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Synthesis of biomimetic cerium oxide by bean sprouts bio-template and its photocatalytic performance

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Abstract: Biomimetic nano CeO_2 materials were prepared by using bean sprouts as bio-template through impregnation and thermal decomposition. For characterization of structure, X-ray diffraction spectroscopy (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), UV-Vis diffuse reflectance spectra (UV-Vis/DRS) nitrogen adsorption-desorption measurements and Labsolar H_2 system were adopted. The results demonstrated that the samples prepared at 550 ºC not only completely removed the original bio-template, but also retained the morphology and microstructure of bean sprouts. Then the biomorphic structure of fluorite structure CeO_2 material was obtained. Micro-pores with a diameter of about 2–3 nm were distributed among the particles, which provided more favorable channel for the photocatalytic reaction. Biomimetic CeO_2 materials exhibited clear red shift (50 nm) compared with powder CeO_2, which could be excited by visible irradiation. Biomimetic CeO_2 materials displayed the superior photocatalytic activity for the hydrogen production by water splitting under the sunlight irradiation, the hydrogen yield could reach 400 μmol/g catalyst after 6 h.

Keywords: bio-template; nano materials; photocatalysis; hydrogen production; rare earths

The evolution of nature has bred a variety of unique structure and excellent properties, which provides a great impetus for the development of science and technology and the progress of social civilization. Biomimetic preparation[1] is a kind of nano material technology that mimics the structure, function, mechanism, and the whole system of the nature. A large number of biological tissues with special types of hierarchical porous structure, viruses, bacterial surface S-layer, diatoms, insect wings, pollen[2,3] and other biological materials have been used in the synthesis of micro/nano porous inorganic functional materials. Using bionic technology, biological materials with hierarchical porous structure can be combined with inorganic functional materials, which can get the superior performance of non-polar porous materials, and avoid the disadvantages of traditional methods. Part of the biological template synthetic materials with large specific surface area and high porosity can effectively increase reaction contact surface, and improve the efficiency of photocatalytic materials. These special materials are shown to have excellent properties in the fields of photo-therm conversion, chemical catalysis, drug delivery and so on. Ceria-based materials[4] have a promising application prospect in the fields of solid fuel cells, oxygen storage components for catalysts, sensors manufacturing, biomedicine[5,6], UV absorbers and biomedical science[7,8].

Hydrogen is a kind of high energy fuel[9], which has the advantages of clean, pollution-free and resistance to storage and transportation. It can be converted into heat or electricity through burning. With the revolutionary potential as energy carrier, it can meet the scale of the world's energy needs. However, the cost of hydrogen production is generally higher and the yield is lower. Facilitating the simple and inexpensive method of hydrogen production has become a common pursuit of a wide range of energy and environmental research workers. At the moment, the photocatalytic decomposition of water to hydrogen is mainly carried out in the UV range. In order to improve the solar energy utilization, it is necessary to develop a catalyst for photocatalytic decomposition of water in the visible region. Due to the high mobility of the oxygen species and the partial reduction of Ce^{4+} to Ce^{3+}, the oxide vacancies in bulk can be derived from its

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fluorite-type structure. On this view, ceria has received the greatest attentions as promising semiconductor photocatalyst. Bionic structure of CeO_2 has a higher catalytic performance both in the UV range and visible region. Therefore, hydrogen production by water splitting should also have high conversion efficiency. On this account, numerous solution-based efforts have been made to design and fabricate particles CeO_2 photocatalyst with high photocatalytic efficiency.

In this paper, the biomimetic morphology of porous cerium oxide materials[10] were prepared by the process of cerium salt impregnation, washing and calcination. The morphology and microscopic characteristics of the bean sprouts were well reproduced by the nano materials, and micro/nano porous structure which is advantageous to set light makes it have a higher photocatalytic activity[11]. Samples were characterized by TEM, XRD, SEM and BET. The results showed that the preparation of cerium oxide nano materials by this method had the advantages of ultra thin structure and rich mesoporous structure[12]. This kind of cerium oxide has a good effect on the hydrogen production by water splitting under the irradiation of the sun[13]. The hydrogen yield reached 400 μmol/g after 6 h, which was higher than that of bulk CeO_2 (40 μmol/g).

1 Experimental

1.1 Preparation of porous CeO_2 bionic material

All reagents used in the experiment were analytically pure and purchased from China National Medicines Corporation Ltd. Right amount of bean sprouts were dipped into dilute hydrochloric acid solution of 0.1 mol/L, then they were filtered out after 24 h. The samples were washed with deionized water for many times. Afterwards the samples without impurities were immersed in 0.1 mol/L of cerium nitrate solution, which were dipped at a constant temperature (25 ºC). After 48 h, the bean sprouts were removed with tweezers, the sample was washed three times with deionized water and then placed under the condition of drying at 40 ºC for 30 min. Eventually, the pretreated bean sprouts were carried into a muffle furnace. The heating rate is 2 ºC/min. When the temperature reached 550 ºC, keeping for 4 h. After these processes, biomimetic nano CeO_2 materials without biological template are obtained.

1.2 Material characterization

The crystalline phase in the samples were characterized by an X-ray diffraction (XRD Rigaku D/MAX-2500PC diffractometer) using Cu Kα radiation at 40 kV and 40 mA at a scanning rate of 5 (º) at 2θ/min ranging from 20° to 70°. The average grain size D was estimated according to Scherrer equation, $D=0.89\lambda/\cos\theta$, where θ was the diffraction angle of the main peak and λ is the full width at half maximum (FWHM). Scanning electron microscopy (SEM) was conducted with a Hitachi S-4800 scanning electron microscope at 15 kV and with a Thermo scientific NORAN System 7 spectrum analyzer to analyse the elements of product. HRTEM characterization was performed using a JEM-2100 electron microscope operating at an accelerating voltage of 200 kV. The N_2 sorption measurement was performed using micromeritics ASAP 2010 at 77 K. The specific surface area was calculated using Brunauer-Emmett-Teller (BET) method. The photocatalytic properties were characterized by electrochemical workstation (Zennium E). Hydrogen production from photolysis of water was determined by Labsolar H_2 system.

1.3 Photocatalytic experiments

The hydrogen production by Labsolar photocatalytic water splitting was tested by the Labsolar H_2 system[14]. Fig. 1 shows Labsolar photocatalytic water splitting producing hydrogen equipment. The 0.1 g catalyst was

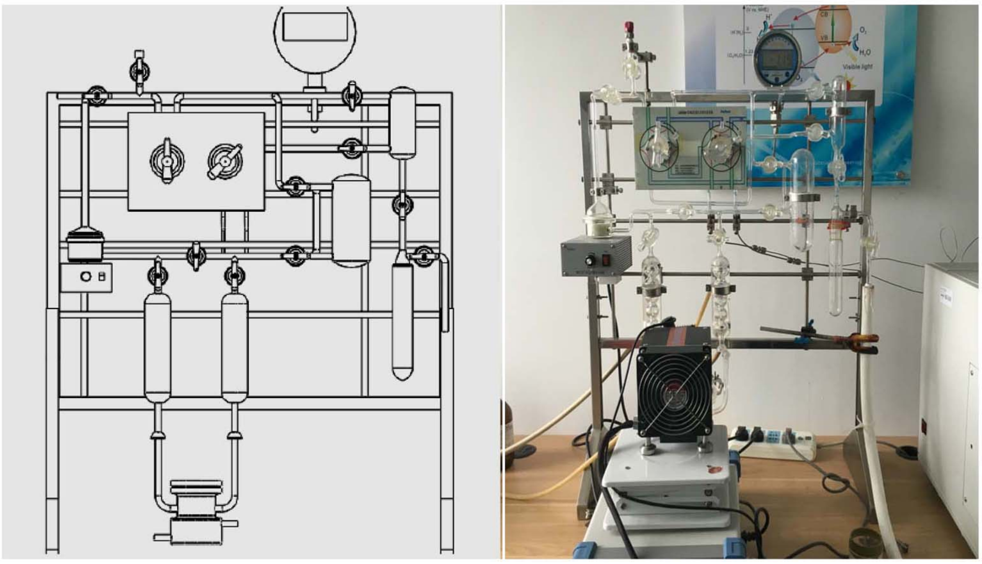

Fig. 1 Hydrogen production by Labsolar photocatalytic water splitting process