

Durable Unsymmetrical Zinc Phthalocyanine for Near IR Sensitization of Nanocrystalline TiO₂ Films With Non-Volatile Redox Electrolytes

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Abstract. We are presenting our results based on unsymmetrical zinc phthalocyanine by adopting ‘push-pull’ concept for the nanocrystalline dye-sensitized solar cells. Using this sensitizer in combination with nonvolatile organic-solvent-based electrolytes, we obtained a photovoltaic efficiency of 1.52% under standard global AM 1.5 sunlight and compared the results with volatile organic-solvent based electrolyte. These devices exhibit admirable stability when subjected to continuous thermal stress at 60 °C for 1000 h. The sensitizer is thermally stable up to 150 °C and can be useful for roof top applications.

Introduction

Phthalocyanines are tetra pyrrolic cyclic organic molecules, which can find applications in several fields: in modeling of some photophysical process of photosynthesis, as photocatalysts in chemical sensors, in photodynamic reactions against cancer, photo degradation of organic pollutants and as a sensitizer in nanocrystalline dye-sensitized solar cells (DSSC's) [1]. The main reason for usefulness of this group of compounds in DSSC's is the strong absorption of visible light in the near-IR/far-red region. The first efficient DSSC was developed by O' Regan and Gratzel in early 1990's. In these devices, the photoactive electrode consists of a nanostructured wide-bandgap semiconductor, often TiO₂, a redox couple (I⁻/I₃⁻) and sensitized with a monolayer of dye. The most successful charge-transfer sensitizers employed so far in such cells are bis(tetrabutylammonium)-cis-di(thiocyanato)-bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (the N719 dye) and trithiocyanato 4,4'4''-tricarboxy-2,2':6',2''-terpyridine ruthenium(II) (the black dye), produced solar-energy-to-electricity conversion efficiencies (η) of up to 11% under AM 1.5 irradiation and stable operation for millions of turnovers [2]. In spite of this, the main drawbacks of these sensitizers are the lack of absorption in the red region of the visible spectrum and also relatively low molar extinction coefficient above 600 nm. In this regard, phthalocyanines are potential candidates as sensitizers in DSSC's applications.

Phthalocyanines have been repeatedly tested in the past as sensitizers of wide-bandgap oxide semiconductors. Although, poor incident photon-to-electric current conversion yields were obtained, remaining below 0.1% efficiency with these systems, which is insufficient for solar cell applications [3]. This may be due to the solubility, aggregation and lack of directionality in the excited state. To overcome these problems, recently, we have reported two unsymmetrical zinc phthalocyanines **PCH001** and **PCH003** (structures are shown in Fig. 1) based on ‘push-pull’ concept [4]. These unsymmetrical phthalocyanines have either three alkyl or alkoxy groups which acts as electron releasing (‘push’), enhance the solubility of phthalocyanine macrocycle in common

organic solvents as well as minimizes the aggregation. It has also two carboxyl groups, which acts as electron withdrawing (*'pull'*) and serves to graft onto nanocrystalline TiO₂. Both the sensitizers were tested in DSSC by using volatile redox electrolyte and found efficiency (η) of 3.05% for **PCH001** and 1.13% for **PCH003**. To the best of our knowledge, these results represent a major breakthrough in the design and development of phthalocyanine-based sensitizers for DSSC applications. However, the DSSC with volatile redox electrolyte is not suitable for roof top applications as the durability of the test cell is short. For this reason, we have designed two new redox electrolytes for the durability improvement of the test cell with **PCH001** sensitizer. The composition of two redox electrolytes is 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPI), 0.1 M I₂ and 0.5 M *n*-methylbenzimidazolium iodide (NMBI) in γ -butyrolactone (AH1) and 0.9 M DMPI, 0.1 M I₂, 0.5 M NMBI and 0.1 M lithium saccharide in γ -butyrolactone (AH4).

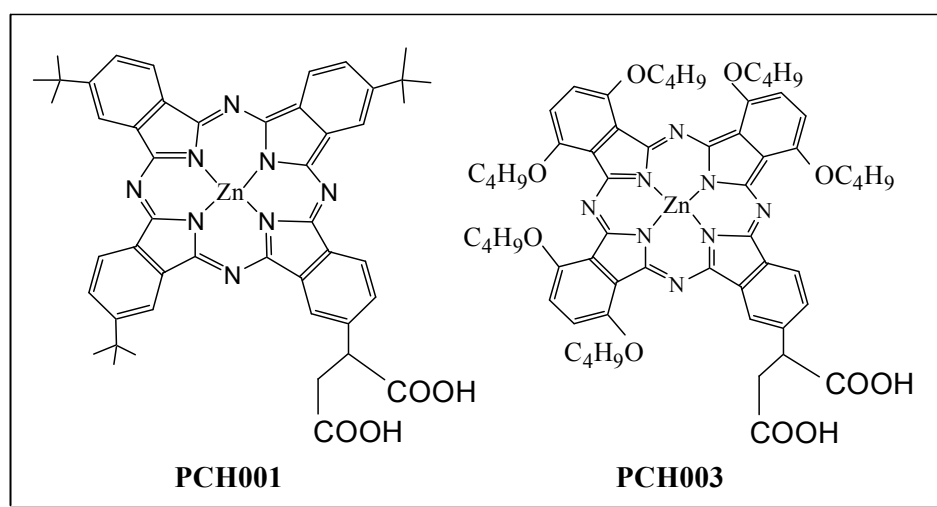


Fig 1. Structure of unsymmetrical zinc phthalocyanines.

Experimental

All the chemicals and reagents were procured either from Aldrich (USA) or Ranbaxy (India) and were purified according to the standard procedure prior to use [5]. The TiO₂ paste consisting of 20 nm sized TiO₂ particles procured from Solaronix. Fluorine doped tin oxide glass substrate was obtained from ASAHI, Japan. Synthesis of **PCH001** was reported elsewhere [4a].

Cyclic- and differential pulse voltammetric measurements were performed on a PC-controlled CH instruments model CHI 620C electrochemical analyzer. Cyclic voltammetric experiments were performed on 1 mM phthalocyanine solution in acetonitrile at scan rate of 100 mV/s using 0.1 M tetrabutyl ammoniumhexafluorophosphate (TBAPF₆) as supporting electrolyte. The working electrode is glassy carbon, standard calomel electrode (SCE) is reference electrode and platinum wire is an auxiliary electrode. After a cyclic voltammogram (CV) had been recorded, ferrocene was added, and a second voltammogram was measured. X-ray photoelectron spectroscopy analyses were carried out on KRATOS AXIS 165 X-ray photoelectron Spectrometer. Thermogravimetric measurements were carried out on a Mettler Toledo TGA/SDTA 851e instrument-heating rate at 10 °C min⁻¹ with 10 mg of sample under nitrogen atmosphere.

Test Cell Preparation

TiO₂ photoelectrode (area: ca. 0.74 cm²) was prepared by a similar method as reported in the literature [6]. The TiO₂ paste was first screen-printed on fluorine doped SnO₂ conducting glass (transmission > 85% in the visible, sheet resistance 10 Ω/square obtained from ASAHI, Japan) to form a transparent layer. Subsequently, a second scattering layer made up of a paste containing 400

nm anatase TiO₂ particles was coated. Finally, the screen-printed double layer film was heated to 450 °C in an oxygen atmosphere and calcinated for 45 min. The sensitizer was dissolved in ethanol at a concentration of $2-3 \times 10^{-5}$ M. The photoelectrode was dipped into the dye solution while it was still hot, i.e., its temperature was ca. 80 °C and kept at room temperature for 16 h. After completion of the dye adsorption, the photoelectrode was withdrawn from the solution and washed thoroughly with ethanol to remove non-adsorbed dye under a stream of dry air or argon.

A sandwich cell was prepared using the dye-sensitized electrode and platinum coated conducting glass electrode as the counter electrode. The later was prepared by chemical deposition of platinum from 0.05 M hexachloroplatinic acid. The two electrodes were placed on top of each other using a thin polyethylene film (50 μm) thick as a spacer to form the space for electrolyte. The empty cell was tightly held, and the edges were heated to 65 °C to seal the two electrodes together. The active surface area of TiO₂ film electrode was ca. 0.74 cm². The electrolyte was introduced into cell through pre-drilled whole of the counter electrode and later covered by cover glass to avoid the leakage of the electrolyte solution. Photoelectrochemical data were obtained using a 450W xenon light source focused to give 1000 W/m², the equivalent of one sun at AM 1.5 (the luminance of the lamp has normalized and corrected by the supplier), at the surface of the test cell.

Photoelectrochemical Measurements

The photovoltaic performance of DSSC test cell was determined using the instrument SOLARONIX SA SR-IV unit type 312. The incident photon-to-current conversion efficiency (IPCE) was measured using a 100-W xenon light source was used to give 100 mW cm⁻² (the equivalent of 1.0 sun at AM 1.5) that was focused onto cell through a double monochromator. The monochromator was incremented through the visible spectrum to generate the IPCE(λ) curve as defined below

$$\text{IPCE}(\lambda) = 12\,400 (J_{SC} / \lambda \phi) \quad (1)$$

Where λ is the wavelength(nm), J_{SC} is the photocurrent density under short circuit conditions (mA/cm²) and φ is the incident radiative flux (mW/cm²). The whole experiment was run automatically using PV measurements software. For *I-V* measurements, a 1000-W xenon light source was used as the irradiation source. The spectral output of the lamp matched the AM 1.5 solar spectrum in the region of 350-750 nm (mismatch 1.9%). Incident light intensities were adjusted with neutral wire mesh attenuators. The current-voltage characteristics were determined by applying an external potential bias to the cell and measuring the photocurrent using a Keithley model 2420 digital source meter. The overall conversion efficiency η of the photovoltaic cell is calculated from the integral photocurrent density (J_{SC}), the open-circuit photovoltage (V_{OC}), the fill factor of the cell (*ff*) and the intensity of the incident light (*I_{ph}*).

$$\eta = J_{SC} V_{OC} ff / I_{ph} \quad (2)$$

The fill factor is defined by the following equation.

$$ff = \frac{J_{PH(max)} X V_{PH(max)}}{J_{SC} X V_{OC}} \quad (3)$$

where $J_{PH(max)}$ and $V_{PH(max)}$ are the photocurrent and photovoltage for maximum power output and J_{SC} and V_{OC} are the short-circuit photocurrent density and open-circuit photovoltage.

Results and Discussions

The unsymmetrical zinc phthalocyanine **PCH001** was synthesized according to the reported procedure in the literature and fully characterized [4]. The electronic absorption spectrum of **PCH001** was recorded in ethanol solution and compared to that of the phthalocyanine adsorbed onto 6 μm thick nanocrystalline TiO_2 films is shown in Fig. 2. The absorption spectrum in solution consists of a Soret band at 350 nm ($\epsilon = 70,000 \text{ M}^{-1} \text{ cm}^{-1}$) and a Q-band at 692 nm ($\epsilon = 1,91,000 \text{ M}^{-1} \text{ cm}^{-1}$) due to the π - π^* transitions of the conjugated macrocycle. The absorption spectrum of the phthalocyanine adsorbed onto 6 μm thick TiO_2 electrode is similar to that of the solution spectra but exhibit a small red shift. This may be due to the presence of the carboxylic protons of the phthalocyanine, which on adsorption on TiO_2 release the proton and bind to Ti^{4+} . The Ti^{4+} acts as electron withdrawing group and produces a red shift in the absorption bands.

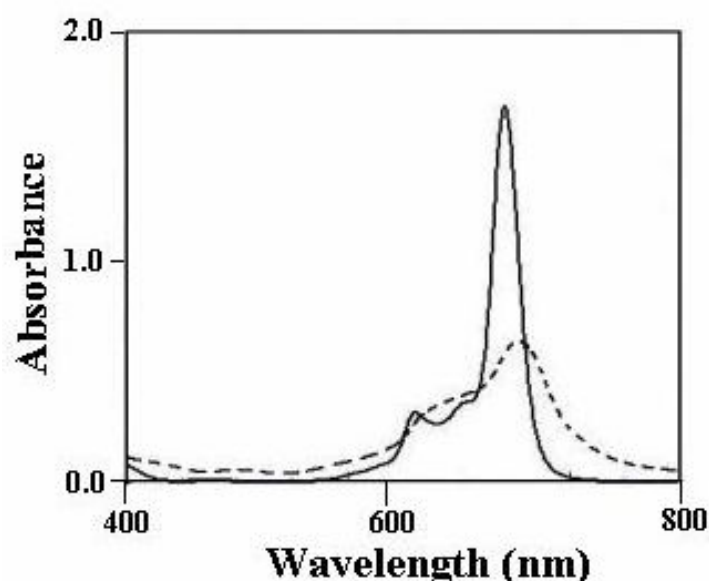


Fig. 2. UV-Vis absorption spectra of **PCH001** (—) in ethanol and (-----) adsorbed onto a 6 μm thick TiO_2 film.

With a view to evaluate the HOMO-LUMO levels of **PCH001**, we have performed the electrochemistry by using cyclic and differential pulse voltammetric techniques in acetonitrile solvent. The oxidation potentials were determined from half-wave potentials ($E_{1/2}$) ($E_{\text{OX}} - E_{\text{red}}/2$) by cyclic voltammetry (CV) or peak potentials (E_p) by differential pulse voltammogram (DPV, dotted line) of **PCH001** are shown in Fig. 3. **PCH001** exhibits a quasireversible one-electron oxidation at 0.51 V, generating π -cation radical and a quasireversible reduction at 1.31 V. With respect to dye-sensitization of wide-bandgap semiconductors, e.g., TiO_2 the oxidation potential of **PCH001** and the E_{0-0} transition energy, the energy levels of the singlet excited states (LUMO) of **PCH001** were determined to be 1.78 V vs. SCE, whereas the energy level of the conduction band edge of TiO_2 is ca. -0.74 V vs. SCE. This makes electron injection from the excited state of **PCH001** into the conduction band of TiO_2 thermodynamically feasible. Furthermore, the HOMO level of the **PCH001** is lower than the energy level of the redox couple I^-/I_3^- (0.2 V vs. SCE) in the electrolyte, enabling the dye regeneration by electron transfer from I^- .

X-ray photoelectron spectroscopy (XPS) was used to distinguish any changes in **PCH001** or TiO_2 upon adsorption. Because XPS is a highly surface-selective technique, it was expected that different forms of surface or bulk material could be distinguished. The spectra of the Ti (2p) and O (1s) regions are shown in Fig. 4. The samples that were compared included a blank nanocrystalline TiO_2 electrode; pure **PCH001** and **PCH001** adsorbed on TiO_2 are shifted to higher binding energies

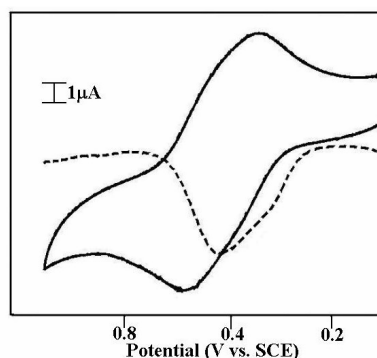


Fig. 3. Cyclic (—) and differential pulse voltammograms (-----) of **PCH001**.

by 0.2-0.4 eV upon **PCH001** adsorption i.e., both the O(1s) and the Ti (2p_{3/2}) peaks. Similarly, the O(1s) peak, attributable to **PCH001**, is also shifted to higher binding energy, by about 0.5 eV in this case. Both the N(1s) and the O(1s) peaks of **PCH001** are shifted. This data suggests that there is a substantial interaction between **PCH001** and TiO₂ and the results observed clearly in absorption spectra. The shifts can be interpreted in terms of an increase in the delocalization of the π -orbital of the phthalocyanine upon adsorption. The two carboxyl groups of the sensitizer serves to graft onto TiO₂ and thereby enhancing electronic coupling between the π^* orbitals of the phthalocyanine and the Ti(3d) orbital manifold of TiO₂. This coupling leads to increase delocalization of the π^* level of the phthalocyanine. The energy of the π^* level of the phthalocyanine is decreased by this delocalization, which explains the observed shift of the peaks. Similar types of interactions were observed in case of porphyrins adsorbed on TiO₂ surface [7].

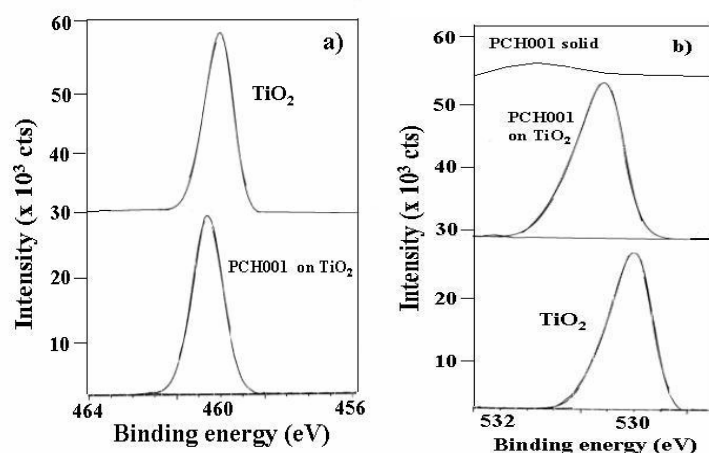


Fig. 4. XPS spectra of a) O 1s region and b) Ti 2p_{3/2} region.

Photovoltaic Performance:

We have reported earlier photovoltaic performance of **PCH001** with volatile liquid redox electrolyte i.e., 1376 [4]. The composition of 1376 redox electrolyte is 0.6 M 1-butyl-3-*n*-methylimidazolium iodide (DMPI), 0.05 M iodine, 0.05 M LiI and 0.5 M *tert*-butyl pyridine in a 50:50 (v/v) mixture valeronitrile and acetonitrile. We have observed an overall efficiency of 3.05%, which is a major break through in the phthalocyanine based DSSC devices. However, the test cell is not durable due to the volatile solvents in redox electrolyte. To overcome these problems, we have designed two new redox electrolytes AH1 and AH4. The composition of two redox electrolytes is 0.6 M DMPI, 0.1 M I₂ and 0.5 M *n*-methylbenzimidazolium iodide (NMBI) in γ -butyrolactone (AH1) and 0.9 M DMPI, 0.1 M I₂, 0.5 M NMBI and 0.1 M lithium saccharide in γ -butyrolactone (AH4) solvent. The reason for using γ -butyrolactone lies in its high boiling point, low volatility,

non-toxic and good photochemical stability, making it viable for practical applications. The viscosity of AH1 and AH4 redox electrolytes is 2.5 cPs and 2.9 cPs, respectively. The photocurrent action spectra of PCH001 with two redox electrolytes are shown in Fig. 5. We have observed an IPCE of 22% with AH1 and 41% with AH4 redox electrolyte in the spectral range 550 – 750 nm, reaching its maximum at 700 nm. Fig. 6 presents the photocurrent density-voltage curve of the device with PCH001 dye having AH1 and AH2 redox electrolytes under AM 1.5 simulated sunlight at a light intensity of 1000 W/m². The short-circuit current density (J_{SC}) open-circuit voltage (V_{OC}) fill factor (FF) and overall conversion efficiency (η) of device with AH1 redox electrolyte are 2.50 mA/cm², 536 mV, 0.69 and 0.92%, respectively. Where as with AH4 redox electrolyte the photovoltaic parameters are 4.04 mA/cm², 570 mV, 0.67 and 1.52%, respectively. At one third of a solar light intensity (300 W/m²), the power conversion efficiency reached up to 1.94 % with AH4 redox electrolyte. Under similar conditions, the device with 1376 redox electrolyte at AM 1.5, the photovoltaic parameters are 6.5 mA/cm², 635 mV, 0.74 and 3.05%, respectively. The detailed photovoltaic parameters for the devices having **PCH001** sensitizer with AH1 and AH2 redox electrolyte under different light irradiance are shown in Table 1. The overall conversion efficiency of device with AH4 redox electrolyte increases from 1.09 to 1.94% mainly because of increasing J_{SC} and V_{OC} . The low efficiency of test cell device with AH1 and AH4 than 1376 redox electrolyte may due to the high viscous nature of the solvent.

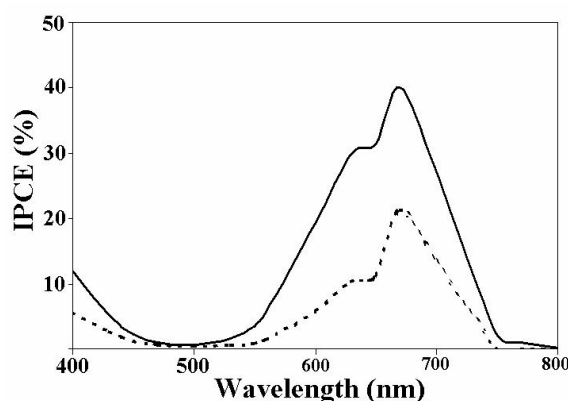


Fig. 5. Photocurrent action spectra of **PCH001** in AH1 (·····) and AH4 (—) redox electrolytes.

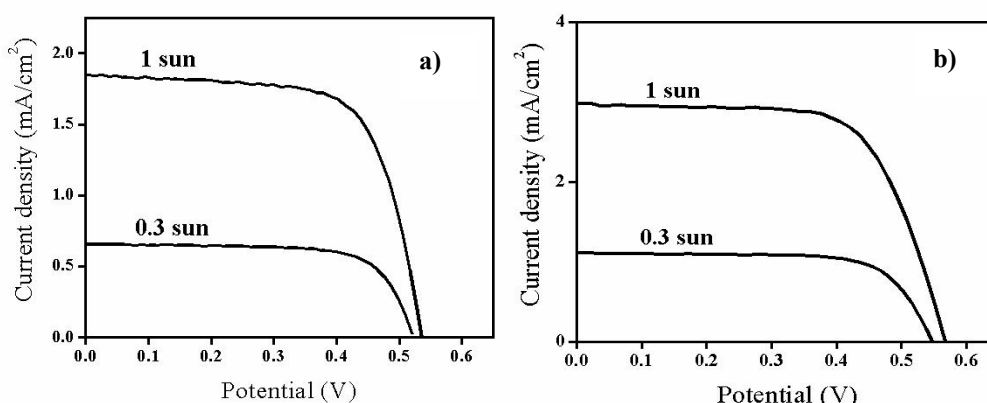


Fig. 6. Current-voltage characteristics of **PCH001** a) in AH1 and b) in AH4 redox electrolytes.

Fig. 7 presents the variation in the photovoltaic parameters at 60 °C in dark with the devices having AH1 and AH4 redox electrolytes. In both the redox electrolytes the cell parameters are increased by 10% over a period of time. This is due to the high viscous nature of the redox electrolytes and takes time to penetrate into the mesoporous TiO₂ nanoparticles. From this figure 7, it is clear that the devices containing both AH1 and AH4 redox electrolytes retains 92% of initial performance after 1000 h of heating at 60 °C. During 1000 h there is a decrease of 60 mV in V_{OC} ,

Table 1. Comparison of Short-circuit Photocurrent Density (J_{sc}), Open-Circuit Photovoltage (V_{oc}), fill factor (ff) and overall conversion efficiency (η) for the DSSC using different liquid redox electrolytes.^a

Electrolyte	Light Intensity	J_{sc} (mA/cm ²)	V_{oc} (mV)	ff	η , (%)
AH1	1 sun	2.50	536	0.69	0.92
AH1	0.3 sun	0.89	522	0.72	1.09
AH4	1 sun	4.04	570	0.67	1.52
AH4	0.3 sun	1.50	547	0.71	1.94
1376 ^b	1 sun	6.50	635	0.74	3.05

^aError limits, J_{sc} , ± 0.1 mA/cm²; V_{oc} , ± 30 mV and ff , ± 0.03 . ^bFrom literature.^{4a}

and a slight increase in fill factor in case of AH1 redox electrolyte. Where as for the device with AH4 redox electrolyte there is an increase 0.3 mA/cm² in short-circuit current density J_{sc} and slight decrease in fill factor.

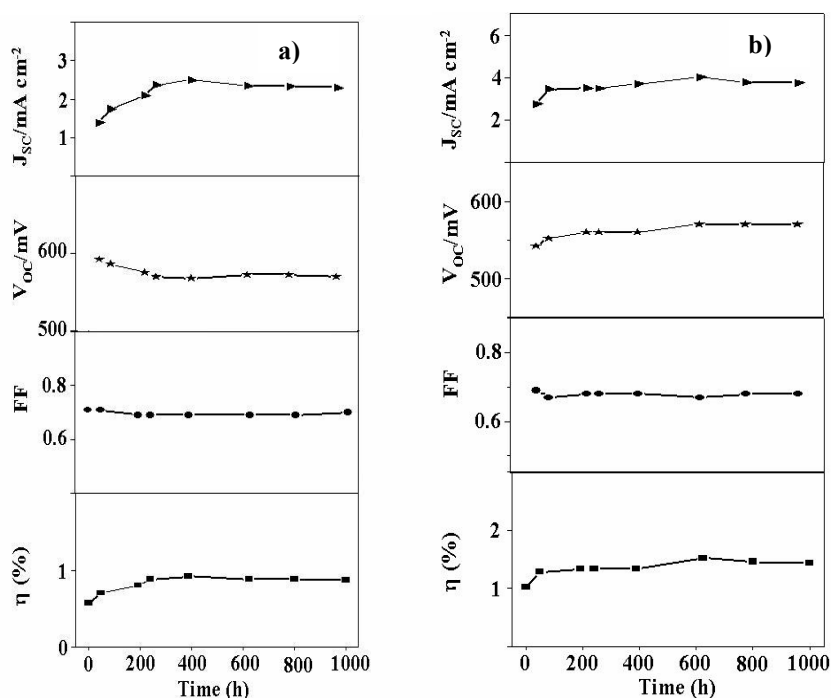


Fig. 7. Variation in photovoltaic parameters (J_{sc} , V_{oc} , FF, η) with aging time for devices based on **PCH001** at 60 °C in dark a) in AH1 and b) in AH4 redox electrolyte.

Fig. 8 shows surface AFM images for TiO₂, TiO₂+sensitizer and TiO₂+sensitizer+AH4 redox electrolyte, respectively scanned over a distance of 5 μ m. Figure 8(a) show the film surface of the sample to be 'forests' of pillars protruding out confirming the film 'rough surface'. The rough surface favor more dye adsorption and also trap more light in comparison to smoother surfaces. Figure 8(c) show the surface AFM image of TiO₂+sensitizer+AH4 redox electrolyte obtained after the sample was dried for a week at room temperature. According to the AFM image the redox electrolyte AH4 submerge the pillars of TiO₂.

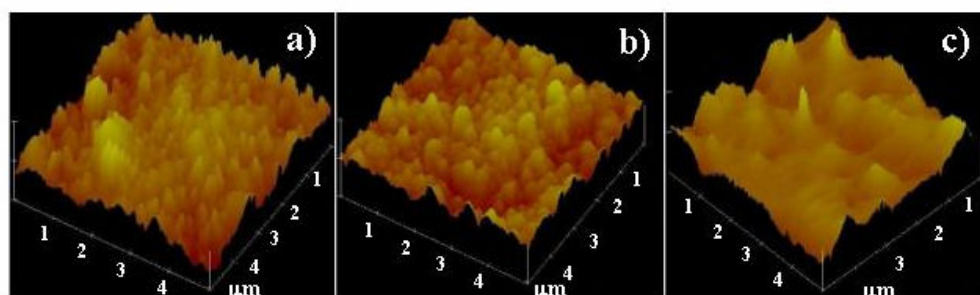


Fig. 8. AFM images of a) TiO_2 b) TiO_2 +sensitizer c) TiO_2 +sensitizer+AH4 redox electrolyte.

Finally, we have examined the thermal stability of the **PCH001** by using thermogravimetric analysis. Fig. 9 shows the thermal behavior of **PCH001**. It is well known in the literature that phthalocyanines and its metallo derivatives are stable up to 400 °C [8]. The thermogram indicates that the **PCH001** sensitizer is stable up to 150 °C. The initial weight loss (4.22 %) observed between 150 to 200 °C is attributed to the removal of carboxyl group.

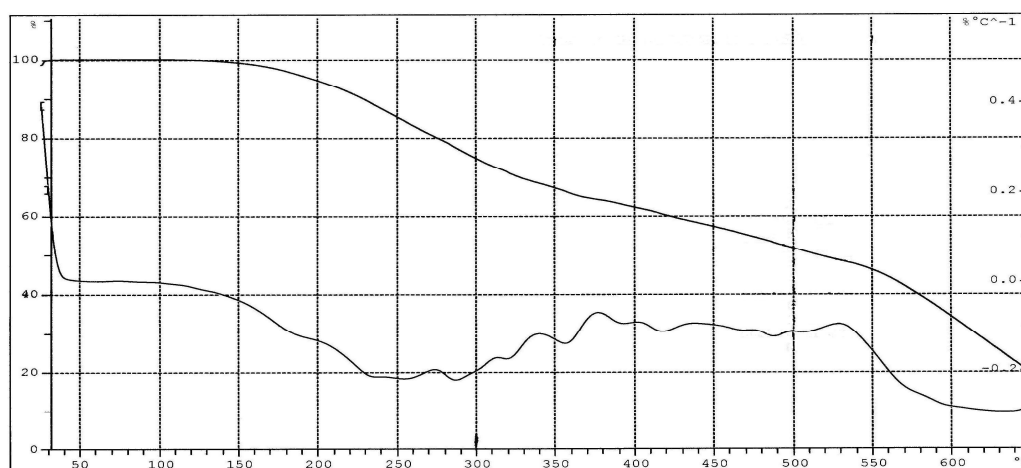


Fig. 9. TG/DTG curves of PCH001 with heating rate 10 °C min⁻¹ under nitrogen.

In conclusion, we have constructed a DSSC device by using nanocrystalline TiO_2 and an unsymmetrical zinc phthalocyanine. Using two new durable redox electrolytes tested the performance of test cell device. We have observed an overall efficiency of 1.09 and 1.94% with AH1 and AH4 redox electrolytes, respectively (0.3 sun). The DSSC devices showed excellent stability when subjected to long-term high-temperature stress. The DSSC device maintains more than 93% of the initial photovoltaic performance after aging at 60 °C in the dark. Finally, the sensitizer is stable up to 150 °C.

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