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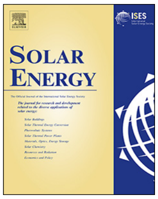

In-situ Cl^- ions formation during photocatalytic reaction of platinized nanocomposite for hydrogen generation

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ABSTRACT

Platinised Titania is emerging as a promising catalyst for its chemical stability, large surface area, and good electronic charge transfer. It is one of the most efficient materials and has been studied over past few decades for photocatalytic hydrogen generation. Photodeposition of Pt nanoparticles on TiO_2 surface enhances trapping of photoexcited electrons and restricts recombination process. In this article we explored the influence of chloride ion formed during in-situ photocatalytic process, on photocatalytic hydrogen generation by scavenging holes. Illumination under UV–Visible light ($400\,nm < \lambda < 700\,nm$) improves interband excitation and transfer of photogenerated electron to the conduction band of TiO_2. Transmission electron microscopy (TEM) results reveal average particle size of Pt nanoparticle in the range of 10 nm with uniform distribution on TiO_2 surface. In-situ photodeposition of Pt nanoparticle on TiO_2 resulted in incredibly active photocatalyst for hydrogen generation due to in-situ generated Cl^- ions. Also, to one of the highest reported (6.72%). The hydrogen evolution rate of $17\,mmol\,h^{-1}$ with apparent quantum yield (AQE). The AQE significantly higher than that for catalyst under solar AM (1.5 G) illumination (0.04%).

1. Introduction

The enormous solar flux at the earth's surface depicts a unique capacity to deliver clean and renewable energy source for the sustainable future. In the recent era, solar to chemical fuel (hydrogen) conversion has drawn significant attention and has also given a promising solution for global energy and environmental crisis. Photocatalysis provides a major way for storing solar energy in chemical bonds that can efficiently capture sunlight and transform photon energy into chemical energy. Platinum-supported titanium catalysts have been widely used in various industrial procedures due to their excellent efficiency to accelerate the rate of reaction with very low price. In early 1970s, Fujishima and Honda reported water splitting and significant hydrogen generation by using TiO_2 and Pt electrode in a photoelectrochemical cell (Fujishima and Honda, 1972). TiO_2 (Titanium(VI)dioxide) has drawn extensive attention in photocatalysis and environmental remediation owing to its non-toxicity, stability, wide availability, durability, and low cost. Several disadvantages often restrict the traditional photocatalyst TiO_2 for photocatalytic water splitting including (i) wide band gap (3.2 eV) and (ii) rapid charge recombination of photogenerated electron and hole pairs leading to low quantum yield and a poor photocatalytic activity (Asahi et al., 2001; Linsebigler et al., 1995; Chen et al., 2011). To generate hydrogen photocatalytically, extensive efforts are being made across the globe to overcome the above disadvantages and improve the performance of TiO_2. The most promising and viable way to overcome the above problem is the incorporation of noble metal nanoparticles (mainly Pt) on TiO_2. Platinum is one of the most promising noble metal and light harvesting cocatalyst for photocatalytic enhancement. Platinum exhibits highest Schottky barrier (Chen et al., 2007; Zielińska-Jurek and Zaleska, 2014) and therefore deposition of Pt on TiO_2 creates an interface. This interface acts as an electron sink and reduces the chances of electron-hole pair recombination. Deposition of platinum (Pt) metal nanoparticle on TiO_2 can absorb visible light and bring significant changes to many aspects of photocatalysis. An increase in activity of photocatalysis is observed when irradiated under visible light due to LSPR effect. Other photocatalysis materials like; MoS2/g-C3N4, Cu2O and CuInZnS nanoparticles have reported as highly photocatalytic performance (Ye et al., 2018; Haijun Huang et al., 2017; Wen al., 2016). This phenomenon occurs when nanoparticles with free electrons interact with an external electric field that matches with the valence electrons oscillating against the restoring force of nuclei (Zielińska-Jurek et al., 2011; Zhang et al.,

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2013). Surface plasmon resonance (SPR) of platinum is relatively unexplored because Pt nanoparticles show SPR below 450 nm, which makes weak absorption of light (Anpo and Takeuchi, 2003; Amano et al., 2009). Gray et al. reported Pt loading on TiO_2 nanotubes with improved photocatalytic activity in visible light for photo-oxidation of acetaldehyde (Bigall et al., 2008). Similarly, Al-Thabaiti et al. synthesized intrinsic decorated TiO_2 nanotubes with Pt leading to highly efficient photocatalyst for hydrogen generation under both UV and visible light (Vijayan et al., 2010). Tian et al. reported selective oxidation of alcohol to aldehyde in water based on surface plasmon resonance of platinum nanoparticle loaded on TiO_2 under visible light irradiation (Basahel et al., 2014). Li et al. explained deposition of Pt on TiO_2 surface with highest activity for H_2 generation (Zhai et al., 2011). There are many reports on effect of inorganic ions on photocatalytic degradation and activity of TiO_2 has been discussed widely.

In this study, TiO_2 was modified by depositing Pt onto TiO_2 surface by a traditional in-situ-photo deposition method using different illumination sources to understand its influence on photocatalytic hydrogen generation (Li et al., 2001). In this approach, TiO_2 has filled VB (Valence Band) & unfilled CB (conduction band) in its electronic structure. When illuminated with photon energy (hv) electron and holes are generated in TiO_2. Platinum precursor gets reduced to zerovalent Pt and gets deposited onto TiO_2 surface in the presence of ethanol and water. The electrons from CB of TiO_2 is trapped by platinum owing to the Schottky barrier created. Ethanol which is added as a sacrificial donor prevents recombination (Kowalska et al., 2009; Kowalska et al., 2012). Such in-situ decorated Pt metal and chloride formation on TiO_2 shows valuable improvement in photocatalytic H_2 generation rate under UV–Vis irradiation.

2. Experimental section

2.1. Materials

All chemicals were of analytical grade and were used without further purification. Aeroxide TiO_2 (P-25) (80–20% anatase to rutile) procured from Evonik Degussa Corporation, U.S.A., was used as the catalyst. Ethanol (99.9%) was purchased from Merck. Hexachloroplatinate (IV) solution (50% assays) was purchased from Merck. Ultrapure water (18 MΩ cm) was used for sample preparation and experiment.

2.2. Synthesis and characterization of catalyst

Platinum was deposited on TiO_2 (Degussa-P25) catalyst by in-situ photo deposition method. TiO_2 powder was mixed with a requisite volume of hexacholoroplatinic acid (H_2PtCl_6) solution (consistent to 1% w/w loading), and ethanol was used as a sacrificial donor. A 20:1 volume ratio of de-ionized water and ethanol was added to the photocatalytic reactor. Then, the reaction mixture was illuminated under anaerobic condition (in presences of N_2) by using a solar simulator (AM 1.5 G filter, 1 sun) and medium pressure mercury lamp (450 W) with vigorous stirring. The white color of solution transformed into a grey color. After centrifugation and washing with ethanol 2–3 times, the powder was dried at 60 °C temperature in a vacuum oven. The sample designated as Pt/TiO_2 (in-situ). The same process as mentioned was carried out except recovered catalyst prior to testing the catalyst for hydrogen generation rate. p-XRD patterns of synthesized materials and crystallinity were determined using Rigaku Miniflex-II Desktop X-ray diffractometer with Cu Kα radiation and data were collected in a 2Θ range. All materials were scanned with a step width of 10 $\min^{-1}$. pXRD recorded pattern were matched with a JCPDS cards. UV–Visible diffuse reflectance spectra were measured by using UV–vis/NIR Agilent spectrophotometer and the absorbance of all materials were analysed the same instrument. Transmission electron microscopy studies carried out on Phillips CM100 electron microscope operating at 100 kV.

2.3. Light source

All experiments were performed with either solar simulator or medium pressure mercury lamp. The simulated solar irradiation was produced using a solar simulator (1000-W Xe arc lamp with an AM 1.5 G filter). It generates simulated 1 sun intensity (100 mW cm^{-2}) 500 W, which matches with the global solar spectrum. Medium pressure mercury lamp was used as a source of UV–visible light (450 W).

2.4. Photocatalytic hydrogen generations

All the experiments were carried out in gas-tight 750 mL borosilicate glass (outer chamber) with quartz inner illumination vessel. TiO_2, 1% hexachloroplatinic acid solution, 400 mL deionized water, and 5% Ethanol were taken in an outer glass chamber. The reaction mixture was then degassed by using ultra-pure nitrogen for 25 min to remove all the dissolved gasses. The temperature of the reaction was maintained at room temperature by continuously circulating water through inner quartz vessel. The solution was stirred at 400 rpm. Photocatalyst was irradiated by 450 W medium pressure mercury lamp. The gas mixture was analysed by using online GC-2014 Shimadzu with molecular sieve 5A packed column and N_2.

3. Results and discussion

3.1. Characterization of catalyst (Pt/TiO_2)

XRD of bare TiO_2 and Pt/TiO_2, synthesized under the irradiation of medium pressure mercury lamp is presented in Fig. 1. Similarly, the pXRD pattern of Pt/TiO_2 and standard TiO_2 is same regarding position and width (Ren et al., 2010) sharp peaks of Pt cannot be detected because its concentration appears to be below XRD detection limit. Another possibility could be due to lower loading and homogeneous dispersion. UV-DRS spectra of bare TiO_2 (P-25) and Pt/TiO_2 are shown in (Fig. 2). The incorporation of Pt metal on TiO_2 matrix show a shift in the spectrum (Chowdhury et al., 2012; Yu et al., 2009). The peak for Pt/TiO_2 shifted towards visible region leading to a reduction in the band gap of TiO_2 from 3.04 eV to 2.38 eV (Red shift).

The UV-DRS spectrum reveals the broadband absorption from (300 to 700 nm) of platinum nanoparticles onto TiO_2 surface. The morphology and size distribution of metal nanoparticles on photocatalyst Pt/TiO_2 was observed by Transmission electron microscopy (TEM). The TEM study of photocatalyst Pt/TiO_2 indicates that Pt nanoparticles were reduced and homogeneously deposited on TiO_2 surface. It is also confirmed from the color transformation from the white color of TiO_2 to

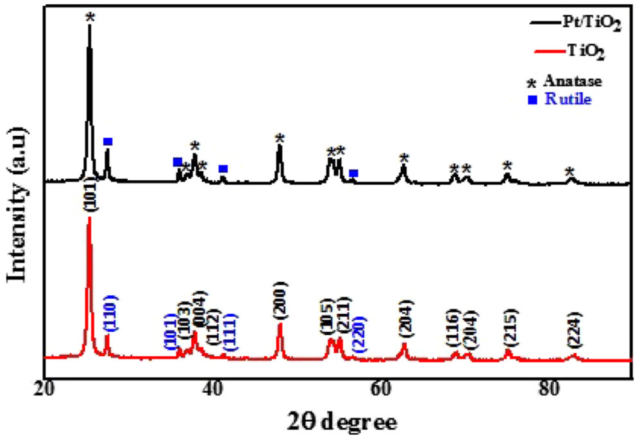

Fig. 1. pXRD graph of TiO_2 (red) and Pt/TiO_2 (black) synthesized by photodeposition method. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)