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THE EFFECT OF GREEN LASER ON HYDROGEN PRODUCTION OF TiO_2/CDS ELECTRODE

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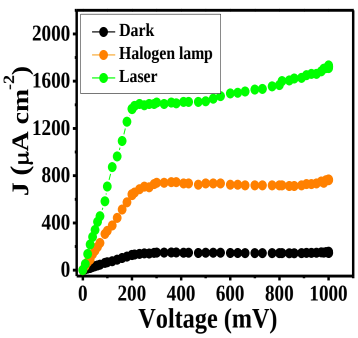
Graphical abstract



Abstract

Enhancing the response of TiO_2 semiconductor nanocomposites to visible light is topically important for hydrogen production. TiO_2/CdSnanocomposite films (NCFs) are grown on p-type [100] silicon substrate using electron beam deposition (EBD). The UV–Vis reflectance spectra and PEC measurement reveal the enhanced absorption and induced photo-currents due to CdS coating on TiO_2 nanofilm. The improved visible light absorption is attributed to the increase in optical path length and subsequent decrease in back-scattered radiation near TiO_2– Si interface. The excellent features of our results suggest that NCF electrodes may be nominated for potential applications in water splitting, renewable energy and environmental fields.

Keywords: Water splitting, green laser, TiO_2, Cds, electrode

Meningkatkan gerak balas TiO_2 nanokomposit semikonduktor kepada cahaya yang boleh dilihat adalah penting untuk pengeluaran hidrogen. TiO2/CdS filemnanokomposit (NCFs) yang ditanam di atas substrat silicon jenis-p [100] menggunakan pemendapan alur elektron (EBD). Pantulan UV-Vis dan PEC mendedahkan penyerapan telah dipertingkatkan dan mengaruh foto-arus kerana salutan CdS pada nanofilem TiO_2. Penyerapan cahaya yang boleh dilihat yang bertambah baik adalah disebabkan oleh peningkatan dalam panjang jalan optik dan penurunan seterusnya dalam sinaran belakang bertaburan berhampiran TiO_2-Si antaramuka. Ciri-ciri yang sangat baik dari keputusan kami mencadangkan bahawa elektrod NCF boleh dinamakan untuk aplikasi yang berpotensi dalam membelah air, tenaga boleh diperbaharui dan bidang alam sekitar.

Kata kunci: Pemisahan air, laser hijau, TiO_2, CDs, elektrod

1.0 INTRODUCTION

Lately, many efforts are dedicated towards solar hydrogen production from semiconductor nanomaterials via heterogeneous photo-catalysis. Undoubtedly, this is considered to be most promising routes for renewable energy generation and environmental applications [1-3]. Titanium dioxide (TiO2) based nanostructured materials are attractive due to their unique photo-catalytic response useful for varieties of applications. Un-doped TiO2 is an n-type semiconductor material with the indirect energy band gap of 3.2 and 3.02 eV in anatase and rutile phases, respectively. TiO2 being non-toxic and photo-stable is an excellent choice as photo-catalyst in the ultraviolet region with ~ 5% conversion efficiency [4]. Their extreme insensitiveness to visible light and strong activity to UV-light limits the application for harvesting solar energy. The association of TiO2 with other semiconductor materials of lower band gaps like CdS is found to be promising for photovoltaic applications [5]. Consequently, the deposition of different types of thin film composites for improving the optical properties of each component remains challenging. Despite intensive work on growth and characterization of TiO2/CdS NCF the literature on photo-current responses and efficient generation of hydrogen is still lacking. The efficiency of solar hydrogen is limited by the weather changes and geographical location. Previous works used conventional UV source and xenon lamps to induce photo-catalysis in NCFs. The main difficulties with conventional light sources are their inherited shortcoming in delivering constant output power over longer period originates from heating effect. In addition, their broad spectral emission lies outside the absorption region of photo-catalyst unfavourable for devices. Therefore, the use of low power laser (green) as excitation source to activate photocatalysis in TiO2/CdS NCFs) for hydrogen production is proposed [6].

We report the efficient hydrogen production from TiO2/CdS NCFs electrode synthesized using EBD technique. The achieved NCFs having wider, uniform, clean and dense surface with a high adhesion to substrate films is optically (UV-Vis) characterized. The PEC measurement under the illumination of green laser and halogen lamp are performed to examine photo-current response. The mechanism of significant enhancement in the water splitting efficiency is analyzed and understood.

2.0 EXPERIMENTAL

Analytical grade TiO2 and CdS (Aldrich, 99.99 % purity) powders without further purification are used to prepare the NCFs on p-type [110] silicon substrates (2 x 2 cm) by EBD method operating at 3 keV and 2 ×10-5 torr pressure with 0.5 nm/min evaporation rate. The TiO2 exist predominantly in the anatase (tetragonal forms). TiO2 film is evaporated on cleaned substrates of thickness 400 nm and annealed for 4 hours at 400 °C under the oxygen flow. The CdS film of thickness 50 nm is then evaporated on the TiO2 film. The thicknesses of the films are measured by crystal thickness monitor type Edwards FTM 5. Finally, the samples are annealed at 400° C for 3 hours in vacuum at a pressure of 10-4torr to enhance the CdS diffusion within TiO2 to achieve high quality TiO2/CdS NCFs.

NCFs electrodes are fabricated on p-type silicon in the [100] direction to measure the PEC and photo-catalytic properties. Silicon wafers are coated with 400 nm thick TiO2 layer deposited in a single cycle. The top electrode is made by depositing aluminium of 100 nm thickness with 1 mm circular pattern on TiO2 layer. The rear contact is made by depositing aluminium on silicon wafer. All the electrical contacts are protected by epoxy. The UV-Vis measurements in the wavelength range of 200–1000 nm are performed via UV-3101 PC UV-VIS-NIR spectrometer.

The PEC and photo-catalytic responses are measured by a PEC cell composed three electrodes with TiO2/CdS NCF as working, platinum (Pt) wire as a counter and silver/silver chloride (Ag/AgCl) as reference electrode. A mixture of Na2S (0.01 Molar) and Na2SO3 (0.02 Molar) electrolyte solution (PH = 11) is used to probe the photo-catalytic properties and water splitting mediated hydrogen generation. The current-voltage (I-V) characteristics of the working electrode illuminated with a 50 W halogen lamp (model MR16 GU10 from Philips) and diode pumped solid state laser with second harmonics (model DPG-2000 at λ = 532 nm) are examined using Source Meter-Keithley 2400. The PEC analyses are carried out using a power meter model Nova Z01500 at bias voltage 0.25 V with power 80 mW/cm2. The reactor is made of borosilicate glass without UV filter and water solution is used as IR filter that kept the temperature constant. Oxygen from the reaction chamber is completely removed by purging and stirring pure Ar gas (99.9%) for 1 h before the measurement.

3.0 RESULTS AND DISCUSSION

The reflectance spectra of S1 and S2 electrodes in the wavelength range of 200 - 800 nm are presented in Figure 1. Extremely low reflectivity in the UV region revealed by the two electrodes is related to the strong absorption by TiO2. A steady decrease in the reflectance with the introduction of CdS is attributed to the enhanced light scattering. The red-shift of the reflectance minima due to the incorporation of CdS interpreted in terms of increasing particle size is consistent with Mie's theory [7].

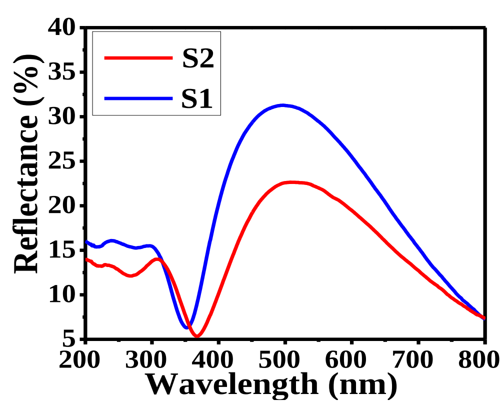


Figure 1 The reflectance spectra of S1 and S2 electrodes

The current-voltage responses of S2 electrode shown in Figure 2 clearly reveal much higher photo-current density under visible light (from green laser) irradiation compare to the illumination using halogen lamp. The open-circuit voltage and short circuit current density are found to be 0.919 V and 191.3 μA/cm2, respectively. The current density in dark remains almost constant at around 156.1 μA/cm2 but increase significantly to 767.13 μA/cm2 and 1732.7 μA/cm2 after illuminated by halogen and green laser, respectively. Sample S1 does not show any response to visible light as expected.

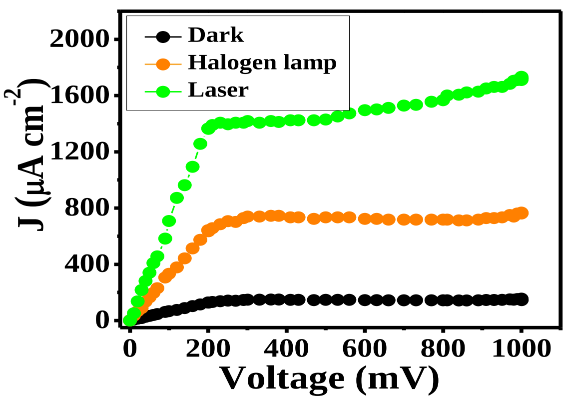


Figure 2 The dark and photo-current response of S2 electrode illuminated under halogen lamp and green laser

The rate of hydrogen generation from water splitting by NCF photo-anode is displayed in Figure 3. The evolution rate of hydrogen determined for illumination via halogen lamp and laser are 0.878 and 1.99 μmole.min-1, respectively.

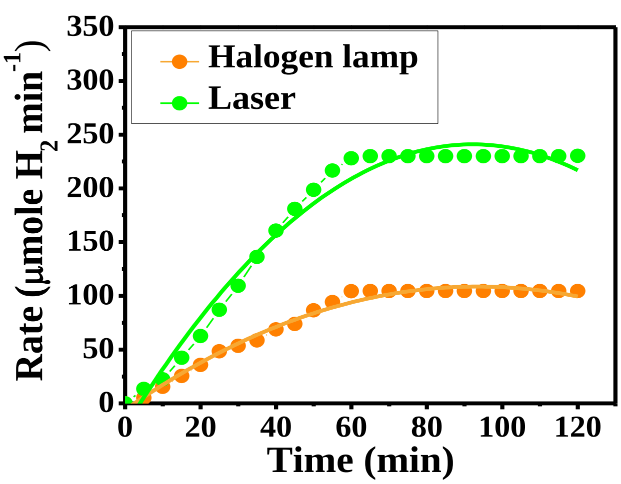


Figure 3 The rate of hydrogen generation from S2 electrode

The amount of H2 produced through laser induced catalyses is 2.26 times higher than that induced via halogen lamp. Generally, the hydrogen produced by photo-electron reaction is directly proportional to the photo-current density of the electrode. The current is generated, when the photo-induced electrons are available for the H2 evolution reaction. The reaction can be described as [8]:

$$2H^+ + 2e^- \rightarrow H_2 \uparrow \quad (1)$$

During the reaction, the photo-generated electrons react with H+ at the counter electrode to yield H2 gas. Factually, the mechanisms of enhanced hydrogen production in NCFs electrode via laser induced photo-catalyses are far from being understood. We establish that the unique combination of green laser and NCFs electrode may serve as a best alternative for producing hydrogen with enhanced efficiencies by means of photo-catalytic reactions [9, 10]

4.0 CONCLUSION

A simple yet accurate method is adopted to make TiO2 and TiO2/CdS NCFs on silicon substrate by electron beam deposition to examine the possibility of photo-catalyses mediated efficient hydrogen generation from NCFs electrode. The photo-anode made from NCFs is further used for hydrogen generation via water splitting. The achieved enhanced efficiency of hydrogen production via laser induced focusing effect suggests that our method may constitute a basis for tuning photo-current response of NCFs decisive for future renewable energy sources.

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References

[1] Fujishima, A., Honda, K. 1972. Electrochemical Photolysis Of Water at a Semiconductor Electrode. *Nature*. 238: 37-8.

[2] Hamadanian, M., Jabbari, V., Shamshiri, M., Asad, M., Mutlay, I. 2013. Preparation of Novel Hetero-nanostructures and High Efficient Visible Light-active Photocatalyst Using Incorporation of CNT as an Electron-transfer Channel Into the Support TiO2 and PbS. *Journal of the Taiwan Institute of Chemical Engineers*. 44(7): 48-57.

[3] Wang, R-C., Fan, K-S., Chang, J-S. 2009. Removal of Acid Dye by Znfe2o4/Tio2-Immobilized Granular Activated Carbon Under Visible Light Irradiation in a Recycle Liquid–solid Fluidized Bed. *Journal of the Taiwan Institute of Chemical Engineers*. 40: 533-40.

[4] Dholam, R., Patel, N., Adami, M., Miotello, A. 2008. Physically and Chemically Synthesized TiO2 Composite Thin Films for Hydrogen Production by Photocatalytic Water Splitting. *International Journal of Hydrogen Energy*. 33: 6896-903.

[5] Peng, S., Huang, Y., Li, Y. 2013. Rare Earth Doped TiO_2-CdS and TiO_2-CdS Composites with Improvement of Photocatalytic Hydrogen Evolution Under Visible Light Irradiation. *Materials Science in Semiconductor Processing*. 16: 62-9.

[6] Gondal, M. A., Hameed, A., Yamani, Z. H., Suwaiyan, A. 2004. Laser Induced Photo-catalytic Oxidation/Splitting of Water Over a-Fe2O3, WO3, TiO2 and NiO Catalysts: Activity Comparison. *Chemical Physics Letters.* 385: 111-5.

[7] Wriedt, T. 2012. *The Mie Theory, Basics and Applications*. Berlin Heidelberg: Springer.

[8] Pareek, A., Dom, R., Borse, P. H. 2013. Fabrication of Large Area Nanorod Like Structured Cds Photoanode for Solar H_2 Generation Using Spray Pyrolysis Technique. *International Journal of Hydrogen Energy.* 38: 36-44.

[9] Gondal, M. A., Hameed, A., Yamani, Z. H., Suwaiyan, A. 2004. Production of Hydrogen and Oxygen by Water Splitting Using Laser Induced Photo-catalysis Over Fe_2O_3. *Applied Catalysis A: General*. 268: 159-67.

[10] Gondal, M. A., Sayeed, M. N., Seddigi, Z. 2008. Laser Enhanced Photo-catalytic Removal of Phenol from Water Using p-type NiO Semiconductor Catalyst. *Journal of Hazardous Materials.* 155: 83-9.