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Research Article

Sensitized solar cell on polymer substrates

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Abstract: TiO_2 films with excellent mechanical adhesion were prepared on indium tin oxide (ITO) coated polyethylene naphthalate (PEN) substrates. Optical properties of TiO_2 films were studied. An organic dye 1-(2-hydroxycarbonyl-phenyl)-5-(2-hydroxy-5-sulfophenyl)-3-phenylformazan (zincon) was used as a sensitizer. Photo-effects of solar cell with the configuration of PEN|Pt|I^-|I_3^-|zincon|TiO_2|ITO|PEN were studied.

Keywords: indium tin oxide, polyethylene naphthalate, coaxial pressing, power conversion efficiency, dye-sensitized solar cell, zincon.

INTRODUCTION

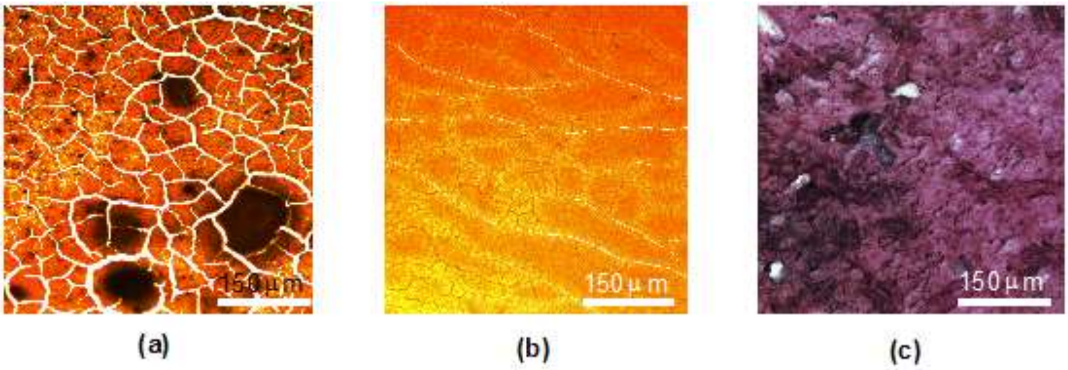
Glass based dye-sensitized solar cell with the efficiency over 10% was fabricated by a Swiss research group [1]. However, rigidness of glass based cells limits their applications in day-to-day life. In this viewpoint, solar cells with polymer or plastic based substrates aroused much attention, due to lightweight and easy usage. The stability of the polymer substrates over 200˚C is identified as one of the major problems compare to glass counterpart. Several attempts have been made to deposit semiconductor thin films on polymer substrates without applying high temperature [2, 3]. Uniaxial pressing is a technique to make semiconductor thin films on polymer substrates [4]. Such pressure-based techniques were able to improve the inter-particle connectivity, as well as the mechanical adhesion of the TiO_2 films on flexible substrate [5]. It would be a challenge to achieve especially uniform large size TiO_2 films with a thickness of 10µm, which is needed for the optimal performance of the cell. In this paper, we discuss the potential of making high quality TiO_2 electrodes on flexible substrates. Morphological and photovoltaic properties of TiO_2 electrodes on indium tin oxide (ITO)-coated PEN substrates were studied.

EXPERIMENTAL

7 g of P-25 TiO_2 powder and 14 ml of ethanol were placed in an agate ball milling jar with different size of agate balls. The mixture was milled with a speed of 250 rpm for 10 hours. TiO_2 slurry was coated on flexible ITO|PEN films (Peccell Technologies, Inc., Japan) with the conductivity of 13 Ωcm^{-2} substrates by either doctor blade or spin coating techniques. TiO_2-coated ITO|PEN substrates were heated at 150˚C for 30 min. TiO_2 coated electrodes were transferred to a polyethylene envelope and sealed under a vacuum of 10^{-1} Torr. Vacuum-sealed electrodes were pressed at room temperature using uniaxial pressing (Yankee hydraulic press, model no. YK20.v3). Morphology of the films was studied through an optical microscope. Transmittance of TiO_2 films was measured from a UV–visible spectroscope (GENESYS 10S, UV Visible scanner). An organic dye zincon, (Tokyo Chemical Industry, Japan) was used as the sensitizer and was coated on TiO_2 electrodes by immersion in acetonitrile solution at room temperature, where the dye concentration was maintained at 0.1 mM. Dye-coated electrodes were then washed in acetonitrile and dried in flowing nitrogen gas. FTIR spectra of dyed samples were obtained from a FTIR spectrophotometer (Jasco 4100) equipped with an attenuated total reflectance (ATR) unit. Dye-sensitized solar cell devices were fabricated by attaching a Pt|ITO|PEN to the dye-coated TiO_2|ITO|PEN electrode. The electrolyte that was composed of 0.04M I_2, 0.4M 4tert-butylpyridine, 0.4M lithium iodide, 0.3M N-methylbenzimidazole in acetonitrile and 3-methoxypropionitrile by volume 1:1 was filled in between the electrodes by the capillary action. Current–voltage characteristics of cells with the configuration of Pt|electrolyte|zincon|TiO_2 were studied under irradiation of white light (100mWcm^{-2}) by using an Oriel solar simulator system. The interfacial electrical properties of cells were investigated by applying -0.6V on the working electrode under a two-electrode configuration with the same electrolyte using

a multi-channel potentiostat (Princeton Applied Research, Oak Ridge, TN, USA) coupled with a computer. The charge transfer resistance at the electrolyte–electrode interface was evaluated from EC lab software (Bio-Logic, Claix, France).

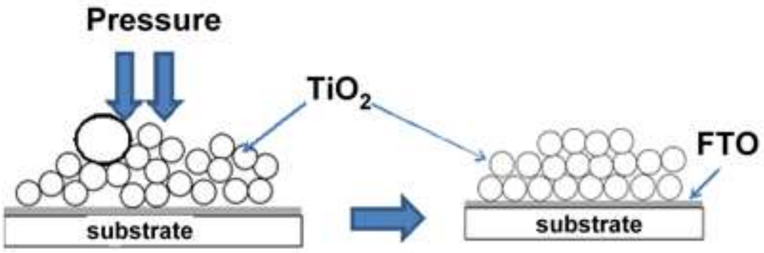
RESULTS AND DISCUSSION



(a) (b) (c)

Fig-: Morphology of a TiO_2 films prepared by using (a) non-milled (b) milled slurry and (c) after pressing

Figure 1 illustrates the morphology of TiO_2 films prepared by using (a) non-milled and (b) milled slurry. As is observed, the TiO_2 films prepared by using non-milled slurry exhibited a high level of cracking on the TiO_2 films. These cracks are essentially formed during air drying process due to the absence of binders in the TiO_2 slurry. Wider cracks are observed around agglomerates [black spots on the image Fig. 1(a)] compared to other region of the film. These wider cracks are formed due to the high stress around agglomerates on drying. The degree of such macroscopic cracks was found to be highly dependent on the thickness of the TiO_2 layer. No larger agglomerates and fewer cracks were observed on the TiO_2 films prepared by using milled slurries [Fig. 1(b)]. These samples were subjected co-axial pressing. Crack free compact film with an improvement of transparency were observed after pressing. Surface morphology of such a film is shown as image c in Fig. 1. De-aggregation of P-25 powder during the pressure process and there by minimization of scattering effect is the most likely explanation for increasing of transparency of the film.



Scheme-1: Application of pressure on TiO_2 films

Scheme 1 represents effect of pressing on TiO_2 films. During the process of pressing friction is applied on TiO_2 grains. The friction between TiO_2 nanoparticles converts to thermal energy thus increasing the temperature in the film. There by an interconnected network of TiO_2 grains was observed. Formation an interconnected network of TiO_2 nanoparticles has been observed previously as a result of applying pressure [5].

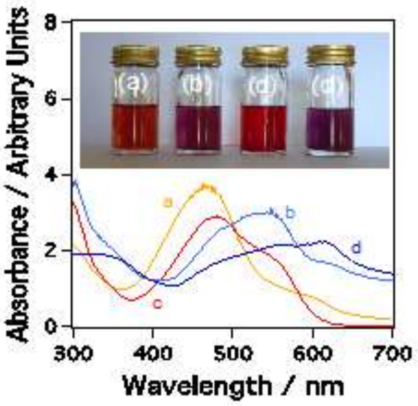


Fig-2: Absorption spectra for zincon in (a) water, (b) acetonitrile (c) 1: 1 mixture of water and acetonitrile and (d) ethyl acetate

Absorption spectra of zincon in different solutions (a) water (b) acetonitrile (c) 1: 1 mixture of water and acetonitrile and (d) ethyl acetate are shown, in Fig. 2. Two major electron transitions were observed at 472 and 600 nm for zincon in water. However, a significant red shift in the absorption spectrum with three different electron transitions correlated at 487, 540 and 628 nm were observed in acetonitrile. Two major electron transitions were observed at 472 and 600 nm for zincon in 1:1 mixture of water and acetonitrile. Three predominant electron transitions were observed at 480, 565 and 620 nm for zincon in ethyl acetate. It is known that dye molecules behave in different manner in different environments, probably due to enforcement of Van der Waals interaction between dye molecules and solvents depending on their polarity [6]. The absorption spectrum seems to be shifted toward the shorter wavelengths with increasing the polarity of the solvent.

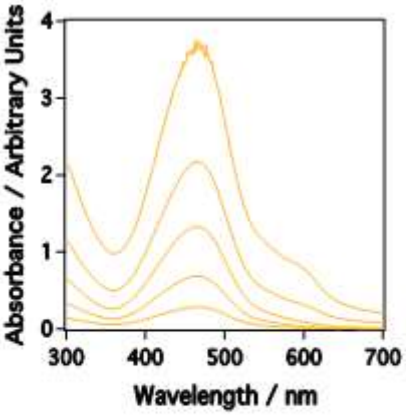


Fig-3: Diluting effect of zincon (water was used as solvent)

In additional, we have measured the absorption spectra by diluting each and every stock solution by respective solvent. A shift of absorption maximum was not observed by diluting them by respective solvents. For an example diluting effect of zincon in water is shown as Fig. 3. This result indicates zincon dye behave as a monomer in respective solutions.

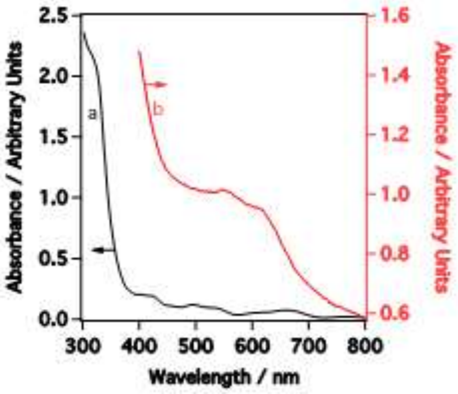


Fig-4: Absorption spectra of (a) bare and (b) dye coated TiO_2 films

TiO_2 electrodes were kept immersed in zincon in (a) water, (b) acetonitrile (c) 1: 1 mixture of water and acetonitrile and (d) ethyl acetate and absorption of dyed TiO_2 films were separately measured. Even though zincon dye behaves as different manner in different solutions, almost similar properties were observed in absorption spectra for dyed TiO_2 films. Absorption spectra of (a) bare and (b) dye coated TiO_2 films are shown in Fig. 4. As is shown in this figure, the onset of absorption of dyed TiO_2 film is extended to 720 nm due to chelation of zincon dye with metal centers [7].

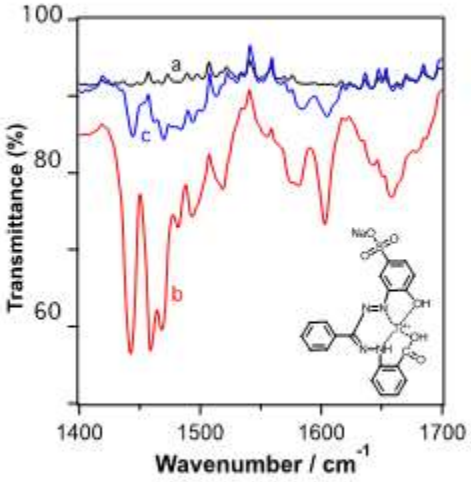


Fig-5: FTIR spectra for (a) TiO_2, (b) zincon dye (c) zincon coated TiO_2 powder. Inset shows the mechanism of chelation of zincon with TiO_2

We have performed FTIR spectroscopy for (a) TiO_2, (b) zincon dye (c) zincon coated TiO_2 powder. FTIR spectra for (a) TiO_2, (b) zincon dye (c) zincon coated TiO_2 powder within the wavenumber region from 1400 to 1700 cm^{-1} are shown in Fig. 5. Significantly enhanced peaks were observed for pure zincon powder samples. However, peaks with moderate intensities were observed for dye coated TiO_2 film most probably due to low concentration of dye on TiO_2 powder. The peak at $\nu = 1666$ cm^{-1} in curve b is correlated with COOH group. This peak has completely disappeared after chelation of dye with TiO_2. Thus indicating enrolment of bonding of COOH group with TiO_2 film. The mechanism of chelation has been proposed elsewhere [7].

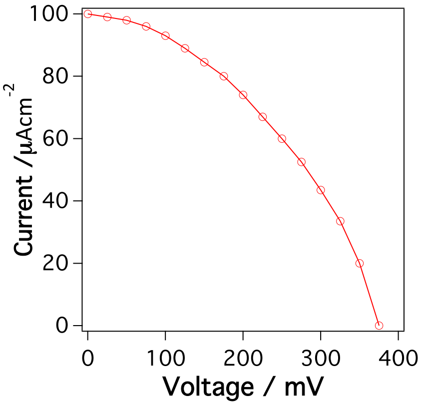


Fig-6: I–V characteristics of the cell under light illumination.

To the best of our knowledge zincon dye has not been used as a sensitizer in plastic based solar cells so far. Figure 6 shows I–V characteristics of the cell under light illumination. The maximum power conversion efficiency of is measured and to be 0.3% with short circuit current (J_{sc}) of 100 µAcm^{-2}, open circuit voltage (V_{oc}) of 372 mV and a fill factor of 46% under 1 sun. These cell parameters are significantly enhanced to that of the composed with un-pressed samples. The maximum power conversion efficiency of 0.1% with J_{sc} of 100 µAcm^{-2}, V_{oc} = 266 mV and a fill factor of 33 % were observed for the cell composed with un-pressed electrode with similar conditions. There has been a noticeable increment in the V_{oc} after applying pressure processed on the films. This could be due to the reduced charge recombination of the cell resulting from the better connectivity of TiO_2 particles due to the compaction of the titania film. However, obtained photo-performances are rather poor with respect to previously reported values by one of the authors of this paper PMS [8]. This effect may be due to un-appropriate HOMO and LUMO levels of dye with band structure of TiO_2. A gradual decrement of photocurrent was observed with increasing pressure by applying over 200 MPa. This may be due to damage of ITO layer on PEN film due to the high pressure. We have also measured the variation of photocurrent of with the light intensity and a liner variation of photocurrent was observed (not shown in the text). A linear variation of photocurrent indicates monophotonic process of the dye-sensitized electrodes. Such monophotonic process also demonstrates the better inter-particle connectivity of the TiO_2 film.

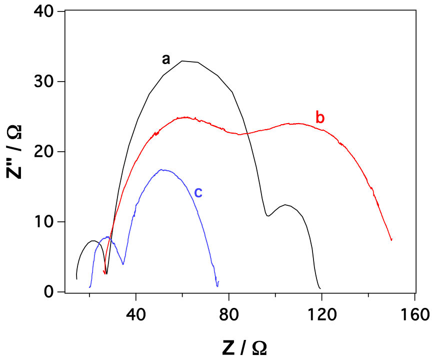


Fig-7: Impedance spectrum for the solar cell cells (a) conventional glass based cell, (b) plastic based without pressing and (c) plastic based with pressing

Internal resistance of the TiO_2 film and the back interface of pressed TiO_2 films were studied using electrical impedance spectroscopy. A typical Nyquist diagram for glass-based counterpart features three semicircles in the order of increasing frequency (curve a, Fig. 7) and is attributed to the diffusion within the electrolyte, the electron transfer at the oxide/electrolyte interface and the redox reaction at the platinum counter electrode [9]. The intercept with the real axis at high-frequency range corresponds to the contact resistance between the TiO_2 film and the transparent conducting oxide coating on the substrate or the ohmic resistance of the cell [9]. Impedance spectra obtained for TiO_2|PEN electrodes exhibited two distinct semicircles in the impedance spectroscopy. The Nyquist diagrams for TiO_2 electrode with (b) un-pressed and (c) pressed electrodes are shown in Fig.7. The semicircle corresponding to the high range of frequencies (the left semicircle, with diameter R_1) and the middle range of frequencies (the right semicircle, diameter R_2) represent the redox reaction at the platinum counter electrode and the electron transfer at the oxide/electrolyte interface within the TiO_2 network, respectively. The reduction of the R_1 and R_2 values with increasing pressure illustrates that the efficient charge transfer process in the relevant interfaces due to better contact after pressure process. Similar properties have been observed by increasing calcinations temperature of TiO_2 electrodes by Hoshikawa *et al.* [10].

CONCLUSIONS

A method was developed for the preparation of highly flexible dye sensitized solar cells at room temperature on polymer substrates. This technique does not require any additives such as organic binders, inter-particle connecting agents in the TiO_2 slurry or any high temperature sintering to form necking between particles. Flexibility, higher mechanical stability and better electrical connectivity of the film are the most important characteristics of the electrodes.

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