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Formation of hybrid WO₃-TiO₂ nanotube and its application to conserve the environment

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A B S T R A C T

Hydrogen could be a significant fuel of the future replacing fossil fuel, which causing a major treat to social and environmental problems, such as carbon emissions, energy security and local air pollution. However, our future will certainly not be based on a simple replacement of fossil fuels by hydrogen but making it available at cheaper cost for everyone to utilize it. This is possible if we could generate hydrogen on renewable basis using water splitting technology. The development of hybrid transition oxide (WO₃-TiO₂) nanotubes (HTON) that capable of producing hydrogen gases in a cleaner, more efficient and cost-effective way by using two natural resources (sunlight and water). HTON has a stable, high chemical and thermal stability, active at room temperature as well as have extended their light absorption spectrum towards visible region, which is responsive to both ultraviolet and visible illumination. The HTON could be served as an efficient photo-induced electrons acceptor to facile better charge carrier separation in splitting water. In conclusion, HTON catalyst is the cornerstones for sustainable energy economy to conserve the environment because it could generate hydrogen efficiently and inexpensively for humankind.

Introduction

Today, newspapers, magazines, and other media often announce reports about the issue related to the pollution and depletion of the state-of-the-art commercial energy such as fossil fuel (e.g., oil, natural gas, coal, petroleum) (Turner, 1999; Ohi, 2005). Recently, public concern about the environment, climate change and limited fossil fuel resources have given rise to the urgent need of fostering development in the area of renewable energies which are

inexhaustible as well as non-polluting (Turner, 1999; Jefferson, 2006; Kreuter and Hofmann, 1998). One of the most likely prospects for an efficient renewable resource is to produce hydrogen gas from water using sunlight (Fujishima and Honda, 1972; Grätzel, 2001). To date, hydrogen gas has been established as a potential future energy carrier and possibly the best substitute for fossil fuel to secure the future supply of a clean and sustainable energy (Grätzel, 2001;

Kitano *et al.*, 2007; Mishra *et al.*, 2003). In order to bring hydrogen to the point of commercial readiness and viability in terms of high efficiency and cost effective, continuous research on the development of PEC with n-type semiconductor for decomposition of water using solar energy is still needed (Leung *et al.*, 2010; Kubacka *et al.*, 2012; Lai and Sreekantan, 2013c). In this manner, photoelectrochemical (PEC) water splitting process is initiated by the direct absorption of a photon from the illumination, which creates separated electrons and holes in the energy band gap of the material (Grätzel, 2001). The photo-induced holes perform work at the TiO₂-electrolyte interface oxidizing water molecules to create oxygen and hydrogen ions. Due to the electric field, the photo-induced electrons will move through the circuit to the platinum electrode (counter electrode) where they reduce hydrogen ions and creating hydrogen molecules (Ni *et al.*, 2007).

Today, in the field of photocatalysis, there are various oxides (WO₃, TiO₂, ZnO, etc) and non-oxide semiconductors (Si, InP, CdTe, GaAs, etc.) which have been tested with the aim of developing stable high efficiency material for this process (Nah *et al.*, 2010). Among these materials, n-type TiO₂ offers great promise because it has great capacity for oxidation, able to absorb light, corrosive resistant and perfectly suitable as a photoanode for PEC water splitting (Kitano *et al.*, 2007– Roy *et al.*, 2011). However, the unmodified TiO₂ photoanode is still far from becoming a practical semiconductor for PEC water splitting cell (Nah *et al.*, 2010; Lai and Sreekantan, 2013e; Zhang *et al.*, 2010). Despite its cost, making high efficient PEC water splitting cell using unmodified TiO₂ is a challenge unless two main issues are addressed. The achievement of high-

efficiency requires a suitable architecture that minimizes the recombination of the electron-hole pairs by separating them quickly. The second issue involves the larger band gap of unmodified TiO₂ (3.0-3.2eV) compared to other oxides mentioned above. This means that only about 5% of the sunlight can be absorbed by TiO₂ and converted into useful chemical and electrical energy (Kitano *et al.*, 2007; Mishra *et al.*, 2003; Kubacka *et al.*, 2012; Lai and Sreekantan, 2013c; Nah *et al.*, 2010; Lai and Sreekantan, 2013e). It is a well-known fact that about 40–45% of the solar energy incident on the earth's surface falls in the visible region ($400 < \lambda < 800$ nm), the efficient use of visible light is essential for generating hydrogen gas through PEC water splitting process (Ni *et al.*, 2007; Nah *et al.*, 2010). To date, no known semiconductor has been discovered that simultaneously meets all the criteria required for economical hydrogen production (Nah *et al.*, 2010, Lai and Sreekantan, 2013e). Therefore, the properties of unmodified TiO₂ are yet to be perfected and further investigated.

In fact, unmodified TiO₂ can be further improved by engineering the architecture through synthesising process by producing the nanotubes structures for optimal architecture of photoelectrode (Mishra *et al.*, 2003; Nah *et al.*, 2010; Lai and Sreekantan, 2013; Roy *et al.*, 2011; Paulose *et al.*, 2006; Mohapatra *et al.*, 2007). The reason attributed to the high quantum efficiency of these nano-scale tubes like structure under solar illumination. However, it is apparent that the remaining challenge is to tune their band gap energy of unmodified TiO₂ for higher efficiency in photons absorption from solar energy and enhance the lifetime of charge carriers (Nah *et al.*, 2010; Zhang *et al.*, 2010). To resolve the above listed problems of the unmodified TiO₂, continuous efforts have been conducted by

coupling a narrow band-gap semiconductor with TiO₂. In this case, the narrow band-gap semiconductor must fulfill several basic requirements for better charge separation efficiency, such as the conduction band of narrow band-gap semiconductor should be more positive than that of the TiO₂, responsive to visible light and photo-corrosion free condition (Navarro Yerga *et al.*, 2009). In the present study, WO₃ was selected as a suitable semiconductor to be coupled with TiO₂ nanotubes due to suitable band edge position relative to TiO₂, strong reversible field-aided ion intercalation, and exhibit higher surface acidity to absorb more ionic species on the surface of TiO₂ (Lai and Sreekantan, 2013c; Lai and Sreekantan, 2013e; Nah *et al.*, 2008; Song *et al.*, 2011). In this manner, conduction band electrons from TiO₂ can be injected to the WO₃ due to the internal electrostatic field from the interpretation of inter-band state. Besides, WO₃ offers relatively small band gap energy (2.5 eV to 2.8 eV) and exhibit strong absorption within solar spectrum (Song *et al.*, 2011; Abe *et al.*, 2011). Another important reason for using hybrid WO₃-TiO₂ as photoelectrode in PEC water splitting system is because of long term inertness to chemical environment and resilience to photocorrosion over a wide pH range in aqueous solution under evolving oxygen conditions (Nah *et al.*, 2008; Song *et al.*, 2011; Abe *et al.*, 2011; Lai and Sreekantan, 2013b). Herein, the WO₃ coupled with TiO₂ nanotubes was defined as hybrid transition oxide nanotubes (HTON). The novelty of this work is to obtain an efficient and desired HTON photoanode, resulting in best PEC water splitting performance under solar illumination.

Materials and Methods

Ti foils (99.6% in purity) were cut into desired dimension (50 mm x 10 mm) and

then placed in ethylene glycol electrolyte with 5 wt% ammonium fluoride (NH₄F) and 5 wt% hydrogen peroxide (H₂O₂) for 1 hour at 60 V. Anodization was performed in a two-electrode configuration bath with Ti foil as the anode and a platinum rod as the cathode. Then, the resultant unmodified TiO₂ nanotubes were loaded with WO₃ species using RF sputtering machine Penta Vacuum. Prior to sputtering treatment, the vacuum chamber was maintained at lower than 1×10^{-5} Torr while the pressure was kept at 10^{-3} Torr. The sputtering was carried out in argon atmosphere with the flow rate of 50 sccm. A high frequency generator was used to generate electromagnetic power in the MHz region (13.56 MHz). The discharges were generated at 150 W and the duration of sputtering was fixed at 30 seconds. After the sputtering process, the HTON sample was thermal annealed at 400 °C in argon atmosphere for 4 hours. Based on our preliminary studies, higher aspect ratio of nanotubular structure could be produced when they are maintained around this value (Lai and Sreekantan, 2013e; Lai and Sreekantan, 2012a). Thus, the direct comparison between the unmodified TiO₂ nanotubes and HTON sample was conducted in this study.

The surface and cross-sectional morphologies of the samples were observed via field emission scanning electron microscopy (FESEM) using a Zeiss SUPRA 35VP. The elemental analysis was determined using energy dispersion X-ray (EDX) equipped in the FESEM. The phase determination of the anodic layer was determined by X-ray diffraction (XRD) using a Philips PW 1729 operated at 45 kV and 40 mV. The electrochemical properties of the samples were characterized using a three-electrode PEC cell with anodic samples as the working photoelectrode, a platinum rod as the counter electrode, and a

saturated calomel electrode (SCE) as the reference electrode. All of the three electrodes were connected to a potentiostat (μ Autolab III), and the current and voltage were measured. A 150 W xenon lamp (Zolix LSP-X150) with an intensity of 800 W/m^2 was transmitted by a quartz glass as the xenon lamp shone on the working photoelectrode. The xenon lamp was switched on after the three electrodes were connected to the potentiostat. A linear sweep potential (LSP) was swept from -1.0 V to 1.0 V at a scan rate of 5 mV/s , and the corresponding photocurrent was measured. The photocurrent density (j_p) applied was plotted versus the potential (V). The evolved hydrogen gas was collected using a reverted burette.

Result and Discussion

In the present study, unmodified TiO_2 nanotubes before loading with WO_3 species are illustrated in Figure 1 (a). It can be noticed that the tubes have an average diameter of 120 nm and length of $10 \mu\text{m}$. This resultant unmodified TiO_2 nanotube was duplicated, and the following experiment was carried out by applying an ion implantation sputtering system for producing the HTON sample as shown in Figure 1 (b). Interestingly, HTON sample has almost similar appearance to that of unmodified TiO_2 nanotubes with clear opening pores without any WO_3 precipitation layers. This result manifested that the small W^{6+} ions might diffuse into the TiO_2 lattice, which introduced lattice substitution with sufficient incident kinetic energy and without any damage to the nanotube structure (Lai and Sreekantan, 2012b). Next, EDX analysis was conducted to determine the average atomic percentage (at%) for unmodified TiO_2 nanotubes and HTON sample. The average elemental compositions for both samples based on the

EDX spectra are summarized in Table 1. The peak of Ti, O, W, and C elements were detected from the EDX spectra (not shown), which indicate that the existence of the Ti, O, C and W elements in the HTON sample. It was noteworthy to mention that the composition of W element ($0.92 \text{ at}\%$) was identified from the HTON sample. Meanwhile, the carbon element was believed came from the organic ethylene glycol electrolyte, which was oxidized to carbonate type species and then these species were further reduced to carbon during heat treatment stage (Allam *et al.*, 2008; Lai and Sreekantan, 2013d). Thus, the presence of the carbon species was found within both samples.

In the present study, XRD measurements were conducted to determine the crystallinity of the unmodified TiO_2 nanotubes and HTON sample. The results are presented in Figure 2. Based on our previous study, heat treatment of $400 \text{ }^\circ\text{C}$ was sufficient to convert amorphous to anatase phase of TiO_2 , which exhibited thermodynamically stable and higher surface stability (Lai and Sreekantan, 2012a; Lai and Sreekantan, 2013a). It was found that the presence of anatase phase was detected in both samples subjected to annealing at $400 \text{ }^\circ\text{C}$ in argon atmosphere. It can be seen that the diffraction peaks of the entire samples are ascribed to the TiO_2 with anatase phase [JCPDS No 21-1272]. The diffraction peaks allocated at 25.37° , 38.67° , and 48.21° are corresponding to (101), (112), and (200), crystal planes for the anatase phase, respectively. It could be noticed that HTON sample hindered the crystallization of TiO_2 significantly. The intensity of the (101) peak at 38.67° decreased after loading with WO_3 species, which indicating the reduced crystallinity of the anatase phase. It is worth noting that no obvious WO_3 phases were observed in the

XRD patterns for the lower content of W (< 1 at% based on EDX analysis). This finding may be attributed to the insufficient sensitivity of the XRD measurements to disclose the small amount of WO₃ phase within the TiO₂ nanotubes (Sajjad *et al.*, 2009).

A scanning potentiostat was used to measure j_p under an applied potential. j_p -V characteristic curves for unmodified TiO₂ nanotubes and HTON sample is plotted in Figure 3. Both samples exhibited non-significant j_p of less than 10 $\mu\text{A}/\text{cm}^2$ under light-off condition. However, the j_p increased under solar illumination. A maximum j_p of 2.0 mA/cm^2 was observed for the HTON sample, which is relatively high compared to the unmodified TiO₂ nanotubes (1.2 mA/cm^2). These results are in line with literatures, which suggested that the presence of optimum WO₃ content (~1 at%) into the lattice of TiO₂ could be acted as photo-induced electron acceptor to enhance the transportation of charge carriers (Nah *et al.*, 2008; Song *et al.*, 2011; Abe *et al.*, 2011; Lai and Sreekantan, 2013b; He *et al.*, 2011). It is a well-known fact that WO₃ states are reported to lie within the band gap of TiO₂ (about 0.2 - 0.8 eV below the conduction band of TiO₂). Therefore, the interpretation of inter-band states (mismatch of the band energies of TiO₂-and WO₃) will act as mediators for trapping photo-induced electrons under solar illumination (Lai and Sreekantan, 2013c; Sajjad *et al.*, 2009; He *et al.*, 2011; Higashimoto *et al.*, 2006). In contrast, photo-induced electrons in the conduction band of the pure TiO₂ nanotubes were rapidly trapped for the recombination with holes.

Next, the evolution rate of hydrogen gas generated from water splitting was measured. Figure 4 shows the hydrogen evolution as a function of time. It was found that H₂ generation rate increased linearly with the exposure time. A maximum hydrogen evolution rate of 14.5 mL/cm^2 was achieved from the HTON sample, which is relatively high compared to unmodified TiO₂ nanotubes (7.5 mL/cm^2). This reveals that the HTON sample exhibited better charge carrier transfer properties, and thus generating more hydrogen gas at counter electrode of platinum (Lai and Sreekantan, 2012c; Lai and Sreekantan, 2013b; Lai and Sreekantan, 2012a; Maeda *et al.*, 2010).

Conclusion

The present work clearly to show a strongly beneficial effect of the WO₃ species existed in HTON sample in improving water splitting performance than that of the unmodified TiO₂ nanotubes. An optimum content of W element (~1 at%) into the lattice of TiO₂ nanotubes demonstrated a maximum j_p -V characteristic of 2.0 mA/cm^2 with hydrogen gas evolution rate of 14.5 mL/cm^2 under solar illumination. This is ascribed to an effective separation of charge carriers and greatly reduces the recombination losses within the HTON sample. Such mechanistic understanding and findings is very important for improving the hydrogen generation via water splitting process, which may be used to realize the pollution-free hydrogen economy in our future.

Table.1 Average at% of unmodified TiO₂ nanotubes and HTON sample obtained by EDX analysis

Sample	Ti (at%)	O (at%)	W (at%)	C (at%)
Unmodified TiO ₂ sample	35.03	56.95	-	08.02
HTON sample	36.91	57.05	00.92	05.12

Figure.1 FESEM images of (a) unmodified TiO₂ nanotubes, and (b) HTON sample. Insets show the cross-section morphology of oxides

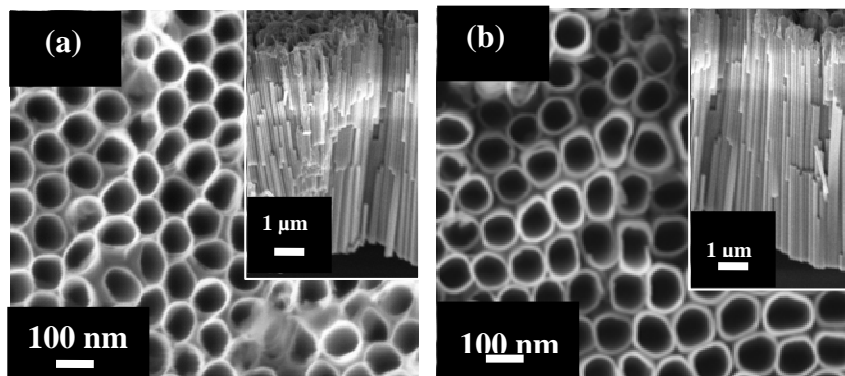


Figure.2 XRD patterns of (a) unmodified TiO₂ nanotubes, and (b) HTON sample annealed at 400 °C under argon atmosphere [A=Anatase; T=Titium]

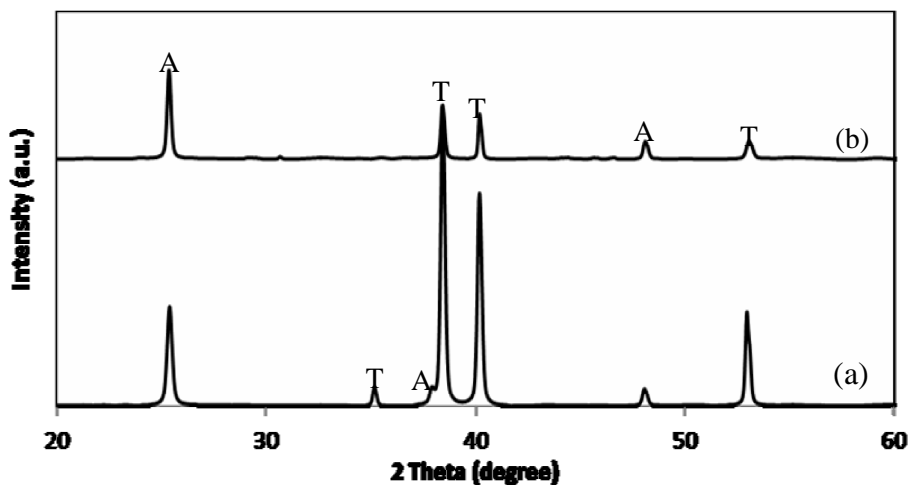


Figure.3 The j_p-V characteristic curves of (a) unmodified TiO₂ nanotubes, and (b) HTON sample under solar irradiation

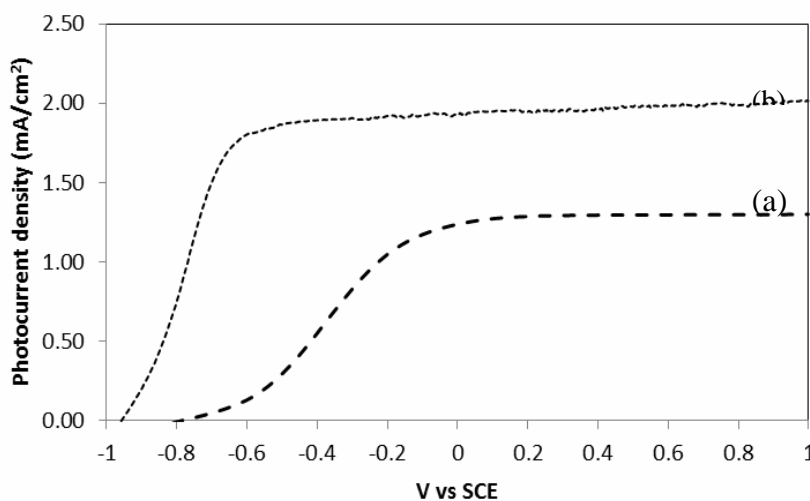
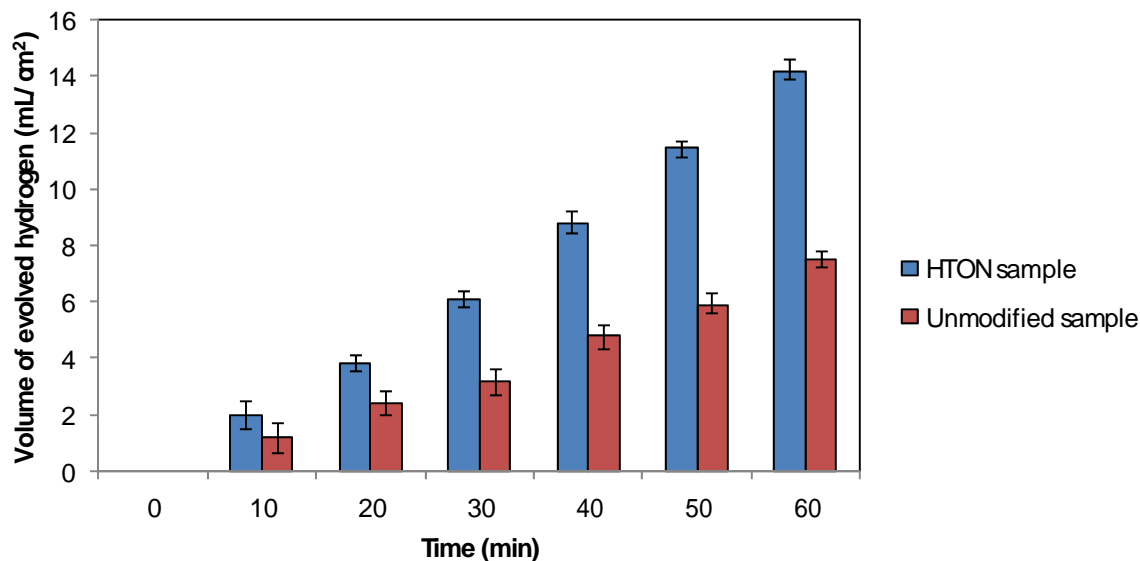


Figure.4 Hydrogen evolution of (a) unmodified TiO₂ nanotubes, and (b) HTON sample under solar irradiation



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