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Enhanced photocatalytic activity of Pt deposited on titania nanotube arrays for the hydrogen production with glycerol as a sacrificial agent

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ABSTRACT

Photocatalytic activity of Pt-loaded TiO₂ nanotube arrays (Pt-TNTA) in the presence of glycerol as a sacrificial agent to produce H₂ has been studied. The effects of Pt loading and the methods by which it is deposited on TNTA (chemical reduction and photo-assisted deposition) were carefully examined. Intermediate products were also identified in order to scrutinise the reaction pathways of hydrogen generation in this particular system. FESEM imaging confirmed the formation of nanotubular structures of TiO₂ with average inner diameter of 80 nm, wall thickness of 20 nm, and length of approximately 2.5 μm. The generated nanotube arrays were of anatase structure with crystallite size within the range of 22–30 nm. Pt was successfully deposited on the surface of TNTA, as corroborated by EDX spectra, elemental mapping and TEM analysis. Band gap narrowing upon Pt loading was implied by UV–Vis DRS analysis, resulting in a band gap value of 2.93 eV, notably lower than a typical value of 3.2 eV associated with anatase. The photocatalyst sample with Pt deposited via a photo-assisted deposition method (Pt-TNTA-PDC) evidently outperformed its bare TNTA counterpart in producing hydrogen by 4.7 times, while that with Pt deposited by chemical reduction could improve H₂ production by 3.8 times. During photocatalytic operations, glycerol served an important purpose in suppressing electron-hole recombination by providing holes an oxidative target which is less energy-demanding than water. It is proposed that glycerol underwent dehydrogenation and decarbonylation processes producing ethylene glycol, followed by dehydration and oxidation towards acetic acid, before transforming into H₂ and CO₂, eventually. We suggest that Pt plays a role not only in the enhancement of H₂ photoproduction, but also in governing the direction of reactions, hence the intermediates and final products.

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Introduction

Utilizing solar energy with TiO₂-mediated photocatalytic reactions have been studied extensively in the last decade especially for production of renewable energy like H₂ [1–9] on the purpose of responding to the ever increasing energy demand as well as circumventing the inevitable depletion of fossils fuels and environmental pollution [10]. To date, nearly 95% of H₂ in the market was produced via conventional technology, such as methane steam reforming and pyrolysis which are generally energy demanding, while offering low H₂ selectivity [7–11]. It is therefore imperative to assemble advanced H₂ generation systems, namely utilizing renewable sources, such as water or biomass, and implementing a cost effective process, such as photocatalysis. In fact, many biomass feedstocks such as methanol, ethanol, glycerol [9,12], or many organic pollutants can be integrated into a photocatalytic reaction system as anodic sacrificial agents, hence kinetically enhancing H₂ production while eliminating pollutants at the same time [5,6,8,13,14]. In this process, photo-splitting of water and photo-reforming of sacrificial agents are believed to take place simultaneously in the absence of oxygen. Introducing sacrificial agents, being from inorganics (H₂S, S²⁻/SO₃²⁻, Fe²⁺ etc) or organics (alcohols, acids, aldehydes, sugar etc) into a photocatalytic system is known to be an effective way to suppressing electron-hole recombination. H₂ yield is significantly improved as the sacrificial agents are oxidized by holes, •OH radicals, and/or oxygen produced by cleavage of water [8–11,15,16]. Furthermore, this arrangement also results in the suppression of O₂-H₂ back reaction [7,8]. The affinity of these agents towards holes would depend upon their polarity, which in turn affects their adsorptive properties on photocatalyst surface [15]. One of the most intriguing sacrificial agents is glycerol because it is considered as a biodegradable, nontoxic, and, nonflammable substrate. Being an undesired by-product in biodiesel industry, the demand for glycerol is relatively limited, so to many it is regarded as waste [10]. Therefore, this would be beneficial as a new avenue for H₂ generation and waste limitation.

Among other light-harvesting semiconductors, TiO₂ is the most studied material and widely considered as the most promising photocatalyst due to its cost effectiveness, non-toxicity, low environmental impact, high photocatalytic activity [6,17–20] and excellent stability (in alkaline and acidic solution as well as under illumination) [21]. The versatility of TiO₂ as a photocatalyst is proven by its wide applications, which include air and water purifications (removal of organic and inorganic pollutants [19,22], photo-driven disinfection of pathogenic micro-organisms as viruses and bacteria [22,23], self-cleaning, self-sterilizing, anti-fogging [19,21], and dye-sensitized solar cells [25]. Compared to others morphologies (nanorods, nanotube, nanowires, nanobelt), well aligned TiO₂ nanotube arrays (TNTA) produced from anodic oxidation of Ti foil are favored in many cases, owing to its tunable structure, effective photon absorption, and extensive internal surface area [20,21,25,26]. However, its applications have been constrained by rapid recombination of photogenerated electron-hole pairs, inactivity under visible, and large overpotential for H₂ generation [1–6,16,17,19–21,24–27]. This is because,

photo-generated electrons and holes resulted by photocatalysis can either react with adsorbed species or undergo undesired recombination [10]. Tremendous efforts have been performed to narrow the band gap in order to enhance the visible light response, including incorporating non-metal doping (C, N, B, and F) to the matrix of TNTA, and coupling with low-band-gap semiconductors such as CdS, CdSe, PbS or WO₃ [1–4,19,24–27]. In order to hamper the fast recombination of photogenerated electron-hole pairs, deposition of high-work-function metals such as Pt, Au, Pd, Ni, Cu, Rh and Ag on TiO₂ have been previously reported to be a useful approach [5,7–9,11,12,20,21,25,26,28,29]. Enhancement of photocatalytic activity can also be performed by the use of TiO₂-Co₃O₄-Pt and TiO₂/WO₃/Pt since co-catalyst Co₃O₄-Pt can suppress recombination and provide extensive active sites [30], while WO₃ and Pt can act as hole and electron collectors, respectively [1]. Branched hydrogenated TiO₂ has also been reported effective to promote the separation of electron-hole [17]. In addition, incorporation of Cu₂(OH)₂CO₃ onto TiO₂ also enhanced the water splitting reaction as reported by He et al [31]. Meanwhile, direct Z-scheme anatase/rutile TiO₂ nanofiber photocatalyst could also enhance photocatalyst efficiency in H₂ production [18].

Increasing attention has been devoted to Cu₂O, CuO, CuO_x that embedded on TiO₂ [11,12,16,31] to enhance H₂ production since these metal oxides are abundant, cheaper, non-toxicity, very active and their bandgaps are suitable for water splitting [11,12]. However, formation of partially oxidized species strongly adsorbed on the surface can lead to deactivation. Moreover, the presence of complexing agent, such as carboxylic acids can lead to the leaching of highly disperse metals. Some researchers also reported that Cu leaching is observed under visible light irradiation and it can be minimized by UV back photodeposition [10,12,16]. On the other hand, Pt is one of the noble metals that occupy the largest work function (5.65 eV), low overpotential for solar harvesting fuel generation [1], and has higher stability compared to others [25]. Therefore, it performed better as electron trapper [5,20–22,25]. When Pt is deposited on TNTA, the formation of Schottky barriers at the interface between TNTA and Pt occurs, hence, the photogenerated electron can be captured easily [5,28]. The availability of Pt on TNTA not only reduce the recombination the photogenerated electron-hole pairs but also modified Pt-TNTA utilizes visible light effectively [15,28,29]. However, the price of this metal is expensive among others [8], therefore the selection of the appropriate method in depositing Pt on TiO₂ is necessary to get the optimum Pt-depositing amount. Recently, various methods have been reported for the preparation depositing Pt on the TiO₂, including impregnation Pt on TiO₂ nanoparticles (TNP) for hydrogen production [14,15], ion-exchange and incipient wetness Pt on TiO₂ nanotube non-arrays (TNT) for water splitting [29], ion sputtering Pt on TNTA for fuel cell [32], dipping and deposition Pt on TNTA [33], modified photo irradiation-reduction Pt on TNTA for degradation of Rhodamine B [25], hydrogen reduction Pt on TNTA [21], electrodeposition Pt on TNTA for methanol oxidation [34], photo-assisted deposition (Pt on TNP for hydrogen production from methanol solution) [35], Pt on TNT for degradation of methyl orange [28], Pt on TNTA for water splitting [20] and chemical reduction Pt on TNT for hydrogen

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