ARTICLE IN PRESS

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–15

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/he

Metal-free hydrogen evolution over defect-rich anatase titanium dioxide

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ARTICLE INFO

Article history:
Received 13 March 2018
Received in revised form
12 June 2018
Accepted 14 June 2018
Available online xxx

Keywords:
Anatase
Hydrogen evolution
Methane steam reforming
Photocatalysis
Ti^{3+}
Titanium dioxide

ABSTRACT

Commercial anatase phase titanium dioxide was annealed under various gases (hydrogen, nitrogen, argon, and air) to induce the formation of defects. While annealing in the absence of oxygen there was a notable increase in the concentration of paramagnetic defects as measured by Electron Paramagnetic Resonance (EPR) and X-ray Photoelectron Spectroscopy (XPS). The presence of these defects increased the metal-free photocatalytic activity of the samples towards hydrogen evolution from photocatalytic methane steam reforming (MSR) under UV illumination. Catalyst activity was stable for over 42 h while illuminated owing to the regeneration of Ti^{3+} defects by UV photoexcitation, but rapidly decayed in the dark. The high concentration of unique Ti^{3+} defect sites generated during annealing catalyze hydrogen evolution, avoiding the need for precious metal cocatalysts, while anatase lacking these defects is inactive. This work shows that the implementation of defect-rich anatase TiO_2 provides new catalytic pathways for hydrogen generation from photocatalytic methane steam reforming.

Introduction

Titanium dioxide (TiO_2) has been a favored material for applications in catalysis and photocatalysis due to its stability, redox properties, and low cost [1–8]. Photocatalysis for hydrogen generation has generated significant scientific interest since the 1972 discovery of water splitting over TiO_2 under ultraviolet light illumination [9]. TiO_2 has two very desirable properties for a photocatalyst. First, it is photoactive in near-visible ultraviolet light while maintaining stability under catalytic conditions. Second, its band energies are well-aligned with reactions such as water splitting, namely the conduction band energy is higher than the reduction potential of the proton. Perhaps due to the potentially limitless material feedstock (water) and energy input (sunlight), solar water splitting for hydrogen production has received much attention, but there are other hydrogen-containing feed stocks from which liberating hydrogen gas is thermodynamically easier, including methanol [10–21] and biomass [22–30].

Hydrogen gas is touted as a clean-burning energy carrier that has potential applications in both stationary [31] and mobile power generation [32,33] and energy storage [34] at higher efficiency than conventional internal combustion engines [35–37]. However, the majority of hydrogen produced commercially is derived from an unsustainable process: Methane steam reforming (MSR) of fossil-fuel derived methane [38–40]. MSR is used to convert fossil methane to hydrogen gas and carbon monoxide as syngas at high temperature. Not only does this process use an unsustainable

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https://doi.org/10.1016/j.ijhydene.2018.06.096
0360-3199/

Please cite this article in press as: Pennington AM, et al., Metal-free hydrogen evolution over defect-rich anatase titanium dioxide, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.06.096

feedstock, but it also suffers from being an endergonic and endothermic reaction that operates at poor atom efficiency based on C and H. This poor efficiency is due in part to the need to burn half of the methane feed to provide heat for the process, which releases CO_2, a greenhouse gas, into the atmosphere [41].

Photocatalytic methane steam reforming by contrast offers several advantages for hydrogen generation. For reaction to proceed spontaneously, the following inequality must hold, $\mathbf{\Delta G < W_e}$, where W_e is the external input of non-PV work. For a thermochemical reaction, there is no external work function ($W_e = 0$), so the reaction proceeds only when $\mathbf{\Delta G < 0}$. In a photochemical reaction, photoexcitation provides external energy input in the form $W_e = h\nu$, where h is the Planck constant and ν is the frequency of irradiated light. Therefore, for photocatalysis, the thermodynamic limitation is $\mathbf{\Delta G < h\nu}$. Since $\Delta G^\circ = 113$ kJ mol^{-1} for MSR, this requires a semiconductor with a band gap energy of 1.17 eV or larger to absorb photons of enough energy. This minimum theoretical band gap energy is readily met by many wide-band gap semiconductors including TiO_2. For example, the band gap energy of the anatase polymorph of TiO_2 is 3.2 eV [42]. In this way, photocatalytic MSR bypasses the thermodynamic equilibrium limitations of thermocatalytic MSR. The addition of photon energy, $h\nu$, means the system is not at thermal equilibrium, therefore the equilibrium limitation is not the same as in the absence of light at the same temperature.

Once the high temperature requirement is relaxed, the process may proceed at lower temperature, and many deficiencies of industrial MSR could be addressed. At lower temperature, residual or waste heat could be used to drive the reaction, eliminating the need for external fuel burn and immediately doubling the atom efficiency and increasing the hydrogen yield of the process. Operating at these conditions would also limit the amount of coke formation, leading to longer process cycles and less reactor down time. The elimination of the furnace when conducting MSR at low temperatures with waste heat would simplify the reactor design and materials of construction, making the process more scalable and applicable to smaller scale and point source operations. The smaller scale of operation will allow biorenewable methane to become a feasible feed stock for MSR. Biorenewable methane can be obtained from landfill gas, and the anaerobic digestion of waste streams, such as food waste and wastewater. Waste-derived biomethane can be considered a renewable and net CO_2-free hydrogen source, as the carbon in the methane was removed from the atmosphere during photosynthesis and returns to the atmosphere after the MSR process. If the energy for the MSR reaction comes from solar photons, the hydrogen synthesized this way is renewable [43,44]. An additional benefit of biomethane utilization at point sources such as landfills and dairy farms is to incentivize capture of methane emissions, instead of releasing the potent greenhouse gas into the atmosphere. Methane has more than twenty times the global warming potential per carbon as CO_2 over 100 years [45], Solar thermal heating for MSR [38,46–48] would couple well with photocatalytic reaction conditions, providing both adequate heat for the endothermic reaction at the desired elevated temperature as well as high photon flux in a solar concentrator.

Photocatalytic methane steam reforming for hydrogen production has been investigated experimentally by the group of Yoshida [49–56]. They found that supporting Pt on a variety of semiconductors is effective for hydrogen evolution from steam and methane with quantum yield up to 30%. In the reaction of water and methane over Pt/TiO_2, CO_2 was the primary carbonaceous product, with trace quantities of CO and ethane formed during an induction period. In these experiments platinum was always included as a cocatalyst as TiO_2 is not able to evolve H_2 gas without precious metal cocatalysts due to a lack of the required active site [57].

It is known that under certain pretreatment conditions, including exposure in vacuum and thermal treatment under reducing atmosphere [58,59], TiO_2 can liberate dioxygen gas by losing lattice oxygen, resulting in defect-rich anatase with oxygen vacancies and reduced Ti^{3+} centers. TiO_2 is known to turn blue under ultra-high vacuum (UHV) conditions due to the high concentration of defects, but this change is reversible, as O_2 from ambient air reoxidizes the reduced TiO_2 once the vacuum is removed, making it white again. Annealing in hydrogen gas can induce oxygen vacancies both on the surface and within the lattice of TiO_2 [60–62]. Studies from Mao and coworkers have shown that annealing TiO_2 under hydrogen gas at 18 bar and 473 K for five days creates black TiO_2 with an increase in surface hydroxyls [63]. Studies by other groups of hydrogen treatment at various temperatures, pressures, and annealing times have synthesized black [64,65], blue [59,65], and brown [64–66], photoactive TiO_2, thus supporting that optical properties and photocatalytic performance of hydrogen-treated TiO_2 depends significantly on the method of preparation [67].

The removal of one oxygen atom from the TiO_2 lattice leads to the formation of an oxygen vacancy (V_O) and two electrons, which migrate to and reduce two Ti^{4+} centers to become Ti^{3+} centers. Both X-ray Photoelectron Spectroscopy (XPS) and Electron Paramagnetic Resonance (EPR) have been used to investigate the presence and concentration of defects in anatase. XPS has been used to identify the percentage of oxygen in three bulk states: lattice oxygen, surface hydroxyl, and defect oxygen proximal to an oxygen vacancy [66,68]. EPR is sensitive to unpaired electrons, and can identify a variety of paramagnetic defect structures in TiO_2, including holes trapped at O atoms (O^-), electrons trapped at oxygen vacancies (F-centers), and electrons trapped at Ti atoms (Ti^{3+} centers) in bulk and surface lattice positions [5,59,66,69].

Though annealing under hydrogen has received much attention, the mechanism by which hydrogen alters the physical and chemical properties of TiO_2 are less well understood. Often, it is assumed that hydrogen is responsible for direct reduction of the metal oxide. To provide insight into the annealing process, in the present work the effect of H_2 gas is compared to annealing under different gases, including diatomic N_2, noble Ar, and oxidizing air. The concentration of defect sites was characterized in each sample by XPS and EPR. The modified anatase samples were then tested for photocatalytic hydrogen evolution under MSR conditions and UV illumination without the use of any metal cocatalyst. The defects produced by annealing under oxygen-excluded atmospheres were found to be highly stable to mildly oxidizing conditions and imparted metal-free photocatalytic hydrogen evolution activity to anatase TiO_2.

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