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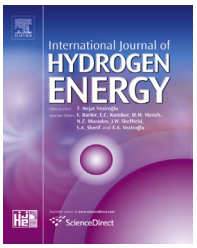

Analyzing the effects of reaction temperature on photo-thermo chemical synergetic catalytic water splitting under full-spectrum solar irradiation: An experimental and thermodynamic investigation

Liang Huaxu [a], *Wang Fuqiang* [a,b,*], *Cheng Ziming* [a], *Hu Shengpeng* [a], *Xiao Bing* [a], *Gong Xiangtao* [a], *Lin bo* [a], *Tan Jianyu* [a], *Li Xiangzheng* [c], *Cao Ruiyang* [a], *Liang Wen* [a], *Liu Linhua* [b,c]

[a] *Harbin Institute of Technology at Weihai, Harbin Institute of Technology, 2, West Wenhua Road, Weihai 264209, PR China*

[b] *Department of Physics, Harbin Institute of Technology, 92, West Dazhi Street, Harbin 150001, PR China*

[c] *School of Energy Science and Engineering, Harbin Institute of Technology, 92, West Dazhi Street, Harbin 150001, PR China*

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ABSTRACT

Photocatalysts currently in use are only able to utilize very small part of the solar spectrum that arrives at the earth's surface (mainly ultraviolet light). Most of the photons that are not absorbed by the photocatalysts are converted to heat. However, there is no consensus on the effect of reaction temperature on photo-thermo chemical synergetic catalysis, which has been studied herein using experimental investigations combined with thermodynamic analysis. An elaborate photo-thermo chemical reaction test rig was initially designed and set up that can test experimental variable while the other influence factors were kept constant. The effects of ultrasonic and operation temperature on Pt/TiO_2 particle cluster distribution during the photo-thermo chemical synergetic catalytic water splitting process were analyzed by an upright microscope for the first time. The results indicated that the H_2 production rate varies with reaction temperature, and 55 °C is the optimum temperature for the photo-thermo chemical synergetic catalytic water splitting process studied here. A maximum H_2 production rate of 11.934 mmol/(h g) could be achieved using a classical Pt/TiO_2 catalyst, when operating under the optimum reaction conditions.

Introduction

In the past decades, population growth associated with modern civilization has led to the serious problems of worldwide fossil fuel energy shortage and environmental pollution [1,2]. Not only is fossil fuel consumption unsustainable, but it also pollutes the environment and increases the amount of CO_2 in the atmosphere [3–6]. Consequently, conventional source of energy resources have been consumed

* *Corresponding author*. Harbin Institute of Technology at Weihai, Harbin Institute of Technology, 2, West Wenhua Road, Weihai 264209, PR China.
E-mail address: Wangfuqiang@hitwh.edu.cn (W. Fuqiang).

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Nomenclature

ΔG	Gibbs free energy, kJ/mol
N_C	effective densities of state in conduction bands, 1/cm^3
$\lvert F_n - F_P \rvert_s$	splitting of quasi-Fermi, eV
E	internal energy, kJ/mol
k_{IT}	reaction rate constant
k_B	Boltzmann constant
$T_{reactor}$	temperature of reactor, K
T_{bath}	temperature of water bath, K
υ_{IT}	rate of electrons, 1/(cm^2 s)
N_v	effective densities of states in valence bands, 1/cm^3
α	absorptivity
ϕ	light intensity, W/cm^2
r_0	radius, cm
Q	activation energy, kJ/mol

to a great extent [7,8]. Therefore, an alternative fuel is necessary, which should in principle be pollution-free [9,10], storable [11,12], and economical [4,13]. Numerous technologies, such as solar energy [14,15], wind energy [16], and nuclear energy [17], have been exploited to replace fossil fuels [18,19]. The production of chemical fuels using sunlight is a promising and sustainable solution to solving global energy and environmental problems [20,21].

Since the Honda–Fujishima effect was reported in the 1970s, splitting water using solar energy has received considerable attention as a possible means for converting solar energy to chemical energy, by creating clean and renewable hydrogen fuel [22,23]. TiO_2 is widely used as a photocatalytic material owing to its good chemical stability [24], no toxicity to the human body [25], and low cost without releasing secondary pollutants [26]. However, the photogenerated electrons and holes in TiO_2 undergo rapid recombination, which can significantly diminish the efficiency of the catalytic reaction. To restrict the electron–hole recombination, Pt is broadly used as a co-catalyst for the photocatalytic production of H_2 from water, because of its high activity and stability under the often harsh operational conditions [27].

H_2 production by water splitting over a Pt–TiO_2 catalyst, with different sacrificial reagents, has been studied by Galińska et al. [28]. Four kinds of sacrificial reagents, Na_2S, EDTA, I^- ions, and IO_3^- ions, were used to obtain effective water splitting to H and O atoms. The maximum H_2 production rate (4.91 mmol/h/g) was achieved when 4 mmol EDTA was used, and the concentration of EDTA decreased to 1.8 mmol after 65 min. When methanol was used as the sacrificial reagent, H_2 evolution was also a result of methanol conversion. Similarly, N-doped TiO_2 particles were synthesized by the two-microemulsion technique and used as a support for Pt toward photocatalytic H_2 evolution by Lin et al. [29]. Their experimental results indicated that the addition of Pt on the TiO_2-xN_x surface could enhance the photocatalytic effect and H_2 evolution. The optimum loading of Pt on TiO_2-xN_x was 0.2 wt.%, and the maximum H_2 production rate was 1.22 mmol//(h g) in 150 mL of 60% methanol solution at pH 5–7. Furthermore, Yu and Jaroniec [30] fabricated Pt/TiO_2 nanosheets with exposed (001) facets by a simple hydrothermal route in a $Ti(OC_4H_9)_4$–HF–H_2O mixed solution, followed by a photochemical reduction deposition of Pt nanoparticles on TiO_2 nano-sheets under Xe lamp irradiation. The experimental results showed that the H_2 production rate using the Pt–P25 (RPt$_2$) catalyst was 1.12 mmol/(h g) with aqueous ethanol solutions, and it was the first report showing that the surface-fluorinated TiO_2 nano-sheets with exposed (001) facets can exhibit excellent photocatalytic activity for water splitting.

The ability of the catalyst to absorb light is very important for photocatalysts. TiO_2 has a wide band gap of ~3.2 eV, which only permits the absorption of ultraviolet (UV) light ($\lambda < 400$ nm). However, UV light accounts for only 4% of the solar irradiation that arrives at the earth's surface (as shown in Fig. 1) [31]. Therefore, effective inhibition of the recombination of photo-generated electron–hole pairs and extension of light absorption to the visible region are key factors for improving the photocatalytic activity of TiO_2. At present, many methods have been adopted to broaden the spectral response range, such as developing composite materials with lower-band-gap semiconductors, dye sensitization, precious metal deposition, and elemental doping of TiO_2 [32]. However, the application of solar energy in water splitting is still hampered by the problems of stability and low H_2 production rate with high cost. Visible light (700 nm>λ > 400 nm) and infrared light (λ > 700 nm) compose almost 96% of the solar spectrum. Most of the photons cannot be absorbed by an adsorbed substrate and will be converted to heat. Therefore, the temperature of the water and photocatalysts would increase during irradiation.

However, the effect of reaction temperature on photocatalysis is controversial, and a consensus on whether it has a positive or negative effect on the H_2 production rate has not yet been reached. Several studies have been conducted to investigate the effects of temperature on photocatalysis. Based on the thermodynamics for a single electron–hole pair, Liu et al. [33,34] deemed that the theoretical energy losses of photo-excited electrons (e–) and holes (h+) would increase and the photocatalytic speed rate would be affected with the rising of reaction temperature. However, other experimental

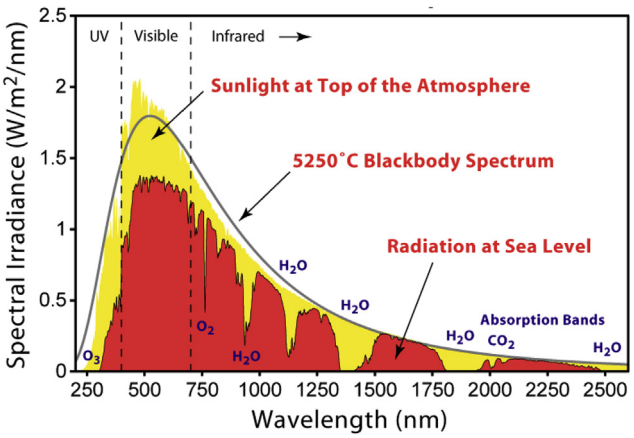

Fig. 1 – Solar radiation spectrum at the top of the atmosphere and sea level [31].

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