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High Capacity Photoelectrochemical Hydrogen Generation Using Hybridized Nanotubular Arrays of TiO2 as Photo Anode And Cathode

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ABSTRACT

The production of hydrogen by directly splitting water at room temperature using solar light is a promising alternate energy resource. However, the advancement of the technology is limited due to the photo conversion efficiency of photo anodes, as well as the expensive nature of Pt cathodes. In this paper, construction of a photo electrochemical cell for generation of hydrogen from water (using band gap modified TiO2 Nan tubes as photo anode and TiO2 nanotubes loaded with Pt nano-particles as cathode) is reported. Both the formation of ordered nanotubes, and modification of the band gap of the anode materials are achieved by a single step ultrasonic assisted electrochemical anodization process in fluoride containing organic solutions (typically ethylene glycol) and subsequent annealing in hydrogen environment. The anodization of Ti foil in organic solutions results in incorporation of carbonaceous species at the walls of the nanotubes, and subsequent heat treatment causes diffusion of carbon into TiO2 lattice, which modifies the band gap to 2.1 eV. The nanotubular TiO2 photo anodes formed by the sono-electrochemical anodization process show more superior charge transport properties and structural integrity than the anodes made of nano-particles. Further, construction of very large area (active on both sides) electrode materials with uniform electronic and mechanical properties is easily achievable using the proposed electrochemical anodization process. Photo electrochemical studies are carried out on these carbon modified double sided nanotubular TiO2 photo anodes and Pt nano-particle loaded TiO2 nanotubular cathodes. Both the electrodes show an equal surface area of 8 cm2. Photo current is recorded as a function of both applied external bias potential and light wavelength using a simulated solar light source. Photo current is observed when wavelength of the light is less than 600 nm, indicating photo activities in the visible region. The double side illuminated TiO2 nanotubes generate a photo current of 86 mA under an external bias of -0.1 VAg/AgCl. The rate of hydrogen generation by this cell is more than 34 cc/h

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KEYWORDS

Nanotubular TiO2, photo electrochemical hydrogen generation, oxide semiconductors, charge transport

INTRODUCTION

Neon-structured semiconductor materials have been considered for photo-electrochemical generation of hydrogen owing to their high surface area and improved charge separation kinetics[i]. Among the available photosensitive materials, TiO2 is considered highly stable against photo corrosion and is relatively inexpensive[ii]. The TiO2 nanocrystalline photo anodes have been fabricated by various methods such as: coating titania slurry on conducting glass, spray pyrolysis, and layer-by-layer colloidal coating on glass substrate followed by calcinations at an appropriate temperature. These processes result in formation of a 3-D network of interconnected nanoparticles. It is suggested that instead of the 3-D configuration of nanoparticles, fabrication of vertical standing nanowires of TiO2 could improve the photoconversion efficiency[iii]. Anodization of titanium metal substrate in acidified fluoride solution results in formation of ordered arrays of TiO2 nanotubes[iv,v,vi]. These vertically oriented TiO2 nanostructures will have better mechanical integrity and photoelectric properties than those of TiO2 nanocoating prepared by the slurry casting route. The main limitation of use of the TiO2 material for photoelectrolysis is its wider band gap, which requires higher energy of light for photo excitation of electron-hole pairs. Therefore, only 3-5% of the solar light (UV-portion) can be used for conversion into photocurrent. Substitutional doping of elements like C, N, F, P or S in the oxygen sub-lattice has been considered to narrow the band gap because of mixing of the p-states of the guest species with O 2p states[vii]. Khan et al.[viii] and Bard et al.[ix] have shown that carbon doping can improve the photo conversion efficiency of the TiO2 film and TiO2 nanotubes, respectively. Recently our research group reported a novel electrochemical method of fabricating highly ordered and low defect density TiO2 nanotubular arrays based on an ultrasonic assisted anodization process in organic solutions, which also enabled effective doping of carbon in the TiO2 lattice after annealing in inert atmospheres[x,xi,xii,xiii,xiv,xv]. This process is considered a single-step method of preparing carbon modified TiO2 nanotubes, because ultrasonication during anodization in organic solutions helps carbonaceous species to adsorb on the surface of TiO2 nanotubes more easily.

In this paper, a novel photo electrochemical cell for hydrogen generation through water splitting is described based on improvised methods of the manufacture of photo-anode and cathode. Conventionally, the photo anode is illuminated either at the front side or at the back. In this new development, the TiO2 nanotubular arrays are formed on both sides of the Ti substrate, and therefore the anode can be illuminated on both sides. Further, a solid Pt foil or nickel electrode is used as a cathode in conventional electrolyzers. Solid Pt electrode is an expensive component. In this communication, a method of manufacture of a low cost cathode material based on a TiO2 nanotubular template loaded with Pt nanoparticles is discussed. It will be shown that the Pt-nanoparticles loaded at a rate of 0.4 mg/cm2 of the cathode electrode area are as effective as the solid Pt foil of the same geometric area, but with more than 100 folds cost reduction.

EXPERIMENTAL

PREPARATION OF PHOTOANODE

Nanotubular TiO2 arrays are formed by anodization of the Ti foils (0.1 mm thick, 99.9% purity) in 300 mL electrolytic solution containing 10 wt% water, and 0.3 wt% ammonium fluoride in ethylene glycol under ultrasonic irradiation using an ultrasonic bath (100 W, 42 KHZ, Branson 2510R-MT). Both sides of the Ti foil are anodized. A two-electrode configuration is used for anodization. A flag shaped platinum (Pt) electrode (thickness: 0.5 mm, area: equal to the Ti foil) serves as cathode. The distance between the two electrodes is kept at 4.5 cm in all the experiments. The anodization is carried out at 20V using a rectifier (Agilent, E3640A). During anodization, ultrasonic waves are irradiated onto the solution continuously. The anodization current is monitored continuously using a digital multimeter (METEX, MXD 4660A). The anodized samples are properly washed with distilled water to remove the occluded ions, dried in an air oven, and processed for characterization. In the as-anodized condition, the TiO2 nanotubes are amorphous. In order to crystallize the nanotubes and to facilitate adsorbed carbon to diffuse into the lattice, the TiO2 nanotubes are annealed using 10% hydrogen under an argon atmosphere at 500 oC for 2 h.

PREPARATION OF CATHODE

The cathode is prepared by synthesizing Pt nanoparticles on TiO2 nanotube-arrays (Pt/TiO2) by the incipient wetness method. For this purpose, TiO2 nanotubular arrays are prepared by the sonoelectrochemical anodization method using an aqueous solution (pH = 2.1-2.2) of 0.5M phosphoric acid (H3PO4) and 0.14M sodium fluoride solution. The anodization is done for 30 min. The TiO2 nanotubes are then kept for activation (to remove adsorbed moisture and atmospheric gases) in an air oven at 100 oC for 12 h. A diluted solution of chloroplatinic acid (H2PtCl6, 8 wt % in water; Sigma-Aldrich) is added drop-by-drop to the pre-activated titania nanotubular arrays. This is then dried under a vacuum overnight. The reduction of the platinum salt into Pt(0) is carried out in a furnace at 500 oC for 2 h under reducing (10% H2 in argon) atmosphere.

PHOTO ELECTROCHEMICAL EXPERIMENTS

Photoelectrochemical studies are carried out in a glass cell with quartz windows for illumination of the photo anode on both sides. Fig. 1 schematically illustrates the experimental set up used in the photoelectrochemical studies. Details of the experimental procedure are given in our earlier publications10-14. Briefly, two 300 W solar simulators are used for illuminating the photo anode (8 cm2) on both sides. The electrolyte is 1 M KOH with a 5 vol% addition of ethylene glycol as a hole scavenger. A potentiostat is used for both the application of an external bias and measurement of the photocurrent.

RESULTS AND DISCUSSION

Fig. 2 (a) shows the morphology of the ordered TiO2 nanotubular arrays as a planar view, and Fig. 2 (b) shows the side view of the nanotubes. The outer diameter of the nanotubes ranges from 70-100 nm with a wall thickness of about 20 -30 nm. Anodization at 20 V in fluorinated ethylene glycol solution for 30 minutes results in 800 – 1000 nm long nanotubes under ultrasonication. Longer nanotubes (more than 2 microns) are obtained with an increase in the anodization time. As noted in Figure 3 (a), ultrasonication results in faster growth kinetics of the nanotubes. The anodization current is higher (more than 50% of that under mechanical stirring) and the time required to reach the steady state growth condition is shorter in the case of the ultrasonicated anodization condition. Further, the nanotubes prepared under ultrasonication contain less defect density as observed from the Mott-Schottky results of Fig. 3 (b). Note that the shallower the slope of the potential Vs 1/C2 plot, the larger the defect density is.

Figs. 4 (a) and (b) show the TEM and HRTEM images of the TiO2 nanotubes loaded with the Pt-nanoparticles, respectively. The Pt loaded TiO2 nanotubular arrays act as a cathode for photo electrolysis of water. The diameter of the Pt-nanoparticles varies between 4 -7 nm. Very uniform distribution of the Pt nanoparticles on the TiO2 template can be observed from Fig. 3 (a).

During formation of TiO2 nanotubular arrays in ethylene glycol solution under ultrasonic field, it is envisaged that carbonaceous species are incorporated in the outer walls of the nanotubes. In the as-anodized condition the nanotubes are amorphous. Upon annealing in inert or reducing conditions, the carbonaceous species dissociates and carbon diffuses into the TiO_2 lattice. This results in a $TiO_{2-x}C_x$ type of structure. Presence of Ti-C type bonds can be observed by XPS analysis.12-14. Further, photo current measurements as a function of light wave length also support the incorporation of carbon in the TiO_2 lattice13. Light wave energy Vs (photocurrent density)$^{0.5}$ plot indicated a band gap energy of 2.1 eV for the carbon doped TiO_2 nanotubes.

Figs. 5(a) and (b) show the results of the photo electrochemical generation of hydrogen using the double side illuminated photo anodes. It should be noted that oxygen evolves at the TiO_2 anode surface and hydrogen evolves at the cathode, preferentially at the Pt-nanoparticles. Fig. 4 (a) shows the photo current as a function of applied potential. Without any external bias, the photocurrent is very small. In order to observe hydrogen generation at the cathode, application of an external bias is required. However, the applied bias is much lower than the theoretically required bias to split the water without light illumination. As observed in Fig. 4(a), the photo current increases with applied potential and reaches almost a plateau value after -0.4 V in the case of single side illumination. Double side illumination doubles the photo current at 0.2 V. Fig. 4 (b) shows the photocurrent transient at an applied potential of -0.1 V Ag/AgCl. Illumination of only one side gives about 48 mA current, which corresponds to a current density of 6 mA/cm^2. Double side illumination gives about 86 mA. The recorded photo current density using simulated solar light is the highest for this type of material. The enhanced photo current density can be attributed to the carbon doping of the TiO_2 and presence of ethylene glycol in the 1 M KOH electrolyte acting as hole scavengers.

CONCLUSIONS

- Ordered arrays of nanotubular TiO_2 are produced by a simple anodization process assisted by ultrasonic irradiation.
- Annealing of the TiO_2 nanotubes formed in ethylene glycol solution results in a carbon doped $TiO_{2-x}C_x$ structure and reduction in the band gap from 3 eV to 2.1 eV.
- A low cost cathode material is developed by loading Pt nanoparticles on to TiO_2 nanotubes.
- The currently obtained maximum photo current density is 6 mA/cm^2 in 1 M KOH + 5 vol% ethylene glycol at - 0.1 V Ag/AgCl.
- Addition of 5 vol% EG to the 1 M KOH electrolyte act as hole scavengers and result in about an 80% increase in the photo current density as compared to 1 M KOH without any addition.
- Double side illumination of the TiO_2 nanotubular photo anode doubled the photocurrent. More than 34 mL/h of hydrogen is produced for a anode with a 8 cm^2 geometric area.

ACKNOWLEDGEMENT

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REFERENCES

- 1 J. van de Lagemaat, N.-G. Park, A. J. Frank, J. Phys. Chem., B 104 (2000) 2044-2052
- 1 T. Tachikawa, Y. Takai, S. Tojo, M. Fujitsuka, H. Irie, K. Hashimoto, T. Majima, J. Phys. Chem. B 110 (2006) 13158-13165

1 S. U. M. Khan, T. Sultana, Solar Energy Materials & Solar Cells 76 (2003) 211-221
1 K. S. Raja, M. Misra, K. Paramguru, Materials Letters 59 (2005) 2137-2141
1 K. S. Raja, M. Misra, K. Paramguru, Electrochimica Acta, 51 (2005) 154-165
1 G. K. Mor, O. K. V Paulose, N. Mukherjee, C. A. Grimes, J. Mater. Res. 18 (2003) 2588-2591
1 R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269-271
1 S. U. M. Khan, M. Al-Shahry, W. B. Ingel Jr., Science, 297 (2002) 2243-2245
1 J. H. Park, S. Kim, A. J. Bard, Nanoletters 6 (2006) 24-28
1 K. S. Raja, M. Misra, V. K. Mahajan, T. Gandhi, P. Pillai, S. K. Mohapatra J. Power Sources, 161 (2006) 1450-1457
1 K. S. Raja, V. K. Mahajan, M. Misra, J. Power Sources, 159 (2006) 1258-1265
1 S.K. Mohapatra, M. Misra, V.K. Mahajan, K.S. Raja, Journal of Catalysis 246 (2007) 362-369
1 S. K. Mohapatra, M. Misra, V. K. Mahajan, K. S. Raja, J. Phys. Chem. C 111 (24) (2007) 8677-8685
1 S. K. Mohapatra, V. K. Mahajan, M. Misra, Nanotechnology, 18 (2007) 445705
1 S. K. Mohapatra, M. Misra, J. Phys. Chem. C 111 (24) (2007) 11506-11510
argheese, M. Paulose, N. Mukherjee, C. A. Grimes, J. Mater. Res. 18 (2003) 2588-2591
1 R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269-271
1 S. U. M. Khan, M. Al-Shahry, W. B. Ingel Jr., Science, 297 (2002) 2243-2245
1 J. H. Park, S. Kim, A. J. Bard, Nanoletters 6 (2006) 24-28
1 K. S. Raja, M. Misra, V. K. Mahajan, T. Gandhi, P. Pillai, S. K. Mohapatra J. Power Sources, 161 (2006) 1450-1457
1 K. S. Raja, V. K. Mahajan, M. Misra, J. Power Sources, 159 (2006) 1258-1265
1 S.K. Mohapatra, M. Misra, V.K. Mahajan, K.S. Raja, Journal of Catalysis 246 (2007) 362-369
1 S. K. Mohapatra, M. Misra, V. K. Mahajan, K. S. Raja, J. Phys. Chem. C 111 (24) (2007) 8677-8685

1 S. K. Mohapatra, V. K. Mahajan, M. Misra, Nanotechnology, 18 (2007) 445705
1 S. K. Mohapatra, M. Misra, J. Phys. Chem. C 111 (24) (2007) 11506-11510
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i J. van de Lagemaat, N.-G. Park, A. J. Frank, J. Phys. Chem., B 104 (2000) 2044-2052
ii T. Tachikawa, Y. Takai, S. Tojo, M. Fujitsuka, H. Irie, K. Hashimoto, T. Majima, J. Phys. Chem. B 110 (2006) 13158-13165
iii S. U. M. Khan, T. Sultana, Solar Energy Materials & Solar Cells 76 (2003) 211-221
iv K. S. Raja, M. Misra, K. Paramguru, Materials Letters 59 (2005) 2137-2141
v K. S. Raja, M. Misra, K. Paramguru, Electrochimica Acta, 51 (2005) 154-165
vi G. K. Mor, O. K. Vargheese, M. Paulose, N. Mukherjee, C. A. Grimes, J. Mater. Res. 18 (2003) 2588-2591
vii R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269-271
viii S. U. M. Khan, M. Al-Shahry, W. B. Ingel Jr., Science, 297 (2002) 2243-2245
ix J. H. Park, S. Kim, A. J. Bard, Nanoletters 6 (2006) 24-28
x K. S. Raja, M. Misra, V. K. Mahajan, T. Gandhi, P. Pillai, S. K. Mohapatra J. Power Sources, 161 (2006) 1450-1457
xi K. S. Raja, V. K. Mahajan, M. Misra, J. Power Sources, 159 (2006) 1258-1265
xii S.K. Mohapatra, M. Misra, V.K. Mahajan, K.S. Raja, Journal of Catalysis 246 (2007) 362-369
xiii S. K. Mohapatra, M. Misra, V. K. Mahajan, K. S. Raja, J. Phys. Chem. C 111 (24) (2007) 8677-8685
xiv S. K. Mohapatra, V. K. Mahajan, M. Misra, Nanotechnology, 18 (2007) 445705
xv S. K. Mohapatra, M. Misra, J. Phys. Chem. C 111 (24) (2007) 11506-11510

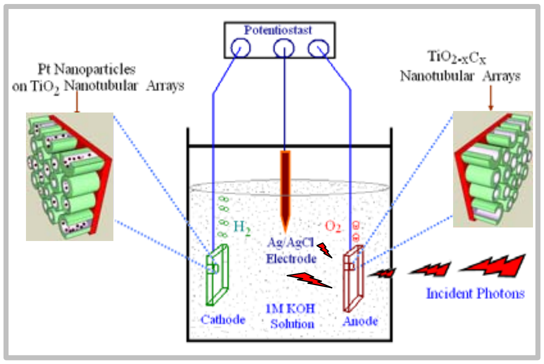

Fig. 1 Schematic experimental arrangement of the photo electrochemical hydrogen generation with double-side illumination of the TiO₂ nanotubular photo-anode and nanotubular TiO₂ template cathode loaded with Pt-nanoparticles.

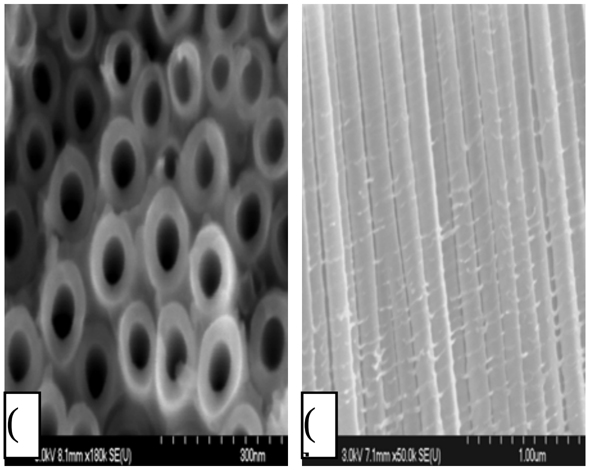

Fig. 2 FESEM images of the TiO2 nanotubes prepared by ultrasonic assisted anodization. (a) planar view of the nanotubes showing the inner diameter (40 – 60 nm) and wall thickness (20-30 nm);

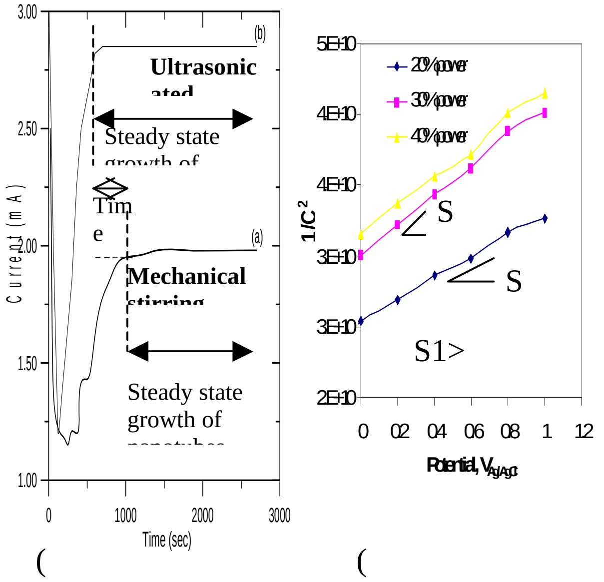

Fig. 3 (a) Comparison of anodic current transients under ultrasonicated and mechanical stirred conditions; (b) Mott-Schottky (M-S) plots of the TiO₂ nanotubes prepared under different ultrasonic

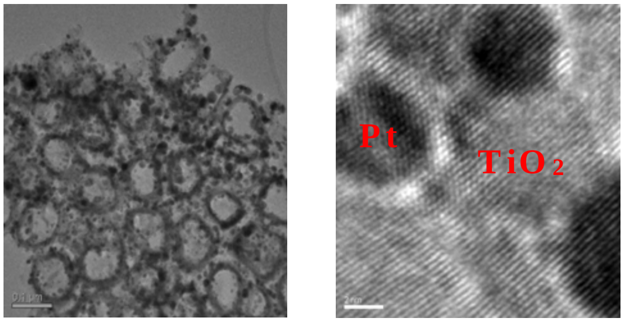

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Fig. 4 (a) TEM; and (b) HRTEM image of the TiO_2 nanotubes loaded with Pt-nanoparticles.

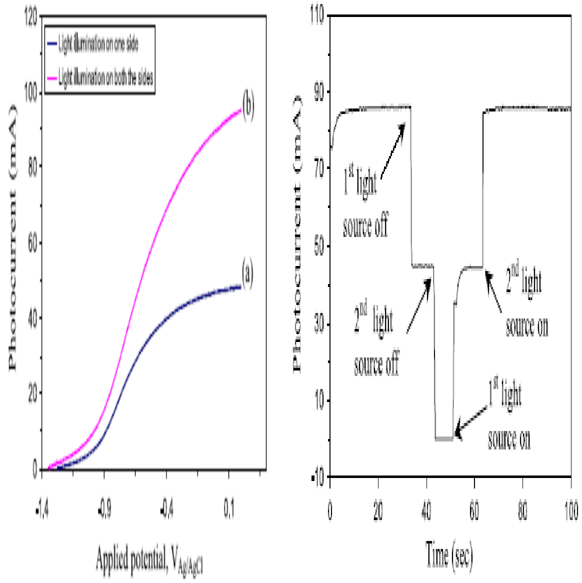

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Fig. 5 Photo current generated by TiO_2 nanotubular arrays during simulated solar light illumination. (a) photo current as a function of