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Original Research Paper

Biotemplating synthesis and photocatalytic activities of N-doped CeO_2 microcapsule tailored by hemerocallis pollen

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ABSTRACT

As one of the most active rare earth, CeO_2 has been receiving considerable attention due to its multifunctional properties. Herein, we present a facile and green route toward hierarchical N-doped CeO_2 hollow microcapsule by using hemerocallis pollen as biotemplate. The resulting sample was characterized by X-ray diffraction spectroscopy, field emission scanning electron microscopy, transmission electron microscopy, nitrogen adsorption and desorption, UV–Vis diffuse reflectance spectra and X-ray photoelectron spectrogram. The obtained N-doped CeO_2 microcapsule exhibits much more superior photocatalytic activity for the hydrogen generation by water splitting, which owing to the nitrogen doping and structural features. This facile method of research provides a rational approach to replicate desired biological structures for semiconductor nanoparticle catalysis in other potential areas.

1. Introduction

Hydrogen as a clean and renewable energy carrier has gained a huge amount of attention due to the great potential for resolving energy and environmental issues toward sustainable progress [1]. The combustion of hydrogen can generate water instead of carbon dioxide and have high energy yield of 122 kJ/g, which is 2.75 times higher than hydrocarbon fuels [2]. Among various techniques for the generation of hydrogen, the photocatalytic water splitting into hydrogen is a promising, environmentally friendly process for the conversion of solar energy into chemical energy over metal-oxide semiconductors such as TiO_2, WO_3 and $BiVO_4$ [3]. However, two of the key limiting factors in these semiconductor photocatalysts are limited applications under visible light irradiation and fast charge carrier recombination [4]. Therefore, tremendous effort has been made to meet the requirements for efficient utilization of the solar energy spectrum.

Compared to other metal oxide nanostructures, Cerium oxide (CeO_2) has attracted attention owing to its high stability, non-toxicity, and photocatalytic activity under ultraviolet irradiation because of its wide band gap. Numerous methodologies have been developed to design and fabricate particles CeO_2 photocatalyst with highly photocatalytic efficiency [5,6]. Among the various researches, there are two ways which could be favorable to improve the photoactivity. One approach is to construct special morphological CeO_2 photocatalyst, which is beneficial to extremely high precision of their self-assembly, replication, functionality and large specific surface areas. Many structures, such as nanorods, nanosheets, nanocubes, and porous structure, had been reported [6–8]. The other approach is doping with noble or transition metals, which inserts a new band into the original band gap of CeO_2 and inhibits charge carrier recombination to enhance the light absorption properties [9,10]. The major drawbacks of the latter technique are the high cost of the reaction setup and the photocorrosion of metal-loaded photocatalysts during the visible light photocatalytic reaction.

Nitrogen doping is quite encouraging, which results in the p-states near the valence band much like other deep donor levels in semiconductors [11]. The doping not only extends the light absorption onset to visible light region, but also suppresses the recombination rate of photogenerated electrons and holes, which leads to enhanced photocatalytic activity [12,13]. In this regard, the nitrogen-rich pollen grains are prominent candidates to be

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used as biotemplates because the tough outer shell (exine) is liable to inorganic mineralization without consequent loss of specific structure. Moreover, pollen has a matching particle size as well as an elaborate and complex spherical morphology. Herein, we develop a rational approach to the facile biotemplate fabrication of hollow CeO_2 spheres with the assistance of hemerocallis pollen. The synthesized N-doped CeO_2 materials showed fine-particle, well-defined ordered mesospheres with high similarities to the pollen. The obtained materials exhibited significantly higher photocatalytic water splitting efficiency. We hope that the results of this study contribute to the design of efficient metal oxide photocatalyst for enhanced solar fuel production.

2. Experimental

2.1. Material

All reagents used in the experiment were analytically pure and purchased from China National Medicines Corporation Ltd. All the chemicals were AR grade, and used as received without further purification. And hemerocallis pollen was collected from campus in autumn. Ultrapure water was used for all experiments.

2.2. Preparation of porous N-doped CeO_2 hollow microcapsule

In a typical experiment to prepare N-doped CeO_2 hollow microcapsule, 0.8 g native pollen produced from Hemerocallis fulva flower was dispersed in ultrapure water by ultrasonic treatment at intervals till to the size of powder needed. Pollen was then pretreated by immersion in ethanol/water mixtures to produce hydrated grains and stirred with an digital mixer. Afterwards, 2.5 g $Ce(NO_3)_3{\cdot}6H_2O$ was added into the resulting mixture and the pH value of the solution was adjusted to about 4 using 5% (mass weight) dilute HCl solution. The cerium ions infiltrated into pollen cell wall at room temperature for 48 h. The pollen grains were filtered out and washed with ultrapure water for several times. The product was dried overnight in a clean bench, followed by calcination at 300 °C in air for 2 h and then at 500 °C under nitrogen atmosphere to obtain biomorphic N-doped CeO_2 hollow microcapsule. The standard sample of CeO_2 was prepared by the same conditions without biotemplate by calcinations of the precipitation of cerium nitrate. The contrastive CeO_2 nanopowder sample was prepared by using $Ce(NO_3)_3{\cdot}6H_2O$ under 550 °C calcination condition.

2.3. Characterization

Inverted fluorescence Microscope (OLYMPUS IX71) was put to use to observe original pollen structure. Powder X-ray diffraction (PXRD) measurement was performed on a Rigaku X-ray diffractometer with Cu Kα radiation (Rigaku, D/max-RB). The surface structure of the N-doped CeO_2 hollow microcapsule was studied by using a Field Emission Scanning Electron Microscope (FESEM) model S-4800. The distribution of CeO_2 nano-particles was investigated by using a JEM 2100 High Resolution Transmission Electron Microscopy (HR-TEM). XPS analysis was carried out by an X-ray photoelectron spectroscopy ESCA (Thermo Fisher Scientific, ESCALAB 250, Mono Al Kα source 1486.6 eV). Nitrogen adsorption-desorption isotherms were determined at 77 K using an ASAP 2020 analyzer. The surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method, and the pore volumes and pore size distributions were obtained using the Barrett-Joyner-Halenda (BJH) model. The ultraviolet–visible (UV–vis) diffuse reflectance spectra were carried out using a spectrophotometer (Shimadzu, UV-2450). The room temperature photoluminescence (PL) spectroscopy measurements at 325 nm excitation were performed by using Edinburgh Instruments FLS980 fluorescence spectrophotometer equipped with a Xenon lamp as a continuous excitation source.

2.4. Photocatalytic H_2 generation

Photocatalytic hydrogen production was carried out with a LABSOLAR–H2 system (Perfect Light Company Labsolar-II, China) equipped with an online gas chromatograph (Techcomp GC-7900). A 300 W Xe lamp with 50% output power (Perfect Light Company Microsolar300) was used to simulate the solar light. For a typical photocatalytic reaction, 100 mg of photocatalyst was placed into 100 mL of aqueous solution containing 20 vol% methanol. Methanol was used as a sacrificial reagent. The amount of generated H_2 was determined by online gas chromatography. The online analysis during the photocatalytic reaction was performed hourly.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 compares X-ray diffraction patterns for the CeO_2 nanopowder (wine curve) and nitrogen-doped CeO_2 (blue curve). It can be seen that all diffraction peaks are recorded at $2\theta = 28.5$, 33.1, 47.48, 56.34, 59.2, 69.46, 76.60 and 79.18°, and could be well-assigned to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), and (4 2 0) planes of CeO_2(JCPDS No. 34-0394). The crystallite size can be estimated by using the Scherrer formula. For undoped CeO_2 nanopowder, the crystallite size is 11 nm and for the N-doped case, it is 6.7 nm on account of the fact that the full width at half-maximum (FWHM) for pure CeO_2 is considerably smaller than the N-doped CeO_2. This phenomenon is largely due to the potential influence of the N incorporation process on particle growth or internal structural incoherence.

3.2. Morphology of N-doped CeO_2 microcapsule

In living nature, hemerocallis pollen was oval and aggregated in the orange stamen, as illustrated in Fig. 2a and b. The grain diameter was about 90 μm. The morphological structures of the pollen was further investigated by scanning electron microscopy. As shown in Fig. 2c, it could be seen that the chimbs checkerboard the raw surface of pollen. After calcination, the surface of

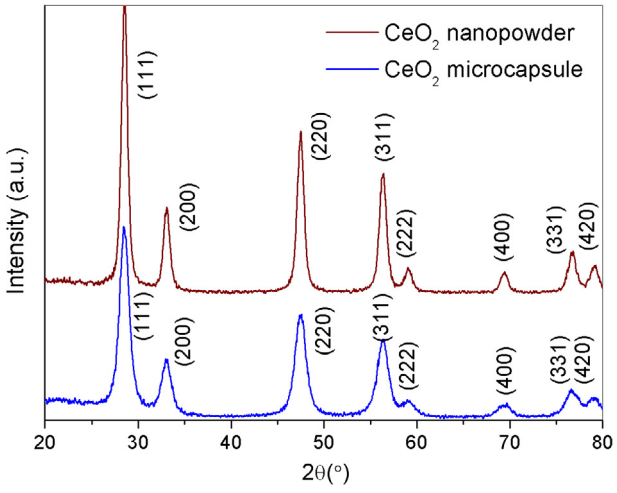

Fig. 1. XRD patterns of CeO_2 nanopowder and N-doped CeO_2 microcapsule.