Materials Letters 133 (2014) 109–112

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Electrospinning preparation of p-type NiO/n-type CeO_2 heterojunctions with enhanced photocatalytic activity

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ARTICLE INFO

Article history:
Received 8 April 2014
Accepted 27 June 2014
Available online 5 July 2014

Keywords:
Heterostructures
Semiconductors
Nanocomposites
Nanofibers
Electrospinning
Photocatalytic activity

ABSTRACT

Novel p-type NiO/n-type CeO_2 heterojunctions, with cubic NiO particles embedded on the CeO_2 nanofibers, were successfully prepared by the electrospinning technique. The photocatalytic activity for MB degradation under UV light irradiation of the NiO/CeO_2 heterojunction is much higher than that of pure NiO or CeO_2. The rate constant of MB degradation by NiO/CeO_2 is about 4 times and 2 times than those of pure NiO and CeO_2 under UV light irradiation, respectively. The excellent photocatalytic activity of the NiO/CeO_2 heterostructures is closely related to the fast transfer and efficient separation of electron–hole pairs between NiO and CeO_2 due to the formation of the heterojunction and their matching band positions.

1. Introduction

Semiconductor photocatalysis is regarded as a promising avenue toward solving the worldwide energy shortage and environment pollution with abundant solar light [1,2]. Of the well-known photocatalysts, cerium dioxide (CeO_2), naturally n-type semiconductors with a wide bandgap (E_g=3.2 eV), has been deemed as one of the most promising photocatalysts for the degradation of organic pollutants and water splitting for hydrogen generation owing to its high incident photon-to-electron conversion efficiencies, low cost, remarkable chemical stabilities along with safety advantage [3,4]. Nevertheless, the photocatalytic activity of CeO_2 system is largely limited by the quick recombination of the photoinduced electrons and holes [5]. To overcome this bottleneck, an effective strategy is the coupling of two semiconductors, CeO_2 and another semiconductor with the matching band positions, to form heterojunctions to increase the separation efficiency of photogenerated electron–hole pairs of CeO_2 photocatalysts [6,7]. So far, various CeO_2-based heterojunctions, such as Ag_3PO_4–CeO_2 [5], ZnO–CeO_2 [8] and $BiVO_4$–CeO_2 [9], have been investigated to suppress the recombination of photogenerated electron–hole pairs by the mutual transfer of photogenerated electrons or holes in the heterojunctions [10–12]. It is known that nickel oxide (NiO), a p-type semiconductor (E_g=3.5 eV) with high hole mobility and low lattice mismatch with CeO_2, is conductive to the fabrication of p–n heterojunction with CeO_2 [13,14]. Theoretically, the formed p–n heterojunction could provide a potential driving force and facilitate the transfer of electron–hole pairs the owing to the building of the internal electric field, with its field direction from the n-type CeO_2 to the p-type NiO [14–17]. Thus, it is significant to synthesize p-type NiO/n-type CeO_2 heterojunction, which might facilitate the easier transfer and efficient separation of photogenerated electron–hole pairs and improve the photocatalytic efficiency.

Herein, novel p-type NiO/n-type CeO_2 heterostructures were successfully prepared by the electrospinning technique. It is interesting that the cubic NiO nanoparticles are uniformly embedded in the CeO_2 nanofibers and form a heterostructure. Moreover, the synthesized NiO/CeO_2 heterojunction photocatalyst displays much higher activity than that of single NiO or CeO_2 under the irradiation of UV light. To the best of our knowledge, this is the first report on the electrospinning preparation of NiO/CeO_2 heterojunction photocatalyst.

2. Experimental section

The p-type NiO/n-type CeO_2 heterojunctions were synthesized using an electrospinning and calcination method. In a typical procedure, 0.0005 mol $Ni(CH_3COO)_2$ and 0.0005 mol $CeCl_3$ were mixed with 2.2 g ethanol and 2.2 g *N*,*N*-dimethylformamide (DMF) under vigorous stirring for 30 min. Subsequently, 0.38 g of poly (vinyl pyrrolidone) (PVP, M_w=300,000) was added to the above solution. After stirring for 12 h, the precursor solution was transferred to a syringe for electrospinning. The positive terminal of a

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http://dx.doi.org/10.1016/j.matlet.2014.06.169
0167-577X/

variable highvoltage power supply was connected to the needle tip of the syringe while the other terminal was connected to the collector plate. In a typical electrospinning process, the precursor solution was electrospun at 20 kV voltage, 20 cm working distance, and 0.4 mL/h flow rate at room temperature. The as-spun samples were calcined at 500 °C for 3 h in air to obtain NiO/CeO_2 heterojunctions with original Ni/Ce molar ratios of 1. For comparision, pure CeO_2 and NiO were also prepared using similar experimental conditions.

The crystal structure of the samples was characterized by a power X-ray diffraction (XRD, Siemens D-5000 diffractometer with Cu *K*α irradiation) and high-resolution transmission electron microscopy (HRTEM, JEOL JSM-2010F). The morphological details of the prepared samples were investigated by field emission scanning electron microscopy (FESEM, S-4800) and transmission electron microscopy (TEM, JEOL JEM 2010F). The Brunauer–Emmett–Teller (BET) specific surface area of the samples was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus.

The photocatalytic performance for the degradation of methylene blue (MB, 10 mg/L, 80 mL) with 30 mg photocatalysts (CeO_2, NiO or NiO/CeO_2) under UV light was explored. A 300 W UV lamp was chosen as the UV light source. Prior to irradiation, solutions suspended with photocatalysts were sonicated in the dark for 10 min to ensure the adsorption–desorption equilibrium of MB on the surface of the photocatalysts. During irradiation, the samples were withdrawn at regular time intervals and centrifuged to remove the catalysts. The photodegradation efficiency was monitored by measuring the absorbance of the solution samples at its characteristic absorption wavelength of 663 nm (MB) with a UV–Vis spectrophotometer at room temperature.

3. Results and discussion

The typical SEM images of pure CeO_2, NiO and the NiO/CeO_2 heterojunction are shown in Fig. 1. It can be seen that the as-spun CeO_2 nanofibers (Fig. 1a), with diameters of ~110 nm, possess smooth and uniform surfaces, whereas the NiO nanofibers (Fig. 1b), with diameter ranging from 50 to 100 nm, are rough and consist of smaller nanoparticles. The SEM image in Fig. 1c and the TEM micrograph shown in the inset of Fig. 1c reveal that the NiO/CeO_2 heterojunction is composed of two distinct phases. The cubic-shaped particles are NiO. It is noticeable that the NiO nanoparticles are uniformly embedded in the CeO_2 nanofibers and form a heterostructure. To further confirm the crystallographic structure of the NiO/CeO_2 heterojunction, HRTEM measurement was carried out. The HRTEM images of NiO/CeO_2 heterojunction in Fig. 1d show two distinct sets of lattice fringes. The uniform lattice fringes have spacings corresponding to the (1 1 1) plane of cubic fluorite-type CeO_2 and the (1 1 1) plane of cubic NiO, respectively.

The XRD patterns of all the samples are shown in Fig. 2. It is observed that all of the diffraction peaks of pure CeO_2 correspond to the cubic fluorite-type CeO_2 structure (JCPDS no. 81-0792), while those of NiO can be indexed to the body-centered cubic structure of NiO (JCPDS no. 78-0643). As expected, the XRD pattern of the NiO/CeO_2 composite shows the mixed patterns of CeO_2 and NiO, and excludes the possibility of any third phase formation, indicating that the NiO/CeO_2 heterojunction has been successfully prepared.

The photocatalytic activity of these samples was evaluated by photodegradation of MB. The degradation efficiency of MB over pure CeO_2, NiO and the NiO/CeO_2 heterojunction photocatalyst, or without the photocatalyst, under UV light irradiation is presented

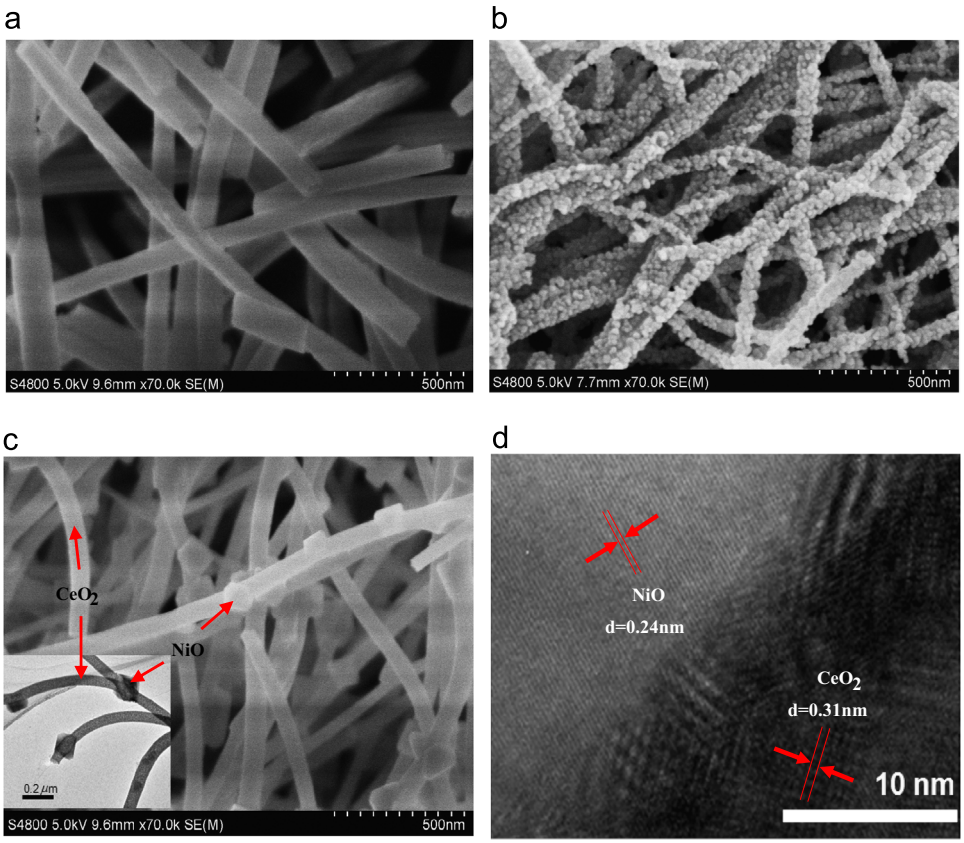

Fig. 1. SEM images of (a) CeO_2, (b) NiO, (c) NiO/CeO_2 heterojunction, and (d) HRTEM image of the NiO/CeO_2 heterojunction.