH_3 gas and graphite at high temperature. These nanostructures are tetragonal in structure with space group of I4/mmm. The thickness and the width of $La_2O_2CN_2$ nanobelts are respectively 180 nm and 2.56 ± 0.68 μm, and the diameter of $La_2O_2CN_2$ nanofibers is 248.10 ± 40.98 nm under the 95% confidence level. $La_2O_2CN_2$ nanostructures exhibit excellent photocatalytic activity in photodegradation of rhodamine B (RhB) under the irradiation of ultraviolet light, and the nanofibers have higher photocatalytic ability than nanobelts under the same experimental conditions. Furthermore, these nanostructures can retain excellent photocatalytic stability after reuse.



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ABSTRACT

La_2O_3 nanofibers and nanobelts were fabricated by calcination of the respective electrospun PVP/[$La(NO_3)_3$] composite nanofibers and nanobelts. For the first time, $La_2O_2CN_2$ nanofibers and nanobelts were successfully prepared via cyanamidation of La_2O_3 respective nanostructures employing NH_3 gas and graphite at high temperature. X-ray powder diffraction (XRD) analysis reveals that $La_2O_2CN_2$ nanostructures are tetragonal in structure with space group of I4/mmm. Scanning electron microscope (SEM) analysis indicates that the thickness and the width of $La_2O_2CN_2$ nanobelts are respectively 180 nm and 2.56 ± 0.68 μm, and the diameter of $La_2O_2CN_2$ nanofibers is 248.10 ± 40.98 nm under the 95% confidence level. Transmission electron microscope (TEM) observation shows that $La_2O_2CN_2$ nanofibers and nanobelts are all composed of nanoparticles. $La_2O_2CN_2$ nanostructures with different morphology exhibit excellent photocatalytic activity in photodegradation of rhodamine B (RhB) under ultraviolet light irradiation, and the nanofibers have higher photocatalytic ability than nanobelts under the same experimental conditions. The possible formation mechanisms of $La_2O_2CN_2$ nanofibers and nanobelts were also proposed.

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1. Introduction

Recently, rare-earth (RE) compounds have attracted much attention of the researchers due to their applications in permanent magnets, superconductors, catalysts and optical devices, etc. [1]. There are many rare-earth compounds, such as RE_2O_2X (X = halogen, S^{2-}, Se^{2-}, Te^{2-}, CO_3^{2-} [2], CN_2^{2-} [3,4] and SO_4^{2-} [5]), in which the crystal structure of the rare-earth compounds consists of $RE_2O_2^{2+}$ layers and their interleaving anion. Different kinds of anions can make structure, physical and chemical properties unique and multiple. A wide variety of function is anticipated by changing interlayer anions between $RE_2O_2^{2+}$ layers [4]. Research interest in C–N containing compounds of the lanthanides has been growing recently with the discovery of new $(N–C–N)^{2-}$ compounds such as $Eu(CN_2)$ [6], $LnCl(CN_2)$ (Ln = La, Ce, Pr) [7], $La_2O(CN_2)_2$ [8] and $La_3Cl(CN_2)O_3$ [9].

The structure and composition of $La_2O_2CN_2$ powders were first reported by Hashimoto et al. The linear anion $(N–C–N)^{2-}$ lies in parallel to the $La_2O_2^{2+}$ layers in structure because of the large ionic size of La^{3+}. The La^{3+} ions are coordinated with 4 oxygen and 4 nitrogen atoms in tetragonal lattice [3]. The $(N–C–N)^{2-}$ anions are also in $RE_2O_2CN_2$ perpendicular with the smaller RE^{3+}, where RE = Ce, Nd, Sm, Eu and Gd. The RE^{3+} cations are coordinated with 4 oxygen and 3 nitrogen atoms in trigonal lattice [10]. All the homologous $Ln_2O_2(CN_2)$ (Ln = La, Y, Gd, Dy, Ho, Er, Tm, Yb) [11] compounds were synthesized following the solid-state metathesis (SSM) method or sol–gel method, and their crystal structures have been reported as tetragonal for Ln = La and trigonal for Ln = Ce, Pr, Nd, Sm, Eu and Gd [10]. It has been reported that $La_2O_2CN_2$ is an excellent matrix for RE^{3+} luminescence [12,13].

Nanofiber and nanobelt are new kinds of one-dimensional nanomaterials with special morphologies. They have attracted increasing interest of scientists owing to their anisotropy, large length-to-diameter ratio and width-to-thickness ratio, unique optical, electrical and magnetic performances [14–20]. Research on the fabrication and properties of nanofibers and nanobelts has become one of the popular subjects of study in the realm of nanomaterials.

Electrospinning is a technique that allows fabrication of continuous fibers with diameters ranging from tens of nanometers up to micrometers [21]. Electrospun nanofibers have already found use in applications that include ultrafiltration, tissue engineering, catalysis, as well as fabrication of solar cells, transistors, sensors, memories, and many other types of devices [21–37]. Advantages of this novel process for fabricating 1D nanostructures include, but is not limited to, low cost, high efficiency and convenient assembly [38]. It has been reported that the rare earth oxide, composite oxide nanofibers, nanobelts [14,15], rare earth oxysulfides nanobelts [16] and rare earth oxyhalide nanofibers [17,18] were successfully synthesized via electrospinning.

Nevertheless, the fabrication of $La_2O_2CN_2$ nanofibers and nanobelts is not reported in the literatures except for $La_2O_2CN_2$ powders [3]. Herein, $La_2O_2CN_2$ nanofibers and nanobelts were fabricated by cyanamidation of the relevant La_2O_3 nanostructures which were prepared by calcination of the electrospun nanostructures of PVP/$[La(NO_3)_3]$ composites in an ammonia atmosphere using graphite at high temperature. The morphology, structure and properties of the resulting samples were investigated in detail, and the formation mechanisms of $La_2O_2CN_2$ nanostructures were also presented.

2. Experimental sections

2.1. Chemicals

Polyvinyl pyrrolidone (Mw = 90,000, AR) were purchased from Tianjin Bodi Chemical Co. Ltd. N,N-dimethylformamide (DMF, AR) was bought from Tiantai Chemical Co. Ltd. La_2O_3 (99.99%) was supplied by China Pharmaceutical Group Shanghai Chemical Reagent Company. Nitric acid (HNO_3, AR) was bought from Beijing chemical Co. Ltd. All chemicals were directly used as received without further purification.

2.2. Fabrication of $La_2O_2CN_2$ nanofibers

La_2O_3 nanofibers were prepared by calcining the electrospun PVP/$[La(NO_3)_3]$ composite nanofibers. 1 g of La_2O_3 powders were dissolved in dilute HNO_3 (1:1, volume ratio) and evaporated to dryness, then dissolved in 15.8 g of DMF, and then 2.2 g of PVP was added into the above solution under stirring for 4 h to form homogeneous transparent spinning solution. In the spinning solution, the mass ratios of PVP, lanthanum nitrate and DMF were 11:10:79. Subsequently, PVP/$[La(NO_3)_3]$ composite nanofibers were prepared by electrospinning technique. The spinning solution was electrospun at a positive high voltage of 13 kV, distance between the capillary tip and the collector was 18 cm, relative humidity was 40–60%, the ambient temperature is 18–25 °C, the diameter of the syringe needle is about 0.5 mm. The flow rate of the spinning solution was determined by the content of PVP in solutions because PVP can adjust the viscosity of solutions. The collected electrospun composite nanofibers were then calcined at 700 °C in air for 8 h with the heating rate of 1 °C/min to obtain La_2O_3 nanofibers.

The La_2O_3 nanofibers were loaded into a graphite boat and then heated to 950 °C at the heating rate of 1 °C/min and remained for 12 h under a flow of gaseous ammonia. Then, the calcination temperature was decreased to 200 °C with a rate of 1 °C/min, followed by natural cooling down to room temperature, and $La_2O_2CN_2$ nanofibers was obtained.

2.3. Preparation of $La_2O_2CN_2$ nanobelts

La_2O_3 nanobelts were prepared by calcining the electrospun PVP/$[La(NO_3)_3]$ composite nanobelts. 1 g of La_2O_3 powders were dissolved in dilute HNO_3 (1:1, volume ratio) and evaporated to dryness, then dissolved in 14 g of DMF, and then 4 g of PVP was added into the above solution under stirring for 12 h to form homogeneous transparent spinning solution. In the spinning solution, the mass ratios of PVP, lanthanum nitrate and DMF were 20:10:70. Subsequently, PVP/$[La(NO_3)_3]$ composite nanobelts were prepared by electrospinning technique. The spinning solution was electrospun at a positive high voltage of 8 kV, the distance between the capillary tip and the collector was 15 cm, and the other preparation conditions were the same as those for the nanofibers. The collected electrospun composite nanobelts were then calcined at 700 °C in air for 8 h at the heating rate of 1 °C/min to acquire La_2O_3 nanobelts.

$La_2O_2CN_2$ nanobelts were fabricated through cyanamidation of the obtained La_2O_3 nanobelts using the same process, as described in Section 2.2.

2.4. Evaluation of photocatalytic performance

In a typical photocatalytic reaction, 0.1 g of the as-prepared $La_2O_2CN_2$ nanomaterials were dispersed into a 100 mL aqueous solution of RhB with the concentration of 5×10^{-3} g/L. Prior to illumination, the mixture was sonicated for 5 min in the dark to make the nanomaterials evenly disperse in solution. Then the solution was directly exposed under the ultraviolet light (500 W ultraviolet lamp with main emission wavelength of 365 nm) with stirring to trigger decomposition of the RhB molecules. At given time intervals, 3 mL suspensions were sampled and centrifuged to remove the photocatalysts. The concentration of RhB aqueous solution