Applied Catalysis A: General 473 (2014) 90–95

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Photocatalytic reduction of CO_2 in cyclohexanol on CdS–TiO_2 heterostructured photocatalyst

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ARTICLE INFO

Article history:
Received 1 September 2013
Received in revised form
26 December 2013
Accepted 29 December 2013
Available online 4 January 2014

Keywords:
Photocatalytic reduction
CO_2
Heterostructured photocatalyst
CdS–TiO_2
Nanosheets
Cyclohexanol

ABSTRACT

A nanosheet of CdS–TiO_2 with heterojunction was prepared by a two-step hydrothermal synthesis method and used as a photocatalyst for reducing CO_2 in cyclohexanol. This heterostructured composite has been characterized by X-ray diffractometer (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and ultraviolet-visible (UV–vis) diffuse reflectance spectroscopy (DRS). The activity of the CdS–TiO_2 composite was tested in a batch slurry bed reactor. The results showed that CO_2 absorbed in cyclohexanol was reduced to cyclohexyl formate (CF) on conduction band and the absorbent cyclohexanol was oxidized to cyclohexanone (CH) on valance band of the photocatalyst. It was revealed that the highest formation rates of 20.2 μmol/(g_{cat} h) and 20.0 μmol/(g_{cat} h) for CF and CH could be obtained when TiO_2/CdS with the molar ratio of 8 was used. Overall, this work provides a novel pathway for photocatalytically reducing CO_2 and preventing the catalyst from photocorrosion.

1. Introduction

In recent years, the increasingly anthropogenic carbon emission has become a severe global environmental issue because of its serious impacts on climate change and energy source exhaustion, such as the “greenhouse effect” [1]. On the other hand, CO_2 provides carbon resource of fossil fuel in natural photosynthesis process. Therefore, seeking for renewable and recycling energies from CO_2 not only meets the increasing energy demand, but also is of environmental benign. Reduction of CO_2 to reusable hydrocarbons using solar light is one of the best mitigation strategies for both the global climate change and the energy shortage problems [2,3].

Many researchers have been devoted to mimicking the natural photosynthesis, at ambient temperature and pressure, photocatalytic converting CO_2 to CH_4, CO, CH_3OH, HCHO, HCOOH and so on by using water as reductant and solar light as photon source [4–7]. But their evolution rates and selectivities were still unsatisfactory, because of the weak reducibility of water and the low solubility of CO_2 in water. Among the various photocatalysts used for photocatalytic reduction of CO_2, TiO_2 is considered as the most potential photocatalyst due to its various advantages including strong stability, low cost, and nontoxicity. By now, many studies reported that nanometer-scale TiO_2 catalyst, such as nanorods, nanotubes, and nanosheets exhibited promising performance as photocatalyst. Especially, for the TiO_2 nanosheets, both the high percentage of exposed (0 0 1) facet and the large surface could offer more effective surface in the photocatalytic reaction [8–10]. However, practical application has been limited by the wider band gap of 3.2 eV and low quantum efficiency. In order to increase the photocatalytic activity of TiO_2, researchers have synthesized new TiO_2-based photocatalysts, involving surface modification by ion dopants [11], photosensitizers [12], depositing noble metals [13], and semiconductor complexes [14].

Among the complexes of semiconductors, coupling TiO_2 with narrow band gap semiconductors such as CdS, which serves as a sensitizer, could improve the charge separation efficiency [15]. Moreover, coupling two different semiconductors can transfer electron from an excited one with narrow band gap into another attached one with proper choice of conduction band potentials. So the separation of photoinduced electron and hole pair is improved and the photocatalytic efficiency is raised dramatically [16]. Published papers [17–19] have proved that the formation of the interface between CdS and TiO_2 was crucial for improving the separation and restraining the recombination of photoexcited electron–hole pairs, which enhanced the photocatalytic activity.

However, CdS–TiO_2 heterostructured photocatalyst was still scarcely employed for the photocatalytic reduction of CO_2. Since CdS has a suitable band gap energy of 2.4 eV and sufficiently

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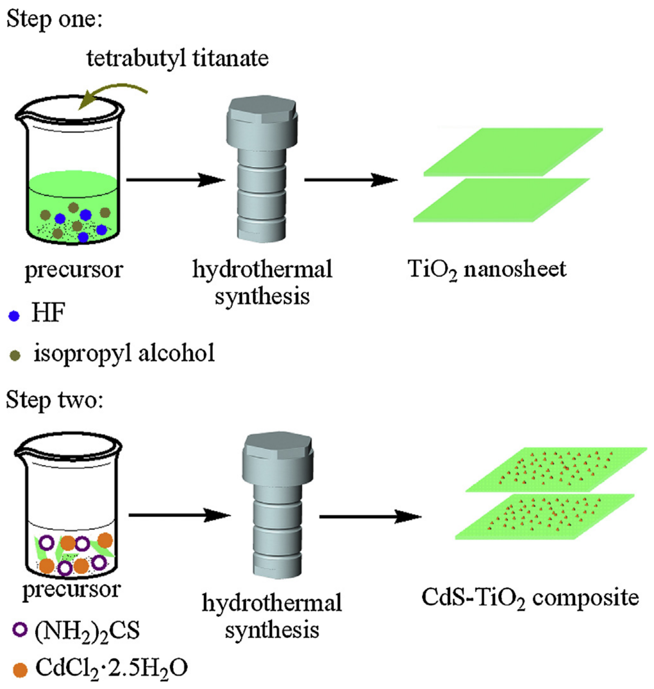
http://dx.doi.org/10.1016/j.apcata.2013.12.035



Scheme 1. Schematic plot for fabrication route of CdS–TiO_2 composite.

negative potential on conduction band of −1.0 V vs. NHE at pH = 7, we deposited CdS particles on the surface of TiO_2 nanosheets via a two-step hydrothermal method. Scheme 1 illustrated the procedure of preparing CdS–TiO_2 heterojunction photocatalyst.

In order to improve carbon dioxide solubility in the liquid phase and reducibility of the sacrificial reagent, cyclohexanol was selected as solvent and reductant because the saturated mole fraction of CO_2 in cyclohexanol is 4.43×10^{-3} [20], which is 7.5 times of that in water [21] at room temperature and normal pressure. CO_2 could be photocatalytically reduced to valuable chemicals by using cyclohexanol as reductant. Photocatalytic oxidation of cyclohexanol to CH and photocatalytic reduction of CO_2 to formic acid were occurred simultaneously, and then esterification of cyclohexanol and formic acid in bulk phase to produce CF.

CH, as one of the intermediates, is mainly used to manufacture Nylon 6, and CF is a normal solvent and synthetic perfume to be widely used in soft drinks, ice cream, frozen foods, candy, and baked food.

2. Experimental

2.1. Materials

Tetrabutyl titanate (TBOT, Ti $(OC_4H_9)_4$), hydrofluoric acid (HF, 40 wt%), isopropyl alcohol (PrOH), cadmium chloride ($CdCl_2$ $2.5H_2O$) and sulfourea ($(NH_2)_2CS$) used in synthesis of catalyst were purchased from Tianjin Guangfu Chemical Reagent Company. All reagents were analytical grade and used without any further purification. GC grade cyclohexanol ($C_6H_{12}O$) used for photocatalytic reduction of CO_2 was bought from Tianjin Xiensi Biochemical Technology Company.

2.2. Catalyst preparation

2.2.1. Preparation of TiO_2 nanosheets

Yang and co-workers [9] found synergistic functions of 2-propanol and HF on the growth of anatase TiO_2 single-crystal nanosheets. Similar to previously described work, in this paper tetrabutyl titanate was used as a titanium source instead of titanium tetrafluoride, HF and isopropyl alcohol were used as synergistic capping agent and reaction medium for preparing TiO_2 nanosheets, respectively. In a typical preparation process, 8 mL tetrabutyl titanate was added dropwise into a mixture of 1 mL hydrofluoric acid and 5 mL isopropyl alcohol with magnetic stirring for 20 min at room temperature. Then, the obtained precursor solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, followed by a hydrothermal treatment at 180 °C for 24 h. After cooling down to room temperature, the collected precipitates were washed with deionized water and ethanol for three times, and dried in a vacuum oven at 80 °C for 10 h. At last, the particles were calcined at 600 °C for 2 h and pure TiO_2 nanosheets were formed.

2.2.2. Preparation of CdS–TiO_2 composite

CdS–TiO_2 composite was synthesized by hydrothermal method. Typically, 0.4 g of above TiO_2 nanosheets were added into 30 mL of deionized water and ultrasonically dispersed. Subsequently, 10 mL aqueous solution of $CdCl_2\cdot 2.5H_2O$ and $(NH_2)_2CS$ with determined concentration were dropped into the as prepared suspension of TiO_2 nanosheets under vigorous stirring, the molar ratio of cadmium to sulfur was kept at 1:1. The final mixture was stirred for 20 min and then hydrothermally treated at 140 °C for 18 h. After centrifugal separation, the obtained precipitates were washed with ethanol and deionized water for three times, and then dried in a vacuum oven at 80 °C for 8 h.

For comparison, a series of CdS–TiO_2 photocatalysts with different molar ratios were synthesized through the same procedure by adjusting amounts of $CdCl_2\cdot 2.5H_2O$ and $(NH_2)_2CS$, which were denoted as CdS–TiO_2-*X*, where *X* represented different molar ratios of TiO_2/CdS. Similarly, pristine CdS was also synthesized following the same procedure as mentioned above.

2.3. Catalyst characterization

The crystal structure and phase identification of the samples were analyzed with a Bruker D8 Avance XRD using Cu $K\alpha$ radiation ($\lambda = 1.54178$ nm) at 40 kV and 40 mA in the 2θ range between 20° and 80°. The morphologies of the samples were observed using Tecnai G2 F20a TEM, with accelerating voltage of 200 kV. The elemental compositions and oxidation state were analyzed by XPS (PHA-5400, SPECS, America) with Mg $K\alpha$ ADES ($h\nu = 1253.6$ eV) source at a residual gas pressure of below 10^{-8} Pa. UV–vis DRS of Shimadzu UV-2550 spectrometer were recorded in the range of 200–800 nm using $BaSO_4$ as a reference.

2.4. Photocatalytic conversion of CO_2

The photocatalytic reduction of carbon dioxide was performed in a batch slurry bed reactor with inner capacity of 50 mL in which 0.02 g of photocatalyst was dispersed in 10 mL cyclohexanol. The reactor was tightly closed during the reaction and stirred continuously by a magnetic stirrer to prevent catalyst from sedimentation. Before irradiation, ultrapure CO_2 was bubbled through the reactor for at least 30 min to purge all of dissolved oxygen and saturate absorbed CO_2. A cooling jacket with cycling water maintained the reaction at room temperature. A 250 W high pressure mercury lamp placed over the reactor to provide light irradiation. A typical run was 10 h.

After a batch, the suspension in the reactor was centrifuged to separate solid catalyst from liquid, and the supernatant solution was analyzed by an Agilent 7890A GC with a flame ionization detector (FID) and a 60 m column of HP Wax. HP1800C GC–MS was used to qualify the products and then CF and CH were found. Blank experiments were also carried out to ensure the reaction to be solely from the photocatalytic reduction of CO_2. One was light illuminated