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Openmouthed β-SiC hollow-sphere with highly photocatalytic activity for reduction of CO_2 with H_2O

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ABSTRACT

A novel hollow spherical 3D structure of β-SiC with an open mouth was successfully fabricated by an environmentally friendly approach starting from ethylsilicate interaction with the P123 and glucose. The proposed growth mechanism of SiC hollow spheres was revealed step by step with SEM and XRD. When the as-prepared SiC was applied for the photocatalytic reduction of CO_2 with pure water, it was found to be highly active for the conversion CO_2 into mainly CH_4 hydrocarbon products due to its unique electronic structure, hollow morphology and high BET surface area. Moreover, the photocatalytic activity of the hollow spherical SiC can be greatly improved by loading Pt cocatalyst. The optimal 2.0 wt% Pt loading led to a stable CH_4 evolution as high as 16.8 μmol/g/h (or 376.4 μl/g/h) with the simulated solar light irradiation, which is higher than that of many reported metal oxides (Pt/TiO_2, CdS/WO_3, Zn_2GeO_4, CeO_2 and g-C_3N_4/$NaNbO_3$ et al.) under similar experimental conditions. This work provides a new strategy for the architecture of thermally and chemically stable non-metallic carbide with unique hollow spherical structure to be a potential nonmetallic photocatalyst for CO_2 reduction into CH_4.

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1. Introduction

Harvesting solar energy for the photocatalytic conversion of CO_2 into chemical fuels is an ideal solution to address global warming and carbon cycle in nature. To achieve this objective reaction, many efforts have been devoted to developing efficient photocatalysts ranging from semiconducting materials, such as TiO_2, Zn_2GaO_4, CdS, and C_3N_4 [1], to metal–organic frameworks (MOFs) including NH_2-MIL-125(Ti) [2], Fe_MOF-525 [3], and Mn(bpydc)-$(CO)_3$Br [4]. However, the efficiency of photocatalytic CO_2 conversion is still very low even in the presence of electron donor sacrificial agent [5]. Searching for suitable photocatalyst materials for efficient CO_2 conversion is one of the fundamental missions in photocatalysis communications.

Silicon carbide (SiC), one of the very important non-metallic oxide semiconductors, has been applied widely from metallurgy to aerospace due to its high thermal conductivity and high strength [6–9]. On the other hand, SiC also possesses several other unique properties, including moderate wide of band gap of Eg ≈ 2.4 eV,

considerable negative conduction band potential (−1.40 V), high chemical stability and environmental friendliness. These make SiC suitable as a photocatalyst, especially for the high reduction potential reactions such as water reduction and CO_2 reduction in efficiently harvesting solar energy. Actually, SiC was reported to has good activity for photocatalytic splitting pure water under ultraviolet light irradiation as early as 1990 [10,11]. However, to the best of our knowledge, SiC has been only a few study as a photocatalyst in the CO_2 reduction up to date [12], although it is more suitable in electron structure than the majority of semiconductor materials.

The morphology commonly has a significant effect on the material properties and applications. One-, two-, and three-dimensional structure of SiC, such as nanofibers [13–17], whisker [18–20], monomolecular layers [21], and hollow spheres [22–26], have been fabricated by various approaches such as carbothermic method [27–29], chemical vapor deposition [30,31], template-directed process [32–34]. The morphologically controlling synthesis of SiC by a simple and friendly approach is still desirable. For diverse structures, the hollow spherical microstructure has attracted intensive attentions as a photocatalyst. Its high surface area, high porosity, low bulk density, and multi-reflections of light within interior cavities are considered to be very favorable for mass transfer and efficient utilization of solar light in the photocatalytic process.

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There has been many methods to be developed for the preparation of hollow spherical metal oxides and sulfides photocatalyst [35]. However, the synthesis of some hollow structure carbide and nitride materials remains a challenge due to high temperature calcination. Zhang et al. [24] prepared SiC hollow spheres by the solid–gas reaction of carbon spheres with excess micro-grade silicon at 1300 °C. Shen et al. [25] have succeeded in synthesizing SiC hollow microspheres by using $SiCl_4$ and C_6Cl_6 as source materials and metallic sodium as reductant. Zhou et al. [26] reported that the ordered SnO_2/SiC hollow sphere nanochains can be prepared through the topological morphology conversion of C@SnO_2 core–shell nanochains in a vapor–solid reaction process. However, these synthesis methods for hollow spherical SiC were involved toxic raw materials or a complicated procedure.

Herein, we report an openmouthed β-SiC hollow-Sphere. It was synthesized by environmentally friendly approach using frequently-used glucose as the carbon resource. The effect of the reaction temperature and time on the hollow sphere morphology was systemically investigated. The possible formation mechanism was suggested according to the analysis results of SEM and XRD. The as-prepared SiC hollow spheres was observed to show a much higher photocatalytic activity for the reduction of CO_2 with H_2O to CH_4 than the commercial SiC or the standard photocatalyst P25 TiO_2. These findings not only show that SiC material is a promising photocatalyst for CO_2 reduction, but also imply that photocatalytic behavior of SiC could be effectively modulated by morphology.

2. Experimental section

2.1. Materials

P123 (PEO-PPO-PEO) and $H_2PtCl_6\cdot6H_2O$ were acquired from ALDRICH and Aladdin, respectively. Other reagents used in the present study, including ethanol, hydrochloric acid, TEOS (ethylsilicate), glucose, sodium hydroxide and methanol, were of analytical reagent grade and obtained from Sinopharm Chemical Reagent Co., Ltd. All of the above chemicals were used without further purification.

2.2. Preparation of SiC hollow sphere

SiC precursor was prepared by Sol-Gel method. In a typical preparation procedure, 2.53 g of P123 was added to the mixed solution containing 3 ml of deionized water, 2.4 ml of ethanol, and 0.3 ml of 1 M hydrochloric acid under magnetic stirring at room temperature until formation of a homogeneous solution. 6.4 ml of ethylsilicate and 10.8 g of glucose were then introduced to the above homogeneous solution by heating at 363 K for 12 h to get a yellow gel. The resulted yellow gel was dried in an oven at 393 K to obtain a brown aerogel SiC precursor.

The SiC samples were prepared by carbothermic reduction of the SiC precursor according to the following steps. Firstly, the brown aerogel SiC precursor was pre-carbonized in flowing N_2 atmosphere at 823 K for 5 h, and then shifted to flowing Ar atmosphere at high temperature (1723 or 1773 K) for a certain time (5, 8, or 10 h). Finally, the carbonized samples were calcined in O_2 atmosphere at 873 K for 5 h to remove residual carbon following by immersing in 10 wt% sodium hydroxide solution to remove unreacted SiO_2. The obtained SiC sample was washed with deionized water serval times and dried at 333 K. The obtained SiC samples were denoted as SiC (xK, yh), where x stands for carbothermic reduction temperature (x = 1723, 1773) and y represents carbothermic reduction time (y = 5, 8, 10).

2.3. Preparation of Pt/SiC

Pt loaded SiC samples (Pt/SiC) were prepared by using incipient-wetness impregnation method. In detail, 0.3 g of the as-prepared SiC (1723 K, 8 h) was added to an aqueous solution with different concentration of chloroplatinic acid. The suspended solution was under ultrasound for 0.5 h to ensure the absorption of chloroplatinic acid on SiC. And then the SiC solids were recovered by centrifugation and dried at 393 K for 5 h. The resulted samples were reduced with 0.1 M of sodium borohydride, followed by the deionized water washing and drying at 333 K. The obtained samples were denoted as z wt%Pt/SiC, where z stands for the weight percentage of the Pt species (z = 0, 1, 2, 3).

2.4. Characterization

The XRD patterns were recorded with Ni filtered Cu Kα radiation at 40 kV and 40 mA on a Bruker D8 Advance X-ray diffractometer. The morphology of sample was characterized by a field emission scanning electron microscopy (FESEM) (JSM-6700F), while the transmission electron microscopy (TEM) images were obtained at an accelerating voltage of 200 kV using a JEOL model JEM 2010 EX instrument. The thermo analysis (TG-DSC) was carried out by a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 K/min under argon atmosphere. The UV–vis diffuse reflectance (UV–vis DRS) spectra were obtained on a UV–vis spectrophotometer (Cary 500) with a self-supporting sample cell, and the pure $BaSO_4$ was used as a reflectance standard. Brunauer–Emmett–Teller (BET) surface area and CO_2 adsorption were measured with an ASAP2020M apparatus (Micromeritics Instrument Corp., USA). Nitrogen adsorption and desorption isotherms were measured at 77 K, and CO_2 adsorption isotherms were measured at 273 K. The elemental composition of samples was analyzed by X-ray photoelectron spectroscopy (XPS, VG, Physical Electrons Quantum 2000 Scanning Esca Microprob, Al Kα$_1$ radiation). The products of the $^{13}CO_2$ and $^{12}CO_2$ isotopic experiment were analyzed by Hiden HPR-20 mass spectrometer. Photoluminescence excitation spectra was recorded on a FL/FS920 spectrofluorimeter (Edinburgh Instruments) fluorescence spectrometer at room temperature, the excitation wavelength is 375 nm.

2.5. Photocatalytic activity measurement

Photocatalytic reduction of CO_2 in the presence of H_2O was carried out as a gas–solid heterogeneous reaction in a 40 ml Schlenk tube with a silicone rubber septum under atmospheric pressure at ambient temperature (298 K). The light source was a 300 W commercial Xe lamp vertically placed outside the reactor. 10 mg of photocatalyst was placed into the reaction tube. The system was evacuated by a mechanical pump and then filled with pure CO_2 gas. This evacuation–filling operation was repeated three times. Finally, 1 ml of pure water was added into the reactor via the silicone rubber septum. The photocatalytic reaction was typically performed for 4 h. After light irradiation, the amount of CH_4 formed was analyzed using a GC-7890A gas chromatograph equipped with a FID detector and a capillary column (GC-GASPRO, 30 m × 0.320 mm). The generated O_2 was detected by HP 7890 gas chromatography (Ar carrier) equipped with a TCD detector and 5A molecular sieve packed column (10 m × 2 mm).

2.6. Photoelectrochemical measurements

Photoelectrochemical measurements were carried out with a BAS Epsilon workstation using a standard three-electrode electrochemical cell with a working electrode, a platinum foil as the counter electrode, and a saturated Ag/AgCl electrode as the refer-