Chemical Physics Letters 700 (2018) 27–35

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

Synthesis and photocatalytic CO_2 reduction performance of Cu_2O/Coal-based carbon nanoparticle composites

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ARTICLE INFO

Article history:
Received 10 January 2018
In final form 3 April 2018
Available online 4 April 2018

Keywords:
Coal
Carbon nanoparticles
Cuprous oxide
Photocatalyst
Cu_2O/CNPs

ABSTRACT

The photocatalytic reduction of CO_2 into hydrocarbons provides a promising approach to overcome the challenges of environmental crisis and energy shortage. Here we fabricated a cuprous oxide (Cu_2O) based composite photocatalyst consisting of Cu_2O/carbon nanoparticles (CNPs). To prepare the CNPs, coal samples from Wucaiwan, Xinjiang, China, were first treated with HNO_3, followed by hydrogen peroxide (H_2O_2) oxidation to strip nanocrystalline carbon from coal. After linking with oxygen-containing group such as hydroxyl, coal-based CNPs with sp2 carbon structure and multilayer graphene lattice structure were synthesized. Subsequently, the CNPs were loaded onto the surface of Cu_2O nanoparticles prepared by in-situ reduction of copper chloride ($CuCl_2{\cdot}2H_2O$). The physical properties and chemical structure of the Cu_2O/CNPs as well as photocatalytic activity of CO_2/H_2O reduction into CH_3OH were measured. The results demonstrate that the Cu_2O/CNPs are composed of spherical particles with diameter of 50 nm and mesoporous structure, which are suitable for CO_2 adsorption. Under illumination of visible light, electron-hole pairs are generated in Cu_2O. Thanks to the CNPs, the fast recombination of electron-hole pairs is suppressed. The energy gradient formed on the surface of Cu_2O/CNPs facilitates the efficient separation of electron-hole pairs for CO_2 reduction and H_2O oxidation, leading to enhanced photocatalytic activity.

1. Introduction

Since the concept of photocatalytic CO_2 reduction was proposed, the exploring and developing of potential catalysts with high efficiency has been a research hotspot [1–3]. Particularly, benefiting from their excellent photocatalytic activity and stability under illumination, semiconductor oxide based catalysts have become one of the most common and extensively studied photocatalysts for CO_2 reduction [4–8]. Among them, nanoscale Cu_2O is a typical p-type semiconductor with direct bandgap of 2.0~2.2 eV, suitable for visible light excitation. In addition, Cu_2O is environmental friendly and inexpensive, which has become a promising candidate for photocatalytic CO_2 reduction into hydrocarbon fuels [9–11]. However, the photo-generated electron-hole pairs in Cu_2O recombine easily, resulting in low photocatalytic efficiency [12]. Furthermore, Cu_2O nanoparticles often form clusters and lose catalytic activity [13]. Thus, these challenges must be overcome before their practical applications.

Discovered in recent years, carbon nanoparticles (CNPs) are a new type of luminescent nanoparticles. The fluorescence of CNPs is comparable to conventional quantum dots (such as strong and stable luminescence, tunable excitation and emission wavelength, upper-conversion ability, and decent visible luminescent emission). Moreover, CNPs are great electron acceptors and donors. After light excitation, the intrinsic surface defects of CNPs can suppress the recombination of generated electron-hole pairs [14–16]. Thus, CNPs can be used as a single photocatalyst or combination with other materials or dopants to form composite photocatalysts with increased catalytic activity [17–21]. So far, there are little reports on CNPs synthesis from coal and their application for composite photocatalysts with semiconductor oxides. For this reason, here we fabricated nanocrystalline carbon by H_2O_2 oxidation, using HNO_3 pre-treated coal sample from Wucaiwan, Xinjiang, China. After linking the carbon sites with oxygen-containing group such as hydroxyl, coal-based CNPs with sp^2 carbon structure and multilayer graphene lattice structure were synthesized. Cu_2O/CNPs composite nanoparticles were fabricated by combining CNPs and

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https://doi.org/10.1016/j.cplett.2018.04.007
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in-situ synthesized Cu_2O particles. The morphology, optical properties of the Cu_2O/CNPs and the photocatalytic performance of CO_2 reduction into CH_3OH were measured.

2. Experimental methods

2.1. Raw materials and reagents

The coal samples were from Wucaiwan coalmine in Zhundong coalfield of Xinjiang, China. The samples were grinded and passed through a 200-mesh sieve, followed by baking at 105 °C for 4 h. Analytical grade hydrogen peroxide (H_2O_2, 30%) and ascorbic acid ($C_6H_8O_6$) were purchased from Tianjin Yongsheng Fine Chemical Co., Ltd. Analytical grade Copper chloride ($CuCl_2{\cdot}2H_2O$) and Polyvinyl Pyrrolidone (PVP, Mr = 30000) were purchased from Tianjin Zhiyuan Reagent Co., Ltd. Analytical grade nitric acid (HNO_3) and sodium hydroxide (NaOH) were purchased from common chemical stores.

2.2. Fabrication of coal-based CNPs

The coal samples from Wucaiwan, Xinjiang, first went through reflux treatment with 2.5 M HNO_3 for 24 h, and were placed into agate mill jars with distilled water (ball milling medium of pickaxe oxide, 6 balls with diameter of 12 mm, 8 balls with diameter of 10 mm, and 8 balls with diameter of 8 mm). The samples were ball-milled at room temperature and 600 rpm for three hours to obtain ultra-fine coal powders. Next, 0.5 g of the obtained powder was dispersed into 10 mL deionized water by ultrasound, followed by adding 30 mL 30% H_2O_2 and reaction at 90 °C for three hours with magnetic stirring (5 mL 30% H_2O_2 was added into the solution every 10 min for a total of four times). After the reaction stopped, the reaction liquid was transferred to a centrifuge tube for centrifugal separation (10000 rpm for 10 min), and the supernatant was dispersed into water and naturally dried to acquire the dark brown coal-based CNPs (yield of 16.5% based on the ultra-fine coal powder).

2.3. Fabrication of Cu_2O/CNPs

25 mg of coal-based CNPs was dispersed into 25 mL 0.02 M $CuCl_2$ solution by ultrasound, and the uniformly dispersed orange yellow liquid was transferred into a reaction bottle. 3.82 g of PVP was added into the bottle with stirring. After stirring for an hour, the bottle was heated to 55 °C, and 5 mL 2.0 M NaOH was dropped into the solution. After reaction for 30 min, 0.6 g of $C_6H_8O_6$ was added into the solution, followed by stirring at 55 °C. The precipitates were centrifuged and washed with water and ethanol, followed by vacuum drying at 50 °C. By varying the CNPs amount, Cu_2O/CNPs with different Cu_2O content can be prepared following the same procedures.

2.4. Characterizations of product

CNPs, Cu_2O, and Cu_2O/CNPs solutions were dispersed onto copper grids and dried. The morphology and structure of the nanoparticles were measured by an H-600 transmission electron microscope (TEM). The element distribution of Cu_2O/CNPs was measured by EDX (HITACHI-SU8010, acceleration voltage of 5 kV, working distance of 8 mm). The crystal structure of CNPs, Cu_2O, and Cu_2O/CNPs was measured by X-ray diffraction (XRD, M18XHF22-SRA, Cu-Ka radiation, measured by X-ray diffraction $2\theta = 10–80°$). The thermogravimetric analysis (TG) was conducted using a PE-DTA/1700 thermal analyzer with scanning range of 25–800 °C. The confocal Raman spectra of CNPs, Cu_2O, and Cu_2O/CNPs were measured by a Raman spectrometer (BRUKER VERTEX 70). The adsorption and desorption performance of N_2 in Cu_2O and Cu_2O/CNPs was tested by a specific surface area and pore size distribution meter (Autosorb-IQ2), and the specific surface area and pore size distribution was calculated by the BET and BJH method. The FTIR measurement of Cu_2O and Cu_2O/CNPs was performed using a Bruker-EQUINOX 55 Fourier transform infrared spectrometer. The surface states of coal-based Cu_2O and Cu_2O/CNPs were obtained by XPS (ESCALAB 250). The ultraviolet–visible diffuse reflectance spectra (UV–vis DRS) of Cu_2O and Cu_2O/CNPs were measured by a UV–vis DRS spectrometer (Shimadzu UV-3100) with $BaSO_4$ as reference and wavelength range of 250–750 mm. The emission spectra of Cu_2O, and Cu_2O/CNPs solutions were measured by a fluorescence spectrometer (Fluorolog-3).

2.5. Photocatalytic CO_2 reduction by visible light

As shown in Fig. 1, 125 mL 1 M NaOH and 0.1 g of photocatalyst were added into a quartz bottle for the photocatalytic reduction reaction. The solution was stirred with CO_2 passing through. After 30 min, the light source (300 W Xenon lamp) was turned on to start the photocatalytic CO_2/H_2O reduction. The samples of the solution were acquired every three hours with syringes, and centrifuged to obtain supernatants, followed by passing through a 200 nm membrane filter. Subsequently, the samples were injected into a gas chromatography (GC8100 with FID detector and PEG-21 packed column). The CH_3OH content in the sample was analyzed using the standard curve method.

3. Results and discussion

3.1. Morphology of Cu_2O/CNPs

The microstructure of coal consists of natural large molecules, including amorphous carbon regions composed of aliphatic compounds and nanoscale crystalline carbon regions composed of polymerized aromatic hydrocarbon [22]. The crystalline carbon regions have large quantity, and the size of each crystalline carbon is similar to quantum dots. Thus, carbon nanoparticles can be obtained using various methods [23,24].

According to the TEM measurement results, the coal-based CNPs from Wucaiwan coal samples using H_2O_2 oxidation/striping method have spherical-like shape with diameter distribution of 2 to 12 nm (Fig. 2A). High-resolution TEM measurement shows that the nanoparticles have graphite-like lattice structure (Fig. 2A inset) with lattice spacing of 0.21 nm, close to the spacing of graphite (1 0 0) crystal surface [25]. The synthesized pure Cu_2O particles have cubic structure with length of 80 nm. The dispersivity of the sample is poor, and the particles are easily clustered (Fig. 2B). Nevertheless, as shown in the TEM image (Fig. 2C) of Cu_2O/CNPs composed of CNPs and Cu_2O, the spherical composite particle consists of CNPs attached to the surface of Cu_2O, and CNPs form a thin shell outside the Cu_2O surface. The diameter of the composite particle is about 50 nm with uniform distribution and few clusters. It is likely that the existence of CNPs suppresses the growth of Cu_2O microcrystal, leading to smaller Cu_2O in the composite, which increases the specific surface area of the composite for more adsorption of CO_2 reactant.

The EDX measurement results show that Cu_2O/CNPs mainly contain four elements (Fig. 2D): C, N, O, and Cu, with content (weight percentage) of 5.78%, 2.07%, 19.85%, and 72.30%, respectively. The result indicates that Cu_2O and CNPs successfully form composite. The C and N come from CNPs, Cu comes from Cu_2O, and O is likely from CNPs and Cu_2O.