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Noble metal modified TiO_2: selective photoreduction of CO_2 to hydrocarbons

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ABSTRACT

CO_2 photoreduction is an indispensable tool to generate carbon containing fuel. A series of noble metal modified TiO_2 were prepared using photodeposition method, and their photocatalytic activities were evaluated towards photocatalytic reduction of CO_2 under gas phase conditions using water vapor as electron donor and UV-A light as energy source. TiO_2 solely produce CO. The addition of noble metals to TiO_2 via photodeposition method significantly increased the photocatalytic reduction of CO_2 with change in product selectivity towards methane under identical conditions. Further combinations of two different noble metals were simultaneously deposited to develop bimetal/TiO_2. The bimetal/TiO_2 further enhances the methane yield with considerable amount of ethane. $Ag_{1\%}Pd_{1\%}/TiO_2$ has been proven as best catalyst among all catalyst and yields maximum methane.

1. Introduction

The environmental issues related to anthropogenic CO_2 have dragged the global attention on CO_2 capture and utilization [1]. CO_2 is very stable molecule, it requires energy rich material or high temperature or voltage to activate the CO_2 [2]. Photocatalytic reduction utilizing solar energy is an attractive approach for CO_2 conversion to fuel [3,4]. Moreover semiconductors have engrossed much attention for photocatalytic reduction of CO_2. such as GaP [5], TiO_2 [6,7], ZnO [8], Ga_2O_3 [9], $ZnGe_2O_4$ [10], CuO [11]. Although TiO_2 has proven a promising material, nevertheless wide band gap, fastest recombination and large over potential for CO_2 reduction limits its efficiency [12,13]. Therefore, several strategies such as engineering the crystal structure, doping, metal deposition [14], sensitization etc. had been adopted to modify TiO_2 for better charge separation [15]. It has been reported that loading of noble metal co-catalysts can promote the quantum yield, as they used to alter the optoelectronic properties of TiO_2 [16]. Noble metals act as electron sink, they retard the recombination due to shift in fermi level and further enhances the activity by providing more catalytic sites [17–19]. Ag, Au, Pd or Pt loaded TiO_2 were reported for CO_2 photoreduction [20–24].

Several approaches were adopted for the preparation of noble metal/TiO_2 composites. Wet impregnation [25] is a simple technique but allows poor control over the particle size, dispersion and composition. Colloid methods provide remarkable particle distributions but long organic ligands suppress the catalytic activity of the nanoparticle surfaces and are difficult to completely remove. Therefore, photodeposition under ultraviolet radiations can be applied to load noble metals over TiO_2 as the process yields smaller metal deposits with homogenous dispersion [26].

Designing of bifunctional co-catalyst with suitable properties is required to obtain higher photoactivity and better selectivity, as metal–metal interaction are supposed to overcome catalyst deactivation with time on stream. It is stated, bimetallic catalyst shows better photocatalytic activities in various chemical reactions [27–30]. $SrTiO_3/TiO_2$ coaxial nanotube arrays loaded with Au–Cu bimetallic alloy nanoparticles, showed enhanced CO and hydrocarbon production from CO_2 photoreduction with hydrazine hydrate [31]. Zhang et al. reported $Au_{0.25}Pt_{0.75}/TiO_2$ nanofiber catalyst exhibited higher activity for CH_4 formation (0.57 μ mol h^{-1}) under UV–vis irradiation. They showed enhanced photocatalytic behaviour could be due to both the electron-trapping effect of Pt nanoparticles and the SPR effect of Au nanoparticles [16]. Gupta and co-workers stated a significant enhancement in the photoreduction of CO_2 with H_2O to CH_4 by co-loading Ag–Pt bimetallic nanoparticles and core–shell $Ag@SiO_2$ particles onto TiO_2 [32].

Despite the broad studies on the versatility of noble metal modified TiO_2, comparative studies of different noble metal loaded

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TiO_2 with bimetallic (Ag-Pd, Au-Pd and Pt-Pd) TiO_2 has not yet been thought as an effective means for assisting CO_2 photoreduction with water vapor under continuous gas phase reaction. In this paper, we introduce a versatile strategy i.e. photodeposition method to synthesize the noble metal/TiO_2 or bimetal/TiO_2 material. It is attributed TiO_2 loaded with bimetallic nanoparticles enhances the photoactivity and selectivity toward methane as fuel by creating Schottky barrier. Ag-Pd loaded TiO_2 shows best photoactivity towards methane production under UV-A irradiation.

2. Experimental section

2.1. Materials

Titanium dioxide (commercial anatase phase, Merck, 99%), palladium chloride (Sigma, 99.99%), dihydrogen platinum chloride or chloroplatinic acid (Alfa Aesar, 99.9%), silver nitrate (Merck, 99.5%), gold chloride (Alfa Aesar, 99.99%), Methanol (Vetec, 99.5%), All material were used as purchased without further purification. HPLC grade water was used for all synthesis.

2.2. Synthesis

Noble metal modified TiO_2 were prepared using photodeposition method. In a typical procedure, required metal precursor was dissolved in 100 mL water having 1 mL methanol as sacrificial hole scavenger with TiO_2. Obtained noble metal/TiO_2 suspension was irradiated under UV-C lamp (8W, Pen ray, UVP, 254 nm) for 3 h. Then material was collected using centrifuge and washed with water thrice and dried in oven at 80 °C for 6 h. The bimetal loaded TiO_2 was prepared by simultaneously photodeposition of noble metals to form the Ag-Pd, Au-Pd and Pt-Pd on TiO_2 (Scheme 1)

2.3. Catalyst characterization

As prepared noble metal loaded TiO_2 were characterized by using XRD, UV–vis diffuse reflectance, SEM, TEM, XPS. X-ray diffraction (XRD) patterns obtained on Bruker D8 advance X-ray diffractometer using Cu Kα irradiation (0.154 nm) at a scan rate of 0.2° s^{-1} were used to analyze the phase structures of the samples studied. The morphology of materials was investigated using FEI Quanta 200F scanning electron microscope (SEM). Energy dispersive Spectroscopic analyzer equipped with SEM was also used for elemental composition. Transmission electron microscopy (TEM) and HRTEM analyses were conducted on a JEOL model JAM-2100 instrument. The accelerating voltage was 200 kV, resolution was 1.4 Å. The UV–vis diffuse reflectance spectra (DRS) were obtained on a Shimadzu 2600 UV–vis spectrophotometer over the wavelength range of 200–800 nm using $BaSO_4$ as an internal standard. X-ray Photoelectron spectroscopy (XPS) analyses were performed on model S/N-10001 (Prevac Poland) with a VG Scienta-R3000 hemispherical energy analyzer.

2.4. Photocatalytic activity measurements

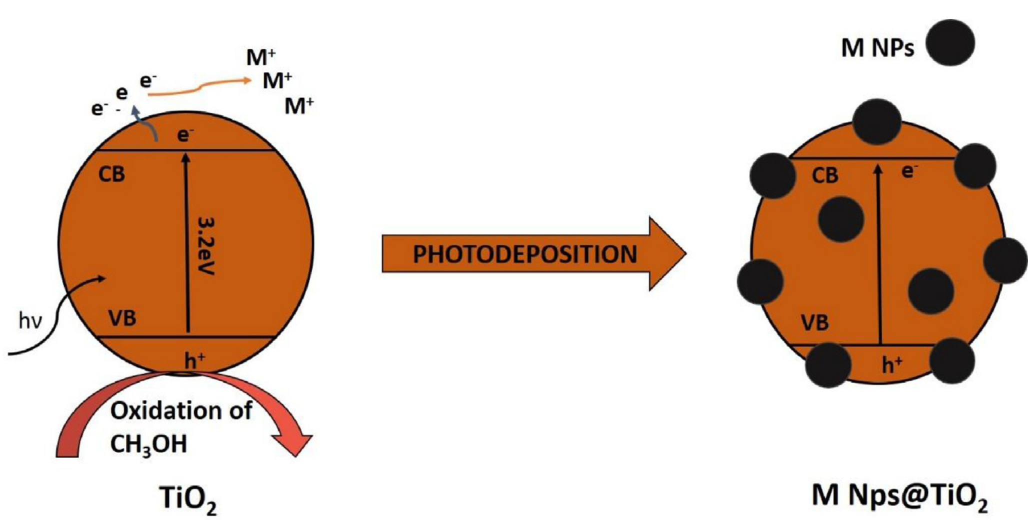
The modified catalysts were subjected to photoreduction of CO_2 in a home-made pyrex reactor. It has cylindrical glass vessel with an effective volume of 270 mL, and provided with a quartz tube at the center of reactor for UV irradiation. The powdered catalyst (250 mg) was dispersed over bottom of glass vessel. CO_2 was bubbled through water bubbler to make it water saturated and passed through gas phase photoreactor. Outline of reactor is directly connected to gas chromatogram. The system was purged with CO_2 for an hour prior to illumination to remove other gases from reactor. After that flow rate was maintained at 8 mL min^{-1} using mass flow controller. UV illumination was done using Lumen dynamics 200 W Hg lamp with wavelength at 320–390 nm and average intensity of 9.0 W/cm^2. The reaction was carried out at room temperature and pressure for period of 0–6 h. Continuous gas chromatography was used to analyze the samples. GC was equipped with TCD (Shincarbon Column) and FID (HP Plot Q Column). Three blank experiments in absence of catalyst, CO_2 and light were also carried out to ensure the products were due to synergistic effect of catalyst, CO_2 and illumination.

3. Result and discussion

3.1. Catalyst characterization

Catalysts were prepared by photodeposition method under UV-C irradiation. Developed materials were well characterized with several techniques as XRD, UV–vis, SEM-EDX, TEM, HR-TEM, and XPS.

The phase purity and crystallographic structure of prepared catalysts were identified by XRD patterns, As shown in Fig. 1a and b major peaks at 25.3°, 37.8° and 48.1° correspond to 111, 004, 200 planes of tetragonal anatase phase of TiO_2 (JCPDS NO-21-1272). The presence of Au can be seen in Fig. 1a at 38.2° (111) and 44.4° (200)



Scheme 1. Strategy to synthesize of M@TiO_2 by Photodeposition.