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## Utilization of poly[2-methoxy-5-(2-ethyl-hexyloxy)-phenylene vinylene] as a hole-conductor in titania-based photovoltaic cell

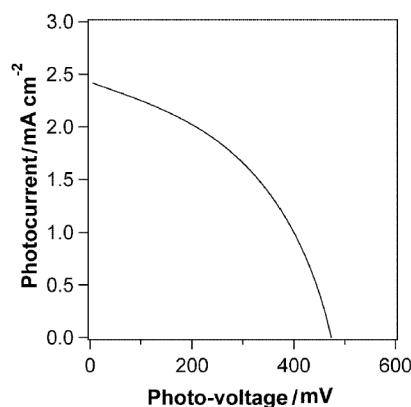
Conjugated polymers have aroused much attention of physicists and chemists all over the world due to their peculiar properties of higher absorption coefficient, luminescence, conductivity and sufficiently fast carrier mobility. For example, poly phenylene vinylene (PPV) and its derivatives exhibit unique absorption band due to electron transitions between  $\pi \rightarrow \pi^*$  bands and emit light in visible wavelengths<sup>1-4</sup>. An efficient separation of excitons is observed in PPV in combination with materials having lower electron affinity<sup>5</sup>. These properties suggest the capability of utilization of PPV and its derivatives in solid-state devices. Recently, dye (or pigment)-sensitized solid-state solar cells have been prepared by replacing the electrolyte of photo-electrochemical (PEC) cells by p-type semiconductors or polymers<sup>6-10</sup>. We have found that poly[2-methoxy-5-(2-ethyl-hexyloxy)-phenylene vinylene] (MEH-PPV) is another suitable candidate to replace the electrolyte of PEC cells due to its sufficiently fast carrier mobility. A photovoltaic cell with a configuration of semiconductor/sensitizer/polymer is fabricated using MEH-PPV as a hole-conductor and our primary observations are discussed.

TiO<sub>2</sub> films with thickness of  $\sim 5 \mu\text{m}$  were prepared by applying a colloidal solution of hydrolysed titanium isopropoxide containing TiO<sub>2</sub> powder (P-25 Degussa, Japan) on preheated conducting glass plates (FTO) as described elsewhere<sup>8</sup>. Dye [*cis*-dithiocyanate-*bis*(2,2'-bipyridyl 4,4'-dicarboxylate) ruthenium (II)] (hereafter abbreviated as N3) was coated on dried TiO<sub>2</sub> electrodes by dipping in a dye solution of  $3 \times 10^{-3} \text{ M}$  (in ethanol at 40°C). Dye-coated TiO<sub>2</sub> electrodes were dried in a hot-air stream followed by washing with ethanol. A thin layer of MEH-PPV was coated on dye/TiO<sub>2</sub> films by a slow solvent evaporation technique as follows: 0.5 mg of MEH-PPV was dissolved in 200 ml of CHCl<sub>3</sub> and used as the stock solution. Dye-coated TiO<sub>2</sub> film was placed at the bottom of the test tube. Next 25 ml of stock solution was added and chloroform was allowed to vapourize under atmospheric conditions in a fume cupboard. MEH-PPV layer with sufficiently enough thickness was obtained by

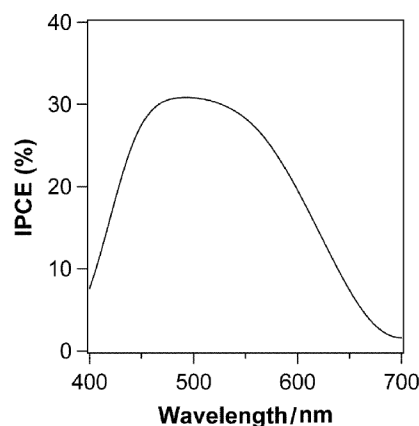
repeating the coating procedure. However, the number of cycles repeated changed with the morphology of titania film. TiO<sub>2</sub>/N3/MEH-PPV electrodes were allowed to dry at room temperature and then a thin layer of graphite was applied on the MEH-PPV layer followed by doping iodine in the polymer film. Iodine was doped by exposing MEH-PPV/N3/TiO<sub>2</sub> electrodes to iodine vapour for 5–10 min. A cleaned FTO electrode was attached to the graphite surface as the back contact of the cell. Photo-properties of solid-state TiO<sub>2</sub>/N3/MEH-PPV/I<sub>2</sub>/graphite cell were studied under illumination of monochromatic and polychromatic light.

A feeble photo-response was observed on solid-state TiO<sub>2</sub>/N3/MEH-PPV cell under illumination. Significant enhancement in photo-voltage (up to 385 mV, under AM 1.5 conditions) as well as conductivity of MEH-PPV film was observed by doping iodine in the polymer film. Iodine accepts electrons from inner bands of the valance band (HOMO level) of the polymer and creates additional holes in the polymer film. Thereby p-type conductivity is increased in the polymer layer, as is proposed in the literature<sup>11,12</sup>. However, the resulting current in the cell was rather poor and had to be further increased. Applying a thin layer of graphite improves the contact between polymer and FTO layers in this type of device<sup>13</sup>. Therefore, a thin layer of graphite was applied on the MEH-PPV layer.

Thereby, significantly enhanced photocurrent was achieved for the cell. Current-voltage characteristics of TiO<sub>2</sub>/N3/MEH-PPV/I<sub>2</sub>/graphite cell are shown in Figure 1. Maximum open circuit photo-voltage of the cell was 475 mV. However, this value is 0.4 of the attainable maximum open-circuit voltage of TiO<sub>2</sub>/N3/MEH-PPV/I<sub>2</sub>/graphite cell, which is approximately determined from the energy difference of the conduction band of TiO<sub>2</sub> and HOMO level of the polymer<sup>14</sup>. Solid-state TiO<sub>2</sub>/N3/MEH-PPV/I<sub>2</sub>/graphite cell exhibited maximum photocurrent of  $2.4 \text{ mA cm}^{-2}$  under AM 1.5 conditions. The overall power conversion efficiency of the cell was 0.8%. It is important to maintain a thickness of the MEH-PPV film not to exceed the excitation diffusion length of MEH-PPV, since this type of cell gives much higher performance when the thickness of the film is equal to the magnitude of diffusion length of the polymer<sup>15</sup>. A drastic decrease in the photocurrent of about 75% was observed in the first 20 s in the absence of MEH-PPV film. This result suggests fast acceptance of photo-generated electrons reached to counter electrode by MEH-PPV than I<sub>3</sub> ions in the polymer layer. Photo-properties of hetero-junctions made of polymer-TiO<sub>2</sub> films or blends have been reported<sup>5,14</sup>. In these studies MEH-PPV has been used as a light-harvesting analogue or hole-conductor itself. However, we have not observed any significant performance in



**Figure 1.** Current-voltage characteristics of solid-state TiO<sub>2</sub>/N3/MEH-PPV/I<sub>2</sub>/graphite cell under illumination of AM 1.5 conditions ( $100 \text{ mW m}^{-2}$ ).



**Figure 2.** IPCE spectrum of solid-state TiO<sub>2</sub>/N3/MEH-PPV/I<sub>2</sub>/graphite cell.

the cell in the absence of a sensitizer. It seems to be charge injection of the cell mainly via excited dye molecules attached to  $\text{TiO}_2$  film. The IPCE spectrum of  $\text{TiO}_2/\text{N3}/\text{MEH-PPV}/\text{I}_2/\text{graphite}$  cell is shown in Figure 2. Maximum IPCE of 33% was observed at 550 nm for the cell. The  $\text{TiO}_2/\text{N3}/\text{MEH-PPV}/\text{I}_2/\text{graphite}$  cell gives a moderate performance compared to other dye-sensitized systems under illumination<sup>9,16</sup>. It has been pointed out that atmospheric oxygen and moisture traps are major concerns in the use of MEH-PPV in similar devices due to fast degradation of the polymer<sup>17</sup>. The  $\text{TiO}_2/\text{N3}/\text{MEH-PPV}/\text{I}_2/\text{graphite}$  cell exhibited poor stability under illumination at atmospheric conditions. Performance of the cell could be further improved by increasing the conductivity of the polymer and finding a proper sealant that prevents the entry of moisture and oxygen into the cell.

MEH-PPV has been used as an electron donor for regeneration of dye molecules in titania-based, dye-sensitized solar cells. Maximum short-circuit photocurrent of  $2.4 \text{ mA cm}^{-2}$  and open circuit voltage of 475 mV were observed for the  $\text{TiO}_2/\text{N3}/\text{MEH-PPV}/\text{I}_2/\text{graphite}$  cell under illumination with the light intensity of  $100 \text{ mW cm}^{-2}$  AM at the electrode.

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## Environmentally benign oxidation of some alcohols with 34% hydrogen peroxide catalysed by $\text{H}_3\text{PW}_{12}\text{O}_{40}$

Selective oxidation of alcohols to the corresponding oxygenated products is of significance to the synthetic organic community and has been a challenge for many years<sup>1–3</sup>. The known chemical protocols for oxidation of hydroxyl groups use either conventional mineral oxidants in stoichiometric amounts<sup>4</sup> or environmentally benign oxidizing agents such as molecular oxygen and hydrogen peroxide in the presence of several transition metal complexes as catalysts<sup>5–12</sup>. The former method generates considerable amount of inorganic waste, and is therefore environmentally not attractive.

Over the last few years, several smart catalytic oxidation methodologies using complexes of noble metals like Pt, Pd and Ru have proved to be promising, as exemplified by numerous examples<sup>13–16</sup>. However, most of the catalytic systems

are expensive and difficult to make. In this context, the polyoxometallates are definitely attractive and challenging while looking for economically viable and easy to manufacture alternatives. These compounds include early transition metal ions with  $d^0$  configuration, e.g. Mo(VI) and W(VI) and have been recognized as potential redox catalysts in many organic transformations<sup>17–20</sup>.

An eco-friendly, simple and efficient method is described here for the oxidation of some alcohols with 34% hydrogen peroxide, catalysed by  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  as the simplest class of heteropolyoxometallates.

Solvents, reagents and other chemicals used in this study were of the highest grade available and were purchased from SD Fine Chemicals (India). The reagents were stored at 5°C and purified just before use. Silica gel 60 (70–230 mesh,

purchased from E-Merck A.G., Germany) was used for column chromatography. Purity of the substances and progress of the reactions were monitored using gas chromatography (GC). GLC analyses were performed on a Shimadzu GC-17A instrument equipped with a flame ionization detector using  $25 \text{ m} \times 0.25 \text{ mm}$  CPB 5-20 and fused silica WCOT  $25 \text{ m} \times 0.23 \text{ mm}$  capillary columns.  $\text{Na}_3\text{PW}_{12}\text{O}_{40} \cdot 7\text{H}_2\text{O}$  was prepared according to the literature<sup>21,22</sup>.

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (30 mmol, 10 g) was slowly added to 20 ml of distilled water and the mixture was warmed to 60°C with complete stirring. Then 85%  $\text{H}_3\text{PO}_4$  (15 mmol, 1 ml) and HCl (100 mmol, 8 ml) were added and the resulting mixture was stirred for 1 h. The white afforded precipitate was washed with water and was recrystallized twice from hot water.