RESEARCH ARTICLE

USAGE OF MIXTURE OF JACKFRUIT LATEX AND ACTIVATED CHARCOAL POWDER AS THE COUNTER ELECTRODE IN PHOTO-ELECTROCHEMICAL CELLS

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Abstract

The counter electrode plays major role in achieving of maximum performance in dye-sensitized solar cells (DSSCs). A mixture of jackfruit latex and activated charcoal is used for the first time in DSSCs as counter electrode material. Maximum short-circuit photo-performances of 3.2 mACm⁻² was achieved for the TiO₂|mercurochrome|(I_/I₃-) solar cells at optimal amount of binder percentage of 15% of jackfruit latex, under AM 1.5 conditions.

Introduction:

Dye sensitized solar cells (DSSCs) have aroused much attention due to its lower fabrication cost. The cell fabricated from sensitized nanoporous TiO₂ by Gratzel and co-workers is the breakthrough in this field (¹). Such a cell composed with counter electrode, photoanode, redox electrolyte, and sensitizer. Counter electrode is one of most important components, since it gathers and transfer electrons from outer circuit. Platinum-coated FTO is the most commonly used counter electrode in DSSCs, due to its higher electro-catalytic action towards the iodide/tri iodide redox reaction and corrosion resistant to liquid electrolytes (²). The performance and cost of DSSCs directly depend on the materials which used to fabricate counter electrode. Several attempts have been carried out to replace platinum counter electrode due to, higher fabrication cost. Activated carbon has been identified as a counter electrode material in DSSCs (³). A binder should mix with activated carbon, in order to fabricate counter electrodes. Thus, there was a high demand in research to find a suitable binder for activated carbon-based electrodes. Jackfruit (Artocarpus heterophyllus) latex is a natural source of binder with several interest physical properties (⁴). Current research has proposed to fabricate counter electrode by using jackfruit latex as the binder for activated charcoal counter electrodes. The photo-performance of the novel counter electrode compared with that of solar cell prepared by binder polyvinyl butyral. The photo-performances of DSSCs those contain carbon and jackfruit latex counter electrodes with mercurochrome as the dye has never been reported so far. Performances of TiO₂|Mecurochrome|electrolyte solar cells were studied. Further, photo-properties of counter electrodes with different ratios of jackfruit latex with activated charcoal were studied.

Methodology:

Deposition of compact TiO₂ layer on conducting glass plates

Fluorine doped tin oxide coated conducting(FTO)glass plates were cut into 1x2.5 cm² pieces, cleaned by detergent, thoroughly washed with distilled water and dried in an oven. One of the edges of FTO (1x1cm²) was covered with...
an aluminium foil and placed horizontally on a hotplate facing the conducting side to air. Temperature of the hotplate was gradually increased to 450 °C. A solution of titaniumdiisopropoxidebis(acetylacetonate) 75wt% in isopropanol (1:9) was sprayed over the FTO quickly at the thermal equilibrium at 450°C and allowed to reach to room temperature by disconnecting power of the hotplate.

**Deposition of mesoporous TiO₂ layer on compact TiO₂ layer**

Titanium tetraisopropoxide (8 ml), 1 ml of glacial acetic acid were mixed with 8 ml of absolute ethanol and steam was passed through the solution. Obtained transparent crystals were mixed with 20 ml of distilled water and were autoclaved for 3 h at 150°C. 20 ml of above solution was mixed with 5.5 ml of glacial acetic acid, 5 drops of triton X-100 and 20 ml of absolute ethanol. The resulting solution was used as the stock solution. Stock was sprayed on top of compact TiO₂ coated FTO glass plates (1×2.5) at 150°C by a spray gun, allowed to dry for few minutes. TiO₂ coated plates were sintered at 500°C for 30 min.

**Dye coating on TiO₂ electrodes**

Mercurochrome was used as the sensitizer, and was dissolved in methanol until concentration reaches to ~10⁻⁵ M. TiO₂ coated FTO glass plates were kept immersed in the mercurochrome solution and temperature of the solution was maintained as 40 °C. Dye coating procedure was carried out in an oil bath.

**Purification of jackfruit latex**

Jacklatex was extracted from ripe jackfruits. Jack latex was dried until get a constant mass, at room temperature. 1 g of dried jackfruit latex was dissolved in 30 ml of absolute ethanol and solution was filtered. The filtrate was dissolved in 70 ml of NaCl (0.4/70 g ml⁻¹). The solution was kept under the room temperature for 12 hours. Deposited jack latex was obtained. Pure jack latex was washed with distilled water and dried under the room temperature until get a constant mass.

**Preparation of activated charcoal**

Coconut shells were cleaned by removing the outer fibers and burned in a closed container. The charcoal produced was dried at 100 °C after washing with distilled water. Burnt coconut shell charcoal was break into small particles, kept in abox furnace at 900°C for 20 minutes and suddenly quenched in water. This quenching process was repeated for ten times and disk milled the activated coconut shell particles for 40 seconds.

**Fabrication of counter electrode by doctor blading method.**

Different amounts of dried jackfruit latex (10 x 10⁻³, 15 x 10⁻³, 20 x 10⁻³ g) were dissolved in 1ml of 2-propanol, each and were mixed with (90 x 10⁻³, 85 x 10⁻³, 80 x 10⁻³ g) of activated charcoal powder respectively. Total mass of the sample was maintained 1 g. Small amount of above mixture was coated on pre heated (120 °C) FTO glass plates by doctor blading method. The commercially available binder polyvinyl butyral(PVB) was used as the reference. Same procedure was repeated by using 0.015 g of PVB and 0.085 g of actvatedcharcoal.

**Assembling of the cell**

Prepared counter electrodes were kept on the dyed TiO₂ film and sandwiched by using alligator clips. The space between the working electrode and the counter electrode was filled by using I/I₃ electrolyte.

**Measurements:-**

IR absorption spectra for dried jackfruit latex was measured using Fourier transform instrument (Thermo scientific, Nicolet IS50FTIR). XRD of activated charcoal powder was obtained by using RigakuUltima IV X-ray diffractometer. Absorption spectra of dye coated TiO₂ plates and mercurochrome dye solutions in different solvents (a) methanol, (b) acetonitrile and (c) water were obtained by using UV-VIS spectrometer (Shimadzu UV-2450). Effect of pH with the absorption of mercurochrome dye was measured. Current-Voltage characteristics of the solar cell were obtained with a solar simulator (LED solar simulator, SPD SS-25, SPD Laboratory, INC. Japan), under 1.5 AM condition. Scan speed was maintained as 0.01 Vmin⁻¹. IPCE curves for solar cells with fabricated counter electrode were obtained as a function of wavelength by using Bentham PVE 300 photovoltaic characterization. EISmeasurement was obtained for DSSCs fabricated with jackfruit latex and activated charcoal electrode by using metrohm, autolab B.V.
Results and Discussion:

FTIR spectrum of jackfruit latex is shown in Fig. 1. Existences of different functional groups are identified in the FTIR spectrum. The FTIR band features at 834 cm$^{-1}$ and 1665 cm$^{-1}$, are accredited for C-H bending and C=C stretching respectively (5). The peaks in the range of 3000-2000 cm$^{-1}$ are due to the C-H stretching vibrations. Two peaks at 1450, 1376 cm$^{-1}$ are due to the C-H deformation of CH$_2$ and CH$_3$ correspondingly. The peaks at 3410 cm$^{-1}$ and 1711 cm$^{-1}$ are due to the O-H group and carbonyl group respectively (6). However, FTIR information given by SambhuBhadra et al. is slightly different than the FTIR data in present research work due to chemical constituent of jackfruit latex can be different according to the area (6).

Fig. 2 illustrates the XRD of activated charcoal powder. According to the Fig. 2, broad diffraction peaks and the nonexistence of a sharp peak reveals the poor crystallinity of activated charcoal. Two broad diffraction peaks can be observed near $2\theta = 23.2^\circ$ and $2\theta = 43.6^\circ$, corresponding to the diffraction of (002) and (100), respectively (7, 8).
A higher degree of solubility of mercurochrome was observed in water, methanol and acetonitrile. Absorption properties of mercurochrome in (a) water (b) methanol and (c) acetonitrile are shown in Fig 3. A shift of the maximum absorption towards the longer wavelengths (red shift) was detected for mercurochrome in acetonitrile and methanol compare to that of water. Red shift generally occurs due to the polarity change of solvents (9). Methanol was used as the solvent for further studies.

Absorption spectrum of mercurochrome in (a) methanol with natural (b) acidic (c) basic is shown in Fig. 4. Addition of few amount of acid to mercurochrome dye reduces the absorption by several fractions (hypochromic shift). However, an enhancement (hyperchromic shift) of absorption was observed with few drops of base compared to that of dye in methanol.
Fig 5: Absorption spectrum of (a) mercurochrome in methanol (b) mercurochrome coated TiO$_2$

Absorption spectrum of (a) mercurochrome in methanol (b) mercurochrome coated TiO$_2$ are shown in Fig. 5. Mercurochrome is an excellent photosensitizer for DSSCs with nanoporous oxide semiconductor materials. Maximum absorption was observed at 520 nm and a shoulder at 480 nm for mercurochrome in methanol. Generally, xanthene dyes produce such type of peculiar properties. An enhancement of absorption in shorter wavelength was observed for mercurochrome coated TiO$_2$. The enhancement in absorbance in liquid form with respect to solid form is due to the chelation of mercurochrome dimers with TiO$_2$. The absorption peak became broader for mercurochrome coated TiO$_2$ films than that of in methanol when the dye chelates with TiO$_2$ substrate. The energy levels of HOMO and LUMO of mercurochrome in methanol changes, because of that beginning of absorption is shifted from 541 to 585 nm (Fig. 5).

Fig 6: IPCE of DSSC fabricated with Jack latex as the binder for activated charcoal counter electrode.

Fig. 6 shows the IPCE of DSSCs fabricated with Jack-fruit latex as the binder of activated charcoal counter electrode. Fabricated DSSCs with carbon electrode with jack fruit latex convert visible light effectively in the range of 381 to 609 nm. The maximum IPCE of 50% was observed at 510 nm for TiO$_2$|mercurochrome|electrolyte (I$^-$/I$_3^-$) solar cell with prepared counter electrode. Efficient IPCE% confirms that excited mercurochrome has transferred
electrons to conduction band of nanoporous TiO$_2$ effectively and also confirms that the counter electrode has collected electrons from the external circuit efficiently.

| Binder    | Binder Percentage | Voc(mV) | Jsc(mAcm$^{-2}$) | FF  | $\eta$(%) |
|-----------|-------------------|---------|------------------|-----|-----------|
| Jack      | 10                | 494     | 3.18             | 19.2| 0.302     |
| Jack      | 15                | 598     | 3.20             | 49.0| 0.937     |
| Jack      | 20                | 502     | 2.82             | 37.2| 0.528     |
| PVB       | 15                | 583     | 2.92             | 43.6| 0.743     |

**Table 1:** Open circuit voltage ($V_{oc}$), Short circuit current ($I_{sc}$), Fill factor (FF) and the Efficiency ($\eta$) of DSSCs with counter electrodes which contain different ratio of binder (jackfruit latex, PVB) as percentages.

Table 1 illustrates the Open circuit voltage ($V_{oc}$), Short circuit current ($I_{sc}$), Fill factor (FF) and the Efficiency ($\eta$) of DSSCs with counter electrodes which contain different ratio of binder (jackfruit latex, PVB) as percentages. The counter electrode with jackfruit latex binder produces higher performance than PVB binder. As is detected, maximum efficiency occurs when the jackfruit latex binder percentage is 15. Activated charcoal with 10% jackfruit latex binder tends to dissolve in the electrolyte due to the lower amount of binder, and it influence to low performance of DSSCs. When the binder percentage is 15% maximum efficiencies of 0.937, 0.743 obtained for counter electrodes with jackfruit latex and PVB binders respectively.

**Fig. 7:** Nyquist plot of DSSCs with charcoal and jackfruit latex electrode.

In this kind of DSSCs, four interfaces can be identified. These four interfaces are FTO/TiO$_2$, TiO$_2$/dye, dye/electrolyte, and electrolyte/counter electrode. Three semi circles in low-frequency, intermediate-frequency and high-frequency regions can be identified in a typical Nyquist plot. Fig. 7 illustrates the Nyquist plot of DSSCs with charcoal and jackfruit latex electrode. According to figure 7, two semi circles can be recognized in the curve. The first smaller semicircle in the region of higher frequency represents the charge transfer resistance ($R_1$) at the electrolyte/counter electrode interface. The second semi-circle in the region of intermediate-frequency attributed to the charge transfer resistance ($R_2$) of the dye coated TiO$_2$ electrode/electrolyte interface (13). Due to the limited range of frequency engaged in this study, the third semi-circle in the region of low frequency related with Nernst diffusion process in electrolyte has been missing. According to the EIS parameters of the DSSCs with charcoal with jackfruit latex electrode determined by fitting experimental data to the equivalent circuit model is shown in table 2.

| Electrode                      | $R_s$ | $R_1$ | $R_2$ |
|-------------------------------|-------|-------|-------|
| Charcoal with Jackfruit latex | 18    | 6     | 119   |

**Table 2:** EIS parameters of DSSC with activated charcoal and jackfruit latex electrode.
Conclusion:
Jackfruit (Artocarpus heterophyllus) latex was used as a binder of activated charcoal powder to fabricate counter electrode for DSSCs. TiO$_2$|Mercurochrome|electrolyte (I$_{3}$/I$_{1}$) form solar cells with jackfruit latex bonded charcoal counter electrode show higher performance than counter electrodes with PVB and activated charcoal. When the binder percentage is 15% (w/w), maximum short circuit currents of 3.2, 2.9 mA/cm$^2$ were obtained for electrodes with jack fruit latex and PVB binders respectively.

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