Enhanced photocatalytic hydrogen production in a UV-irradiated fluidized bed reactor

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ABSTRACT

UV-irradiated fluidized bed reactor system and Pt-loaded TiO_2 spheres were developed for photocatalytic water splitting. This novel approach was explored as a means to minimize the parasitic back reaction, mass transport and radiation distribution effects that limit the performance and scalability of immobilized-film and suspended slurry photocatalysts typically employed for photocatalytic hydrogen production. By fluidizing Pt-loaded TiO_2 spheres in a 2.2 M Na_2CO_3 solution, steady hydrogen production rates up to 211 μmol/h with an apparent quantum efficiency of 1.33% were achieved upon UV-irradiation. This demonstrates a marked 44% increase in the apparent quantum efficiency when compared to the performance of a traditional Pt-loaded TiO_2 suspended slurry photocatalyst in the same reactor. It is hypothesized that this enhanced performance is primarily due to improved separation of the evolved H_2 and O_2 from the Pt-loaded photocatalyst particles, thus reducing the parasitic back reaction.

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1. Introduction

Photocatalytic water splitting has long been sought after as a direct solar-to-chemical energy conversion process, with much of the focus on creating a sustainable and emissions-free source of hydrogen. Titanium dioxide (TiO_2) has been one of the most widely researched water splitting photocatalyst materials due to its low-cost and high stability when irradiated in solution [1–3]. While the application of pure TiO_2 is largely limited to the ultraviolet spectrum due to its wide band gap, it remains a popular candidate as a water splitting photocatalyst.

Though photocatalytic water splitting over pure TiO_2 surfaces is possible, it is often found to proceed at low to negligible rates. It has been shown that the rate of hydrogen evolution can be dramatically improved by depositing platinum nanoparticles (2–3.4 nm) [4,5] onto the TiO_2 surface, typically at loadings of 0.5–1 wt% [4,6]. The presence of platinum sites, however, catalyzes the parasitic back reaction of hydrogen and oxygen to form water and waste heat, thus reducing the overall efficiency of the system. Platinum loadings beyond 1 wt% are often found to decrease the overall rate of hydrogen production [4,6].

Interestingly, while the addition of platinum to the titanium dioxide surface allows the hydrogen evolution reaction to proceed, it has been demonstrated in a number of publications that, in pure water, little to no oxygen is detected throughout the course of the experiment [2,4,7–10]. The absence of stoichiometric oxygen evolution suggests that parasitic or side reactions are "trapping" the oxygen and otherwise hindering the reaction. Sayama and Arakawa demonstrated [11,12] that when photocatalytic water splitting over TiO_2 was carried out in a Na_2CO_3 solution at an optimal Na_2CO_3 concentration of 2.2 M, not only was stoichiometric evolution of hydrogen and oxygen observed, but the hydrogen evolution rate increased by nearly 600 times. The researchers hypothesized that this remarkable increase in performance may be due to the formation of a carbonate layer over the platinum nanodeposits, which reduces the parasitic back reaction of hydrogen and oxygen. It was also suggested that the carbonate ions afford an alternate reaction mechanism for water splitting in which carbonate species scavenge holes (thus preventing the photoadsorption of O_2 and the formation peroxo-titanium species) and facilitate the desorption of O_2 from the TiO_2 surface [11,12].

Since the first demonstration of photocatalytic water splitting over TiO_2 by Fujishima and Honda [13,14], TiO_2 photocatalysts have typically been deployed as either suspended nanoparticle slurries or as immobilized films. From a reactor design point-of-view, suspended photocatalyst nanoparticle slurries offer good radiation distribution throughout the reaction volume, excellent mass transfer and a high photocatalyst surface area with respect to the reactor volume. In suspended nanoparticle systems, however, the evolved hydrogen and oxygen remain in contact with

the platinum-loaded photocatalyst particles for extended periods of time, thus exacerbating the parasitic back reaction. This, in turn, limits the scalability and performance of suspended nanoparticle systems. Immobilized thin film photocatalysts address this issue in that the reaction products are easily separated from the platinum-loaded photocatalyst. However, immobilized film photocatalysts tend to suffer from poor radiation distribution, limited rates of mass transfer and low photocatalyst surface area (with respect to the reactor volume) [15]; all of which limit the performance and scalability of immobilized film systems.

Fluidized bed reactors operate by suspending particles (larger than the nanoparticles typically employed) throughout the reactor volume by the upward flow of a liquid phase. When used for photocatalytic processes such as water treatment, fluidized bed reactors offer improved mass transfer, excellent radiation distribution, and a photocatalyst surface area-to-volume ratio approaching that of suspended nanoparticle systems [16–18]. This approach also yields fast and simple separation of the reaction products from the platinum-loaded photocatalyst particles as the products are carried from the reactor by the fluid flow while the photocatalyst particles are retained in the reactor. The product gases can then be separated from the fluid by downstream separation processes.

Fluidization does, however, introduce the issue of mechanical stability, as the photocatalyst particles must be able to withstand particle-to-particle and particle-to-wall collisions. To our knowledge, there have been no other reported attempts of photocatalytic water splitting in fluidized beds by other researchers; however, there have been several endeavors to employ fluidized TiO_2 photocatalysts for both air and water treatment [16,18–32]. Previously reported attempts of producing fluidizable photocatalysts employ sol-gel [16,18–24], slurry dip-coating [25–30], or CVD methods [31–34] to affix the photocatalyst material onto fluidizable substrates, such as glass beads, though this was often met with limited success. In most instances, the adhesion of the photocatalyst material to the fluidizable supports was not great enough to withstand the rigors of fluidization and significant attrition of the TiO_2 photocatalyst from the fluidizable support material was often observed; in most instances, the photocatalyst material would be ablated from the substrate surface in a short period of time.

From the literature, the critical failure point for supported titanium dioxide films are at the support/TiO_2 film interface, where the TiO_2 film is attached by weak Van der Waals forces, or at fractures and stress points induced by shrinkage during the drying process [35,36]. One research group attempted to improve the mechanical strength of the TiO_2-substrate interface by hydroxylating the surface of soda glass beads with a strong NaOH bath such that residual OH^- surface groups could chemically bind with a TiO_2 sol-gel [23]. While this did achieve an improvement over slurry deposited films, the mechanical strength of the film was still limited and unsuitable for fluidization.

Keshmiri et al. [36] developed a novel TiO_2-TiO_2 composite film where commercially available Degussa P25 nanoparticles where combined with a TiO_2 sol-gel binder. The sol-gel binder caused the P25 nanoparticles to bond to each other, and to a supporting substrate; this resulted in a remarkable improvement in the adhesion of the TiO_2 photocatalyst to the supporting substrate. Vega et al. [24] further developed this TiO_2-TiO_2 composite technique to form self-supported spherical beads of pure TiO_2, which were formed by combining the still wet composite solution with a polymer matrix and cast into spheres by a drop forming technique. By removing the weak TiO_2-support interface entirely, the TiO_2 particles demonstrated dramatically improved attrition resistance and outstanding performance when used for the degradation of model water contaminants in a fluidized bed reactor.

We previously reported our preliminary findings on photocatalytic water splitting in a UV-irradiated fluidized bed reactor where it was found that, on a per reactor volume basis, the fluidized bed approach yielded a marked increase in the hydrogen evolution performance over conventional photocatalyst slurries
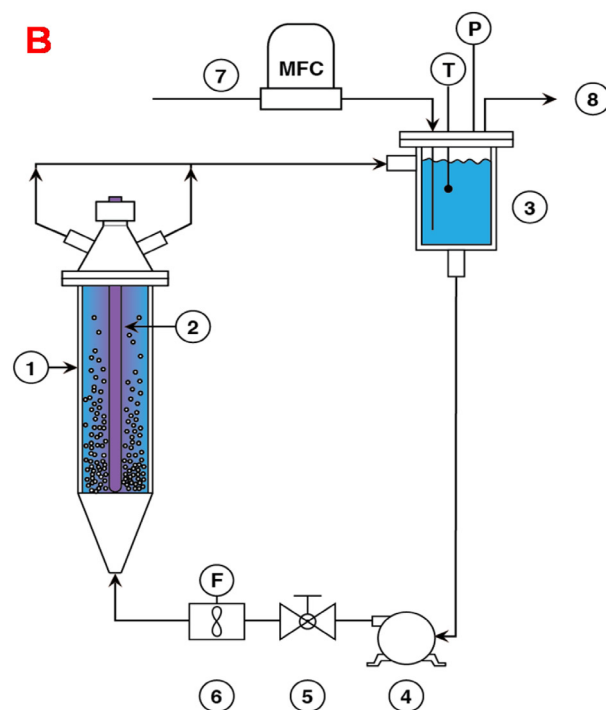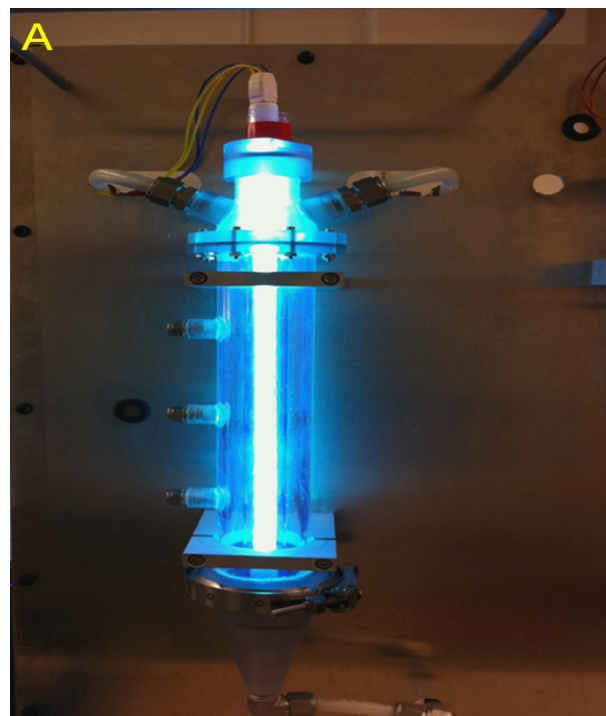
Fig. 1. (A) Photograph of the annular fluidized bed reactor, and (B) schematic diagram of the fluidized bed photoreactor system: (1) fluidized bed reactor, (2) inner quartz annulus with UV lamp, (3) separator, (4) pump, (5) flow control valve, (6) turbine flow meter. A N_2-gas sparge fed by a (7) mass flow controller is employed to purge the reactor system and to sweep product gases to (8) the gas chromatography system for analysis.