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Kelp-inspired N–I-doped ZnO photocatalysts with highly efficient catalytic activity

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ABSTRACT

Efficient N–I-doped ZnO photocatalysts with hierarchical structures are fabricated with kelp as the template. Abundant nitrogen and iodine are successfully simultaneously introduced into the bulk ZnO crystals though calcination under high temperature (600 °C). The morphology, structure, composition, and optical absorption properties of the kelp-templated ZnO are characterized by X-ray diffraction (XRD), field-emission scanning microscopy (FESEM), transmission electron microscopy (TEM), and diffuse reflectance spectra (DRS), respectively. The band gap of the kelp-templated ZnO is narrowed by the N–I coping. The photocatalytic activity under UV-irradiation of the kelp-templated ZnO is about 23.1 times and 1.1 times that of common ZnO and P25, respectively. In addition, no obvious activity of the kelp-templated ZnO is decreased, during five cycle runs. The efficient photocatalytic activity of the kelp-templated ZnO is attributed to the sufficient UV-light utilization and efficient separation of electron–hole pairs.

1. Introduction

Photocatalysis can provide environmentally benign and low-cost methods for the removal of organic compounds. To date, numerous efforts have been made to improve the photocatalytic activity of photocatalysts, including development of the hydrothermal method [1], elemental doping [2–4], semiconductor coupling [5], noble metal loading [6,7] and dye sensitization [8,9]. Recently, bio-templating has attracted much attention. Natural organisms – such as lotus leaves [10], rose petals [11], aquatic grass [12], and butterfly wings [13] – present complex, elaborate, and hierarchical structures at the micro- and nanoscale. It is possible to employ these delicate organism structures as hard templates to find new routes to mediate the morphologies and structures of photocatalysts with excellent photocatalytic activity. For example, Li et al. have produced an artificial TiO_2 leaf with macro/mesopores derived from a dual template of aquatic plant leaves and surfactants [12]. The as-obtained TiO_2 possessed hierarchical nanostructures and under ultraviolet (UV) light it photodegraded methylene blue at a roughly three times higher than P25 (a known commercial TiO_2 nanocrystalline photocatalyst).

TiO_2 and ZnO are recognized as classical and excellent photocatalysts due to their high photosensitivity, non-toxic nature, and low-cost, and have been extensively studied [14–17]. As a result, commercial TiO_2, such as P25, has been produced in great quantities in industry. Compared with TiO_2, ZnO has been thought to be a suitable alternative to TiO_2 because of its higher electron mobility and longer carrier lifetime [18]. However, practical application of ZnO has not gained as wide of an acceptance as TiO_2 in industrial applications because of the generally lower photocatalytic activity of ZnO compared to that of TiO_2. However, there have been a few reports so far indicating that ZnO has a higher efficiency than TiO_2 in the photodegradation of organic pollutants [19–21]. Thus, much research is still necessary toward the improvement of the photocatalytic activity of ZnO.

Herein, kelp (a typical water plant of the class *Phaeophyceae*) has been adopted as a bio-template for the fabrication of artificial leaves for photocatalysis. Kelp is rich in nitrogen and iodine (including formations such as I^-, IO_3^- and organic iodine, etc.), which can be self-doped into the final products via calcination. Additionally, kelp has an elaborate and hierarchical architecture, which can help control the growth and morphology of ZnO crystals in a small three-dimensional space. Recently, Fan et al. have reported that kelp-templated TiO_2 presents higher photocatalytic activity than typical N–TiO_2 [22]. Nevertheless, to the best of our knowledge, there is little information available in the literature regarding achieving both morphological control and elemental

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self-doping for ZnO nanostructures with kelp as the template. In this paper, although the final products have not completely copied the architecture of the kelp due to the quick rate of change in the calcination temperature (20 °C/min), kelp-templated ZnO still retain a hierarchical morphology due to limitation of the kelp cells. The kelp-templated ZnO has enhanced photocatalytic activity as compared with P25 and common ZnO when calcined under the same conditions and without a bio-template.

2. Experimental

2.1. Materials

All chemicals were analytical grade reagents and used as received without further purification. Glutaraldehyde (Tianjin Bo Di Chemical Co., Ltd), hydrochloric acid (Tianjin Yong Da Chemical Reagent Development Center, 99%), and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%, Aldrich) were used for the preparation of the kelp-templated ZnO. Kelp was purchased from Qingdao city, Shandong province. Fluorine-doped tin oxide (FTO) conducting glass substrates were acquired from Asahi Glass Company, Japan.

2.2. Pretreatment

Before the fixation procedure, the fresh kelp samples were carefully rinsed with pure water carefully several times to remove the impurities adhering to the kelp surface. Afterwards, the kelp samples were cut into the fixed size (3 cm × 3 cm) and treated with 2% glutaraldehyde/phosphate buffered saline (PBS; pH=7.2) solution at 4 °C for 7 h for the fixation of cells and tissues. The fixed samples were then rinsed with 0.2 M PBS solution and pure water and kept under 4 °C for further use.

2.3. Synthesis procedure of the kelp-templated ZnO

The pre-fixed kelp samples were immersed in 5% HCl solution for 14 h at room temperature. After rapidly rinsing with pure water, the as-treated samples were placed in a 1.2 M $Zn(NO_3)_2 \cdot 6H_2O$ solution in an oven at 60 °C for 72 h. The samples were then rinsed with pure water and dried at 80 °C for 15 h. Finally, the samples were calcined in air at 600 °C with a heating rate of 20 °C and tempered for 2 h. Hereafter, the products are referred to as "kelp-templated ZnO". A common ZnO reference was also synthesized by directly calcining zinc nitrate powder in the muffle furnace under the same experimental conditions as described above.

2.4. Characterization

The central thallus of the Kelp was fixed with a 4% formaldehyde solution and then sealed by a routine paraffin-section method. The thallus was precisely examined and photographed by a Nikon-E400 microscope with a Nikon E-995 digital camera. The phase and structure of the samples were characterized by X-ray diffraction (XRD, Germany Bruker D8-ADVANCE, Cu-$K\alpha$ radiation). The morphologies of the samples were investigated by field emission scanning electron microscopy (FESEM, Hitachi S-4800 with an energy-dispersive X-ray spectroscopic measurement). Transmission electron microscopy (TEM) analysis was conducted with a Tecnai G2 F20 S-TWIN microscope (FEI, Holland) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) of the samples was performed on the ESCALab 220i-XL spectrometer (Thermo VG Scientific, UK) with an Al-$K\alpha$ source. The carbonaceous C 1s line (284.8 eV) was used as the reference to calibrate the binding energies (BE). Diffuse reflectance spectra (DRS) were recorded with a Hitachi U-4100 spectrophotometer. The Brunauer–Emmett–Teller (BET) specific surface area of the as-prepared products was investigated by a Micromeritics 3Flex surface characterization analyzer. Photoluminescence (PL) spectra of the samples were measured with a Hitachi F-4600 florescence spectrophotometer, with an excitation wavelength of 325 nm. All of the spectra mentioned here were measured at room temperature.

Photoelectrochemical measurements were performed by an electrochemical system (CHI-660E, China), with a conventional three-electrode cell. An FTO glass (20 mm × 33 mm) was first ultrasonically cleaned with acetone and deionized water. One longitudinal edges of the FTO glass was covered with insulating tape, with the exposed effective area measuring 1 cm^2. Typically, 10 mg of the products were added to 2 mL ethanol and then ground with pestle for 20 min. Afterwards, the viscous paste was bound onto the FTO glass, which formed the products/FTO glass working electrode, and was then dried at 70 °C. The variations of the photoinduced current density with time (i–t curve) were measured at a 0.5 V bias potential (vs SCE) during five cycles when light was switched on and off. A 300 W Xe-lamp with a D300 monochromator was used to provide 254 nm irradiation light. A Pt wire and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. A Na_2SO_4 solution (0.5 M) was used as the electrolyte.

Electron paramagnetic resonance (EPR) measurements were carried out on a JEOL JES FA200 EPR spectrometer operating in the X-band at 9.07 GHz and 0.998 mW. Small portions of the products (~20 mg) were investigated and the measurements were taken at 123 K in an atmosphere of liquid nitrogen. A low-pressure mercury lamp (10 W, 365 nm wavelength) was used as the light source.

2.5. Photocatalytic experiments

The photocatalytic activity of the sample was evaluated with rhodamine B (RhB). A 10 W UV lamp with its wavelength centered at 365 nm was used as the irradiation source. In a typical experiment, a 50 mg ZnO sample was suspended in a 100 mL RhB aqueous solution (5 mg/L). The distance between the lamp and the aqueous surface was 10 cm. Before being exposed to the UV lamp, the suspension was stirred in the dark for 60 min to ensure the establishment of an adsorption–desorption equilibrium. During the photocatalytic process, a 4 mL reaction suspension was periodically withdrawn from the reactor. The obtained suspension was then centrifuged and then the RhB concentration was quantified with a UV–vis spectrophotometer at a 553 nm wavelength.

The main oxidative species generated in the photocatalytic process were detected through trapping by using iso-propyl alcohol (i-PrOH) and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na).

Total organic carbon (TOC) of RhB was also investigated using vario TOC cube analyzer, when some reaction suspension was withdrawn and centrifuged.

3. Results and discussion

Optical image of a piece of fresh kelp is shown in Fig. 1a. Due to the numerous chlorophylls in its cells, the kelp appears green in color. Kelp has hierarchical and porous structures at scales ranging from the macroscale down to the nanoscale, due to the arrangement of organelle in cell interior, as shown in Fig. 1b. These complex structures are benefit to capture the light for kelp. The optical image of a cross-section of organism of the kelp is shown in Fig. 1c. Many of the kelp cells are clearly observed, which act as a framework and can provide confined spaces in which ZnO crystal