Synthesis of TiO_2 Nanotube Arrays for Hydrogen Production From Photo-Assisted Water Splitting Reaction

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ABSTRACT

This study focuses on the preparation of Pt sensitized TiO_2 nanoparticles and nanotube arrays and their application in hydrogen generation from photo-assisted water-splitting reaction. For the synthesis of TiO_2 nanotubes arrays an electrochemical anodization in fluorine (F-) based electrolyte was adopted. Further, these TiO_2 nanotubes arrays were sensitized with Pt using hexachloroplatanic acid. The presence of platinum on the surface of TiO_2 nanotubes arrays provided the reductive sites for the hydrogen generation in a photocatalytic cell. The effectiveness of Pt sensitized TiO_2 nanoparticles towards the H_2 generation from photo-assisted water-splitting reaction was compared with Pt sensitized TiO_2 nanotube arrays.

Keywords: Pt/TiO_2 nanoparticles, Pt/TiO_2 nanotube arrays, photocatalysis, H_2 production

1 INTRODUCTION

Hydrogen is one of the cleanest sources of energy with energy density higher than gasoline. At present our global energy requirements are getting fulfilled by fossil fuels. However the rate of consumption of the fossil fuel is very high leading to depletion of fossil fuels. Moreover combustion of fossil fuels leads to the formation of CO_2, which is believed to be one of pollutants responsible for global warming. Hence there arises a need to look for the cleaner and green fuel to meet the present energy demand.

Solar energy is one of the cleanest sources of energy. Many different technologies such as photovoltaic, fuel cell and photochemical water-splitting can be used to harness the solar energy. Solar energy can be used to produce hydrogen through photoassisted water-splitting reaction. It is believed that the photoassisted water-splitting reaction on the semiconductor surface is one of the promising technologies for the hydrogen production [1-3]. Among several semiconductor materials that have been investigated for photocatalytic applications, TiO_2 remains the most promising candidate because of its high photoconverison efficiency, low cost, chemical inertness, and photostablity.

Since the pioneering work of Fujishima and Honda in 1971[4] on the photolysis of water with the use of single crystal TiO_2 rutile wafer, many researchers had reported different nanostructures of TiO_2 [2, 5-7] for the photoassisted water-splitting reaction in photoelectron-chemical cells (PEC) or photocatalytic cells. Photoelectrochemical cell comprises of two electrodes where semiconductor electrode constitute for one of the electrodes, whereas in a photocatalytic cell, the photocatalysts used are in the form of particles or powder suspended in aqueous solution. In particulate system, each particle acts as a micro electrode and both oxidative and reductive half cell reactions occur on the same microelectrode.

With the use of PEC, researchers had reported higher photoconverison efficiency towards hydrogen generation through photoassisted water-splitting reaction. Paulose et al. [8] reported higher photoconverison efficiency of 16.25% using 1D TiO_2 nanotubes arrays in PEC. The 1D nanostructure is promising candidate in photoassisted water-splitting reactions because of their superior electronic properties.

In this paper, we are presenting the photocatalytic effectiveness of TiO_2 nanotubes arrays towards hydrogen generation from photoassisted water-splitting reaction. TiO_2 nanotubes arrays synthesized by electrochemical anodization were decorated with platinum and used as a photocatalyst. In addition photocatalytic effectiveness of Pt/TiO_2 nanoparticles suspension was also studied in presence of methanol as a scavenging agent.

2 EXPERIMENTAL

2.1 Preparation of Pt/TiO_2 nanoparticles

Commercially available TiO_2 nanoparticles (P-25 Degussa) reagent grade were purchased from Sigma Aldrich. The BET surface area of as purchased TiO_2 nanoparticles was 50 m^2/gm with mean particle size of 25 nm. About 2.0 gm of P-25 TiO_2 nanoparticles were dispersed in 0.1M aqueous solution of hexachloroplatanic acid. The dispersion was initially dried at 100 ^oC and annealed at 650 ^oC for 1hr in air.

2.2 Preparation of TiO_2 nanotubes

To synthesize TiO_2 nanotubes, Ti foils of 250 μm were purchased from Alfa Aesar. As purchased Ti foil was ultrasonically cleaned sequentially with acetone,

isopropanol and water for 15 minutes each in order to degrease the Ti foil, which was subsequently dried in air. This degreased Ti foil was then placed in an electrochemical cell comprised of platinum gauze (counter electrode). The electrochemical anodization experiments were performed using organic electrolyte. The electrolyte comprised of ethylene glycol containing 0.3 wt % NH_4F and 2 wt % water. Electrochemical anodization was performed at ambient conditions at anodization potential of 45 V for anodization time of 15 hr. The as-anodized TiO_2 nanotubes arrays were detached from Ti foil in methanol.

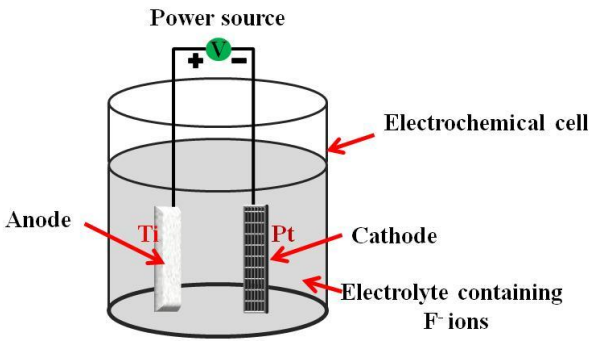

Figure 1: Electrochemical anodization setup for the synthesis of TiO_2 nanotubes arrays from Ti foil.

2.3 Deposition of co-catalysts on the surface of TiO_2 nanotubes arrays

The as-anodized TiO_2 nanotubes arrays obtained through electrochemical anodization were sensitized with 0.1 M dilute aqueous solution of hexachloroplatanic acid and sonicated for 5 minutes and finally annealed in argon environment containing 10 vol % H_2 at 400 ^oC for 1hr.

2.4 Photocatalytic experimental setup

The photocatalytic reactions using TiO_2 nanostructures (nanoparticles and nanotube arrays) were performed in a quartz cell. The solar simulator (λ = 180 to 2400 nm) equipped with 500 W high pressure Xe lamp (Newport Oriel) was used. In order to get actual solar spectrum, the solar simulator was additionally equipped with air mass 1.5 global (AM = 1.5 G) and infra red (IR) cut off filter supplied by Andover Corp., which allowed a light with wavelength of 220 to 400 nm. The power density was maintained at 21.96 $W.cm^{-2}$ with the help of power density meter supplied by Thor Labs.

Accurately weighed 3.1 mg of P-25 TiO_2 nanoparticles sensitized with platinum were dispersed in 4.0 ml of water containing 10 vol % or 20 vol % CH_3OH. The colloidal dispersion was degassed with Ar for 30 min to remove O_2 and irradiated with the light of wavelength ranging from 220 nm to 400 nm for 6 hr with different power densities. Two different power density 100 mW/cm^2 and 21.9 mW/cm^2 (AM 1.5 G) were used to irradiate the suspension of TiO_2 nanoparticles.

TiO_2 nanotubes arrays sensitized with Pt was placed in a quartz cell (7 ml capacity) containing water mixed with 10 vol% CH_3OH and irradiated with light of wavelength 220 nm to 400 nm for 6 hr. The gas samples from the head space (approx 3 ml) of the quartz cell were withdrawn periodically at 1 hr interval using a gas syringe (100 µl) and analyzed using chrompak capillary column on gas chromatograph (HP 6890) equipped with TCD.

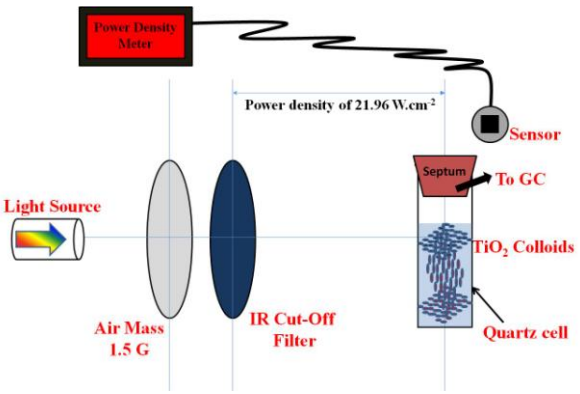

Figure 2: Schematic of the experimental setup used to investigate the photocatalytic performance of Pt/TiO_2 colloidal suspension and single sided Pt/TiO_2 nanotubes arrays for hydrogen generation from aqueous solution containing 10 vol % CH_3OH.

3 RESULTS AND DISCUSSION

3.1 Synthesis of TiO_2 nanotubes arrays

As anodized Ti foil was examined using scanning electron microscopy (SEM) and the SEM image obtained for open end and closed end of as-anodized TiO_2 nanotubes arrays are shown in Figures 3A and 3B respectively. The SEM images of as-anodized TiO_2 nanotubes arrays further indicate that the average pore size (inner diameter) of the as-anodized TiO_2 nanotubes arrays is 145 nm and average outer diameter is 165 nm. It was also observed that the TiO_2 nanotubes obtained after 15 hrs of electrochemical anodization of Ti foil produced nanotubes of 120 µm in length.

3.2 Hydrogen generation using Pt/TiO_2 nanoparticles

Pt/TiO_2 nanoparticles were suspended in de-ionized water and exposed to UV radiation. However, no hydrogen was observed even after 10 hrs of irradiation. It is believed that the rapid recombination of photogenerated excitions and also the backward reaction of photogenerated hydrogen and oxygen on the surface of platinum might have prevented formation of H_2. The backward reaction however can be suppressed by the addition of sacrificial or scavenging

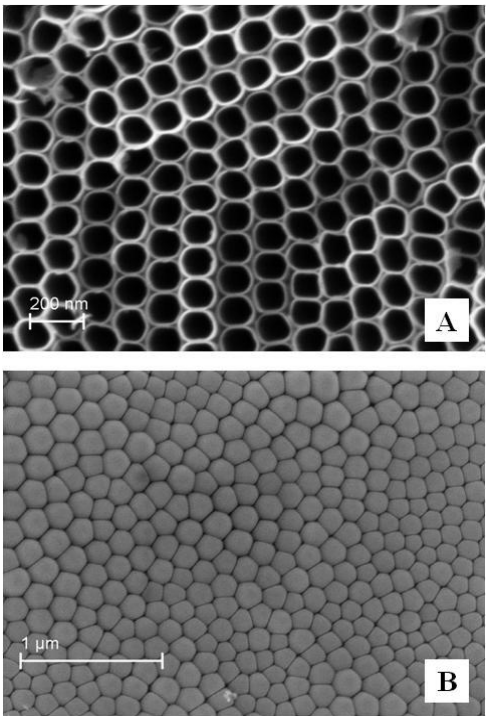

Figure 3: SEM images for as-anodized TiO_2 nanotubes arrays displaying A) open end and B) closed end.

agents. Several investigators have reported the use of EDTA and methanol [5, 9-11] as oxygen scavenger.

In this study methanol was used as a scavenger during photoassisted water-splitting reaction for hydrogen generation. Pt/TiO_2 nanoparticles were dispersed in an aqueous solution containing 10 vol % or 20 vol % CH_3OH and exposed to light with a wavelength of 200 - 400 nm. While the reaction was in progress, gas samples were withdrawn and analyzed using gas chromatography. The hydrogen generation results are presented in Figure 4. It can be observed that the volume of hydrogen generated for 20 vol% CH_3OH aqueous suspension of Pt/TiO_2 nanoparticles is slightly higher than that in case of 10 vol % CH_3OH aqueous suspension containing Pt/TiO_2 nanoparticles.

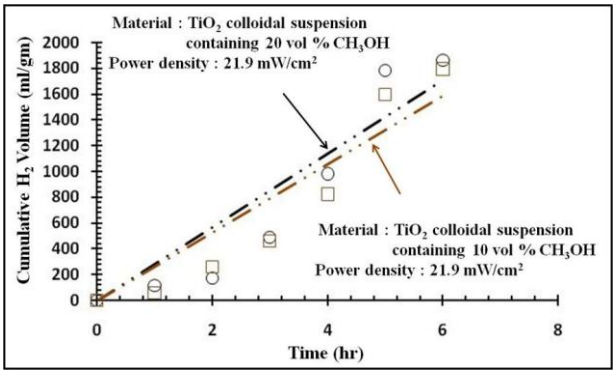

Figure 4: Comparison of photocatalytic H_2 generation using Pt/TiO_2 nanoparticles from water containing 10 vol % and 20 vol % CH_3OH at 21.9 mW/cm^2.

3.3 Hydrogen generation using Pt/TiO_2 nanotubes arrays

Single sided TiO_2 nanotubes arrays were decorated with platinum and used as a photocatalytic semiconductor material for the hydrogen generation from water splitting reaction. In the experiment performed Pt/TiO_2 nanotubes arrays with and without nanograss (120 µm long) were placed in the water containing 10 vol % CH_3OH and irradiated with simulated solar irradiation at a power density of 21.9 mW/cm^2. The area of the TiO_2 nanotube arrays sample exposed to irradiation was approximately 1 cm^2.

It can be observed that the hydrogen generation profile presented in Figure 5, the hydrogen volume generated after 1 hr of irradiation using TiO_2 nanotubes was 14 ml/m^2. It can also be observed that the hydrogen volume increased gradually to 375 ml/m^2 after 6 hr of water splitting reaction.

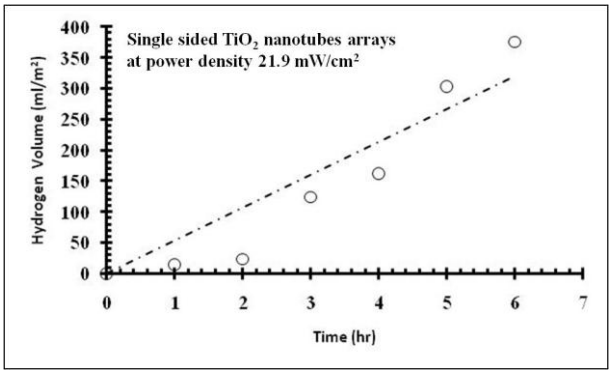

Figure 5: Photocatalytic H_2 generation from self standing platinized TiO_2 nanotubes arrays in water containing 10 vol% CH_3OH.

In general the outcome of photocatalytic reactions is influenced by the surface irradiation. As UV being high energy wave, it gets absorbed on the skin depth of the material up to 300 nm to 400 nm and the remainder of the photocatalytic material does not take part in the reaction due to no accessibility of photons. In the case of suspension of TiO_2 nanoparticles, the entire suspension is believed to be exposed to photons, however in the case of TiO_2 nanotubes arrays, only the irradiated surface translated into photocatalytic activity. It is reasonable to mention that the actual mass of TiO_2 nanotubes arrays taking part in the photocatalytic activity is thus significantly lower as compared to TiO_2 nanoparticles suspension.

4 CONCLUSIONS

The photocatalytic effectiveness of two different nanostructures of TiO_2 was studied in aqueous solution of methanol. TiO_2 nanotubes were electrochemically grown using Ti foil and were used as photocatalyst. TiO_2 nanotubes appeared to be more promising nanostructure for the photocatalytic applications as compared to their particulate

counterparts. After 6 hr of UV irradiation, Pt/TiO_2 nanoparticles generated H_2 of 1795 ml/gm and 1861 ml/gm using 10 vol % and 20 vol % CH_3OH aqueous solution, respectively under the radiation of 21.9 mW/cm^2.

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