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Invited paper

Construction of multivariate functionalized heterojunction and its application in selective oxidation of benzyl alcohol

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ABSTRACT

In this work, a new, multifunctional heterojunction Au-CeO_2-TiO_2/CNFs was constructed through the some methods including electrostatic spinning, high-temperature calcination, solvothermal, impregnation and gas reduction, and it was applied in the selective oxidation of benzyl alcohol under heating and optical radiation in which it shows a certain catalytic activity (the conversation was 50% and 40% respectively). It implements the functionalization and concept of green chemistry, offering a new idea for the material preparation and its application.

1. Introduction

Selective oxidation of alcohols to their corresponding aldehydes and ketones is of significant importance [1,2] and because these carbonyl compounds were widely used as valuable intermediates in the fragrance, confectionary, and pharmaceutical industries [3–6]. But traditional synthesis of them is accomplished using oxidizing agents such as $KMnO_4$, MnO_2 and CrO_3 [7], and the residue would lead to environmental problems [8,9].

The capture and conversion of solar energy has gained immense attention by the scientific and engineering world because of the great potential in resolving energy and environmental issues in the sustainable processes [10]. Among different types of semiconductor, the TiO_2 has been extensively investigated and is one of the most widely used in photocatalysis due to its excellent photocatalytic activity, high thermal and chemical stability, low cost, and non-toxicity [11,12]. Notably, the noble metal (Au, Ag, Pt, Pd et al) could effectively reduced the photogenerated electron/hole recombination owing to it is able to serve as electron sinks to facilitate interfacial electron transfer [13,14]. So they have been used for modification of TiO_2, in order to improve its photocatalytic activity.

The ceria plays a key role in many catalytic reactions owing to its high oxygen storage capacity, which is associated with the ability to undergo a flexible conversion between Ce (III) and Ce (IV) as well as its high thermal stability [15–18]. However, the band gap energy of ceria is ~3.2 eV, which makes CeO_2 only responsive to ultraviolet light, and photogenerated carriers in ceria can hardly transport to the surface or interface to participate make the catalytic of ceria can hardly be driven light [19].

Comprehensive above factors, firstly, the composite materials was prepared through the method contained high-temperature calcination, solvothermal and impregnation, and it is made up of CNFs (carbon nanofiber), TiO_2, cerium oxide and nanogold. Then the selective oxidation of alcohols was choosed as reaction system to investigate the performance in different catalysis conditions include light and thermal.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, Mw = 80,000) was purchased from Kunshan Hongyu Plastics Co., Ltd (China). Chloroauric acid ($AuCl_3 \cdot HCl \cdot 4H_2O$, Au ≥ 47.8%, AR) and absolute ethyl alcohol (C_2H_6O, AR, 99.7%) were bought from Sinopharm Chemical Reagent Co., Ltd. The N, N-dimethylformamide (C_3H_7NO, AR, 99.5%), glacial acetic acid (CH_3COOH, AR, ≥99.5%) and ethyl acetate ($C_4H_8O_2$)

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were from Tianjin Fuyu Fine Chemical Co., Ltd. The tetrabutyl titanate (Ti $(OC_4H_9)_4$, CP, 98.5%) was obtained from Xiya Reagent and the $Ce(NO_3)_3{\cdot}6H_2O$ was supplied from Recovery of Tianjin institute of fine chemicals. The KOH was bought from Tianjin HengXing Chemical Reagent manufacturing Co., Ltd. All above chemical reagents were used as received without further purification.

2.2. The preparation of Au-CeO_2-TiO_2/CNFs composite material

Five drops of glacial acetic acid (about 0.0941 g) was added into 20 mL absolute ethyl alcohol and then 0.5 mL (1.4×10^{-3} mol) of tetrabutyl titanate was added into the above mixture, which was stirred for 4 h at room temperature and subsequently transferred into a 100 mL autoclave reactor lined with Teflon. After that, 0.1 g carbon nanofibers (CNFs) that made through the processes of electrospinning and high temperature calcination was used as support and added into the above system. After physical adsorption for 24 h, followed 0.5 mL distilled water and 9.5 mL absolute ethyl alcohol was added into the system and then it was maintained at 180 °C for 9 h. When cooled to room temperature, the product was collected, washed with distilled water for three times, and dried at 85 °C in vacuum oven. The product was calcined at 550 °C in N_2 atmosphere for 2 h, and the product was named as TiO_2/CNFs.

At room temperature, 0.1 g of TiO_2/CNFs was added into a certain concentration of aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$ (0.01 M, 25 mL), and the system was put into vacuum drying chamber for 1 h under the condition of −60 kPa pressure and then it was transferred into atmospheric environment for another 5 h, after dried at 100 °C and followed by calcined under 300 °C for 4 h in air atmosphere and the product was called CeO_2-TiO_2/CNFs.

According to the same method, 0.1 g of CeO_2-TiO_2/CNFs was immersed in a known concentration of aqueous solution of $HAuCl_4$ (0.1 g/L, 20 mL) and the system was put into vacuum drying chamber for 1 h under the condition of −60 kPa pressure and then it was transferred into atmospheric environment at room temperature for another 5 h, after dried at 80 °C and it was put into the high pressure reaction vessel, in which it was full of H_2 and the temperature and pressure was 100 °C and 2.5 MPa respectively. After 9 h, the product Au-CeO_2-TiO_2/CNFs was obtained. The preparation of functional heterojunction process was shown in Fig. 1.

2.3. Catalyst testing

In order to test the catalytic activity of the catalyst, the sample was applied to catalyze the reaction of selective oxidation of benzyl alcohol in different conditions. On the one hand, 30 mL of distilled water, a certain amount of alkali, 15 mmol benzyl alcohol and 0.05 g catalyst were added into the steel reactor, successively. And the whole process was in the atmosphere of O_2 and heat.

On the other hand, the reaction was proceed in another condition, in which 30 mL of distilled water, 1.5 mmol KOH, 15 mmol benzyl alcohol and 0.05 g catalyst were added into the quartz reactor (which provided a 500 W high pressure Hg lamp with a 365 (±15) nm band-pass filter and the distance between the liquid level of solution and lamp was 10 cm). The whole process was in the atmosphere of air and under the optical radiation.

After the reaction was finished, the catalyst was removed and the resulting solution was extracted by ethyl acetate, then the organic phase was analyzed by Gas Chromatograph (Shimadzu, GC-2010 Plus) with FID using the DB-WAX column. On the other side, the Agilent (5975C) gas chromatography mass spectrometer (GC–MS) was also used to ensure the component of the product. The computational formula of conversion and selectivity for reaction as follows:

$$Con.(\%) = [(C_0 - C_t)/C_0] \times 100$$

$$Sel.(\%) = [C_p/(C_0 - C_t)] \times 100$$

where C_0 is the initial concentration of benzyl alcohol, and C_t and C_p are the concentration of reactant and product at t (reaction time), respectively.

3. Characterization

The morphologies of the materials were observed by field-emission scanning electron microscope (FE-SEM, FEGQUANTAN 650) and the condition of nanoparticles distributed on the surface of carbon nanofibers was studied by transmission electron

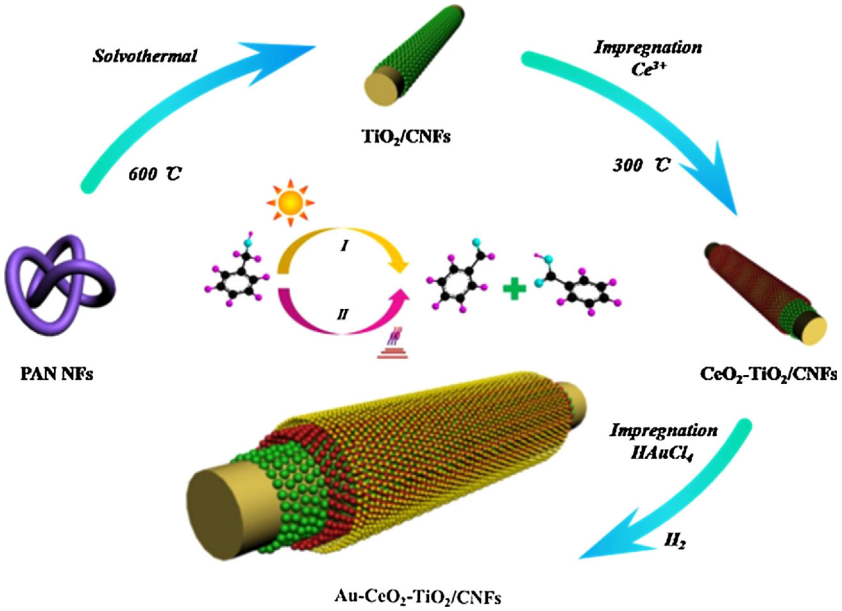

Fig. 1. Schematic illustration of the synthesis process for the composite materials.