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Fabrication of Heterostructured g-C_3N_4/Ag-TiO_2 Hybrid Photocatalyst with Enhanced Performance in Photocatalytic Conversion of CO_2 Under Simulated Sunlight Irradiation

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ABSTRACT

Heterostructured g-C_3N_4/Ag-TiO_2 (CN/AgTi) hybrid catalysts were fabricated through a facile solvent evaporation followed by a calcination process, using graphitic carbon nitride (g-C_3N_4) and Ag-TiO_2 (AgTi) as precursors. The phase compositions, optical properties, and morphologies of the catalysts were systematically characterized. The heterostructured combination of g-C_3N_4, titania (TiO_2) and silver nanoparticles (Ag NPs) resulted in significant synergy for catalytic conversion of CO_2 in the presence of water vapor under simulated sunlight irradiation. The optimal CN/AgTi composite with a g-C_3N_4 to AgTi mass ratio of 8% exhibited the maximum CO_2 photoreduction activity, achieving a CO_2 conversion of 47 μmol, CH_4 yield of 28 μmol, and CO yield of 19 μmol per gram of catalyst during a 3 h simulated sunlight irradiation. Under the experimental conditions, the rate of electron consumption was calculated to be 87.3 μmol/g·h, which was 12.7 times, 7.9 times, and 2.0 times higher than those for TiO_2, g-C_3N_4 and AgTi, respectively. The combination of g-C_3N_4 and AgTi resulted in more sunlight harvesting for electron and hole generations. Photoinduced electrons transferred through the heterjunction between g-C_3N_4 and TiO_2, and further from TiO_2 to Ag NPs with lower Fermi level greatly suppressed the recombination of electron-hole pairs, and hence resulted in electron accumulation on Ag NPs deposited on the TiO_2 surface in the CN/AgTi. Abundant electrons accumulated on the Ag NPs were further energized by the surface plasmon resonance effect with the aid of visible light. Therefore, the CN/AgTi catalysts exhibited superior catalytic performance in CO_2 reduction by water vapor under simulated sunlight irradiation.

1. Introduction

Photocatalytic reduction of carbon dioxide (CO_2) with water (H_2O) vapor utilizing low energy density solar energy to convert greenhouse gas CO_2 into high energy density chemical energy has been considered as one of the best solutions to partially alleviate the energy shortage crisis and decrease the concentration of CO_2 in the atmosphere. Since Inoue and co-workers first reported photocatlalytic conversion of CO_2 in aqueous suspensions containing semiconductor powders [1], more and more photocatalysts have been developed by scientists to achieve a more efficient CO_2 photocatalytic conversion [2]. Among them, titania (TiO_2) was the most extensively studied photocatalyst, because of its high stability, non-toxic nature, low cost, and wide availability [3]. However, its wide bandgap and high electron-hole recombination rate restrict its practical application in CO_2 conversion [4]. Therefore, it is of great interest to modify the crystal structure, electronic structure, lifetime of charge carrier, and electron-hole (e-h) recombination probability of TiO_2 to enhance its photocatalytic activity in CO_2 conversion [5] via several different strategies such as doping with ions and heterostructuring of semiconductor photocatalysts [6].

To avoid the fast e-h recombination issue, doping or deposition of noble or coinage metals such as platinum (Pt) [7], gold (Au) [8], or silver (Ag) [9] to TiO_2 has been proposed. These noble or coinage metals can improve the e-h separation through formation of Schottky barriers [10,11]. For example, Pt nanoparticles (NPs) can hinder e-h recombination by serving as electron sinks and facilitating interfacial electron transfer [12,13]. However, because of Pt NPs are lack of visible light absorption capacity, loading of Pt NPs would usually not improve the solar-harvesting capability of TiO_2-based photocatlysts [14,15]. More importantly, Pt is a rare and costly metal. In contrast, the relatively abundant and inexpensive Ag not

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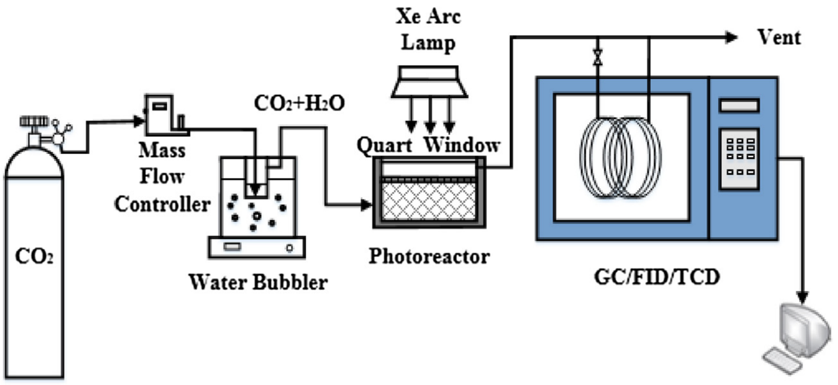

Fig. 1. Schematic diagram of the experimental set up.

only can serve as electron sink [16], but also can strongly absorb visible light and facilitate the separation of photo-excited e-h pairs due to the surface plasmon resonance (SPR) [17,18]. Accordingly, the silver NPs incorporated TiO_2 (Ag-TiO_2) showed effectiveness in CO_2 photoreduction in several studies [19–21]. Even though the SPR effect attributed to silver doping enhances visible light adsorption of TiO_2, the light-harvesting capacity of Ag-TiO_2 (AgTi) catalyst is still poor due to its wide bandgap [21].

To effectively increase the light-harvesting capacity of TiO_2 based catalysts, a novel metal-free polymeric graphitic carbon nitride (g-C_3N_4) has attracted abundant scientific interests due to its suitable bandgap for absorbing visible light [22], photocatalytic stability [23], and effective charge transfer ability [5]. Although g-C_3N_4 is of visible light response, its ultraviolet (UV) response is relatively lower, as compared to TiO_2 [24]. Coupling wide-bandgap TiO_2 with small-bandgap g-C_3N_4 as visible light sensitizer to form heterojunction can superpose the light response of both semiconductors, owing to the special electronic band structure [25,26]. Therefore, it is possible to harvest more sunlight through the combination of g-C_3N_4 and TiO_2 forming the g-C_3N_4/TiO_2 heterojunction.

Moreover, formation of heterojunction is a promising strategy for improving charge separation, because the build-in electric field of heterojunction can drive the photogenerated electrons and holes to transfer to contrary directions, consequently inhibiting their recombination [27]. In the photocatalyst system of the g-C_3N_4/TiO_2 composites, the photoinduced holes tend to pass from the valence band (VB) of TiO_2 to the VB of g-C_3N_4 under UV light irradiation, while the electrons pass from the conduction band (CB) of g-C_3N_4 to the CB of TiO_2 [24]. As the Fermi level of Ag NPs is lower than the CB of TiO_2 [20], electrons accumulated on the CB of TiO_2 could further transfer to Ag NPs, if there are Ag NPs on the surface of TiO_2 [28]. The electrons transfer from TiO_2 to Ag could further facilitate charge separation on the photocatalyst system of g-C_3N_4/TiO_2. Under visible-light irradiation, no hole can be exited on TiO_2, abundant electrons in TiO_2 limit electrons on the CB of g-C_3N_4 to transfer to TiO_2, and hence result in a high e-h recombination rate [25]. In this case, Ag NPs on the TiO_2 surface could act as an electron sink to extract electrons from TiO_2, and hence overcome the fast e-h recombination on the g-C_3N_4/TiO_2. In a word, Ag NPs on the TiO_2 surface will benefit the photocatalytic activity of the g-C_3N_4/TiO_2 under the full spectrum solar irradiation. Therefore, we hypothesis that combination of g-C_3N_4 with Ag NPs coated TiO_2 could combine advantages of g-C_3N_4/TiO_2 heterojunction and Ag NPs, i.e., superior light-harvesting capacity and slower e-h recombination rate, and hence yields enhanced performance in photocatalytic conversion of CO_2 under sunlight irradiation. However, only limited studies utilized the ternary g-C_3N_4/Ag-TiO_2 for photodegradation of organic pollutants [25,29,30], in which the ternary g-C_3N_4/Ag-TiO_2 exhibited remarkably improved photocatalytic activities compared to pristine TiO_2, g-C_3N_4, and single-component modified catalysts, i.e., Ag-g-C_3N_4, Ag-TiO_2 and g-C_3N_4/TiO_2, much less the synergistic effect between heterojunction and Ag NPs on CO_2 photocatalytic reduction.

Herein, we fabricated heterostructured g-C_3N_4/Ag-TiO_2 hybrid photocatalysts via a facile solvent evaporation followed by a calcination process using g-C_3N_4 and Ag-TiO_2 as precursors, and investigated the photocatalytic CO_2 reduction by H_2O over the g-C_3N_4/Ag-TiO_2 catalysts for the first time. This study demonstrated that synergistic effect in enhancing the photoconversion of CO_2 under simulated sunlight illumination into carbon monoxide (CO) and methane (CH_4) was achieved by coupling g-C_3N_4 with Ag NPs coated TiO_2. The possible mechanism for the enhanced photoactivity of the g-C_3N_4/Ag-TiO_2 composite was also proposed based on the experimental results. The ultimate goal was to develop a more efficient photocatalyst for conversion of greenhouse gas CO_2 into renewable fuels.

2. Experimental

2.1. Catalyst preparation

g-C_3N_4 powder was prepared according to the literature [31]. In specific, 10.0 g urea (AR, Sinopharm Chemical Reagent Co. Ltd) was put in an alumina crucible with a cover, and calcined in air at 550 °C for 2.5 h. The resulted light yellow product was collected and ground into powder for further synthesis.

AgTi was prepared through a $NaBH_4$-reduction process. In a typical synthesis, 1.0 g of TiO_2 (P25, Degussa) was added into a beaker containing 50.0 ml deionized water. Then, the beaker was placed into an ultrasonic bath for 30 min. Subsequently, 42.5 mg $AgNO_3$ was added into the suspension after the ultrasonic treatment. After vigorous stirring for 30 min, 5.0 ml $NaBH_4$ solution (0.05 g/ml) was quickly added into the suspension under vigorous stirring for another 180 min. After reduction, the suspension was filtered, washed several times with deionized water and dried in an oven at 60 °C overnight. The nominal atomic ratio of Ag to Ti was fixed at 2% in preparation of all catalysts.

The g-C_3N_4/Ag-TiO_2 composites were prepared as follows. 0.5 g Ag-TiO_2 and different mass of g-C_3N_4 (2%, 5%, 8%, and 12% of 0.5 g) were dispersed in 50.0 ml methanol by ultrasonic treatment for 1 h. Then, the mixture was stirred at room temperature for 24 h. After complete volatilization of the methanol, the mixtures were dried at 60 °C for 12 h, and then calcined at 400 °C for 1 h (heating rate during the warming process was 5 °C/min) to obtain the g-C_3N_4/Ag-TiO_2 composites with different g-C_3N_4 to Ag-TiO_2 mass ratios. For simplicity, the g-C_3N_4/Ag-TiO_2 composites with g-C_3N_4 to Ag-TiO_2