Flame spray pyrolysis synthesized ZnO/CeO$_2$ nanocomposites for enhanced CO$_2$ photocatalytic reduction under UV–Vis light irradiation

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ABSTRACT

CO$_2$ photocatalytic reduction over semiconductor materials has attracted worldwide attentions. In this paper, ZnO/CeO$_2$ nanocomposites with different Zn/Ce molar ratios were one-step synthesized through flame spray pyrolysis (FSP) and their photocatalytic activities for CO$_2$ reduction were investigated. The results indicate that the addition of CeO$_2$ enhances the surface area and extends the light response to visible light region. The introduction of ZnO enhances the interaction between CO$_2$ and the nanocomposites. In addition, the formation of ZnO/CeO$_2$ heterojunction and co-existence of Ce^{4+}/Ce^{3+} remarkably promote the separation of photogenerated electron-holes pairs within the composites. Due to the special composition and structure, the ZnO/CeO$_2$ nanocomposites exhibited enhanced CO$_2$ photocatalytic reduction under UV–Vis light irradiation.

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1. Introduction

The CO$_2$ emission from the consumption of fossil fuels has been widely recognized as the main contributor to global warming. One of the best solutions to this issue is to convert CO$_2$ into solar fuels, which can not only reduce CO$_2$ emission but also provide valuable fuels [1–4]. Since Inoue et al. [5] first reported CO$_2$ photocatalytic reduction on semiconductors in 1979, the photocatalytic properties of different semiconductors such as ZnO [6,7], TiO$_2$ [8–11], SnO$_2$ [12], CdS [13,14], WO$_3$ [15,16], and C$_3$N$_4$ [17,18] have been reported in succession. Among them, ZnO has attracted wide attention due to its high catalytic activity, high photosensitivity, low cost, and environmental friendliness [19–21]. However, the properties of ZnO still cannot meet the requirements of practical application because of low quantum efficiency and low utilization rate of visible light, resulting from fast recombination of photogenerated charges and wide band gap of ZnO (3.37 eV) [22].

In the past decade, researchers found that the combination of ZnO with other semiconductor materials [19,23–25] or carbon materials can not only promote the separation of photogenerated charges but also enhance the visible light absorption of ZnO, resulting in enhanced photocatalytic activity. Among these composites, ZnO/CeO$_2$ composite is one of the most promising materials since the introduction of CeO$_2$ can maintain their original features and give the composites additional properties [24,26]. Recently, Ma et al. [24] reported enhanced UV and visible light photocatalytic activity of porous ZnO/CeO$_2$ composited for Rhodamine B degradation because of the co-existence of Ce^{3+} and Ce^{4+} on the surface of the composites as well as enhanced visible light absorption. Li et al. [27] reported the synthesis of ZnO/CeO$_2$ nanofibers through electrospinning and their results showed that ZnO/CeO$_2$ nanofibers demonstrated excellent photocatalytic activity for Rhodamine B degradation due to the effective separation of photogenerated electron-hole pairs caused by the formation of ZnO/CeO$_2$ heterojunction. However, to the best of our knowledge, few papers reported CO$_2$ photocatalytic reduction over ZnO/CeO$_2$ composites.

The synthesis method also has great influence on the structural and physico-chemical properties of nanomaterials. Binary metal oxide nanocomposites have been synthesized by wet chemistry routes including sol-gel method [28] and hydrothermal method [24], etc. However, these methods have significant limitations, which usually need multiple steps of washing, purification, drying and annealing. In recent years, flame spray pyrolysis (FSP) processes has received much interest as they enable the production of a broad range of materials in the form of nanostructured powders with high specific surface area and

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primary particle size in the range of few nanometers. FSP allows a precise control over the powder structural characteristics. Properties such as crystallite size, crystalline phase, degree of aggregation and agglomeration, surface area and porosity can be controlled by flame conditions [29–31]. Compared to wet chemistry routes, flame synthesis can produce binary metal oxide nanocomposites in a single step by mixing different metallorganic precursors before feeding them into the spray nozzle, which is very simple and convenient. For example, Choi et al. [32] reported the flame synthesis of core-shell structured $NiO@TiO_2$ nanopowders and Pratsinis' group [33] reported one-step flame made WO_3/CeO_x-TiO_2 catalysts. However, to date, one-step flame synthesis of ZnO/CeO_2 nanocomposites has not been reported.

Here, for the first time, we reported the one-step synthesis of ZnO/CeO_2 nanocomposites through FSP and examined their photocatalytic activities for CO_2 reduction under UV–vis light. The effect of ZnO/CeO_2 molar ratio on the physico-chemical properties and CO_2 reduction activities of ZnO/CeO_2 composites was analyzed. The roles of ZnO and CeO_2 during CO_2 photocatalytic reduction were investigated. Finally, the cycle performance and the deactivation of ZnO/CeO_2 composites were discussed.

2. Experimental

2.1. Catalyst preparation

The experimental apparatus for FSP is shown in Fig. 1. The apparatus consists of an external-mixing atomizing nozzle that is made of a capillary tube that lies in an opening orifice creating an annular gap. The solution containing precursor and fuel flows through the capillary tube, while the dispersion gas rapidly passes through the annular gap. Thereby, the solution is dispersed into small droplets and then is ignited by a supporting flame. The resulting droplets of dissolved precursor are combusted and generated small clusters of the product powder, which grow up by agglomeration and sintering processes occurring in the high temperature environment of the flame. The powders are collected in a glass fibre filtering system placed above the flame. In this work, the precursor solution was prepared by dissolving 50 mmol of Zn $(NO_3)_2$·$6H_2O$ and $Ce(NO_3)_3$·$6H_2O$ with different Zn/Ce molar ratios (0.5, 1.0, and 2.0) into 100 mL of absolute ethanol. The feed rate of precursor solution was 5 mL min⁻¹. The oxygen dispersion gas, methane for supporting flame, and oxygen for supporting flame were 5 SLM (with atomization pressure of 1.5 bar), 0.75 SLM, and 1.5 SLM, respectively. The obtained ZnO/CeO_2 nanocomposites
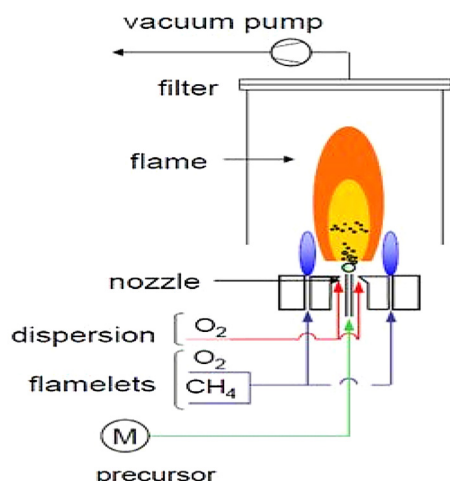
with different Zn/C molar ratios (0.5, 1.0, and 2.0) were donated as ZnCe-0.5, ZnCe-1, and ZnCe-2, respectively. For comparison, pure ZnO and pure CeO_2 were also prepared by the same method.

2.2. Catalyst characterization

For all samples, X-ray diffraction (XRD) patterns were recorded on an Empyrean diffractometer using Cu Kα radiation (λ = 0.1542 nm) in the range of 20–80°. Transmission electron microscopy (TEM) images were obtained by using an FEI Tecnai G^2 F30 instrument. The specific surface areas and pore size distribution were measured by a Micrometrics ASAP 2020 surface area and porosity analyzer. X-ray photoelectron spectra (XPS) were recorded on a Shimadzu/KRATOS AXIS-ULTRA DLD-600W instrument equipped with Al/Mg Kα radiation. Steady and time-resolved photoluminescence (PL) spectra were recorded on a confocal laser Raman microscope (Horiba JobinYvon, LabRAM HR800) and a time-resolved fluorescence spectrometer (Edinburgh Instruments, F900), respectively, by using a 325 nm excitation light source. The photocurrent response and electrochemical impedance spectra (EIS) measurements were performed in three-electrode quartz cells with a 0.1 mol/L Na_2SO_4 electrolyte solution. Platinum wire was used as the counter electrode, and saturated calomel electrodes were used as the reference electrodes. The sample coated ITO glass served as the working electrode. The photoelectrochemical test results were recorded by an electrochemical system (CHI-660D, China). A 500W Xe lamp was used as a light source. UV–vis absorbance spectra were measured by a UV–vis spectrophotometer (Perkin Elmer, Lambda 950). The molar ratio of Zn to Ce in the bulk was measured by an X-ray fluorescence (XRF) spectrometer (EDAX Inc., EAGLE III).

In order to verify the behavior of the catalysts in the presence of CO_2, all samples were analyzed by temperature programmed CO_2 desorption (TPD-CO_2). This technique enables us to analyze the types of CO_2 species adsorbed on the materials. For the procedures in detail, 50 mg sample of powder was placed into a quartz tube reactor first, which was heated under ultra-high purity He flow (30 mL min⁻¹) up to 300 °C at a rate of 25 °C min⁻¹ for 1 h and then cooled to ambient temperature. After the pretreatment, CO_2 flow (30 mL min⁻¹) passed through the catalyst bed for 30 min, subsequently the sample was flushed by He flow (30 mL min⁻¹) for 1 h. Finally, the TPD analysis was performed under He flow (30 mL min⁻¹) by heating the reactor up to 750 °C (Rate: 10 °C min⁻¹). The effluent gas flow was monitored by a TCD detector.

2.3. Photocatalytic reduction of CO_2

CO_2 photocatalytic reduction under UV–vis light irradiation (300 nm < λ < 400 nm, 18.7 mW cm⁻²; 400 nm < λ < 800 nm, 45.0 mW cm⁻²) was carried out in an internal circulated reaction system reported in our previous work [34]. The system mainly includes a 500 W Pyrex glass reactor, a 300 W Xe lamp positioned 10 cm above the reactor, and an online gas chromatography (GC). 10 mL of deionized water was added in the bottom of the reactor, and then 20 mg of catalyst powders was placed on a Petri plate positioned 2 cm above the water in the reactor. Prior to illumination, the reactor was first vacuumed and then was purged by ultra-pure CO_2 (99.999%). The pressure in the reactor was 71 kPa and the temperature of the reactor was kept at 20 °C by cooling it with circulating water. The vapour pressure of water was 2.3 kPa under such a situation. During 4 h UV–vis light irradiation, the amounts of H_2, CO, and hydrocarbons in the reactor were analyzed by the GC/FID/TCD every 15 min. The GC was equipped with a carbon molecular sieve column (TDX-01) and a molecular sieve 5A column.

Fig. 1. Experimental setup for flame spray pyrolysis.