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Short communication

Selective photocatalytic carbon dioxide conversion with Pt@Ag-TiO_2 nanoparticles

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ABSTRACT

Pt@Ag-TiO_2 nanocomposites were prepared and tested for photocatalytic CO_2 conversion in the presence of H_2O. The characterizations showed that Pt@Ag core@shell structures were formed. The photocatalytic activity of Pt@Ag_x-TiO_2 catalysts with different Ag content showed that the deposition of Ag shell could increase the photocatalytic CO_2 reduction efficiency and selectivity by suppressing H_2 generation. Pt@$Ag_{1.0}$-TiO_2 with an Ag content of 1.95 wt.‰ showed a maximum CH_4 formation rate of 160.3 $\mu mol \cdot g^{-1} \cdot h^{-1}$, together with a CO_2 reduction selectivity of 87.90%. PL spectra and photocurrent measurements indicated that Pt@$Ag_{1.0}$-TiO_2 had the highest photogenerated electron-hole separation efficiency among all the prepared photocatalysts.

1. Introduction

Fossil fuel shortage and global warming mainly caused by CO_2 emission are two urgent challenges confronting human beings. Converting CO_2 into useful chemicals and clean fuels can solve these two issues at the same time. Nevertheless, CO_2 is a very stable molecule and the activation of CO_2 is energy intensive. A potentially cost-effective approach is to utilize solar energy and convert CO_2 with photocatalysts [1]. Since the pioneering report of Inoue et al. [2], lots of studies have been conducted with semiconductor-based photocatalysts to convert CO_2 with H_2O into H_2, CH_3OH, CO, and CH_4 [3–6]. Among various photocatalysts, TiO_2 has gained its popularity due to its robust reactivity, commercial availability and chemical stability. However, the disadvantages of TiO_2 including the limit to only UV light absorption and low quantum efficiency are apparent and nettlesome [7].

The enhancing effects of metal co-catalysts have been recognized and widely reported for photocatalytic conversion of CO_2 with H_2O [5,8–11]. It is generally accepted that metal co-catalysts can serve as reaction sites and promote the separation of photogenerated electrons and holes through trapping electrons, improving the quantum efficiency and the photocatalytic activity [12]. Among all the metal co-catalysts, platinum (Pt), with its large work function, is the one of the best candidates for trapping electrons. Pt decorated TiO_2 nanostructured films are reported to exhibit a CO_2 conversion efficiency which is more than 10 times that of pure TiO_2 [9].

However, the loading of Pt nanoparticles usually doesn't improve much of the light-harvesting property of TiO_2 due to its poor visible light absorption. Gold (Au) and silver (Ag) nanostructures can strongly absorb visible light due to localized surface plasmon resonance (LSPR) derived from the resonant oscillation of free electrons coupled by light [13]. For example, coupling Ag nanoparticles with TiO_2 would largely improve the light-harvesting capability and form visible-light-active photocatalysts. Nevertheless, as for the role of photogenerated charges separation, in general Ag has much lower activity than Pt [14]. Thus, to achieve high efficiency for photocatalytic CO_2 conversion, the co-loading of Ag nanoparticles onto Pt-TiO_2 composite nanostructures would be desirable by combining the advantages of both LSPR effect of Ag nanoparticles and the “electron sink” effect of Pt nanoparticles.

It is accepted that CO_2 conversion to CH_4 through accepting photogenerated electrons is a competitive process with water splitting to produce H_2 [15]. Since different co-catalysts may provide different selectivity for photocatalytic CO_2 conversion versus water splitting, bifunctional co-catalysts with a proper structure may improve CO_2 conversion efficiency and selectivity at the same time [12]. However, the rational design of bifunctional co-catalysts for high efficiency photocatalytic CO_2 conversion is still deficient.

In this work, TiO_2 nanoparticles with a high surface area were prepared by a solvothermal method [3]. Then Pt and Ag were deposited stepwise on the surface of TiO_2 nanoparticles through photodeposition methods. Through characterizations, the prepared Ag and Pt decorated

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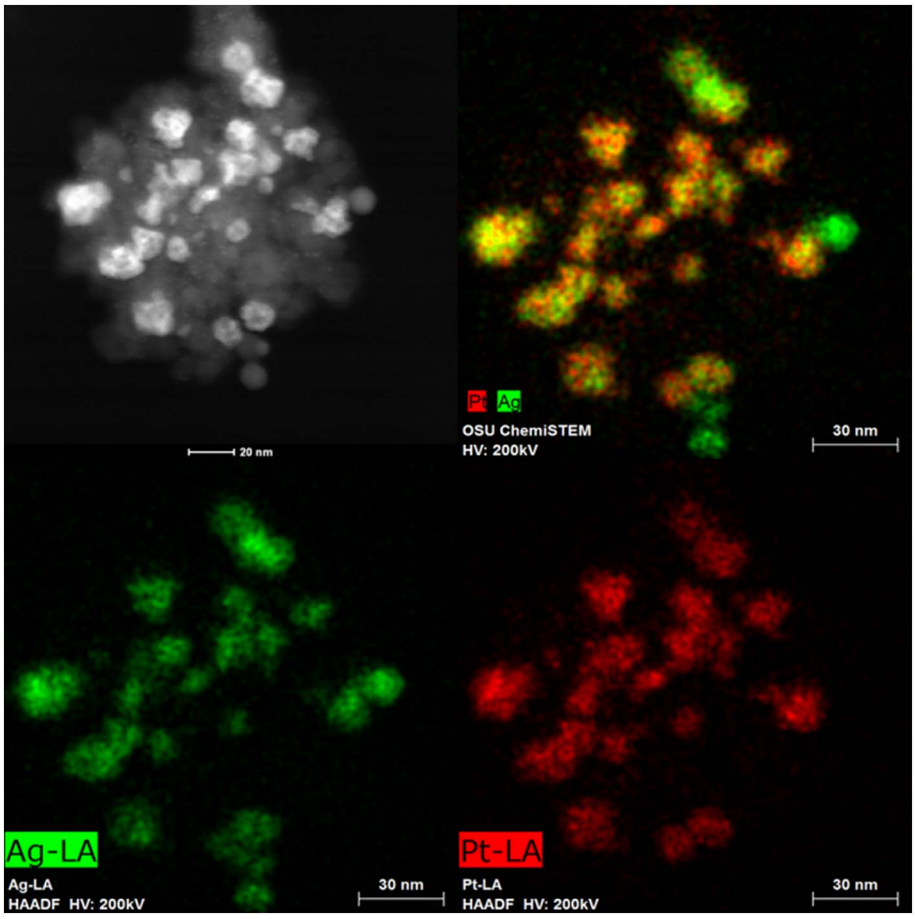

Fig. 1. STEM and STEM-EDS mapping images of Pt@$Ag_{1.0}$-TiO_2.

TiO_2 nanoparticles had a core-shell structure (denoted as Pt@Ag-TiO_2), and was used for photocatalytic CO_2 conversion. The deposition of Ag nanoparticles greatly improved the visible light absorption of Pt-TiO_2 and the influence of Ag content on the selectivity of CO_2 conversion versus water splitting was investigated. It is found out that with a certain amount of Ag as a second co-catalyst, the photocatalytic CO_2 conversion efficiency and selectivity to CH_4 are both notably improved. This paper provides some insights for the easy and rational design of bifunctional co-catalysts for efficient photocatalytic CO_2 reduction.

2. Experimental

The preparation of TiO_2 followed the procedure developed by [3], and is not described here. The Pt@Ag-TiO_2 nanoparticles were prepared by a two-step photoreduction method. The deposition amount of Pt is optimized by suspending 0.2 g TiO_2 into a mixture of 30 mL deionized H_2O, 6 mL 1 mg/mL H_2PtCl_6 and 10 mL 0.1 mol/L CH_3OH, and then irradiating the whole suspension under a 500 W Xe lamp (Newport) for 1 h [3]. For the deposition of Ag, 0.2 g prepared Pt-TiO_2 was first suspended in a mixture of 30 mL deionized H_2O, a certain amount of 1 mg/mL $AgNO_3$ solution and 5 mL 0.1 mol/L CH_3OH solution. Then, the whole suspension was stirred for 0.5 h before being irradiated with a 500 W Xe lamp for 0.5 h. Next, the prepared Pt@Ag-TiO_2 samples were filtered, washed repeatedly with deionized water, and dried at 80 °C in a vacuum oven for 24 h. Photocatalysts with different Ag contents were prepared. With a $AgNO_3$ addition amount of 0.5 mL, 1.0 mL, 1.5 mL, 2.0 mL and 2.5 mL, the photocatalysts were denoted as Pt@$Ag_{0.5}$-TiO_2, Pt@$Ag_{1.0}$-TiO_2, Pt@$Ag_{1.5}$-TiO_2, Pt@$Ag_{2.0}$-TiO_2, and Pt@$Ag_{2.5}$-TiO_2 (Pt@Ag_x-TiO_2 series). Ag-TiO_2 was prepared for comparison with addition of 1 mL $AgNO_3$.

Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and energy-dispersive X-ray spectroscopy (EDS) mapping were taken on a FEI Titan 80–200 TEM/STEM operated at an acceleration voltage of 200 kV. CO chemisorption was carried out on a Micromeritics ASAP 2020 chemisorption analyzer at 35 °C. Electrochemical measurements were performed by a CHI 660B electrochemical workstation with a standard three-electrode cell at room temperature. The prepared sample, an Ag/AgCl electrode (saturated KCl), and a Pt wire were used as the working electrode, the reference electrode, and the counter electrode, respectively. The preparation of working electrodes was based upon reported literature [16]. For photocurrent (PC) measurement, a 350 W Xe arc lamp was served as light source, and a Na_2SO_4 (0.5 mol/L) aqueous solution was used as the electrolyte.

All the other characterization techniques as well as the experimental apparatus and photocatalytic CO_2 conversion experiments are described in detail by Wang et al. [3]. The selectivity for CO_2 reduction on an electron basis has been evaluated using Eq. (1) [12]:

$$\text{Selectivity}\ (\%) = 8n(CH_4)/[8n(CH_4) + 2n(H_2)] \times 100\% \quad (1)$$

where $n(CH_4)$ and $n(H_2)$ are the amounts (moles) of the detected products CH_4 and H_2.

3. Results and discussions

3.1. Characteristics of photocatalysts

The structure of photocatalysts was characterized by XRD. Fig. S1 shows the XRD patterns of the samples. Only typical anatase peaks were observed on prepared TiO_2. The deposition of either Pt or Ag did not