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Novel photocatalytic conversion of CO_2 by vanadium-doped tantalum nitride for valuable solar fuel production

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ABSTRACT

In this study, Ta_3N_5 and V-doped Ta_3N_5 (V–Ta_3N_5) were synthesized as catalysts for the conversion of CO_2 into valuable fuels under visible light. As compared with Ta_2O_5, the synthesized Ta_3N_5 and V–Ta_3N_5 exhibited great increases in visible light adsorption and decreases in band gap energy. Therefore, the synthesized Ta_3N_5 and V–Ta_3N_5 photocatalytically converted CO_2 into CO and CH_4 even under visible light. The V dopants, which existed in the Ta_3N_5 lattice, could act as an intermediate band (V3*d*) between the valence band (N2*p*) and the conduction band (Ta5*d*) of the Ta_3N_5 to increase the electron–hole separation efficiency of the photocatalyst. Thus, the photocatalytic activity of V–Ta_3N_5 was much higher than that of Ta_3N_5. However, an increase in the V doping ratio led the formation of VN particles distributed on the Ta_3N_5 surface. The formed particles eclipsed the light reaching the photocatalyst surface, resulted in a decrease in photocatalytic activity. The optimal V doping ratio in V–Ta_3N_5 was found to be 2 wt.%. As a result, the production rates of CH_4, CO, O_2, and H_2 generated from the photocatalytic reduction of CO_2 by 2 wt.% V–Ta_3N_5 under visible light were 425, 236, 1003, and 56 $\mu mol\ g^{-1}cat\ h^{-1}$, respectively.

1. Introduction

Atmospheric concentrations of CO_2 have greatly grown since the Industrial Revolution and the current rate of ambient concentration increase is alarming [1,2]. Photocatalytic conversion of CO_2 into valuable fuels, such as CH_4, HCHO, HCOOH, CH_3OH, and CO, has become one of the most attractive technologies to overcome these issues. Various photocatalysts, such as ZnO, $ZnGe_2O_4$, Ga_2O_3, Co_3O_4, TaO_3, $BiVO_4$, g-C_3N_4, Si nanocrystals, and TiO_2, have been investigated for their performance in the photocatalytic conversion of CO_2 [3–8]. The photocatalysts utilized ultraviolet and/or visible light as the excitation source to generate electron–hole pairs, which participated in reactions with CO_2 and H_2O to produce various valuable fuels [9]. For instance, Parayil et al. reported that the CH_4 yield from CO_2 conversion of carbon and nitrogen co-doped sodium titanate nanotubes was approximately 9.75 $\mu mol\ g^{-1}cat\ h^{-1}$ [6]. However, the development of efficient photocatalytic systems for CO_2 conversion still remains in the embryonic stage. For example, TiO_2, the most extensively studied material, only exhibits photocatalytic activity under UV irradiation because of its wide band gap (3.2 eV) and high recombination rate of photogenerated electron–hole pairs [10,11]. In addition, photocatalytic CO_2 conversion is thermodynamically highly endothermic and requires multiple electrons and protons [12]. Bera et al. presented that eight electrons and four protons were required to convert one molecule of CO_2 to CH_4, while six electrons and four protons were necessary to form a CH_3OH molecule [12]. Therefore, photocatalytic CO_2 conversion efficiency is still low for expanding commercial production.

Recently, many active visible light absorbers, which are narrow-band-gap materials, in particular Ta-based materials, such as tantalum nitrides (Ta_3N_5) and tantalum oxynitrides (TaON), have become main candidates for efficient solar light water splitting [13]. TaON and Ta_3N_5 have narrow band gap energies of 2.4 and 2.1 eV, respectively, which make them suitable to absorb visible light (low energy consumption) to initiate photocatalysis [14]. Several studies have been conducted on application of Ta_3N_5 for water splitting and photocatalytic degradation of organic pollution [15,16]. The obtained results indicated that the T_3N_5 is a promising candidate as a visible-light-driven photocatalyst. However, the

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application of Ta_3N_5 for CO_2 conversion to produce valuable fuels seems not to have been conducted yet. Due to low band gap energy, Ta_3N_5 could generate a significant number of electrons and holes even under visible light. The generated holes could react with H_2O to produce protons (H^+). The generated electrons could directly reduce CO_2 into a radical anion, CO_2^{*-}. However, the direct formation of the CO_2^{*-} intermediate requires a very negative equilibrium potential of −1.9 V (vs. NHE at pH 7). Therefore, the formation of CO_2^{*-} radicals could involve a series of multiple proton-coupled electron transfer (PCET) processes, which provide reaction pathways for simultaneously transferring protons and electrons to avoid high-energy intermediates [17,18]. Finally, the formed protons could react with the formed radical anions to produce valuable fuels such as CO, CH_4, CH_3OH, and HCOOH [19,20]. Therefore, the first aim of the study is to use synthesized Ta_3N_5 as a photocatalyst for reduction of CO_2 to produce valuable fuels under visible light.

More recently, the modification of Ta_3N_5 to prevent fast recombination of the generated electrons and holes, a major drawback of Ta_3N_5 photocatalyst, has been actively pursued to further enhance the efficiency of the photocatalyst [21,22]. Cong et al. reported that modifications in structure and size of Ta_3N_5 led to a threefold increase in the its photocurrent response [21]. Several researchers coupled Ta_3N_5 with other semiconductors, such as Bi_2O_3, Co_3O_4, and $AgPO_4$, to enhance the transfer efficiency of the generated electrons and holes in order to prevent their recombination [23–25]. Doping Ta_3N_5 with different metals has also been conducted to increase the electron–hole separation efficiency of the photocatalyst [13,14,26]. For example, Kado et al. reported that the band gap energy of Na-doped Ta_3N_5 was approximately 1.6 eV, which is much lower than that of pure Ta_3N_5 (2.1 eV), leading to an increase in electron–hole separation efficiency and a decrease in recombination of generated electrons and holes in the doped material [13]. Vanadium has been popularly used as a dopant to enhance photocatalytic activity of TiO_2 [27–31]. Pham and Lee reported that V dopants defected into the TiO_2 lattice led to formation of Ti^{3+} and V^{4+} in the lattice [27]. The presence of Ti^{3+} and V^{4+} in the TiO_2 lattice increased the electron–hole pair generation capacity and electron–hole pair separation efficiency and also prevented the recombination of generated electrons and holes, leading to enhancement in photocatalytic activity. However, attempts to dope V into Ta_3N_5 lattices have not yet been reported in the literature. Thus, the second aim of the proposed project is to dope V into the Ta_3N_5 lattice. It was believed that the V dopants could defect the Ta_3N_5 lattice (based on similar roles of V dopant in the TiO_2 lattice) to maximize photocatalysis for CO_2 conversion to produce valuable fuels.

2. Experimental

2.1. Material synthesis

Ta_2O_5 powder (Sigma-Aldrich, 99.9%) was calcined for 10 h at 1000 °C in a quartz tube furnace under a flow of ammonia gas (50 mL/min) to obtain Ta_3N_5 [32]. To synthesize V-doped Ta_3N_5 photocatalyst, the Ta_2O_5 powder was added into a 0.05 M NH_4VO_3 solution, which was prepared by dissolving NH_4VO_3 in deionized water at 50 °C. The obtained mixtures were ultrasonicated and stirred for 1 h and 24 h, respectively, to achieve a uniform suspension. Then the suspension was dried at 150 °C in the oven for 12 h and calcined in the quartz tube furnace under a flow of ammonia gas at 1000 °C for 10 h to obtain the V–Ta_3N_5 material. The weight of Ta_2O_5 and the volume of NH_4VO_3 solution were controlled to synthesize 1, 2, and 3% V–Ta_3N_5 materials, in which the V/Ta ratios were 1, 2, and 3 wt.%, respectively.

2.2. Photocatalyst characterization

X-ray diffraction (XRD) spectra of the pristine Ta_2O_5, the synthesized Ta_3N_5, and the V–Ta_3N_5 photocatalysts were obtained using a Bruker AXN model with a CuKα radiation (λ = 1.5418 Å) source, operated at a scan rate of 0.02° s^{-1} over a 2θ range of 15°–55°. X-ray photoelectron spectroscopy (XPS) of the V–Ta_3N_5 photocatalysts was carried out on a Thermo Fisher K-Alpha X-ray photoelectron spectrometry system. Gaussian multipeak shapes were applied to determine the elemental states of the vanadium dopant in the synthesized materials. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images of the synthesized Ta_3N_5 and V–Ta_3N_5 were obtained using a JEOL TEM-2010F at an acceleration voltage of 200 kV. The BET surface area of the Ta_2O_5, the synthesized Ta_3N_5, and the V–Ta_3N_5 photocatalysts were calculated, based on a Bru nauer–Emmett–Teller isotherm determined by nitrogen adsorption and desorption at 77 K. An Evolution 300 spectrophotometer (UV-1700 Shimadzu) was used to measure the optical absorption of the pristineTa_2O_5 and the synthesized Ta_3N_5 and V–Ta_3N_5 photocatalysts in the wavelength range 300–700 nm.

2.3. Experimental system

A continuous gas system was designed for photocatalytic CO_2 conversion. A CO_2/H_2O vapor, which was produced by passing compressed high-purity CO_2 gas (99.99%) through a water vaporizer, was used as input gas. The flow rate and the relative humidity of the input gas were 30 mL/min and 60%, respectively. The input gas was oriented to a top-and-bottom quartz reactor (20 × 2 × 1 cm), which was placed in a reaction chamber, a cask with a dark cover. The residence time of CO_2 in the reactor was 80 s. The top and bottom of the reaction chamber had two 20 W white bulbs (ES 220/N EX-L, Orex Co. Ltd., Korea) equipped with ultraviolet cutoff filters to generate visible light ($\lambda \geq 400$ nm) with a power density of 0.06 W/cm^2. Before the photocatalytic conversion experiments, the reactor, containing 100 mg synthesized photocatalysts, which were uniformly dispersed on the reactor floor, was purged three times with high–purity CO_2 gas in order to drive off the air inside. Then the CO_2/H_2O mixture gas was oriented to the reactor and the bulbs were turned on to generate visible light for the CO_2 conversion process. To analyze the produced gases, 100 μL of product was automatically injected into the gas chromatography (GC) system at intervals of 30 min. The GC system contained two detectors, a flame ionization detector (FID) equipped with a methanizer for CO and CH_4 analysis and a thermal conductive detector (TCD) for H_2 and O_2 analysis. Control experiments were also conducted to determine carbon sources of the CH_4 and CO and also sources of O_2 and H_2 (see the Supplementary Material).

3. Results and discussion

3.1. Material characteristics

3.1.1. Crystalline structure

XRD patterns of the pristine Ta_2O_5, the synthesized Ta_3N_5, 1% V–Ta_3N_5, 2% V–Ta_3N_5, and 3% V–Ta_3N_5 are shown in Fig. 1. The obtained XRD pattern of the Ta_2O_5 indicated that it existed in the orthorhombic form [33]. Fig. 1 also shows that the XRD pattern of the synthesized Ta_3N_5 photocatalyst corresponded to the typical XRD pattern of pure Ta_3N_5 [34]. As observed in the XRD pattern of the synthesized Ta_3N_5, there was no impurity peak, indicating that the Ta_2O_5 was completely nitrided to Ta_3N_5 during the sintering in ammonia gas at a high calcination temperature. As