



Fabrication of a modified straw cellulose and cerium oxide nanocomposite and its visible-light photocatalytic reduction activity



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ABSTRACT

A straw cellulose-cerium oxide (SC-CeO₂) nanocomposite has been synthesized through a hydrothermal method. Before this, the SC is oxidized and functionalized by a 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation. The as-obtained SC displays carbon nanotube-like nanocellulose. When composited with CeO₂, the nanocellulose grows on the surface of CeO₂. The synergistic effect between SC and CeO₂ results in an efficient separation of photogenerated carriers in the SC and CeO₂ coupling system. It is confirmed in this work that the SC-CeO₂ nanocomposite has good visible light-induced photocatalytic activity on reduction of aqueous Cr(VI) under acid condition (pH 4–6). More than 95% Cr(VI) (3–5 ppm) can be reduced under visible light irradiation for 60 min. Photocatalyst dosage and Cr(VI) concentration affect the conversion rate greatly.

1. Introduction

In recent years, development of technologies for water purification has been attracting great attention. Heterogeneous photocatalysis has been considered as a viable water treatment method [1]. Utilization of solar energy has become one of the hot spots in the field of photocatalysis because solar energy is a natural abundant energy source [2]. Numerous attempts have been made to develop the semiconductor photocatalysts which have wider light absorption range for more effectively utilizing the solar energy [3]. Cubic fluorite cerium dioxide (CeO₂), a semiconductor with a band gap energy about 3.2 eV [4,5], also shows promising photocatalytic activity for the removal of various water pollutants, such as organic dye pollutants [6,7], phenol and chlorinated phenol under UV illumination [5]. However, CeO₂ can absorb only a small portion of the solar spectrum in the ultraviolet region because of the wide band gap energy (3.2 eV), and meanwhile, the fast recombination of the photogenerated electron/hole reduces the photonic efficiency and represents the major draw-back of photocatalytic applications [8,9]. The way to solve this problem is to develop multiphase photocatalyst system by doping with metal/nonmetal elements or by forming heterojunctions between CeO₂ and other narrow band gap semiconductors in order to generate visible light-driven catalysts [10].

So far, lots of works have been done on designing CeO₂-based solar light-driven semiconductor multiphase photocatalyst system. For example, a bismuth vanadate and cerium dioxide (BiVO₄/CeO₂) has been prepared by Wetchakun and coworkers [4], which has high visible-

light-induced photocatalytic activity to Methylene Blue, Methyl Orange and a mixture of Methylene Blue and Methyl Orange solutions. Karunakaran et al., have reported a CeO₂-TiO₂ nanocomposites are not only visible-light-induced photocatalysts but are bactericides as well [11]. Xu's group has reported a rotary vacuum evaporation and support driven nanoassembly of tiny Pd noble metal particles on nanosized CeO₂. The resulting Pd/CeO₂ nanocomposite can be used as an active visible light photocatalyst toward organic redox transformations in water [12]. Ag@CeO₂ visible-light-induced photocatalysts have been reported by Cho's, Ge's and Muthuraj's groups through different methods [9,13,14]. To enhance the photocatalytic activities of CeO₂ under solar light, multiphase photocatalyst system has been confirmed a successful way. However, more efforts on fabrication of cheap, effective CeO₂-based solar light-driven photocatalyst are still needed.

As we know, various carbon-based supporting materials are reported to construct catalysts, such as graphene (oxide) [15], activated carbon [16], carbon nanotubes [17] and cellulose [18]. Among them, cellulose is the most abundant, renewable, biodegradable natural polymer resource on earth, which can be found in nature almost exclusively in plant cell walls (wood, cotton, bamboo, straw etc) [19]. It has been reported that cellulose can convert to carbon nanotube-like structure under proper TEMPO-mediated oxidation [20–22], and it can be a good supporter for catalyst [23]. For example, Li and coworkers have reported a novel regenerated cellulose (RC)/TiO₂/ZnO nanocomposite, which has been prepared via electrospinning technology and sol-gel process followed by hydrothermal method [24]. Very recently, Mesquita et al., have presented the fabrication of a α Fe₂O₃/

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highly hydrophilic carbon dots hybrid heterostructures with photocatalytic activity [25]. The highly hydrophilic carbon dots can be prepared by dehydration and oxidation of cellulose. With the aid of hydrophilic carbon dots, the photocatalytic activity of $\alpha\text{Fe}_2\text{O}_3$ enhances obviously. Under visible light irradiation, more than 90% Indigo carmine dye can be degraded with 90 min.

In the present work, the natural obtained straw cellulose was oxidized through TEMPO-mediated oxidation. The resulting SC-CeO₂ composite was obtained by hydrothermal method. SEM and TEM images display carbon nanotube-like nanocellulose was obtained. When composited with CeO₂, the nanocellulose grows on the surface of CeO₂. Cr(VI) was chosen as the target pollutant to test the photocatalytic reduction activity of the SC-CeO₂ nanocomposite. It is confirmed that the SC-CeO₂ nanocomposite has good visible light-induced photocatalytic activity on reduction of Cr(VI) in solution. The mechanism is also presented based on the results of XPS, PL and LSV.

2. Experimental

2.1. Materials

Cellulose (straw pulp) was provided by Yongfeng Yu life paper (Yangzhou) Co., Ltd. (Yangzhou, China). 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), sodium bromide (NaBr), sodium hypochlorite (NaClO), Cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), polyvinylpyrrolidone ($(\text{C}_6\text{H}_9\text{NO})_n$), ethanol, sodium hydroxide (NaOH), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and other chemicals were purchased from Sinopharm Chemical Reagent Company. All the reagents were of analytical grade and used as received without further treatment. All solutions were prepared with DI water.

2.2. TEMPO-mediated oxidation of straw cellulose (SC)

10 g straw slurry was suspended in 1000 mL DI water containing 0.16 g TEMPO and 1 g NaBr. 0.1 M HCl was added into NaClO (5 w%), adjusting pH to be 10. Then a certain amount of the NaClO solution, corresponding 5 mmol/g of the SC was added to the slurry. The mixture was violently stirred at room temperature and the pH was maintained to be 10 by adding 0.5 M NaOH. After two hours, the oxidized cellulose was washed thoroughly with water on filter papers set in a filter flask. The wet cellulose was dried at a temperature of 60 °C in the oven.

2.3. Preparation of SC-CeO₂

In a typical synthesis procedure, 0.4343 g Cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), 0.223 g polyvinylpyrrolidone ($(\text{C}_6\text{H}_9\text{NO})_n$) and 0.1 g oxidized SC were dissolved in a 7 mL DI water and 33 mL ethanol. Then the solution dissolved under magnetic stirring. The obtained transparent solution was transferred into a 50 mL polytetrafluoroethylene (PTFE) (Teflon)-lined steel autoclaves and heated at 140 °C for 16 h. After cooling to ambient temperature, the precipitate was centrifuged, washed several times with DI water and ethanol, and

dried at 60 °C in an oven. As a control experiment, CeO₂ was prepared under the same conditions without adding SC.

2.4. Characterization

The FT-IR spectra of the samples were measured on a Cary 610/670 microscope (Varian, US). Thermogravimetric analysis (TGA) was performed to investigate the thermal stability on a PE Pyris-1 instrument at a heating rate of 10 °C min⁻¹ under argon atmosphere. Scanning electron microscopy (SEM) was examined on a field-emission scanning electron microanalyzer (Hitachi S-4800, Japan). The photoluminescence (PL) spectra were measured with a JY HRD double grating monochromator with an excitation wavelength at 532 nm. High-resolution transmission electron microscopy (HRTEM) was recorded on a Tecnai G2 F30 S-TWIN transmission electron microscopes. The specific surface area was determined by nitrogen adsorption-desorption measurements were performed on a Beishide 3H-2000PM2 surface area and porosity analyzer. The bath and the outgas temperatures were 77.3 and 333.2 K, respectively. XPS measurements were performed to identify surface chemical composition and chemical states of the catalysts on an ESCALAB 250 Xi photoelectron spectrometer using Al K α radiation (Thermo-Fisher Scientific, US).

2.5. Photocatalytic testing

Photocatalysis experiments were carried out in a BL-GHX-V photochemical reactor (Shanghai Bilon Instrument Co., Ltd). The visible light source ($\lambda > 420$ nm) was provided by a 400 W high-pressure halogen lamp. In a typical run, 6 mg of SC-CeO₂ was dispersed in a 20 mL Cr(VI) (3 or 5 ppm). Then the suspension was stirred for 30 min in the dark to ensure adsorption/desorption equilibrium before light illumination. At each specific sampling time, aqueous sample was withdrawn by a 5 mL syringe, and filtered immediately by a 0.22 μm filter film to remove the catalyst particles before analysis. The concentration of Cr(VI) was then determined by measuring the absorbance at λ_{max} 540 nm via UV-vis spectrophotometer (UV 2700, Shimadzu).

2.6. Photoelectrochemical measurements

All photoelectrochemical characteristics were performed in the electrolytic cell consisted of a CeO₂, SC or SC-CeO₂ composites (2 mg mL⁻¹, 100 μL) coated FTO glass working electrode (4 cm²), a platinum wire counter electrode and a saturated calomel reference electrode (SCE) on a Model CHI 660D electrochemical workstation under a 300 W visible light irradiation.

3. Results and discussion

3.1. Materials characterization

The FT-IR spectra of the samples are shown in Fig. 1a. It is clearly seen that the SC-CeO₂ nanocomposites exhibits both characteristic

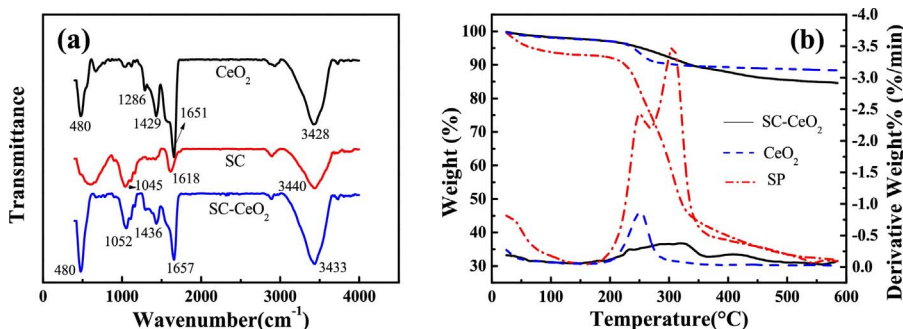


Fig. 1. (a) FT-IR spectra and (b) TGA curves of the SC, CeO₂ and SC-CeO₂.

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