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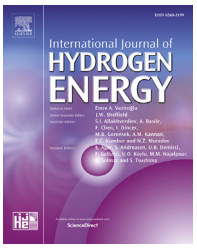

Fabrication of CeO_2 nanorods for enhanced solar photocatalysts

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ABSTRACT

In this work, CeO_2 NRs were synthesized by a hydrothermal approach and their microstructures were controlled by modifying the concentration of the hydroxide ions. The as-synthesized CeO_2 NRs appeared highly crystallized with a cubic structure, while their lengths increased from ~20 to 50 nm as the concentration of the hydroxide ions increased. By tuning their surface properties, the CeO_2 NR samples exhibited favorable band structures, which enabled them to effectively absorb large amount of photon energies and enhance the photocatalytic properties. The optimum CeO_2 sample showed the highest H_2 production rate (~25.10 μmol/g after solarlight irradiation for 5 h), largest Brunauer-Emmett-Teller specific surface area (65.26 m^2/g), smallest pore size (7.0 nm), and largest amount of oxygen vacancies. The photocatalytic H_2 evolution properties were attributed to the preferred planes of the CeO_2 NRs and the redox capacity of CeO_2. The photocatalytic process is mainly related to the conversion of Ce^{3+}/Ce^{4+} cycle of CeO_2, and the redox capability of CeO_2 is related to the amount of its oxygen vacancies.

Introduction

Owing to its energy capacity and zero pollution emission, compared with traditional fossil fuels, H_2 has recently attracted considerable research interest [1,2]. In the attempt to build a new H_2-based economy, tremendous efforts have been dedicated to the development of effective and low-cost approaches for the production and utilization of H_2 [3–5].

Water is the most abundant source of H_2, and it can be used for its production via photocatalytic water splitting [4]. Thus, a photocatalyst, solar energy, and water are necessary for the production of H_2. Solar energy is by far the most abundant renewable energy source; it is estimated that around 0.01% of the energy of one second of sunlight irradiation is sufficient for the annual energy consumption of human society [6,7]. The photocatalytic water splitting technology is not only clean, but it can also efficiently utilize the solar energy; besides, no dangerous by-products or pollutants are released in the process [8–11]. Therefore, it promises to provide a great contribution to the solution of energy and environmental issues in the near future. Currently, the major challenge is the development of efficient photocatalysts capable of absorbing sunlight to split the water.

Functionalized nanomaterials with various microstructures have shown to exhibit a few remarkable properties that suit for applications in catalysis, adsorption, environmental remediation, and energy conversion [12–17]. Nowadays many

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researchers have investigated the photocatalytic properties of various semiconductor nanomaterials such as ZnO, TiO_2, CeO_2, CdS, $SrTiO_3$ [1,2,8,18–28], Among these photocatalysts, CeO_2 has attracted considerable attentions as a promising photocatalyst for environmental applications due to its abundant resources, low cost, environmental-friendly, and long-time stability [29,30]. CeO_2 is also one of the most important rare-earth materials and it has been extensively studied for energy conversion applications including fuel cells and solar cells because of its high oxygen storage capacity [31–34]. Various microstructures of CeO_2 nanocrystals have been reported. The dimensions of the CeO_2 NRs are significantly affected by the synthesis method adopted. For instance, the solvothermal method produced CeO_2 NRs with lengths ranging from 0.3 to 2 μm [35], whereas CeO_2 NRs with diameters of ~10 nm were synthesized by using a precipitation method [36]; on the other hand, when the cathodic electrode deposition method was adopted, CeO_2 NRs with diameters of 200–400 nm were successfully grown on Ti substrates [2]; furthermore, CeO_2 NRs synthesized using the hydrothermal method exhibited widths of ~20 nm and lengths of several hundreds of nanometers [37]. However, facile and large-scale fabrication of homogeneous CeO_2 nanostructure with good photocatalytic activity is still difficult, which hinders its commercial application. Therefore, getting a uniform, homogeneous size and a good morphology of CeO_2 with excellent performance is still challenging. Moreover, CeO_2 with different nanostructures (NRs and nanowires) possessing of the redox couple between Ce^{3+}/Ce^{4+} have been applied in photocatalytic H_2 evolution, exhibiting excellent performances [22,23]. However, the relationship of the redox coupling and the oxygen vacancies in the catalytic performance of CeO_2 still needs to be further clarified.

In this work, we have demonstrated the preparation of CeO_2 NRs by using a facile hydrothermal method and investigated the effect of the concentrations of the hydroxide ions (OH^-) in the reaction system on photocatalytic performance. Synthesis of one dimension CeO_2 nanostructures in the absence of any organic templates or surfactants is desirable, even though it is more difficult to achieve. The synthesized CeO_2 samples were used as efficient photocatalysts for H_2 production under solar light irradiation. A novel feature was found that the CeO_2 NRs with the largest specific surface area, smallest pore size, and largest amount of oxygen vacancies possessing of highest hydrogen production, which was attributed to the heterogeneous structure between redox coupling of Ce^{3+}/Ce^{4+} in CeO_{2-x} NRs reactors. This will promote the further development of photocatalytic materials in practical energy applications. The developed photocatalytic reactor can also support light-catalyzed reactions well, and may inspire further development of photocatalytic reactors.

Experimental section

Synthesis of CeO_2 NRs

First, 1.74 g of $Ce(NO_3)_3{\cdot}6H_2O$ (Shanghai Zhanyun Chemical Co., Ltd, China) was dissolved in 40 mL of distilled water, and a certain amount of NaOH (National Pharmaceutical Group Chemical Reagent Co., Ltd. China) was rapidly added under vigorous stirring. Subsequently, the mixture was transferred into a Teflon-lined stainless steel autoclave. All these chemical reagents were of analytical grade.

The concentrations of the hydroxide ions (OH^-) in the reaction system were adjusted to 0.1, 0.2, 0.3, 0.4 and 0.5 mol/L. The autoclave was maintained at 130 °C for 18 h, and then cooled to room temperature. The precipitate was collected by centrifugation, washed repeatedly with distilled water, dried in vacuum at 60 °C for 24 h, and calcined at 300 °C for 4 h to obtain the final product. The as-prepared CeO_2 samples were denoted as C1, C2, C3, C4, and C5, which corresponded to the OH^- concentrations of 0.1, 0.2, 0.3, 0.4, and 0.5 mol/L respectively.

Characterization of CeO_2 NRs

Analytical grade chemical reagents were used for the preparation. The structural properties of the CeO_2 NRs were investigated by X-ray diffraction (XRD, Bruker D8; Cu K_α radiation, $\lambda = 1.5406$ Å) analysis. The XRD data were collected over a 2θ range of 5°–70° with steps of 0.01°. The Brunauer–Emmett–Teller (BET) surface areas of the samples were measured at liquid N_2 temperature (77.4 K), using a N_2 adsorption apparatus (ASAP-2020, Micromeritic, Norcross, GA, USA).

The morphologies of the prepared samples were studied by scanning electron microscopy (SEM; Hitachi SU-8010, Tokyo, Japan). A high-resolution analytical transmission electron microscope (FEI Tecnai GI F30) was utilized to obtain high-resolution transmission electron microscopy (HRTEM). X-ray photoelectron spectroscopy (XPS) analysis was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical, Manchester, UK) equipped with an Al K_α X-ray source and an electrostatic hemispherical electron analyzer. UV–vis spectra of solid powders were obtained using a Lambda 35 double-beam UV–vis absorption spectrometer equipped with a deuterium lamp and a tungsten halogen lamp (Perkin-Elmer, Norwalk, CT, USA).

Photocatalytic activity measurements

The photocatalytic H_2 evolution activity was evaluated in a 250 ml glass vessel as our earlier reported [26]. In a typical procedure, a sample of 100 mg was dispersed in 100 mL of an aqueous solution containing 0.43 M Na_2S mixed with 0.50 M Na_2SO_3 in a Pyrex reaction cell. The simulated solar light was supplied by a 300 W Xe lamp (PLS-SXE-300UV, Beijing Changtuo). The reactor was irradiated with Xe-lamp and stirred magnetically. The amount of produced H_2 was analyzed using an on-line gas chromatography system (Techcomp, GC7900) (TCD detector, 5 Å molecular sieve column) equipped with a thermal conductivity detector and a N_2 carrier for every one hour.

Results and discussion

Structural and morphological analysis

Fig. 1 shows the typical XRD patterns of the CeO_2 NRs prepared using different concentrations of hydroxide ions. The CeO_2

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