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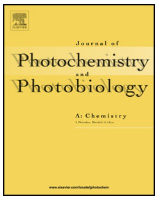

Laser induced H_2 production employing Pt-TiO_2 photocatalysts

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ABSTRACT

The photocatalytic production of hydrogen from water as well as from an aqueous methanol solution employing pre-treated TiO_2 and various Pt-TiO_2 photocatalysts was studied by using an Nd:YAG laser as irradiation source. The photocatalysts (0.5, 1.0, 1.5 and 2.0 wt% Pt-TiO_2) were prepared by utilizing a photocatalytic reduction method upon which characterization by TEM and EDX were conducted. EDX indicated that the loading method was successful and TEM analysis confirmed the presence of Pt on the surface of TiO_2 with a particle/cluster size between 11 nm and 22 nm. The impact of the loaded Pt on the band gaps of the different photocatalysts was investigated by diffuse reflectance spectroscopy (DRS) and calculated by means of the Kubelka–Munk method. The band gap values shifted sequentially from 3.236 to 3.100 eV as the loading increased. The amount of H_2 produced from the individual photocatalysts dispersed in both pure water and aqueous methanol solutions, was measured manually with a gas chromatograph. As soon as irradiation was initiated, a distinct color change from shades of gray to dark blue-gray was observed for all the photocatalysts. XRD confirmed that this was due to the part conversion of the anatase phase to the rutile phase. No H_2 was detected for the various photocatalysts suspended in water, i.e. in the absence of methanol. The amount of H_2 produced from the various Pt photocatalysts suspended in the aqueous methanol solution was found to be the highest for the 0.5 wt% and 1.5 wt% Pt-TiO_2 photocatalysts and the lowest for the 2 wt% Pt-TiO_2.

1. Introduction

At present technologies related to the combustion of fossil fuels supply approximately 88% of the world's energy needs and therefore dominate compared to clean and renewable energy supply technologies [1]. Views concerning available/remaining world fossil fuel reserves and predictions of exactly when supplies will be exhausted differ substantially, and this uncertainty, coupled with growing environmental concern, the continuous increase of global energy demand and the depleting state of non-renewable fossil fuels, have many companies and researchers working on the development of technologies and processes which can efficiently exploit the potential of hydrogen as a competitive and clean alternative energy carrier [2]. Much attention has been focused on the photo-assisted stoichiometric production of H_2 and O_2 from water employing solar energy as a renewable energy resource [3]. Exploiting solar light, however, is still extremely challenging and the photocatalytic production of sufficient amounts of H_2 through water splitting employing sunlight is still far from being a practical application [4,5]. TiO_2 is one of the most extensively studied oxide semiconductors employed in photocatalytic reactions due to its abundance, low cost, high stability in aqueous environments and favorable band gap (3.2 eV for anatase) [4,6–10]. TiO_2 photocatalysis is achieved by the irradiation of an aqueous suspension of the semiconductor with light having energy equal to or greater than the band gap of the semiconductor. This absorbed energy results in charge separation producing excited electrons (e^-) and positive holes (h^+) which can participate in H_2 production redox reactions. It has, however, been reported that fast, undesirable e^-–h^+ recombination occurs within TiO_2, which impacts negatively on the overall efficiency of the process. The most common technique to counter recombination is to load TiO_2 with Pt. The excited electrons then migrate to the Pt through the metal–support interface [11]. A further means of enhancing overall H_2 production is by employing sacrificial agents. Methanol was reported to be the most employed and reactive alcohol to inhibit/prevent this recombination by acting as an electron-donor- or electron–acceptor scavenger, which in turn enhances the photocatalytic activity of TiO_2 in H_2 production studies [12,13]. Many studies have been conducted where conventional light sources were employed as the irradiation source for photocatalytic H_2 production [14,15]. The basic problems, however, associated with the use of conventional lamps in commercial heterogeneous photocatalysis are very long reaction times (h), low photonic efficiencies and overall higher H_2 production rates are required. If these problems are resolved, heterogeneous

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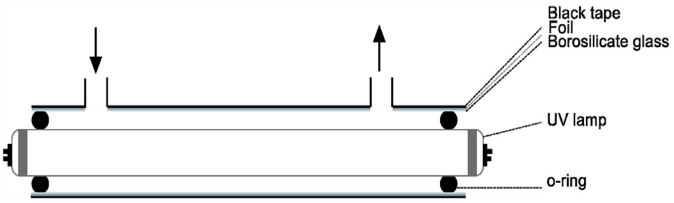

Fig. 1. Borosilicate glass cylinder containing a 0.7 W/m^2 UV light.

photocatalysis can be employed as an economically viable and environmentally friendly technique. A possible way to address these problems according to Gondal, Hameed and associates is by employing lasers as the light source [16–18], not considering the economic viability as laser light, in contrast to light generated from lamps, consists of unique properties such as high beam intensity, directionality, monochromaticity and tunability. This combination of properties allows for controlled experimental working conditions resulting in higher amounts of photons being introduced in a shorter time period as a result of directionality and high beam intensity, which can be tuned as desired. This does not necessarily result in higher photonic efficiencies as photonic efficiencies are influenced by various experimental parameters/factors. These specific properties are not that easily achieved with light generated from lamps. To date, a limited number of studies have been conducted employing lasers as the irradiation source as part of hydrogen production studies. The photocatalysts used during these studies include NiO, TiO_2, Fe_2O_3 and WO_3, all operating under different experimental conditions. For these studies the amount of hydrogen that evolved after 60 min at 100 mJ of incident laser energy was in the range of 1.5 and 1.9 mmol, which is substantially more in a shorter period of time compared to conventional non-monochromatic UV-light [16–18]. Our aim in this study is to investigate the activity of different Pt-TiO_2 photocatalysts toward H_2 production when exposed to monochromatic UV-light at mild energies (40 mJ), as no studies incorporating these Pt-modified TiO_2 photocatalyst in conjunction with a laser has been reported to date. For studies employing conventional non-monochromatic UV-light, it was observed that Pt enhanced the overall amount of hydrogen produced. However, this study shows that much lower amounts of H_2 are produced employing Pt-TiO_2 and mono-chromatic (laser) UV-light.

2. Experimental

2.1. Materials

Commercially available Degussa P-25 TiO_2 powder with an anatase/rutile ratio of 86.3/13.7 was used throughout. Chloroplatinic acid ($H_2PtCl_6.6H_2O$), methanol (CH_3OH, 99.5%), hydrochloric acid (HCl, 32%) and ethanol (CH_3CH_2OH, 99.5%) were obtained from MERCK and Sigma–Aldrich and used without further purification.

2.2. Preparation of Pt-TiO_2 photocatalysts

A photocatalytic method was employed to prepare all photocatalysts. A stock solution containing water (400 mL), HCl (100 mL) and $H_2PtCl_6.6H_2O$ (25 g) was prepared, using all the available salt due to the hygroscopic nature of $H_2PtCl_6{\cdot}6H_2O$. All photoreduction experiments were conducted in a photocatalytic reactor system, which consisted of a borosilicate glass cylinder housing a UV lamp (0.7 W/m^2) (Fig. 1). TiO_2 (1 g) was placed in a water (500 mL), $H_2PtCl_6{\cdot}6H_2O$ and ethanol (3 g) solution to produce a suspension through magnetic stirring. The suspension was pumped through the continuous flow-through UV light reactor with a flow rate of 400 mL/min for 25 min at 20 °C as shown in Fig. 2. The solution was subsequently filtered to yield Pt deposited TiO_2 powder and placed in a vacuum oven at 80 °C for 30 min to dry and to evaporate all the ethanol. Unsupported TiO_2 was prepared by pre-treating TiO_2 in an identical fashion to the corresponding Pt-TiO_2 samples, but without incorporating the metal.

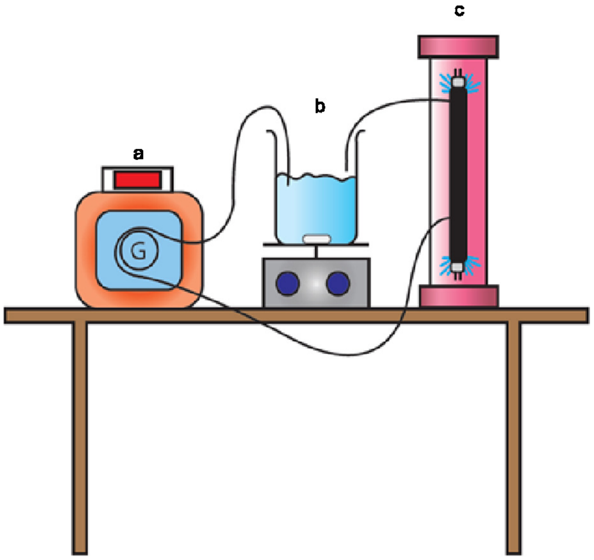

Fig. 2. Schematic diagram of the photocatalytic reaction system used for loading 0.5–2.0 wt% Pt-TiO_2: (a) peristaltic pump, (b) suspended Pt-TiO_2 solution and magnetic stirrer, (c) UV light reactor.

Table 1
Parameters used for DRS.

Parameter	Value
Lamp	Halogen (HL)
Integration time (ms)	780–822
Accumulation	5
Dark current correction	Yes

2.3. Characterization of Pt-TiO_2 photocatalysts

Transmission electron microscopy (TEM) analyses were conducted employing a Philips CM10 electron microscope (Philips, Netherlands) employing a 100 kV accelerating voltage. The samples were sonically dispersed in an ethanol solution for 2 min and a drop of the resultant solution was deposited onto a copper grid covered by a porous carbon membrane for observation.

Energy dispersive X-ray (EDX) analysis was conducted on a FEI QUANTA 200 ESEM with an integrated OXFORD X-SIGHT EDS system operating at 15.00 kV. The samples were deposited on a standard aluminum holder and coated with Pt for observation.

The UV–vis reflectance spectra of the photocatalysts were recorded by making use of a Specord S600 (Analytik Jena) UV–vis spectrophotometer incorporating a diffuse reflectance module with standard white spectralon as reference. Settings used in the DRS measurements are tabulated in Table 1. The band gaps for the individual photocatalysts were calculated by means of the Kubelka–Munk equation [19,20].

2.4. H_2 production and measurements

The setup used to study the photocatalytic production of H_2 is illustrated in Fig. 3.

A special glass cell (40 mm diameter, 150 mm length and 3 mm thick), equipped with optical grade N-BK7 windows (40 mm diameter) for transmission of UV and visible laser beams, was fabricated.