



Dramatic CO₂ photoreduction with H₂O vapors for CH₄ production using the TiO₂ (bottom)/Fe–TiO₂ (top) double-layered films



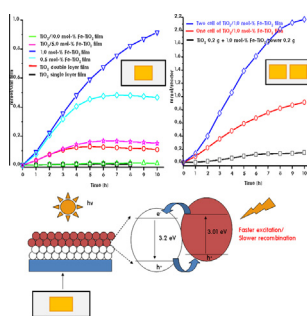
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HIGHLIGHTS

- x mol.% Fe-doped TiO₂ powders were prepared using a conventional solvothermal method.
- The powders were fabricated as double-layered films for the photoreduction of CO₂.
- The CH₄ increased remarkably over the TiO₂/Fe–TiO₂ double-layered films.
- The CH₄ gas evolved over the TiO₂/1.0 mol.% Fe–TiO₂ film was 7 times higher.
- The effective charge separation and inhibited recombination of photogenerated electron–hole (e[−]/h⁺) pairs.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper reports the production of a catalyst for the efficient photoreduction of CO₂ to CH₄. TiO₂ and x mol.% Fe-doped TiO₂ (Fe–TiO₂, $x = 0.5, 1.0, 5.0, 10.0$ mol.%) were prepared using a conventional solvothermal method. The prepared powders were fabricated as TiO₂ (bottom)/Fe–TiO₂ (top) double-layered films for applications to the photoreduction of CO₂. The amount of CH₄ generated from the photoreduction of CO₂ with H₂O increased remarkably over the TiO₂/Fe–TiO₂ double-layered photocatalytic films compared to the TiO₂ (bottom)/TiO₂ (top) double layered film. In particular, the amount of CH₄ gas evolved over the TiO₂/1.0 mol.% Fe–TiO₂ double layered film was 7 times higher than that produced over the TiO₂ (bottom)/TiO₂ (top) double layered film. A proposed model suggested that the photoactivity over the TiO₂/Fe–TiO₂ double layered films can be enhanced by the effective charge separation and inhibited recombination of photogenerated electron–hole (e[−]/h⁺) pairs on interfacial transfer between TiO₂ and Fe–TiO₂.

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1. Introduction

Since the CO₂-associated greenhouse effect was first noted by Joseph Fourier in 1824 and Svante Arrhenius in 1896 [1], the present CO₂ levels in the atmosphere are higher than at any other time

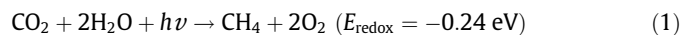
[2,3]. Rapid civilization and industrialization have not only brought convenience to human society, but also pollution and emissions from factories, vehicles and chemical plants. Several governments have attempted to control CO₂ emissions, and signed and ratified the Kyoto Protocol of the United Nations Framework Convention on Climate Change aimed at reducing CO₂ gas emissions [4]. Recently, the International Energy Agency (IEA) revealed that the CO₂ emissions will increase 63% from today's level by 2030, which

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is almost 90% higher than those measured in 1990 [2]. Therefore, improved actions, which include new technology options for cutting CO₂ emissions and on the reuse of CO₂, are needed to avoid further increases over the next few decades. In the first step, many researchers are willing to capture CO₂ gas (CCS: carbon dioxide capture and storage) generated at the major outlets from power plants and the cement industry, and then prevent it from entering the atmosphere by suitably storing it in safe places [2]. On the other hand, they have realized that the CCS process cannot be the final solution, and many industrial methods with an encouraging influence on atmospheric CO₂ have been developed so that it will not need to be buried as a part of the CCS process. Currently, CCS technology was tackled by the carbon dioxide capture and reuse process (CCR) with the demands not only on carbon management but converting it to value-added chemicals and fuels.

The challenges for converting CO₂ to value-added chemicals including methane are great, but the potential rewards will be enormous. The conversion of CO₂ to methane using energy that is not produced from fossil fuels has been suggested as one of the best ways of solving both global warming and energy crisis problems to a great extent. The photocatalytic reduction of CO₂ and H₂O is one of the leading and most environmentally friendly methods for methane production [5,6]: CO₂ reduction with H₂O through photocatalysis is vital in the development of the solar energy-based carbon neutral cycle, as shown in Eq. (1):



Among the various semiconductor materials on the photocatalytic reduction of CO₂, TiO₂ has been widely researched because of its many advantages including higher oxidative potential, relatively inexpensive, abundantly available, non-toxic, and chemically/thermally stable. On the other hand, the lower CO₂ reduction efficiency over TiO₂ has been reported because of the immediate recombination of photogenerated charges (e⁻/h⁺) [7]. New materials or modifications of the TiO₂ structure are needed to impede the recombination of electron and hole pairs to achieve effective CO₂ photoreduction to value-added chemicals and fuels, such as metallic- or non-metallic-TiO₂ materials doped with Ag, Cu, Rh, Pt, I, Br, or N with a high reduction potential [8–14], and Ti materials doped with the porous MCM series [15,16] or zeolites [17]. Despite this potential, there have been few catalytic developments on CO₂ photoreduction to CH₄, and a variety of approaches will be needed to develop new catalysts to increase the production of methane.

Based on the literature, there are no reports on the utilization of Fe-modified TiO₂ for the photoreduction of CO₂ to CH₄. Fe was selected based on the literature data concerning the degradation of organic compounds [18] and hydrogen production [19], which reported that Fe could increase the catalytic activity of TiO₂ photocatalysts induced by the absorption of visible radiation. In general, Fe-modified TiO₂ can be divided into two main groups: (1) loaded on the surface of TiO₂ particles [20,21] and (2) inserted (or incorporated) into the TiO₂ lattice (framework) [22,23]. The photoactivities on these catalysts vary according to the reaction types and conditions. In the present research, two types of well-known catalysts, TiO₂ and *x* mol.% Fe-dopes TiO₂ (Fe–TiO₂, *x* = 0.5, 1.0, 5.0, 10.0 mol.% per 1 mol of Ti) were prepared using a conventional solvothermal method. The prepared powders were fabricated as TiO₂ (bottom)/Fe–TiO₂ (top) double-layered films for applications to the photoreduction of CO₂. The most appropriate amount of Fe for efficient CH₄ production was determined. The synthesized TiO₂ and *x* mol.% Fe–TiO₂ materials were characterized by spectroscopic analysis, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV), ultraviolet–visible (UV–vis) absorption spectroscopy, and photoluminescence (PL) spectroscopy.

2. Experimental

2.1. Synthesis and characterization of *x* mol.% Fe–TiO₂

The *x* mol.% Fe–TiO₂ nanomaterials, which partially placed Fe ions into the Ti sites in the TiO₂ lattice frameworks, were prepared using a conventional solvothermal treatment [24]: Ferrous chloride (FeCl₂·*x*H₂O, 99.9%, Junsei Chemical, Japan) as a Fe precursor was dissolved in absolute ethanol, and the ferrous solution was then stirred for 2 h. TTIP (TTIP, 98.0%, Junsei Chemical, Tokyo, Japan), as a Ti source, was added slowly to the ferrous solution with stirring. The amounts of Fe were varied by Fe/Ti molar ratios of 0, 0.5, 1.0, 5.0, and 10.0 mol.% per 1.0-mol Ti. The solution was fixed to pH = 3 using acetic acid. After stirring for 2 h, the final homogeneous solution was transferred to an autoclave for thermal treatment. To eliminate the gaseous impurities in the reactor, the reactor was purged three times with nitrogen gas, and then the valve was locked. The pressure was confirmed to be atmosphere pressure at this time. The reactor was raised until 200 °C with a rate of 10 °C/min, and then the temperature was maintained for 8 h. The reactor pressure, meaning ethanol vapor pressure, exhibited 40.0 atm. After 8 h, the temperature was cooled to room temperature and the pressure was lowered slowly by opening the pressure valve. The resulting precipitate was washed with distilled water, and dried at 60 °C for 24 h. The five types of materials obtained were called TiO₂ and 0.5, 1.0, 5.0, and 10.0 mol.% Fe–TiO₂.

The synthesized *x* mol.% Fe–TiO₂ nanomaterials (*x* = 0, 0.5, 1.0, 5.0, and 10.0) powders were examined by XRD (MPD, PANalytical) using nickel-filtered CuK α radiation (30 kV, 30 mA). Transmission electron microscopy (TEM, JEOL 2000EX at Yeungnam University Instrumental Analysis Center of Korea) at acceleration voltages of 120 and 200 kV was performed to determine the particle sizes and morphologies of the *x* mol.% Fe–TiO₂ materials, and the atomic compositions of the film was measured by energy dispersive X-ray spectroscopy (EDAX, EX-250, Horiba) operated at 120 kV. CV (BAS 100B) of the *x* mol.% Fe–TiO₂ powders was performed at room temperature and a scan rate of 100 mVs⁻¹ in a 0.1 M KCl supporting electrolyte with platinum wire as the working and counter electrodes, and Ag/AgCl as the reference electrode. The UV–vis spectra were obtained using a Cary 500 spectrometer with a reflectance sphere in the range, 200–800 nm. The recombination tendency of the photogenerated electron–hole pairs (e⁻/h⁺) was estimated by PL (Perkin Elmer) using a He–Cd laser source at a wavelength of 325 nm.

2.2. Photocatalytic activity test

Fig. 1 presents a schematic diagram of the batch type photoreactor for CO₂ photoreduction designed in the authors' laboratory. TiO₂ (bottom)/Fe–TiO₂ (top) double-layered films were fabricated from the prepared powders before being applied to the photoreduction reaction of CO₂. 0.2 g of the TiO₂ or Fe–TiO₂ powder was added to a mixture containing 0.5 g of α -terpinol, 0.05 g of cellulose and 2 mL of ethanol. The mixture was stirred and sonicated for 24 h at 1200 W cm⁻², and a TiO₂ or Fe–TiO₂ paste was prepared. Before coating with the Fe–TiO₂ paste, a formulated TiO₂ paste was coated onto a Pyrex glass plate (height 9 mm and width 20 mm) as a bottom layer using the squeeze printing technique [25]. The TiO₂ bottom layer film (height 5 mm and width 8 mm) was heated to 450 °C for 30 min. On the TiO₂ bottom layer, the Fe–TiO₂ paste was coated using the same method. The double layered film was also treated by heating at 450 °C for 30 min to remove the additives. The reactor consisted of a rectangular quartz cell with a total volume of 8.2 mL. The photocatalytic activities were measured using the fabricated TiO₂/Fe–TiO₂ double-layered

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