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PVA Based Polymer Electrolyte with Layered Filler Graphite for Natural Dye Sensitized Solar Cell**Kumari Pooja Priyanka Chawla Mridula Tripathi***

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ABSTRACT

Graphite nanopowder is synthesized by mechanical method using ball mill and used as filler in polymer electrolyte film based on Polyvinyl alcohol (PVA) for application in natural dye sensitized solar cell (DSSC). In the present work dye sensitized solar cell has been assembled using electrolyte system composed of PVA as host polymer, ethylene carbonate as plasticizer, LiI: I₂ as redox couple and graphite as filler; TiO₂ modified with Copper oxide (CuO) photoanode in order to provide inherent energy barrier and natural cocktail dye as sensitizer. The obtained solar cell conversion efficiency was about 3.2 % with fill factor 52% using an irradiation of 100 mW/cm² at 25° C.

1. Introduction

Dye sensitized solar cells which come under the category of third generation photovoltaics, have appeared as a bewitching and promising low-cost solar cell device with potential power conversion efficiency. Sensitizers, nanocrystalline porous semiconductor based photoanode, electrolyte and counter electrode are the four major components of DSSCs^[1]. The properties of metal oxide, as well as the choice of electrolyte and dye are the major components on which the performance of DSSCs depends. Therefore, the researchers working in the field of DSSCs are focusing their attention on improving one or the other component of DSSCs so that efficiency comparable to silicon based solar cell can be achieved.

The liquid electrolyte which is the most important

component of DSSCs hinders its stability as the electrolyte leaks and vaporizes with time. Thus, scientists are focusing their attention in the solidification of electrolyte such as inorganic or organic hole conductors, ionic liquids, polymer electrolyte^[2-3]. For absolute performance and outstanding efficiency, polymer electrolyte should have high ionic conductivity so that transfer of oxidised and reduced species to respective electrodes can be done efficiently and also it should possess good mechanical strength and film forming properties. In this respect Poly (ethylene) oxide (PVA) has much of such exceptional properties. It has excellent ability to form complexes with the ionic salts. PVA shows good salvation property due to the presence of unpaired electrons on the ether oxygen atoms which lead to good ionic ability^[4]. Thus, in the present work we have

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prepared PVA based polymer electrolyte film for DSSC. In order to make film more amorphous which will aid in fast conduction of ions we added nanoparticle of graphite as filler.

Generally, the beautiful colours of plants are due to the natural pigments such as betacyanin, anthocyanin, carotene, chlorophyll, tannins etc. These natural pigments present in various parts of the plants (fruits, flowers, stem etc) can easily be extracted and then can be used as photosensitizers in dye sensitized solar cells. These natural pigments are low in cost and environmentally safe. The synthesis of these pigments in plants is promoted by light and they appear colourful because they selectively absorb and reflect certain wavelength of visible light. As it is the known fact that white light is a roughly equal mixture of the entire spectrum of visible light with the wavelength range of 400-780 nm. When the light comes in the contact of these pigments then the conjugate bonds present in them absorb the part of the spectrum while other part is reflected or scattered. Like the transition metal compounds these pigments are also charge transfer complexes with broad absorption bands that absorb most of the colours of the incident white light ^[5-6].

The photoanode made up of semiconductor oxide is the heart of DSSCs. Generally, TiO₂ is used as semiconductor oxide for DSSCs due to its vivid properties such as easy synthesis, good stability, low toxicity and wide band gap. But TiO₂ can absorb only 6% of the spectral region which creates hinderers in the performance of DSSCs. In order to overcome this drawback various metal ions as well as Non-metal dopants such as nitrogen, carbon, sulphur, phosphorus etc are used for enhancing the visible light photoactivity of TiO₂ ^[7]. In this direction copper oxide has received considerable interest due to its interesting physical properties such as a superior gas sensing material, potential field emitter, powerful catalytic agent, huge application in optoelectronics and solar cells ^[8].

In the present work we fabricated DSSC with polymer electrolyte system composed of PVA as a host polymer, LiI: I₂ as a redox couple, EC as plasticizer, graphite as filler with cocktail dye and CuO modified TiO₂ photoanode. The properties like short-circuit photocurrent density (J_{sc}), open circuit voltage (V_{oc}), fill factor (ff) conversion efficiency and stability of the fabricated DSSC has been studied.

2. Materials and Methods

All the materials were purchased from sigma Aldrich. For the preparation of dye black grapes and spinach leaves were purchased from local markets.

2.1 Preparation of Polymer Electrolyte

The appropriate amount of PVA along with LiI:I₂ was dissolved in distilled water for the preparation of thin film polymer electrolyte. The prepared solution was stirred for 7 hours with the help of magnetic stirrer for obtaining a homogenous solution. In the above prepared solution plasticizers EC and PC along with 1 weight percent of graphite powder with respect to PVA was added and then it was mixed thoroughly for one night. This graphite powder was synthesized by ball milling process (Retsch PM 100) the raw material was put in planetary ball milling machine for 48 hours at a rotation speed of 300 rpm. Then the final solution was cast in the polypropylene dish and by slow evaporation in ambient temperature followed by vacuum drying, a solvent free polymer electrolyte film was obtained.

2.2 Extraction and Purification of Dyes from Natural Sources

2.2.1 Beetroot (Betacyanin) Dye

Fresh beetroot pieces were washed with deionized water and crushed in mortar and soaked in ethanol for one week. Solutions were filtered out, and filtrates were concentrated in rotavapor at 40°C and the resulting dye solution was used as sensitizers.

2.2.2 Spinach (Chlorophyll) Dye

The spinach leaves were washed thoroughly with deionized water and crushed in mortar and soaked in ethanol for one week. Solutions were filtered out, and filtrates were concentrated in rotavapor at 40°C and the resulting dye solution was used as sensitizers.

2.2.3 Cocktail Dye

The betacyanin dye obtained from beetroot and chlorophyll dye from spinach leaves were blended at volume ratio of 1:1 to serve as natural cocktail dye sensitizer for DSSC. Chromatographic techniques were used for the purification of prepared dye.

2.3 Preparation of TiO₂-CuO Admixed Photoelectrode

TiO₂-CuO based nanoparticle was prepared as per our previous work ^[9]. The cleaned ITO conductive glass plates having a sheet resistance of 18–20 Ω/cm² were used and over these plates prepared TiO₂-CuO nanoparticle paste was applied using doctor blade technique. The resulting film substrate was annealed in oven at 150°C for 10 minutes.

2.4 DSSC Fabrications

For the fabrication of DSSC we immersed the prepared photoelectrode in the prepared dye inside the petridish and left undisturbed for 24 hours and it's was covered to prevent the photo decay of the dye. Then in between the photoanode and photocathode we sandwiched the prepared polymer electrolyte.

3. Results and Discussion

Figure 1 shows the XRD pattern of 99 {80 PVA- 20 LiI: I₂} : 1 graphite film prepared by solution cast technique. The XRD pattern of pure PVA film shows sharp and intense peaks at 19.5 ° and 23.52° respectively whereas for pure graphite film it is at 25°. The peak intensity decreases randomly due to the intermolecular chain reaction resulting in enhancement of the amorphous phase. The amorphous nature of polymer is very important as this allows free ionic transportation which aids in better ionic conductivity.

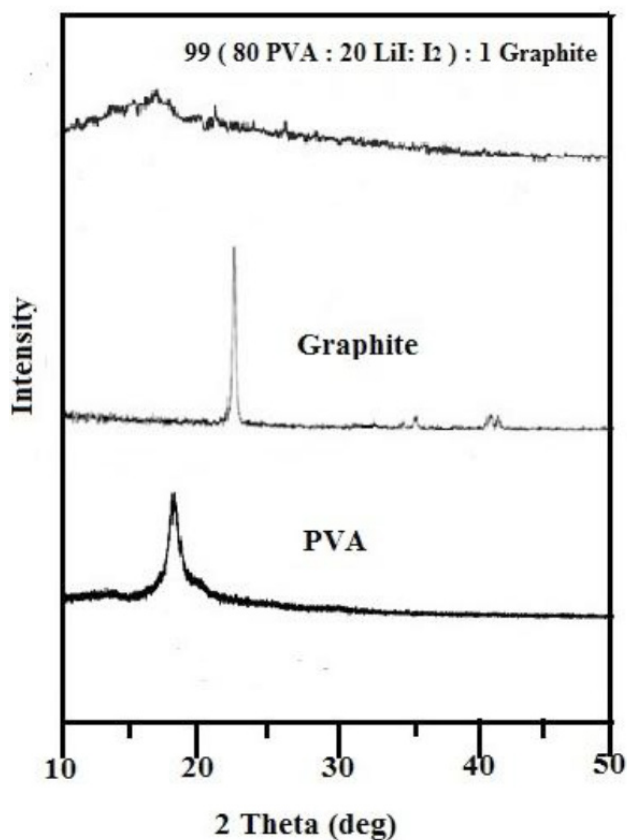


Figure 1. XRD pattern of polymer electrolyte system

The surface morphology of 99 {80 PVA - 20 LiI: I₂} : 1 graphite film prepared by solution cast technique at 80X magnification are shown in Figure 2(a) and (b).

The morphology of the film changed drastically upon the addition of graphite filler. The apparent strings like structure of PVA are not found which can be attributed to the destruction of crystalline structure of PVA resulting in amorphous fractions in the film.

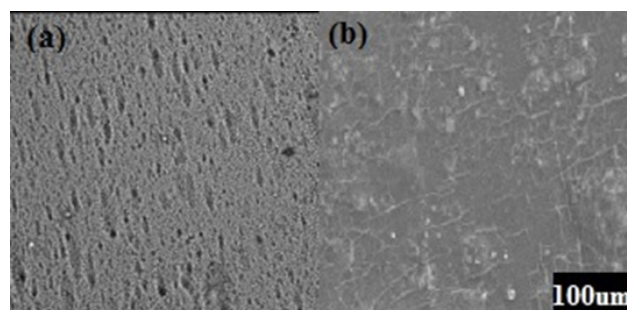


Figure 2. Optical micrograph of the polymer electrolyte film (a) pure PVA (b) 99 {80 PVA- 20 LiI: I₂} : 1 graphite

Figure 3 shows that the ambient ac conductivity of the PVA based polymer electrolyte reaches 10⁻³ S/cm. The conductivity increases linearly up to 5 kHz. The obtained conductivity is very significant to be used as polymer electrolyte for DSSC.

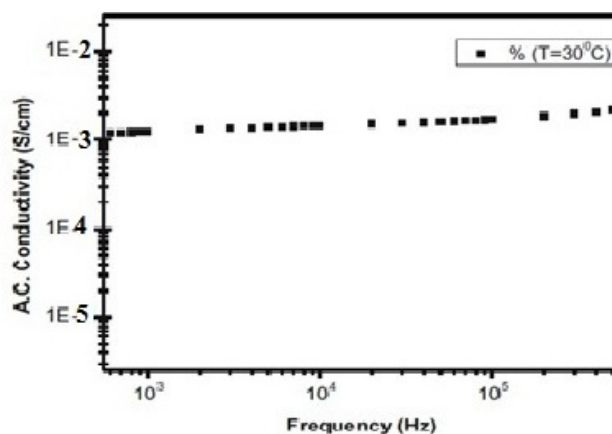


Figure 3. Variation of ac conductivity of the film with frequency

Figure 4 shows the light absorption behavior of betacyanin, chlorophyll and cocktail dye coated TiO₂-CuO photoelectrodes. The pigments betacyanin, chlorophyll and mixture of both dyes show distinctive wavelength due to various sub atomic structure. The wavelength for betacyanin dye was found at 550 nm range while for chlorophyll it was found in the range of 440 nm and the mixture of both dyes a clear enhancement in the wavelength range of about 660 nm. The mixing of dyes produced wider wavelength which will increase the dyes' ability to capture the maximum photons from sunlight and produce a continuous cycle of electrons which will results

in improved performance of DSSCs.

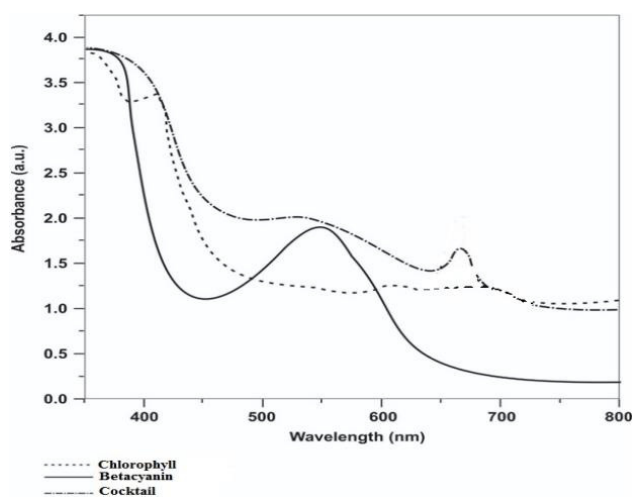


Figure 4. Absorption spectra of Chlorophyll, betacyanin and co-sensitized dye coated TiO₂-CuO photoelectrode on ITO glass substrate

The XRD graph of prepared nanomaterial TiO₂-CuO is of crystalline nature devoid of amorphous phase and it is also clear from the XRD graph that no new nanocomposite material is formed (Figure 5).

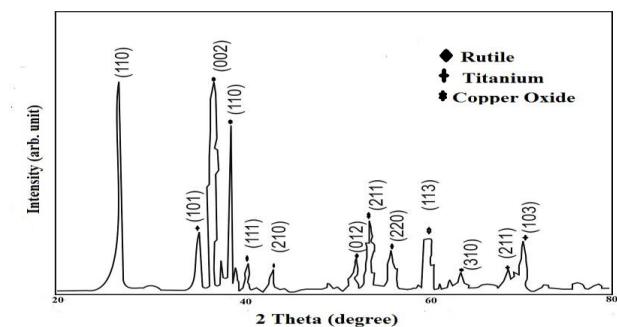


Figure 5. XRD pattern of TiO₂-CuO nanopowder

SEM (scanning electron microscopy) image of the prepared TiO₂-CuO nanomaterial is shown in Figure 6(a) and (b). The small grain size (25-30 nm) absorbs large amount of dye molecules resulting in enhanced efficiency of DSSC.

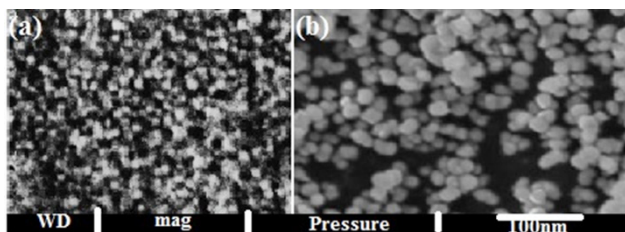


Figure 6. Scanning Electron Micrograph of (a) ns-TiO₂ (b) ns-TiO₂-CuO

The cell performance of the PVA based DSSC with TiO₂-CuO photoelectrode sensitized with cocktail dye is shown in Figure 7. The photocurrent (I_{sc}) was found to be 9.0 mA/cm² and photovoltage (V_{oc}) 0.680 V. The conversion efficiency and fill factor of cocktail dye coated TiO₂-CuO photoanode were found to be 3.2 % and 52 % respectively.

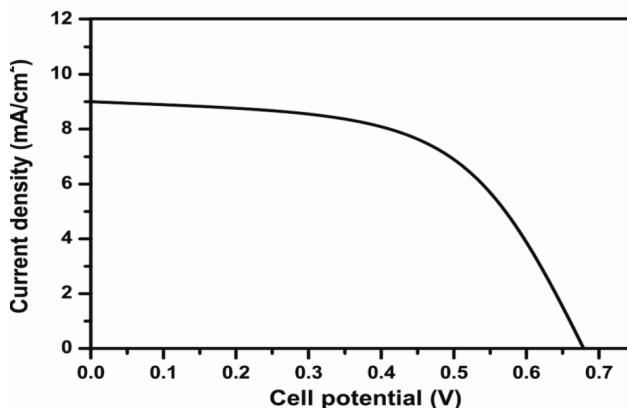


Figure 7. Current-Voltage characteristic curve of cocktail dye coated TiO₂-CuO photoelectrode

4. Conclusions

In the present study, the effect of graphite filler in PVA polymer electrolyte on the performance of DSSC was verified. Ionic conductivity of the prepared polymer electrolyte was investigated by electrochemical impedance spectroscopy which was found in the range of 10-3S/cm. This is due to increase in the amorphous nature of the polymer matrix and increase in the ions mobility in the polymer system. Then the cell performance of the TiO₂-CuO coated DSSC is investigated. CuO is responsible for reducing the recombination rate by providing the inherent energy barrier which results in improved efficiency of the cell. Cocktail dye showed better complexation with TiO₂-CuO surface which aided in better charge transfer between dye molecules and TiO₂-CuO surface. Therefore, this dye provides more efficient incident photon to electron conversion.

Conflict of Interest

No potential conflict of interest was reported by the author

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