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Insight into the enhanced CO_2 photocatalytic reduction performance over hollow-structured Bi-decorated g-C_3N_4 nanohybrid under visible-light irradiation

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ABSTRACT

In this study, hollow-structured Bi decorated g-C_3N_4 hybrids were successfully fabricated by a simple solvothermal method and applied for the first time to the photocatalytic reduction of CO_2. Remarkably, the composites exhibited excellent CO_2 conversion efficiencies in the presence of H_2O under visible light irradiation compared to unmodified g-C_3N_4, especially for the production of CH_4. The optimum photocatalyst 30-Bi/g-C_3N_4 presented the best production of CO and CH_4, approximately 3 times and 9 times as high as those of unmodified g-C_3N_4, respectively. A series of characterizations were conducted to explore the essence behind such an enhancement; we found that enhanced light harvesting, quick separation of photoinduced carriers and more negative conduction band, due to the formation of a Schottky junction between g-C_3N_4 and Bi metal and the solvothermal process, co-contributed for the enhanced CO_2 conversion; A more important finding was that the surprising improvement of CH_4 yield stem primarily from the introduction of the hollow-structured Bi, which enabled the accumulation of electrons on its surface exhibiting the metal-like property. The CO_2 photocatalytic conversion process was also investigated by in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) spectroscopy and we found that HCO_3^- and CO_2^- were active intermediates over 30-Bi/g-C_3N_4 and Bi doping could promote the activation of CO_2. In summary, this work presented hollow-structured Bi decorated g-C_3N_4 composites as new materials for energy applications, proving once more the meta-like nature of bismuth, and laying the groundwork for the utilization of Bi in CO_2 photocatalytic reduction processes.

1. Introduction

As the environmental concerns regarding greenhouse effects and the depletion of fossil resources grow, studies on the conversion of CO_2 into energy fuels have attracted intensive attention worldwide, especially by means of photocatalytic reduction processes utilizing the inexhaustible solar light following the pioneering work by Inoue and coworkers [1], in which CO_2 is not only converted into value-added hydrocarbons such as HCOOH, CO, CH_4, etc. [2,3], but the CO_2 levels in the atmosphere are reduced. However, CO_2 is such a thermodynamically stable molecule with C═O bonds possessing a dissociation energy of ~ 750 kJ mol^{-1} [4]; therefore, the search for highly efficient semiconductor photocatalysts with characteristics of efficient photon utilization (that is, an appropriate bandgap), suitable redox potentials, fast separation of photoinduced carriers, and excellent stability has long been a challenging but rather significant research hotspot [5,6].

Graphitic carbon nitride (g-C_3N_4), an environmentally-benign semiconductor, displays several merits such as low cost, a two-dimensional structure with relative high surface area, tunable band structure and outstanding chemical stability [7,8]. Recent times have witnessed its extensive photocatalytic applications under visible-light irradiation [9,10]. However, the photocatalytic performance of pristine g-C_3N_4 still suffers from quick recombination rates of the photogenerated carriers, poor electrical conductivity, and inefficient visible-light harvesting [11], thus pressing for the development of g-C_3N_4 modifications.

Owing to the easy anchoring features of the g-C_3N_4 surface [10,12], the construction of noble metal-semiconductor hybrid nanocomposites has been considered as an effective strategy to improve the photocatalytic performance of g-C_3N_4, among multifarious modification methods [13–15]. On the one hand, noble metal nanoparticles may

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serve as electron trapping sites in metal-semiconductor hybrids, accelerating the separation of charges at the interface via Schottky barriers [16,17]. On the other hand, noble metals such as Au, Ag, Cu, Bi, etc. may strongly enhance the light harvesting and local electric field to activate more electrons and holes due to surface plasma resonance (SPR) effects [18,19]. Thereinto, the CO_2 photoreduction performance of Au, Ag, Cu, and Pt coupled to common semiconductors has been thoroughly investigated [20–23], however, the SPR effect of Bi has not been studied for CO_2 photocatalysis, although this element has been recognized a promising substitute for noble metals and applied in diverse fields of science and technology [24,25]. More encouragingly, Bi nanoparticle-containing composites have been found to exhibit advanced photocatalytic activity compared to the unmodified semiconductors [24,26–28].

Furthermore, photocatalysts with a hollow structure have recently gained intensive interest on account of their unique properties [29,30]. It has been reported that hollow-structured photocatalysts consist of nanoparticles with not only a large specific area, providing more active sites for the reactants, but also that they allow the multiple reflection of light within their inner cavities [31] reducing the diffusion length of photoinduced carriers, thus challenges related to light harvesting and charge separation can be overcome [32]. Accordingly, such hollow structures may impose a considerable influence on the photocatalytic performance of photocatalysts.

Hence, the combination of the advantages of g-C_3N_4 and low-cost Bi to construct metal-semiconductor photocatalysts could be a feasible approach for the photocatalytic reduction of CO_2. Here, the surface of g-C_3N_4 was uniformly anchored with bismuth hollow nano-spheres by a previously-reported one-pot solvothermal in situ reduction method [33] to study its CO_2 photoreduction activity under visible-light illumination. Morphology structures, light absorption, photo-electrochemical properties, and separation of charge carriers of the photocatalysts were characterized to gain insight into the mechanism of such an enhanced CO_2 photoreduction performance, and in-situ diffuse reflectance infrared Fourier transform spectroscopy (in-situ DRIFT) is also utilized to investigate the possible CO_2 photocatalytic conversion process over the samples.

2. Experimental

2.1. Sample preparation

2.1.1. Chemicals

Urea and polyvinylpyrrolidone (PVP, M_W of 24,000) were purchased from Aladdin Industrial Corporation. $Bi(NO_3)_3{\cdot}5H_2O$, HNO_3, and ethylene glycol were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the chemicals employed in our experiments were of analytical purity and used without any further purification.

2.1.2. Synthesis of Bi/g-C_3N_4 nanohybrids

Graphitic carbon nitride (g-C_3N_4) was firstly prepared by polymerization of urea. Typically, 20 g urea was placed in a 100 mL crucible with a cover, and then introduced in a muffle furnace at 550 °C for 2 h with a programmed ramping rate of 10 °C min^{-1}. After the heat treatment, yellow g-C_3N_4 was obtained and kept for further research. The hybridized Bi/g-C_3N_4 nanocomposites were synthesized according to a literature method [33]. Specifically, $Bi(NO_3)_3{\cdot}5H_2O$ (0.364 g) was firstly dissolved in a diluted nitrate solution (1 M, 10 ml) with intensive stir, then 55 ml ethylene glycol and 0.6 g PVP was consecutively added with constant stir until a completely clear solution was obtained and transferred to a 100 ml Teflon-lined autoclaves, then the pre-synthesized g-C_3N_4 with a certain mass was added, after ultrasonic for 30 min, the autoclaves were heated at 160 °C for 12 h in a dry oven. The mass ratio of Bi to g-C_3N_4 was modulated at 15, 30, 50, 75, and 100% by adjusting the mass of the g-C_3N_4 added, and the resulting specimens were denoted as x-Bi/g-C_3N_4 where x stands for the mass percentage. For comparison, pure Bi hollow nanospheres and g-C_3N_4 nanosheets (denoted as Solvo-CN) were also prepared, following the same synthetic process in the absence of g-C_3N_4 and $Bi(NO_3)_3{\cdot}5H_2O$, respectively. In addition, Solvo-CN and Bi nanospheres at a mass ratio of 10:3 were evenly mixed and thoroughly grounded with a pestle for 30 min. The obtained sample was denoted as solid-mixed 30-Bi/g-C_3N_4.

2.2. Characterization methods

The morphology structure was investigated by scanning electron microscopy (SEM, HITACHI UHR FE-SEM, SU 8010) and transmission electron microscopy (TEM, H-600, Hitachi, Ltd., Japan, Voltage: 200KV). X-ray diffraction (XRD, Model D/max RA, Rigaku Co., Japan with Cu Kα radiation) analysis was performed to analyze the crystal phase of the as-synthesized samples. The surface properties were studied by X-ray photoelectron spectroscopy (XPS) on a Thermal ESCALAB 250 instrument with a monochromatic Al Kα source (150 W, 500 μm, 1486.6 eV). The C1 s level at 284.8 eV was used as the reference to calibrate the binding energy. The specific area and pore structure were calculated from the N_2 adsorption–desorption isotherms by the multipoint Brunauer–Emmett–Teller (BET) method. UV–vis diffuse reflection spectra (UV–vis DRS) were recorded on a UV–vis spectrophotometer (TU-1901, China) equipped with an integrating sphere assembly. Photoluminescence (PL) spectra were acquired on a fluorescence spectrophotometer (FLS920, Edinburgh Instruments, UK) equipped with a xenon lamp at an excitation wavelength of 380 nm. The time-resolved fluorescence was measured using the same analytical instrument excited at 380 nm and monitored at 405 nm. Photoelectrochemical characterizations were performed on an electrochemical system (CHI-660B, China) in a three-electrode cell made of quartz containing a 0.2 M Na_2SO_4 electrolyte solution. Platinum wire (CHI115) was used as the counter electrode, saturated Ag/AgCl (CHI111) as the reference electrode. The working electrode was prepared with a piece of ITO glass, in the middle of which, an area of 1 × 1 cm^2 was coated with our samples with the help of a coating solution. Electrochemical impedance spectroscopy (EIS) measurements were carried out at 0.0 V on a 12,608 W electrochemical system (Solartron Mobrey, England), with a sinusoidal ac perturbation of 5 mV applied to the electrode over the frequency range of 100 –1.8 M Hz. In-situ DRIFT spectra were recorded on a Tensor 27 spectrometer (Thermo Nicolet Corporation, USA) with a Harrick low-temperature chamber.

2.3. Photocatalytic performance

The CO_2 photoreduction activity was evaluated in a continuous-flow system with controllable temperature, reported by us in previous work [34]. To be specific, 40 mg photocatalysts was firstly dispersed at the bottom of a stainless steel cylindrical reactor with a dip-coating method, after the catalyst became dry, the reactor was covered with a quartz glass, through which the light source from a 300 W Xenon lamp (PLS-SXE300UV) can cast upon. A 420 nm light cut filter was equipped for the Xenon lamp to obtain the visible light. Before the formal experiments, a pure CO_2 flow from a steel gas cylinder was purged to the reactor through a water bubble for 60 min with a controlled flow rate of 120 ml min^{-1}. Next the flow was adjusted to a stream of 3 ml min^{-1}, stabilized for about 1 h, during which the coating photocatalysts was saturated with CO_2 and H_2O. It needs to be mention that the temperature of the water bubble was controlled at 30 °C to maintain a fixed water content and simultaneously eliminate external environmental effects. The light was then turned on for 8 h, during which the gaseous products were qualitatively and quantitatively monitored at twenty minutes each interval by a gas chromatography (GC, Agilent 7890 A, USA) on a basis of standard curves. The GC was equipped with three quantitative loops, separately connected with a Porapak culumn, a DB-Wax column and a combination of Porapak and 5 A column, followed