Generation of Hydrogen by Water Splitting with Visible Light

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The major goals that were realized from January to December 2006 are:

- A new method for deposition of nanocrystalline Fe_2O_3 photoanode films from $Fe(CO)_5$ and tetraethoxysilane on SnO_2 is developed, and the novel Fe_2O_3 photoanode films oxidize water under visible light with unprecedented efficiency; *IPCE* = 42% at 370 nm and 2.2 mA/cm^2 (corrected by a spectral mismatch factor of 0.82) in AM 1.5 G sunlight of 1000 W/m^2 at 1.23 V_{RHE}.
- Another important discovery is the deposition of monolayer of cobalt on the hematite surface, which catalyzes the water oxidation and improves solar photocurrents by more than 15%.
- We have designed and developed novel unsymmetrical zinc phthalocyanine sensitizers carrying *tert*-butyl and carboxylic acid groups that act as electron "*pushing*" and "*pulling*"entities, respectively, yielded 85% IPCE in the near IR, and 3.56% power conversion efficiency under one sun from selective harvesting of near IR light.

1 Introduction, state of the art of the research

The research carried out initially in collaboration with the groups of Prof. Augustynski and Prof. Calzaferri from the University of Geneva and Bern, respectively focuses on the development of a water photolysis device combining two mesoscopic semiconductor oxide films [1, 2]. In order to optimize the performance and efficiency of the device, it is desirable that the optical responses of the two oxides in the visible wavelength range are complementary. Nanocrystalline tungsten trioxide was used previously capturing photons from the blue part of the solar emission and serving as photo-anode in the system. However the band gap of this material is 2.6 eV limiting the harvesting of visible light [3]. Hence, the visible light response of WO_3 is not sufficient to allow for optimal operation of the tandem cell. To overcome this problem we looked at promising alternative materials such as Fe_2O_3 (hematite) as a photoanode [4, 5]. This has a band gap of 2.1 eV absorbing blue and green light up to 610 nm. The role of the photo-anode is to generate oxygen from water directly, i.e. without resorting to an additional electrode or redox catalyst. The oxidation process is initiated by light induced electron-hole pair separation in the iron oxide (eq.1), followed by reaction of valence band holes with water (eq. 2).

$$h\upsilon + Fe_2O_3 \longrightarrow Fe_2O_3 \quad (h^+ + e^-) \qquad (1)$$

$$4h^+ + 2H_2O \longrightarrow O_2 + 4H^+ \qquad (2)$$

The present embodiment of our water photolysis system employs a translucent Fe_2O_3 film, which is superimposed on the nanocrystalline dye injection solar cell. The dye solar cell adsorbs the light in the green and red spectral region, which is transmitted by the Fe_2O_3 photoanode [3]. The solar cell serves as a photo-driven bias increasing the electrochemical potential of the photoelectrons produced by band gap excitation of the Fe_2O_3 to render reduction of water to hydrogen feasible (eq. 3).

$$2e^- + 2H^+ \longrightarrow H_2 \qquad (3)$$

The optimal conversion efficiency with tandem devices requires band gaps of 1.4 eV for the dye solar cell, and 1.8 eV for photo-anode. The spectral onset of the black dye and phthalocyanines that is used in the dye sensitized solar cell corresponds to 1.4 eV.

2 Results and Discussion

2.1. High efficient iron oxide photoanodes.

Thin films of silicon-doped Fe_2O_3 were deposited by APCVD (atmospheric pressure chemical vapor deposition) from $Fe(CO)_5$ and TEOS (tetraethoxysilane) on SnO_2-coated glass at 415 °C. HRSEM reveals a highly developed dendritic nanostructure of 500 nm thickness having a feature size of only 10-20 nm at the surface. Real surface area determination by dye adsorption yields a roughness factor of 21. XRD shows the films to be pure hematite with strong preferential orientation of the [110] axis vertical to the substrate, induced by silicon doping [6]. The photocatalytic activity of these films with regard to photoelectrochemical water oxidation, under sunlight illumination in 1 M NaOH, water is oxidized at the Fe_2O_3 electrode with higher efficiency (IPCE) 42% at 370 nm and 2.2 mA/cm2 in AM 1.5 G sunlight of 1000 W/m2 at 1.23 VRHE) than at the best reported single crystalline Fe_2O_3 electrodes (Figure 1). This unprecedented efficiency is in part attributed to the dendritic nanostructure, which minimizes the distance photogenerated holes have to diffuse to reach the Fe_2O_3 /electrolyte interface while still allowing efficient light absorption. Part of the gain in efficiency is obtained by depositing a thin insulating SiO_2 interfacial layer between the SnO_2 substrate and the Fe_2O_3 film and a catalytic cobalt monolayer on the Fe_2O_3 surface.

The morphology of the α-Fe_2O_3 was strongly influenced by the silicon doping, decreasing the feature size of the mesoscopic film [6]. The silicon-doped α-Fe_2O_3 nano-leaflets show a preferred orientation with the (001) basal plane normal to the substrate. The best performing photoanodes were obtained with silicon doped hematite films prepared by APCVD, producing the cauliflower-type nanostructure. Top view and cross-section of both structures are illustrated in Figure 2. From the top view images it becomes apparent that the addition of silicon decreases the feature size in both films. This is thought to enhance the photo response because it renders the feature size commensurate to the diffusion length of holes in hematite crystals.

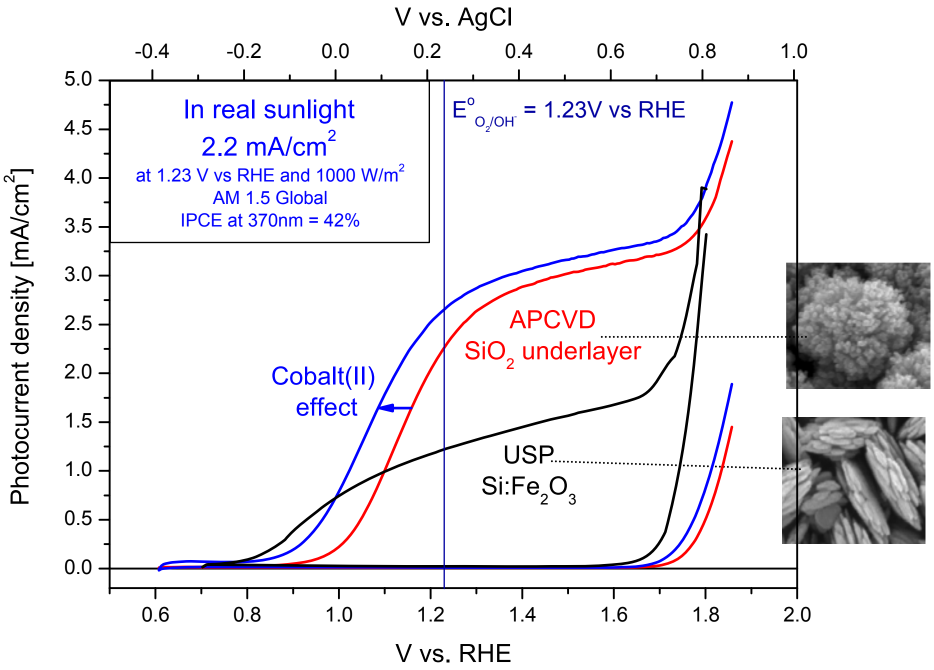

Figure 1: Current-voltage characteristics and morphology of silicon doped iron oxide photo anodes obtained from ultra-sonic spray pyrolysis (USP) and atmospheric pressure chemical vapour deposition (APCVD). Measured in darkness and under simulated sunlight. a) unmodified APCVD Fe_2O_3, b) the same electrode after cobalt treatment, c) unmodified USP Fe_2O_3.

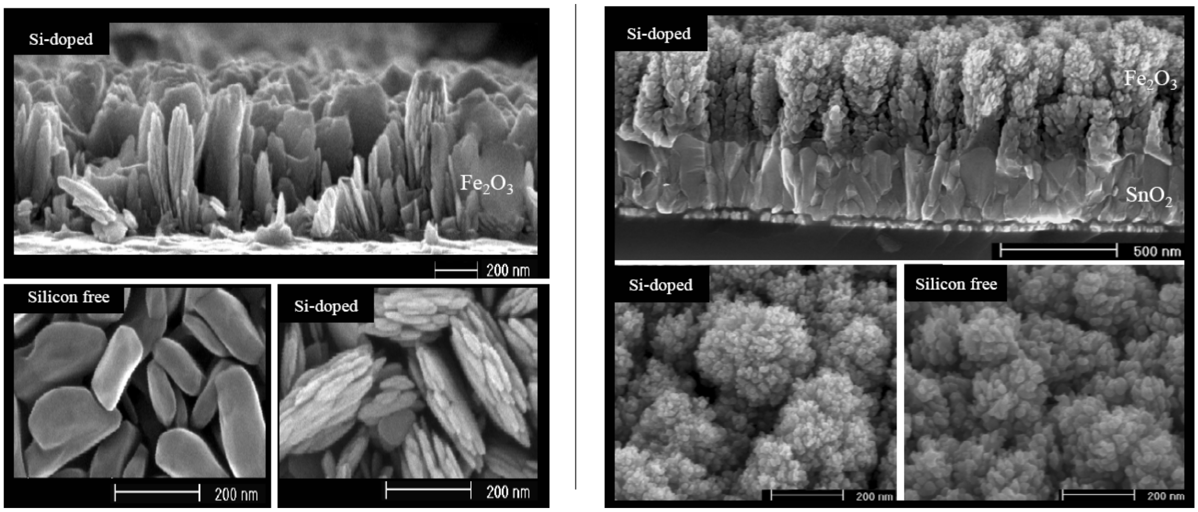

Figure 2: morphology of silicon doped and undoped iron oxide photo anodes. Left: ultra-sonic spray pyrolysis (USP) and Right: Atmospheric pressure chemical vapour deposition (APCVD).

2.2 Development of near IR Sensitizers for the bottom part of the tandem cell

We have reported (see August 2006 report) detailed synthesis and characterization of unsymmetrical Zinc Phthalocyanine (PCH001) sensitizer, which shows absorption maximum at

672 nm (ε = 1 91 000 dm^3 mol^{-1} cm^{-1}). When the PCH001 sensitizer is excited within the charge transfer absorption band at 298 K in an air-equilibrated ethanol solution, it exhibits a luminescence maximum at 682 and 750 nm. The absorption spectra of PCH001 sensitizer adsorbed on a 2 μm TiO_2 film, which exhibit features similar to those seen in the corresponding solution spectra but exhibit a slight red shift 8 nm due to the interaction of the anchoring groups to the surface. The cyclic voltammogram of PCH001, obtained using a glassy carbon disk electrode in acetonitrile solvent with 0.1 M tetrabutyl ammonium tetrafluoroborate, exhibits a quasi-reversible oxidation at $E_{1/2} = 0.65$ V vs. ferrocene (Fc). When scanning towards negative potentials one quasi-reversible wave at $E_{1/2} = -1.31$ is observed, which is assigned to the phthalocyanine based reduction. The photocurrent action spectra obtained with a sandwich cell using an electrolyte of 0.6M M-methyl-N-butyl imidiazolium iodide, 0.05 M iodine, 0.05 M LiI and 0.5 M tert.butylpyridine in 50/50 (v/v) mixture of valeronitrile and acetonitrile (1376) show 75% incident monochromatic photon-to-current conversion efficiency. The PCH001 sensitized cell gave under standard global AM 1.5 solar condition, a short circuit photocurrent density (i_{SC}) of 6.50 ± 0.20 mA/cm^2, an open-circuit voltage of 635 ± 30 mV and a fill factor of 0.74 ± 0.03, corresponding to an overall conversion efficiency η of 3.05% (see August 2006 report). The PCH001 sensitizer contains a saturated carbon between the anchoring group and the phthalocyanine

The new unsymmetrical Zinc Phthalocyanine TT1, that contains anchoring group directly attached to phthalocyanine ring and three *tert*-butyl groups, which act as "*pull*" and "*push*", respectively (Figure 3). The function of the carboxylic acid group is to graft the sensitizer on the semiconductor surface, and to provide intimate electronic coupling between its excited state wave-function and the conduction band manifold of the semiconductor. The purpose of the three *tert*-butyl groups is to enhance the solubility, to minimize the aggregation, and to tune the LUMO level of the phthalocyanine that provides directionality in the excited state.

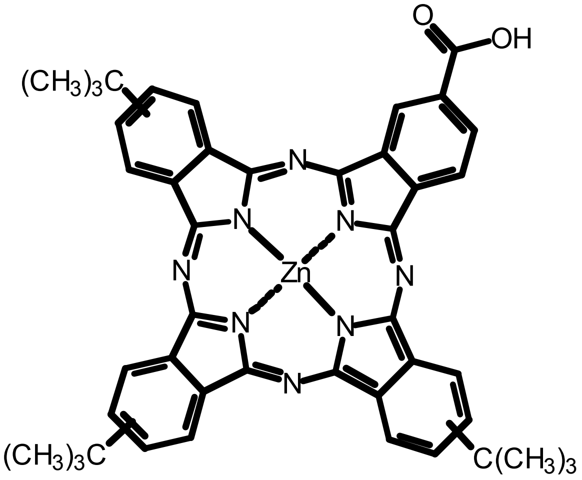

Figure 3. Chemical structure of TT1.

The TT1 sensitized cell gave under standard global AM 1.5 solar condition, a short circuit photocurrent density (i_{SC}) of 7.78± 0.20 mA/cm^2, an open-circuit voltage of 611 ± 30 mV and a fill factor of 0.74 ± 0.03, corresponding to an overall conversion efficiency η of 3.56%. Table 1 shows effect of dye concentration on photocurrent-voltage characteristics of TT1 sensitized cell. The optimum concentration of the dye seems to be 5 X 10^{-5} M, and the higher and lower concentrations resulted slightly lower efficiency. Figure 4 shows current-voltage characteristics of photocurrent action spectra obtained with a sandwich cell using TT1 and an electrolyte of 0.6M M-methyl-N-butyl imidiazolium iodide, 0.05 M iodine, 0.05 M LiI and 0.5 M tert.butylpyridine in 50/50 (v/v) mixture of valeronitrile and acetonitrile.

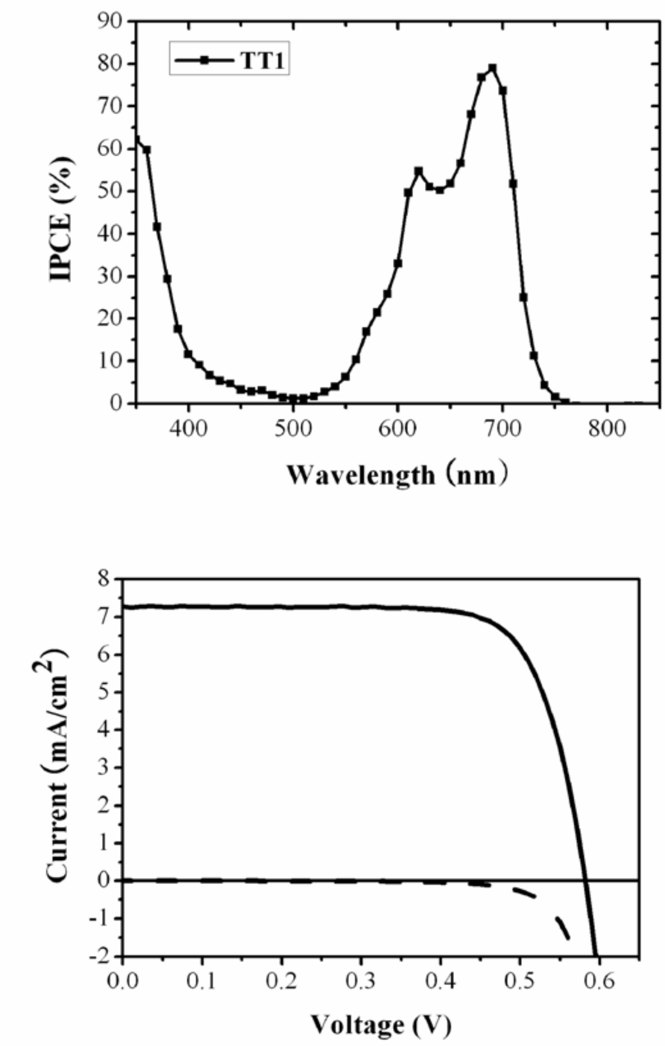

Figure 4. Photocurrent action spectrum (top) and current-voltage characteristics (bottom) of TT1 obtained with a nanocrystalline TiO_2 film supported onto a conducting glass sheet and derivatized with monolayer of TT1 in presence of Chenodeoxycholic acid. A sandwich type cell configuration was used to measure this spectrum.

Table 1: Current current-voltage characteristics of TT1 with various concentrations adsorbed onto 10+ 5 μm TiO_2 films.

Dye concentration	Dipping time (hours)	Short circuit current at 1 sun (mA/cm^2)	Open-circuit potential (mV)	Fill factor	Efficiency under 1 sun
2.5 X 10^{-5} M	4	7.36	606	0.75	3.35

5 X 10^{-5} M	4	7.78	611	0.75	3.56
1 X 10^{-4} M	4	7.18	626	0.75	3.34

3 Conclusions

We have designed and developed novel nanocrystalline hematite Fe_2O_3 photoanodes containing a monolayer of cobalt, which oxidize water under visible light with unprecedented efficiency. Also, developed is the new unsymmetrical zinc phthalocyanine sensitizers with “push” and “pull” groups those exhibit record overall solar to electrical conversion efficiency in the near infrared region.

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