Production of Renewable Solar Hydrogen using Nanotubular Semiconductor Heterostructures by Water Photoelectrolysis

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ABSTRACT

Currently, there is a great interest in developing clean-fuel powered automobiles based on hydrogen. About 150 million tons of hydrogen per year would be needed if all the vehicles in the United States run with hydrogen. This presentation focuses on the development of an efficient photoelectrolytic cell using band gap modified TiO_2 nanotubes as the photo anode and TiO_2 nanotubes loaded with Pt nano-particles as the cathode to generate a high volume of hydrogen by the photoelectrochemical method. The cell gives a photo-current density of 6 mA/cm^2, has an efficiency of ~5% (solar-to-hydrogen), is stable (six months) and the technology can be transformed into large scale hydrogen generation. Synthesis of a composite photoanode comprised of CdS nanoparticles and 1D TiO_2 nanotubes has also been discussed that give an enhanced photo-current density of 8.2 mA/cm^2.

Keywords**:** nanotubes, TiO_2, photoelectrochemical, hydrogen, CdS.

1 INTRODUCTION

Production of hydrogen by water splitting using sunlight by photoelectrochemical method is one of the most promising methods since the process is renewable and environmentally benign [1-2]. In 1999, Zwilling et al. [3] successfully demonstrated TiO_2 nanotube formation on an anodized Ti surface. These self-organized, one dimensional TiO_2 nanotubes prepared by anodization can transport the charges more efficiently than the randomly oriented nanoparticles or nanotubes prepared by the sol-gel process [4-5]. The enhanced electronic properties of the self-ordered nanotubes make them a versatile catalyst for photoelectrolysis of water [6-7]. These titania nanotubes are widely used as gas sensors, radiation sensors, in biomedical implants, hydrogen storage medium, and templates to grow one dimensional nanomaterials [8]. TiO_2 is a high band gap (~3.2 eV) semiconductor material. Therefore only 4–5% of the solar spectrum (UV portion) is harvested by the TiO_2. Thus, band gap modification of TiO_2 nanotubes is necessary so that a larger portion of the sunlight spectrum can be harvested in a more efficient way. The reduction of the band gap can be achieved by doping with foreign elements, such as N, P, C, and transition metals. In this presentation we describe synthesis of double side anodized material with $TiO_2/Ti/TiO_2$ configuration that is used as both photoanode (carbon incorporated titania nanotubes) and cathode (Pt nanoparticles dispersed on TiO_2 nanotubes; $PtTiO_2/Ti/TiO_2Pt$). These electrodes are arranged in a specially designed photoelectrochemical cell to generate hydrogen by water splitting at a rate of 38 mL/h under solar illumination [9]. When narrow band gap semiconductors are combined with TiO_2 as sensitizers, more of the visible part of the solar spectrum can be harvested. CdS forms well matched heterojuncntion photocatalysts with TiO_2 [10-12]. Synthesis of a composite photoanode comprised of CdS (for visible light absorption) and carbon-doped TiO_2 (UV light absorption) results in a better photocatalyst (~7% solar to hydrogen efficiency) compared to the TiO_2 nanotubes alone (4.25% solar to hydrogen efficiency).

2 EXPERIMENTAL

2.1 Preparation of Photoanode Covering TiO_2 Nanotubes on Both the Sides of Titanium ($TiO_2/Ti/TiO_2$)

Nanotubular TiO_2 arrays on both the sides of titanium substrate are prepared by modifying the earlier reported anodization methods [13-15]. Ti foils (ESPI) are cut into the required size and shape, cleaned in acetone, dried, and then anodization is carried out using ultrasonic waves (100 W, 42 KHz, Branson 2510R-MT) by immersing a part of the titanium foil (16 cm^2) in the electrolytic solution (1000 mL). Water (10 wt%), ammonium fluoride (NH_4F, 0.5 wt%, Fischer) and ethylene glycol (Fischer) are mixed together thoroughly and used as the electrolytic solution. The titanium foil acts as the anode. Two platinum meshes kept on both sides of the titanium foil at equal distances serve as the cathode. The anodization of titanium is carried out by applying 20 V for 60 min using a rectifier (Agilent, E3640A) under ultrasonic conditions. The anodization current is monitored continuously using a digital multimeter (METEX, MXD 4660A). The as-anodized samples after anodization are washed with distilled water to remove the occluded ions, dried in an air oven, then annealed under a reduced atmosphere (10% H_2 in argon) at 500 ^oC (1 ^oC/ min) for 2 h using a tubular furnace for crystallization. For synthesizing the cathode template ($TiO_2/Ti/TiO_2$) TiO_2 nanotubular arrays are prepared by the sonoelectrochemical anodization (30 min) method using an aqueous solution of 0.5M phosphoric acid (H_3PO_4, Sigma-Aldrich) and 0.14M sodium fluoride (NaF, Fischer) solution. The nanotubes are then kept for activation in an air oven at 130 ^oC for 12 h. A dilute solution of chloroplatinic acid (H_2PtCl_6, 8 wt % in water; Sigma-Aldrich) is prepared and the template is immersed into it. The acid solution and the TiO_2 template are ultrasonicated for 1-2 minutes, and then dried under vacuum for 12 h. The reduction of the platinum salt into Pt(0) on the TiO_2 nanotubular surface is done in a tubular furnace at 500 ^oC for 2 h under a reduced (10% H_2 in argon) atmosphere.

2.2 Synthesis of TiO_2 Nanotubes and CdS-TiO_2/TiO_2 Nanocomposites

TiO_2 nanotubes are synthesized by anodizing Ti foil in ethylene glycol (Fischer) and ammonium fluoride (Fischer). The CdS nanoparticles are dispersed in the $TiCl_4$ solution and this solution is applied onto pre-activated as-anodized TiO_2 nanotubes/Ti sample, dried under ambient conditions and annealed under N_2 atmosphere to form a thin layer of CdS-TiO_2 composite on TiO_2 nanotube arrays. In this process CdS is coated with a thin layer of TiO_2 forming a core-shell configuration. The CdS core-TiO_2 shell nanoparticles are uniformly loaded onto the TiO_2 nanotubes forming a composite photoanode.

2.3 Characterization

A field emission scanning electron microscope (FESEM, Hitachi S-4700) is used to analyze the morphology and distribution of the double-sided titania nanotubes and the CdS-TiO_2/TiO_2 composites. High resolution transmission electron microscopic studies (HRTEM, JEOL 2100F and Phillips CM 300) are carried out at 200 kV. A scanning transmission electron microscopy (STEM) equipped with ESVision software is used for mapping and crystal distribution of the samples. Fast Fourier transformations (FFT) are measured to find the crystal phases. X-ray photoelectron spectroscopy (XPS, Surface Science Instruments) is used to analyze Pt nanoparticles on the TiO_2 nanotubular surface. It uses a focused monochromatic Al Kalpha X-ray source and a hemispherical sector analyzer operated in fixed analyzer transmission mode. Surveys are run with a pass energy of 25 eV and the take-off angle is 35º. Diffuse reflectance ultraviolet and visible (DRUV – vis) spectra of the samples are measured from the optical absorption spectra using a UV-vis spectrophotometer (UV-2401 PC, Shimadzu). Energy dispersive X-ray spectroscopy (EDS) analysis is obtained using an Oxford detector.

2.4 Photoelectrolysis of Water

H_2 generation by photoelectrolysis of water is carried out in a specially designed quartz cell (Figure 1 – shown only for double-sided TiO_2 nanotubes). The cathodic compartment is separated from the rest of the cell by a fine porous glass frit. The reference electrode (Ag/AgCl) is placed closer to the anode using a salt bridge (saturated KCl) Luggin probe capillary. The cell is provided with a 60 mm diameter quartz window for light incidence. The electrolyte used is 5 vol.% ethylene glycol in 1M KOH. A computer-controlled potentiostat (SI 1286, England) is employed to control the potential, and to record the photocurrent generated. Two solar simulators (300 W, 69911, Newport-Oriel Instruments, USA) are used for illumination of light on both sides of the carbon doped $TiO_2/Ti/TiO_2$ photoanode. An AM 1.5 filter is used to get a sun intensity. The $PtTiO_2/Ti/PtTiO_2$ electrode is used as the cathode. The samples are anodically polarized at a scan rate of 5 mV/s under illumination and the photocurrent is recorded.

For the CdS-TiO_2/TiO_2 composites photoelectrolysis of water is carried out in a glass cell with photoanode (nanotubular CdS-TiO_2/TiO2 specimen) and cathode (Platinum foil) compartments. The electrolyte used is an aqueous solution of 0.35M Na_2SO_3 and 0.24M Na_2S.

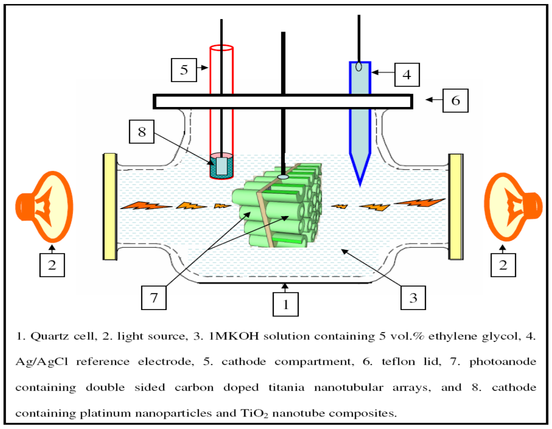

Figure 1: A schematic of the photoelectrochemical cell to generate hydrogen by water splitting using double side illuminated titania nanotube arrays.

3 RESULTS AND DISCUSSION

3.1 Characterization of Photoanode ($TiO_2/Ti/TiO_2$) and Cathode

Figure 2 shows the FESEM image of TiO_2 nanotubular arrays prepared using the sonoelectrochemical anodization method on both of the sides of the titanium foil. The average pore diameter of these nanotubes is found to be ~ 60 nm, and the tube length ~1.2 μ. The wall thickness of the titania nanotubes is found to be in the range of 15-20 nm. It is also observed that the TiO_2 nanotubes are one dimensional in nature and are vertically oriented. The titania nanotubes are covered uniformly on both of the sides of the titanium foil. TEM, STEM and FFT measurements of the annealed TiO_2 nanotubes show crystalline anatase TiO_2 (Figure 2, insets). The highly-ordered titania nanotubes remain intact during scale up of the photoanode (0.7 cm^2 to 16 cm^2 size).

XPS analysis (Figure 3) shows the presence of Ti, O and Pt in the Pt/TiO2 sample. Some common impurities like carbon and nitrogen are also detected. The expanded form of the XPS profile on Pt 4f (Figure 3, inset) shows two peaks at 70.9 and 74.3 eV, corresponding to Pt 4f7/2 and Pt 4f5/2, respectively. These peaks confirm the presence of metallic Pt on the TiO_2 nanotubular surface.

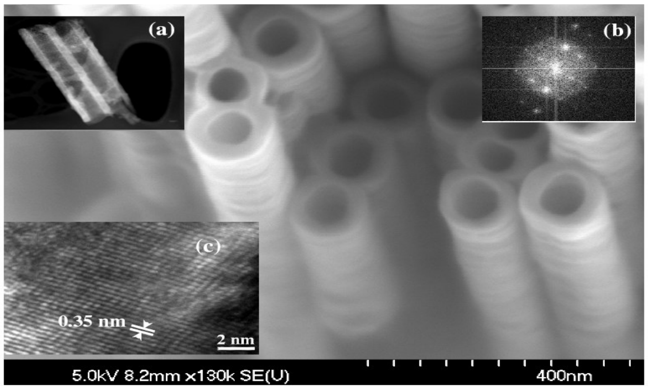

Figure 2: FESEM image showing the self-organized titania nanotube arrays prepared by sonoelectrochemical anodization method using an aqueous solution of ethylene glycol and ammonium fluoride at 20V for 60 min. Inset (a) STEM image of the titania nanotubes, (b) FFT pattern and (c) HRTEM image of a wall of the titania nanotube. This shows the multi-walled nature of the titania nanotubes with anatase crystal structure (lattice spacing of 0.35 nm).

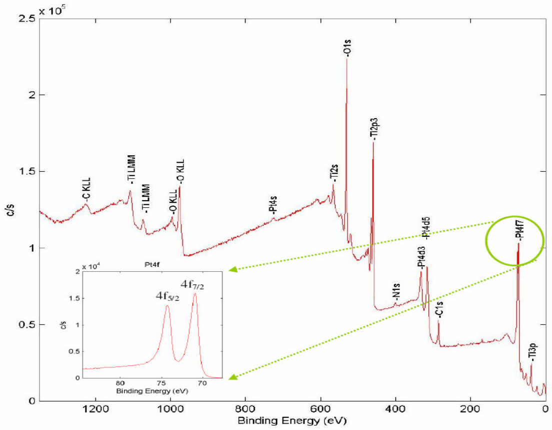

Figure 3: XPS spectrum of Pt/TiO_2 composite material showing the major peaks for Pt, Ti and O. Inset shows the XPS of Pt 4f, which confirms the formation of metallic Pt(0) nanoparticles on TiO_2 nanotubes.

3.2 Photoelectrochemical Generation of Hydrogen

The carbon doped $TiO_2/Ti/TiO_2$ photoanode and $PtTiO_2/Ti/PtTiO_2$ cathode are tested for photoelectrolysis of water in the quartz cell (Figure 1) containing 5% ethylene glycol in 1M KOH solution. Figure 4 shows the photo current generation as a function of applied potential. A photocurrent of 48 mA (6 mA/cm^2 at 0.2 VAg/AgCl) is obtained when light is illuminated on a single side of the photoanode. The photocurrent is increased to 96mA (equivalent to 38 mL/h H_2 generation) when light is illuminated on both sides of the photoanode. A potentiostatic measurement is also carried out by applying an external bias of –0.1VAg/AgCl to confirm that the photocurrent obtained from the PEC cell is due to the photocatalytic activity of the titania nanotubes (Figure 5). The photocurrent is reduced to almost half when one light source is switched off and there is no photocurrent obtained when both the light sources are turned off.

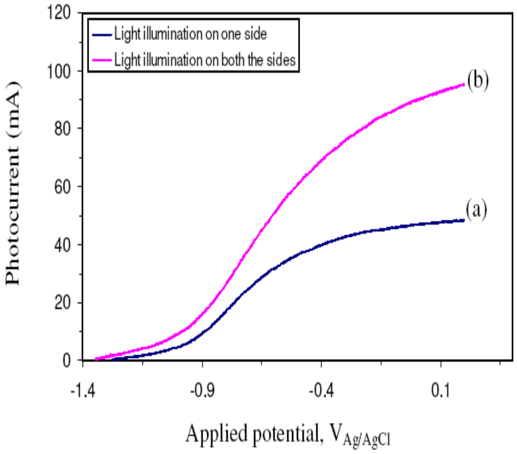

Figure 4: Photocurrent density as a function of potential of a single side (a) and double side (b) illuminated carbon doped titania nanotubular photoanode ($TiO_2/Ti/TiO_2$). $PtTiO_2/Ti/PtTiO_2$ serves as the cathode.

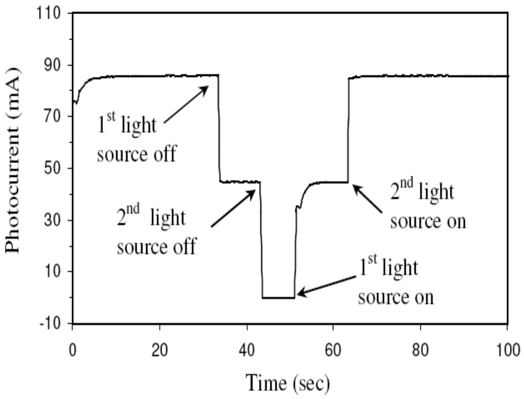

Figure 5: A potentiostatic plot of a double side illuminated PEC. The photocurrent is reduced to half when one light source is turned off and it becomes zero when both the light sources are turned off.

3.3 Characterization and Photoelectrochemical Activity of CdS-TiO_2/TiO_2 Composites

The SEM (Figure 6) and DRUV vis spectra shows formation of a core-shell composite photocatalyst consisting of CdS particles and TiO_2 nanotubes. A small blue shift is observed in the absorption edge of CdS in the CdS-TiO_2/TiO_2 nanotube/Ti composite material compared to the bulky CdS and the TiO_2 nanotubes (figure not shown). The photoactivity (Figure 7) of the CdS-TiO_2/TiO_2 nanotube composite photoanode is higher than that of a simple CdS thin film coated on to Ti foil.

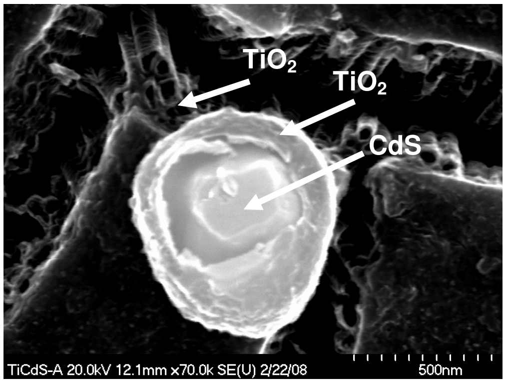

Figure 6: SEM image showing the CdS particle covered with a thin layer of TiO_2 (confirmed by EDS). Beneath the CdS-TiO_2 particles, TiO_2 nanotubes are visible. The image was taken by mechanically scratching the sample.

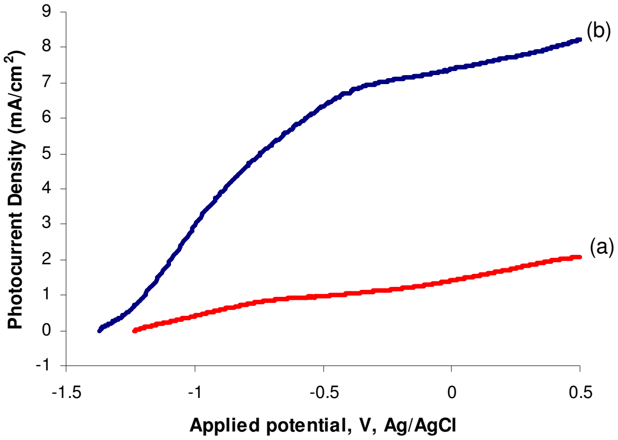

Figure 7: Photocurrent density as a function of potential of CdS thin film on Ti foil (a) and composite of CdS-TiO_2 core-shell onto TiO_2 nanotubes (b).

4 CONCLUSION

A double side anodized TiO_2 nanotubular photo anode with modified band gap states has been developed. Anodization of titanium on both sides (total exposed area of 16 cm^2) is successfully carried out using an acidic and ethylene glycol medium under the influence of ultrasonic waves. The double sided titania nanotube photoanode (TiO_2/Ti/TiO_2) prepared using organic media is found to possess good photoactivity to generate a high volume of hydrogen (38 mL/hour) under the illumination of a simulated solar spectrum on both sides of the photoanode.

The core-shell CdS-TiO_2 onto TiO_2 nanotubes composite photoanode showed an enhanced photocurrent density (8.2 mA/cm^2 at 0.5 V Ag/AgCl) as compared to CdS particles alone. The enhanced light absorption of CdS in combination with the high charge transport properties of 1D TiO_2 nanotube arrays makes this composite a promising material for photoelectrolysis of water.

5 ACKNOWLEDGEMENT

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6 REFERENCES

[1] J.A. Turner, Science 285**,** 687, 1999.
[2] J.A. Turner, Science 305**,** 972, 2004.
[3] V. Zwilling V, E. Darque-Ceretti, A. Boutry-Forveille, D. David, M.Y. Perrin and M. Ancouturier, Surface and Interface Analysis*,* 27, 629, 1999.
[4] J.H. Park, S. Kim and A. Bard, Nano. Lett., 6 24, 2006.
[5] K. Zhu, N.R. Neale, A. Miedaner and A.J. Frank, Nano. Lett., 7 69, 2007.
[6] A. Fujishima and K. Honda, 238**,** 37, 1972.
[7] G.K. Mor, K. Shankar, M. Paulose, O.K. Varghese and C.A. Grimes, Nano.Lett., 5 191, 2005.
[8] O.K. Varghese, D.W. Gong, M. Paulose, K.G. Ong and C.A. Grimes, Sens.Actuators B, 93, 338, 2003.
[9] S.K. Mohapatra, V.K. Mahajan and M. Misra, Nanotech., 18, 445705. 2007.
[10] Y. Yin, Z. Jin and F. Hou, Nanotech., 18, 495608, 2007.
[11] S. Biswas, M.F. Hossain, T. Takahashi, Y. Kubota, and A. Fujishima, Thin Solid Films, 2008 (doi: 10.1016/j.tsf.2008.01.006).
[12] W-T. Sun, Y. Yuan, H-Y. Pan, X-F. Gao, Q. Chen and L-M. Peng, J. Am. Chem. Soc., 130, 1124, 2008.
[13] S.K. Mohapatra, M. Misra, V.K. Mahajan and K.S. Raja, J. Catal., 246**,** 362, 2007.
[14] S.K. Mohapatra, M. Misra M, V.K. Mahajan and K.S. Raja, J. Phys. Chem. C, 111, 8677, 2007.
[15] Handbook of X-ray Photoelectron Spectroscopy, ed. J. Chastain, Perkin-Elmer Corporation, Eden Prairie, MN, 1992.