

Deposition of polyaniline via molecular self-assembly on TiO₂ and its uses as a sensitiser in solid-state solar cells

G.K.R. Senadeera^a, T. Kitamura^b, Y. Wada^b, S. Yanagida^{b,*}

^a Institute of Fundamental Studies, Hantane Road, Kandy, Sri Lanka

^b Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

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Abstract

Volatile solvent free quasi-solid solar cells were fabricated using acid-doped polyaniline (PANI) covalently grafted on surface-modified nanocrystalline TiO₂ substrates via self assembled monolayer (SAM) of silane-bearing aniline compound (C₆H₅NHC₃H₆Si(OMe)₃) (SAM) and investigated their photovoltaic performances with different additives. PANI was able to sensitize TiO₂ efficiently in the presence of SAM. Introduction of ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethyl)sulfonylamid and LiTf₂N enhanced the photocurrent of TiO₂/PANI/Au cell by more than two-fold. The cell treated with 1-methyl-3-*n*-hexylimidazolium iodide delivered a photocurrent of ~450 μA cm⁻² with photovoltage of ~565 mV, giving an efficiency of ~0.12% (FF = 0.47).

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1. Introduction

There has recently been great interest in the development of dye-sensitized solar cells (DSCs) owing to their potential low cost alternative to the conventional inorganic counter part [1]. In general these DSCs consist of sensitizers (dyes), which absorb light and inject electrons to the semiconductor where the dye is chemically attached on the surface. In order to complete the charge transfer mechanism, these dye-sensitized electrodes are combined either with a hole conducting material or a redox couple usually iodide/triiodide in an electrolyte [2,3]. However, due to some limitations, such as encapsulation problems, practical applications of these cells have not been fully realized yet. Therefore, to overcome these problems it is important to fabricate efficient dye-sensitized solid-state solar cells (DSSSCs) by replacing the liquid electrolyte with suitable hole conductor like CuI, CuSCN, PPy, OMeTAD, etc. [4–9].

On the other hand, since the sensitizers used in these DSCs are expensive and generally they employed noble metal complexes, investigations have been widened to explore the possibilities of replacing these by various materials such as organic pigments, conducting polymers (CP's), etc [10,11]. In this context, conducting polymers with extended

π-conjugated electron systems such as polypyrrole, polythiophenes, polyanilines, etc have shown great promises due to their high absorption coefficients in the visible part of the spectrum and high mobility of charge carriers. Further, many CP's in their undoped or partially doped states are electron donors upon photo-excitation and they are known as good hole conductors, which can carry current with several milliamperes [11]. Therefore, CPs may replace, in principle, the dye and the electrolyte, bringing together the function of the sensitizer and hole conductor within a single material. To use these CP's effectively as sensitizers in these devices, rigid bondings, such as by carboxylic moieties in the ruthenium based dyes, with semiconducting metal oxide substrate are required [1]. However, due to the difficulties encountered in the synthesis of these materials with suitable carboxylic moieties, it is generally accepted that self-assembled monolayers are highly promising to construct such a molecular architecture on metals and semiconducting surfaces. This approach has several advantageous such as; it permits the fabrication of highly ordered, appropriately oriented 2D and 3D structures at a fraction of the cost over traditional band-gap engineering like molecular beam epitaxy [12–14]. In this context, several publications revealed that polyaniline could be successfully grafted on to glass substrates (SiO₂) via self-assembled monolayers (SAM) compounds due to their suitable structural compatibilities [14,15].

* Corresponding author. Tel.: +81-668797925; fax: +81-668797875.
E-mail address: yanagida@mls.eng.osaka-u.ac.jp (S. Yanagida).

On the other hand, recently, some ammonium salts like imidazolium salts have attracted much attention as ionic liquids or room temperature molten salts and are reported to improve the physical properties of the conducting polymers [16–18]. In addition, one of the authors (S.Y.) has clarified that the adsorption of cationic species like imidazolium cations to nanoporous TiO_2 electrodes enhances electron diffusion coefficients of the TiO_2 electrodes in dye-sensitized solar systems [19].

Therefore, by considering these facts, here we investigated the capability to inject electrons to TiO_2 upon excitation of covalently grafted polyaniline via $(\text{C}_6\text{H}_5\text{NHC}_3\text{H}_6\text{Si}(\text{OMe})_3)$ (SAM) to TiO_2 . Relatively high photovoltaic performances than the reported values for the polymer sensitized cells were obtained when the ionic liquids, 1-methyl-3-*n*-hexylimidazolium iodide and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfone)imide (EMImTf₂N) with LiTf₂N were added to the cell.

2. Experimental

2.1. Preparation of mesoporous nanocrystalline TiO_2 films

Dense less porous (compact) nanoporous films of TiO_2 were coated on fluorine doped conducting tin oxide (FTO) glasses (sheet resistance $\sim 10 \Omega/\square$) by the following method. Prior to use, FTO glasses were cleaned in an ultrasonic bath using detergent, distilled water and isopropanol and dried with dry air-flow and followed by UV- O_3 treatments

for 18 min (Technovision Inc., Model 208). An ethanolic solution of titaniumtetra-isopropoxide $\text{Ti}[\text{OCH}(\text{CH}_3)_3]_4$ containing a few drops of HNO_3 (pH 2) was spin coated on pre-cleaned FTO at 1000 rpm for 1 min. The films were then sintered at 500°C for 1 h and cooled down to room temperature. The above procedure was then repeated and ~ 100 nm thick compact layer of TiO_2 was obtained.

Nanoporous TiO_2 electrodes were then deposited on the compact layer by “doctor blade” method using a TiO_2 paste from Solaronix (Solaronix Nanoxide-T). Electrodes were then sintered at 500°C for 1 h and cooled down to room temperature in the furnace. The thickness of the films on FTO substrates were determined by a Dektak profilometer (Veeco, Dektack 3) and found to be $\sim 4 \mu\text{m}$.

2.2. Surface modification of substrates with silane compound

As shown in the Fig. 1(A) the grafting of silane compound was carried out as follows. TiO_2 electrodes were first exposed to water vapour for 1 min and dried at 120°C and dipped in a methanolic silane solution (10 mM $\text{C}_6\text{H}_5\text{NHC}_3\text{H}_6\text{Si}(\text{OMe})_3$) for 24 h in a glove box. Films were then washed thoroughly with MeOH and dried at room temperature.

2.3. Polymerisation of PANI

For the surface oxidative polymerization of aniline (emeraldine), SAM grafted TiO_2 electrodes were immersed

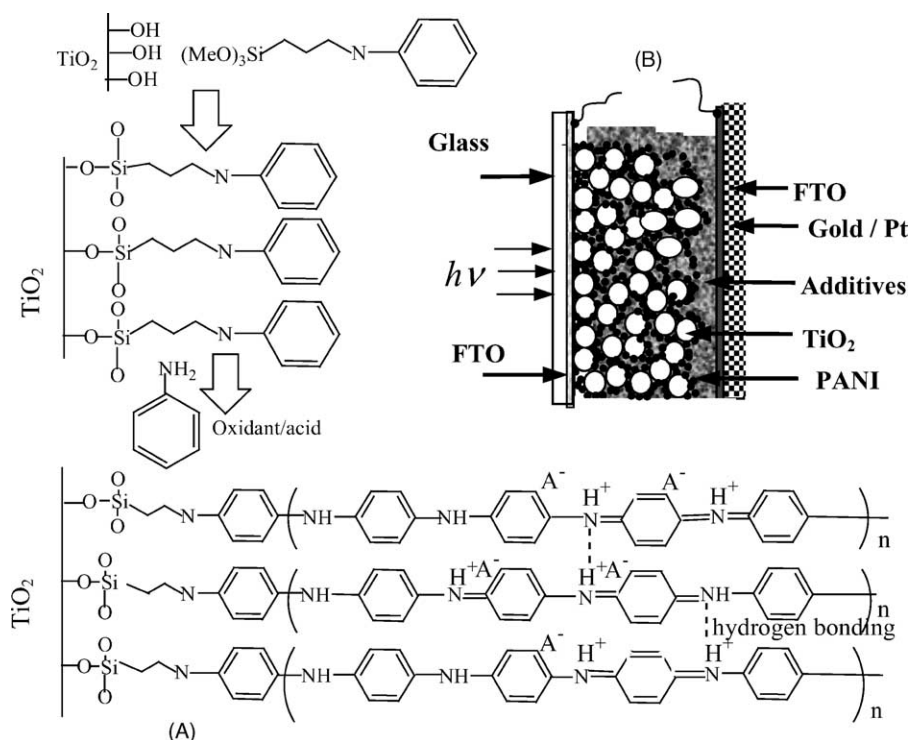


Fig. 1. (A) Schematic illustration for the preparation of PANI grafted on TiO_2 . (B) Construction of the cell n- TiO_2 /PANI/Au or Pt.

in a 50 ml of 1 M HCl aqueous solution containing aniline monomer (0.37 g). A solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was then added with keeping a mole ratio of aniline to $(\text{NH}_4)_2\text{S}_2\text{O}_8$ at 1:1. Polymerisation was carried out for 3 min and films were washed with 1-methyl-2-pyrrolidinone (NMP) to remove the physically absorbed PANI chains, followed by rinsing with ethanol and dried with a dry airflow. PANI grafted films were then immersed in aqueous 0.01 M HCl solutions for 1 min and washed with ethanol and dried in a glove box filled with N_2 . The prepared PANI films were p-type with green colour and thus a n-TiO₂/p-PANI heterojunction could be formed.

2.4. Characterisation of electrodes

The X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI ESCA 5700 spectrometer with monochromated Al K α radiation (1486.6 eV). The samples were placed on a standard sample holder and the spectra were recorded at take-off angle of 45° with respect to the surface of the sample. All binding energies were referred to the C 1s peak of an adventitious contamination hydrocarbon at 285.0 eV. The optical absorption spectrum of the polymer was recorded on a JASCO (V-570) UV-Vis-NIR spectrophotometer. IR measurements of bare TiO₂ and SAM modified TiO₂ in the range from 5000 to 500 cm⁻¹ were performed using a Perkin-Elmer system 2000 FT-IR spectrometer.

2.5. Solar cell fabrication and characterisation

Photocells were constructed as depicted in Fig. 1(B), by sandwiching a gold-coated FTO glass and TiO₂/SAM-PANI electrodes (cell area ~ 0.25 cm²). Photo-energy conversion efficiency was evaluated using standard solar irradiation of 100 mW cm⁻² (AM1.5) with a solar simulator (YSS-50A, Yamashita Denso) and a computer controlled voltage current sourcemeter (R6246, Advantest) at 25 °C. The effectiveness of the cell to convert light of various wavelengths into electrical current was measured as the incident photon to current conversion efficiency (IPCE) defined as the number of electrons generated by light per number of photons incident on the cell, formulated by $\text{IPCE}\% = 1240 J_{\text{sc}}/\lambda W_i$, where J_{sc} is the short circuit current density ($\mu\text{A cm}^{-2}$), λ the excitation wavelength (nm) and W_i the photon flux (W m^{-2}) [14] using a commercial setup for IPCE measurements (PV-25DYE, JASCO).

3. Results and discussion

3.1. PANI on TiO₂

Fig. 2 shows the IR spectra of (a) SAM and TiO₂ before (b) and after (c) the treatments of SAM. Chemical anchoring of SAM onto TiO₂ surfaces can be identified by the

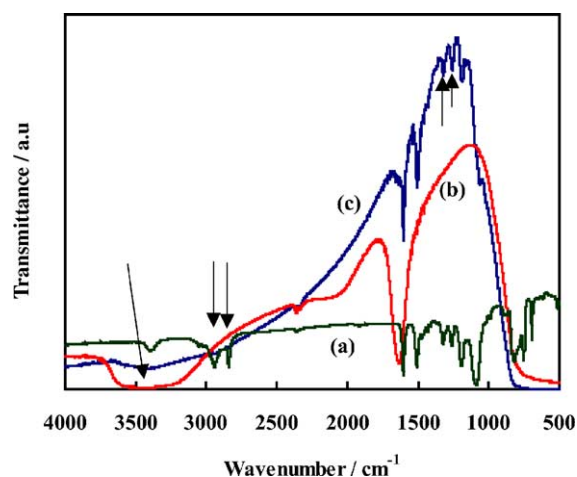


Fig. 2. (a) IR spectra of (a) $\text{C}_6\text{H}_5\text{NHC}_3\text{H}_6\text{Si}(\text{OMe})_3$ (SAM) and TiO₂ (b) before and (c) after the surface modification by SAM.

disappearance of bands assigned to the various functional groups as follows. Complete disappearance of the peaks at 2837 and 2933 cm⁻¹ in the SAM/TiO₂ shows splitting of methoxy groups during grafting processes. In addition to that disappearance of the broad band at 3440 cm⁻¹ in the SAM treated TiO₂, which is assigned to the stretching vibrations of OH groups in the untreated TiO₂ also an indication for this grafting. Further, the appearance of new bands (d (CH₂) 1500, 1316 cm⁻¹) in the spectra of the SAM treated TiO₂ are also an indication for this attachment. These bands correspond to the SAM molecules adsorbed on the TiO₂ surface. Fig. 3 shows the wide scan XPS spectra of silane modified TiO₂. In analogous to previous workers, [15,16] appearing of weak N 1s peak at binding energy of 399.2 eV which is close to the bonding energy of nitrogen in the amine site of emeraldine base of aniline accounts for this grafting. Similar observations were reported by Wu and Chen [16] who confirmed the chemical deposition of polyaniline on SAM modified surface on SiO₂.

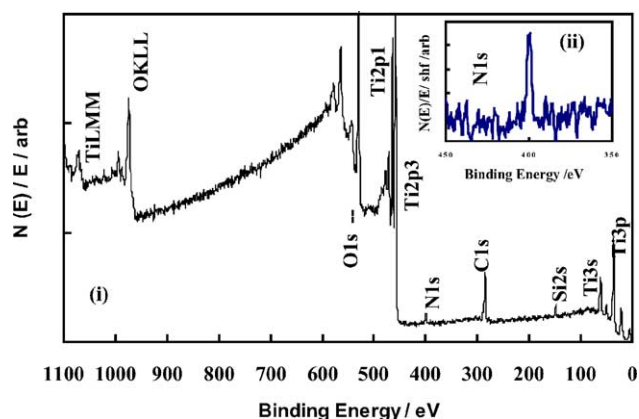


Fig. 3. (a) XPS wide scan spectra of TiO₂ substrate with monolayer of silane and (b) enlargement of part of the spectra.

3.2. Solar cell performances

The (from seven samples) average I - V characteristics of the junction $\text{TiO}_2/\text{PANI}/\text{Au}$ are shown in Fig. 4 (i) in the presence and (ii) absence of light illumination. The curves (a) and (b) show the photoresponses of $\text{TiO}_2/\text{PANI}/\text{Au}$ before and after the treatments with EMImTf_2N and LiTf_2N , respectively. The cell $\text{TiO}_2/\text{PANI}/\text{Au}$ delivered a short circuit current density (J_{sc}) of $\sim 150 \mu\text{A cm}^{-2}$ with photovoltage (V_{oc}) $\sim 375 \text{ mV}$ (FF = 0.38, η = 0.02%). Dramatic increment in photoresponses of this cell was observed with the treatments of EMImTf_2N and LiTf_2N . The corresponding values of the treated cell were $J_{\text{sc}} \sim 325 \mu\text{A cm}^{-2}$, $V_{\text{oc}} \sim 516 \text{ mV}$ with improved fill factor FF = 0.42 (η = 0.07%). One of the reasons for this enhancement is attributed to the reduction of charge recombination due to the surface modification by these additives [17,20]. However, application of graphite (Sri Lanka) on the PANI surface increases the J_{sc} to $\sim 380 \mu\text{A cm}^{-2}$, with slight decrease in V_{oc} ($\sim 460 \text{ mV}$) as well (curve c). The fill factor and the efficiency were 0.43 and 0.08%, respectively. Application of graphite might have reduced the resistance at PANI/Au interface [21], but partially short-circuited the cell, resulting low photovoltage. It should be worth mentioning that in all those cases both the Pt- and Au-coated counter electrodes were used and tested cell performances and better performances were observed with Au-coated counter electrodes. The higher conductivity of the Au-coated counter electrodes than the Pt counter part might be one of the reasons for this better performances.

In order to further see, the sensitizing behaviour of the PANI in the DSCs TiO_2/PANI electrodes were sandwiched with Pt-coated counter electrodes and introduced a drop (14 μl) of 1-methyl-3-*n*-hexylimidazolium iodide (MHImI) (from a 0.6 M solution in acetonitrile), dried with hot stream of air and tested their photovoltaic performances

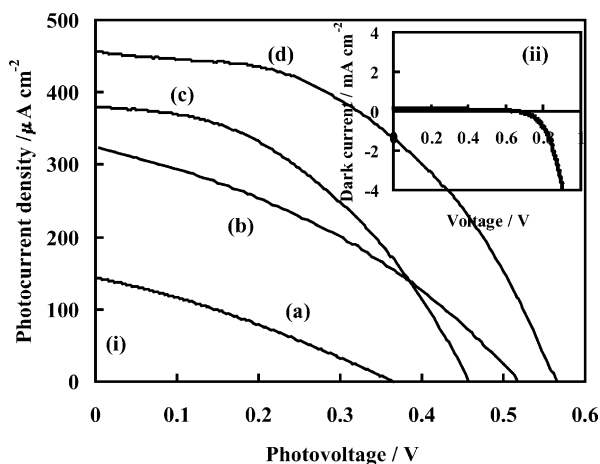


Fig. 4. I - V characteristics for the TiO_2/PANI cell (i) under the illumination of 100 mW cm^{-2} at 1.5 air mass. (a) $\text{TiO}_2/\text{PANI}/\text{Au}$, (b) TiO_2/PANI with EMImTf_2N and $\text{LiTf}_2\text{N}/\text{Au}$ (c) TiO_2/PANI with EMImTf_2N and $\text{LiTf}_2\text{N}/\text{C}/\text{Au}$ (d) TiO_2/PANI with MHImI/Pt and (ii) TiO_2/PANI with EMImTf_2N and $\text{LiTf}_2\text{N}/\text{C}/\text{Au}$ in dark.

(curve d). The cell $\text{TiO}_2/\text{PANI}/\text{MHImI}/\text{Pt}$ delivered a $J_{\text{sc}} \sim 450 \mu\text{A cm}^{-2}$, with an open circuit voltage of $\sim 565 \text{ mV}$ with $\sim 0.12\%$ efficiency (FF = 0.47). The reason for this improvement may be due to the formation of redox couple (I_3^-/I^-) from the MHImI in the presence of acidity of the PANI film. Therefore, the cell must be working as a typical dye-sensitized cell with very small amount of I^-/I_3^- redox electrolytes. Together with dark, as shown in the Fig. 4(ii), and light J - V characteristics (i), these devices behave like a diode showing excellent junction properties. These results are comparable or some times better than reported values where the polymers were employed as either a photosensitizer or a holeconductor or both [3,17,21–24]. In order to further confirm the advantage of this grafting, a separate experiment was carried out depositing PANI on unmodified TiO_2 and fabricated the cells as in the previous case. No or very poor photocurrent ($J_{\text{sc}} < 10 \mu\text{A cm}^{-2}$) was observed as reported elsewhere [24]. Therefore, it is evident that grafting of PANI on surface-modified TiO_2 could work as an efficient sensitizer.

The dependence of the photo current on the light intensity of the $\text{TiO}_2/\text{PANI}/\text{MHImI}/\text{Pt}$ cell is shown in Fig. 5(i). Photocurrent increased linearly with the light intensity, showing the potential use of these cells practically in different environmental conditions. Fig. 5(ii) illustrates (a) the absorption spectra of PANI and (b) TiO_2 and (c) with the action spectrum (IPCE) of the $\text{TiO}_2/\text{PANI}/\text{MHImI}/\text{Pt}$ cell. As depicted in the figure the UV-Vis absorption spectrum of PANI shows an intense absorption at 435 nm. The maximum IPCE obtained at 470 nm was $\sim 2.5\%$ (peak around 350 nm is related with the direct band-gap photo-electron excitation of the TiO_2) giving the IPCE performances mainly in the 400–450 nm range. Therefore, the photocurrent action spectrum resembled well with the absorption spectrum of PANI indicating that photocurrent is generated

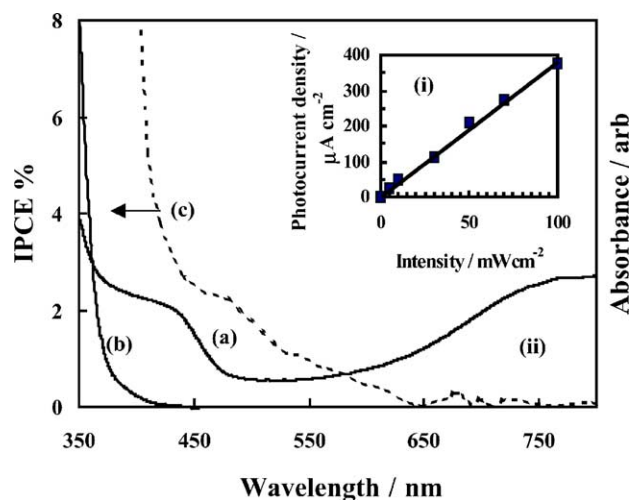


Fig. 5. (i) Incident light intensity dependence of the cell $\text{TiO}_2/\text{PANI}/\text{MHImI}/\text{Pt}$ and (ii) Optical absorption spectra of (a) PANI and (b) TiO_2 and (c) photocurrent action spectrum (incident photon conversion efficiency, IPCE) of the cell $\text{TiO}_2/\text{PANI}/\text{MHImI}/\text{Pt}$.

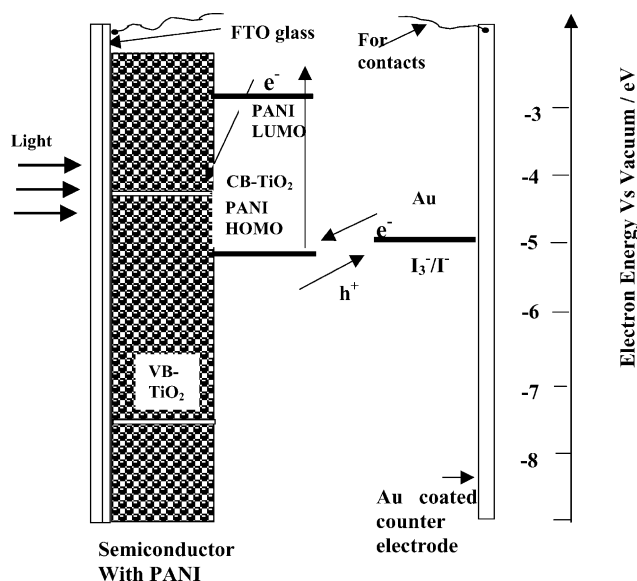


Fig. 6. Schematic energy band diagram of the TiO_2 and energy levels of the ground and the excited levels of the PANI.

by the electron injection from the excited PANI molecules into the conduction band of the TiO_2 phase. Further, as generally observed in the dye-sensitized solar cells, the red shift of the action spectra with the optical absorption spectrum is an indication for the chemical attachment of the polymer to the semiconductor. The no photocurrent at the longer wavelength than 650 nm might be due to the low electronic potential of the excited electrons.

The phenomenon of the photoinduced rectification in TiO_2 /PANI electrodes can be explained using a schematic energy diagram as shown in Fig. 6. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of PANI, the work function of gold and the redox potential of the I_3^-/I^- were shown as reported in the literature [22–25]. When the cell is illuminated both TiO_2 and PANI absorb the photons at their interface and efficient charge separation occurs at the interface. Since the conduction band of TiO_2 and the LUMO level of the PANI are compatible for the charge transfer, the generated electrons can then be transferred to the conduction band of the TiO_2 . Due to the internal electric field these electrons can then transfer to the other side of the cell via the external circuit giving reasonable efficiency.

4. Conclusion

An organic solvent free heterojunction of n- TiO_2 /p-PANI with enhanced photovoltaic properties could be constructed by chemical polymerisation of aniline followed by covalent grafting via $\text{C}_6\text{H}_5\text{NHC}_3\text{H}_6\text{Si}(\text{OMe})_3$ compound. Further improvement could be obtained by employing another conducting polymer such as derivatives of thiophenes as hole conductor in this system because PANI film can transfer the

holes effectively and rapidly to the counter electrode side when another hole conductor is employed. On the other hand, the application of controlled polymerisation processes such as electrochemical polymerisation of PANI would further enhance the photovoltaic performances of these organic/inorganic hybrid solar cells with no volatile solvents. Therefore, a further improvement of these inorganic/organic hybrid cells remains as future research.

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