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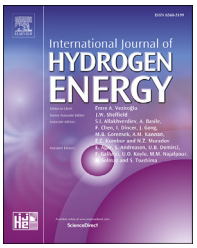

Development of hydrogen production by liquid phase plasma process of water with Ni–TiO_2/carbon nanotube photocatalysts

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ABSTRACT

Hydrogen evolution by water photocatalysis using liquid phase plasma system was disserted over metal-loaded TiO_2 photocatalysts. Carbon nanotube was applied as a support for the metal-loaded TiO_2 nanocrystallites. Photocatalytic activities of the photocatalysts were estimated for hydrogen production from water. Hydrogen was produced from the photodecomposition of water by liquid phase plasma irradiation. The rate of hydrogen evolution was improved by the metal loading on the TiO_2 surface. TiO_2 nanocrystallites were incorporated above 40 wt% onto the carbon nanotube support. The carbon nanotubes could be applied as a useful photocatalytic support for the fixation of TiO_2. Hydrogen evolution was enhanced by the Ni loading on the TiO_2 nanocrystallites supported on the carbon nanotube. Hydrogen evolution was increased apparently with addition of the alcohols which contributes as a kind of sacrificial reagent promoting the photocatalysis.

Introduction

Photocatalytic decomposition of water is an effective method for converting solar energy to hydrogen as clean and renewable energy [1,2]. Because solar energy can be used sustainably and efficiently [3,4]. This process for hydrogen production is attractive economically more conventional methods compared to steam reforming process and water electrolysis [5,6]. Several attempts have been made to develop photocatalysts that work not only under UV light, but also under visible light irradiation [2,7]. It has been developing an effective photocatalysts reacting to the light source [3,8]. Recently, the development of the visible light sensitive photocatalysts for hydrogen generation from water has attracted attention [9,10]. The light sources for the photocatalysts are very important in a photocatalytic reaction [11,12]. Although various light sources have been employed in photocatalysis,

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there have been few studies on photocatalysis using liquid phase plasma (LPP) by irradiation directly into water [13,14].

Plasma reforming has been carried out usually in the gas phase [15,16]. In contrast, there are few reports of discharging in a liquid for hydrogen production [17,18]. Discharge in a liquid has been used in water treatments based on its simple electrical configuration and the use of plasma [19,20]. Similar technical approaches can also be applied in liquid hydrocarbon reforming [21,22]. On the other hand, there are few attempts on its application to hydrogen production [23,24]. Discharging in liquid can generate a higher density of plasma and larger spatial distribution compared to UV lamp irradiation [25,26]. Therefore, these advantages can lead a decomposition of raw materials and an improvement of hydrogen production. The plasma in liquid discharges a strong UV and visible light, simultaneously. Therefore, the plasma in liquid can lead to an effective photocatalytic reaction with photocatalysts.

It has been used TiO_2 nanocrystallines as a typical photocatalyst. Nanocrystalline TiO_2 photocatalysts are suspended into water or hydrogen-containing substances during the photocatalytic reaction. In order to separate and recover the photocatalysts from the reactant solution, photocatalytic supports should also be developed, which can fix the nanocrystalline photocatalysts appropriately. Some of the porous materials have been applied in the preparation of photocatalysts as a photocatalytic support [27]. Carbon nanotubes (CNTs) have also a porous structure and a large specific surface area. The uniform porous structure of CNTs declines the mass-transfer limitations of reactants from solution to active sites on the catalyst [28]. Furthermore, CNTs have a good thermal stability and resistance to acidic and basic media. Because of these reasons, CNTs have been attracted as excellent catalyst support.

CNTs can serve as an ideal building block in hybrid catalysts and improve the performance of photocatalysts due to their excellent mechanical, electrical and optical properties. CNTs can be either semiconducting or metallic depending on their diameter and chirality. CNTs have a large electron-storage capacity [29]. When in contact with TiO_2 nanoparticles, CNTs prompt electron transfer from the conducting band of TiO_2 to the CNT surface due to their lower Fermi level. Thus, CNTs accept and store photo generated electrons and restrain the recombination of electrons and holes.

This paper reports about the hydrogen evolution by LPP irradiation on metal-loaded TiO_2 photocatalysts to obtain a high efficient photocatalytic activity. Effect of LPP irradiation was also evaluated in the photocatalytic hydrogen production. CNT was employed as a photocatalytic support for Ni-loaded TiO_2 photocatalyst. Addition of alcohols into water was evaluated in the photocatalysis by LPP irradiation to obtain a high hydrogen production.

Experimental

Materials

TiO_2 (P25, Degussa), consisting of anatase and rutile was used as a parent photocatalyst. Ni, Fe, and Co ions were introduced as the metal ions loaded onto the TiO_2 photocatalysts. Nickel (II) nitrate hexahydrate (Daejung, 98%), iron (II) chloride hydrate (Daejung, 98%), and cobalt (II) chloride hexahydrate (Aldrich, 98%) were used as the precursor of the metal loaded TiO_2 photocatalysts. The metal-loaded TiO_2 photocatalysts were prepared using the typical incipient wetness impregnation method. The metal ions were loaded on the TiO_2 at a 2 wt% theoretical content. The appropriate amount of metal ions loading on TiO2 was identified as 2 wt% as described in previous work [24]. All chemicals were of analytical grade and used without further purification.

CNT (Kumho Petro. Chem. Co., Korea; MWCNT, K-nanos-1000) was introduced as a support for the photocatalyst in the reaction. To incorporate the TiO_2 nanocrystallites on the support, the TiO_2 sol was prepared by dissolving of titanium isopropoxide (Daejung, 99.9%) into anhydrous ethanol (Daejung, 99%). The content of titanium isopropoxide was adjusted to 10 wt% of the mass of TiO_2. After the solution was stirred at ambient temperature for 2 h, distilled water was added dropwise to initiate hydrolysis. Nanocrystalline TiO_2 (TS) was obtained from the TiO_2 sol by drying and calcination at 500 °C. TiO_2/CNT photocatalyst were prepared by the wetness impregnation method for CNT in TiO_2 sol. CNT was soaked into a TiO_2 sol. After stirring for 4 h, the sample was calcined at 500 °C for 5 h.

Water photocatalysis by LPP irradiation

Distilled water and alcohol-contained water were employed as the reactants. Methanol and ethanol were introduced as the additives. The TiO_2, metal-loaded TiO_2, and TiO_2/CNT were introduced as photocatalysts in the photocatalytic reaction. The amounts of reactants and photocatalysts were adjusted as 200 mL and 0.5 g, respectively. These conditions were defined as the most efficient to obtain a high evolution rate of hydrogen in previous work [30]. A schematic diagram of the apparatus of the photocatalytic reaction using the LPP system was presented in Fig. 1. The photocatalytic reaction was performed in a completely air-free system connected to a gas chromatograph (GC). The gas products generated during the photoreaction were carried by a N_2 gas at a continuous flow to the GC at a 20 mL/min flow rate. The temperature of the photocatalytic reactor using LPP was maintained at 25 °C with cooling water, which was controlled by a circulating water bath. The gas products were analyzed by GC (Younglin, M600D) equipped with a thermal conductivity detector (TCD) and a molecular sieve 5A packing column. The liquid products and remaining alcohols were also analyzed by GC (Shimadzu, 8A) using a FID analyzer and HP-1 capillary column, 50 m length. Deviation of measuring errors are below 5%.

The electric discharge was generated from a needle-to-needle electrode system in a double annular tube reactor within a liquid. The plasma within the liquid reactant was generated by the plasma power supply. Tungsten electrodes with a ceramic coated insulator were inserted with a 0.3 mm interelectrode gap. A bipolar pulse power supply with high frequency (Nano Technology Inc., NTI-1000W) was used to generate the pulsed electrical plasma discharge within the liquid directly. The range of applied voltages, frequency, and pulse width, were 230–250 V, 25–30 kHz, and 3–5 μs, respectively.

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