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An Enhancement of Photoproperties of Solid-state TiO_2|dye|CuI Type Cells by Coupling Mercurochrome with Natural Juice Extracted from Pomegranate Fruits

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Electrostatic coupling of mercurochrome with an anthocyanin pigment extracted from pomegranate fruits results an enhancement of the photovoltaic properties of TiO_2|dye|CuI solid-state solar cells.

Dye-sensitized solar cells receive much attention as promising system for conversion of solar energy. A dye-sensitized photo-electrochemical cell with over 10% conversion efficiency was fabricated by Grätzel and co-workers using nanoporous TiO_2 film covered with a metal centered dye and liquid electrolyte.[1] The electrolyte based in photoelectrochemical cells leads some technological drawbacks. A dye-sensitized solid-state cell with similar structure was fabricated by replacing the electrolyte from p-type semiconductor (CuI) by Tennakone et al.[2] In this cell cyanidin extracted from red anthurium flower was used as the sensitizer. Thereafter, a series of solid-state photovoltaic cells has been demonstrated by using several natural pigments such as red sandalwood,[3] tannin,[4] gallic acid,[5] and cyanin derivatives[6] as the sensitizer. However, out of these organic pigments cyanin exhibited more stability and best performance in the application of solid-state photovoltaic cells.

Meso-porous TiO_2 films with the thickness of 5 µm were prepared by using a colloidal solution of hydrolyzed titanium isopropoxide admixture with TiO_2 powder (P-25 Degussa) as described elsewhere.[7] Natural juice of pomegranate fruits was extracted by squeezing pomegranate seeds coat in the laboratory afresh to avoid denaturation. Mercurochrome-coated TiO_2 films were kept immersed in pomegranate fruits juice for 5–10 min at room temperature. Similar coating procedure was used to deposit mercurochrome on TiO_2 films. Pomegranate fruits juice and mercurochrome-coated TiO_2 films were dried in a hot air stream. The photoactive electrode was completed by deposition of CuI on pomegranate pigment and mercurochrome-coated TiO_2 films. Brifely, 1.2 g of CuI powder was dissolved in 20 mL of acetonitrile and residue was separated. Triethylamine hydrothiocyanate was added to this filtrate until its concentration is reached to 10^{-6} M. Small amount of this solution was spread on preheated (ca. 150 °C) sensitized TiO_2 electrodes. TiO_2|dye|CuI type solar cells were fabricated by attaching a conducting glass plate on top of the electrode as the back contact. Cells were characterized by illuminating with monochromatic and polychromatic light from a Xe lamp (or tungsten lamp) through a mask with a hole of 0.4 cm^2. The intensity of light on the surface of the cell was maintained as 100 $mW\,cm^{-2}$ in the case of polychromatic illumination. Illumination was carried out through the TiO_2 layer of the cell. Absorptiion spectra were obtained by UV–vis spectrometer (Shimadzu UV-3000).

Absorption spectrum of (a) mercurochrome, (b) mercurochrome-coated TiO_2, (c) pomegranate pigment (mostly contains cyanidin 3-glucoside and its derivatives[8]), and (d) pomegranate pigment-coated TiO_2 are shown in Figure 1.

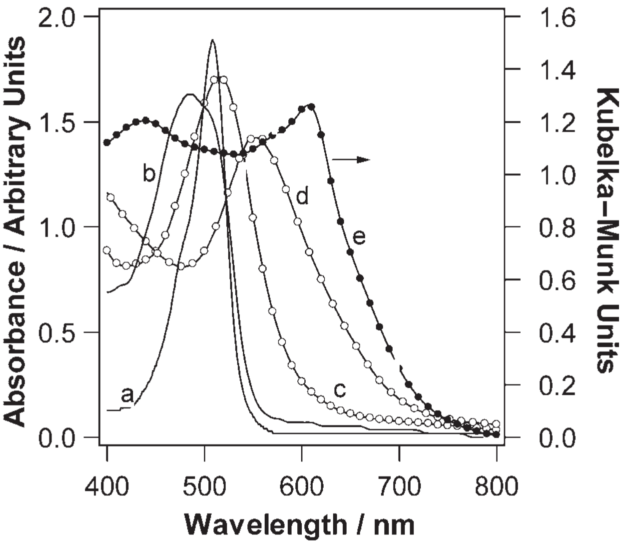

Figure 1. Normalized absorption spectrum of (a) mercurochrome in ethanol, (b) mercurochrome-coated TiO_2 film, (c) natural pomegranate juice, (d) natural pomegranate juice-coated TiO_2 film, and (e) diffuse reflectance spectrum of natural pomegranate juice, mercurochrome-coated TiO_2 film.

Mecurochrome and its derivatives with TiO_2 exhibited an optical absorption onset at 550 nm. Chelation of mercurochrome dimers with TiO_2 results an enhancement in the absorption in shorter wavelengths.[9] Natural pomegranate juice exhibited an optical absorption onset at 610 nm (curve c). Chelation of natural pomegranate juice with TiO_2 extended the onset of optical absorption toward the longer wavelength region (curve d). Diffuse reflectance spectrum of TiO_2|mercurochrome|pomegranate pigment is also shown in Figure 1 (curve e). Electrostatic coupling of mercurochrome with pomegranate anthocyanin results broadening of the spectrum with a shift of the absorption edge toward the longer wavelengths. Mott–Schottky plots of (a) TiO_2, (b) mercurochrome-coated TiO_2, and (c) pomegranate pigment| mercurochrome-coated TiO_2 electrodes shows distinct differences (Figure 2). The more positive shift is noted in TiO_2| pomegranate pigment|mercurochrome-coated electrodes, possibly better surface coverage or coupling of the two dyes makes an apparent shift of the flat band potential.

We have fabricated TiO_2|dye|CuI type solid-state solar cells using mercurochrome, natural pomegranate juice, and their mixtures. The maximum IPCEs of 60 and 31% were observed for solid-state TiO_2|dye|CuI type cells fabricated with mercurochrome and natural pomegranate juice, individually (curves a and b, in Figure 3). These values are comparable to that of values

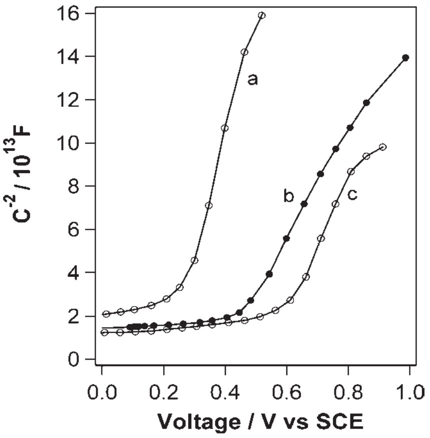

Figure 2. Mott–Schottky plots of (a) TiO_2 film, (b) mercurochrome-coated TiO_2 film, and (c) pomegranate juice|mercurochrome-coated TiO_2 film in 0.1 M $NaClO_4$.

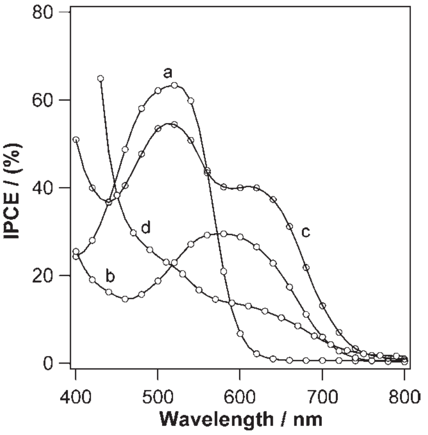

Figure 3. Photocurrent action spectrum of TiO_2|dye|CuI cell sensitized with (a) mercurochrome, (b) natural pomegranate juice, (c) mercurochrome-pomegranate pigment, and (d) pomegranate pigment-mercurochrome.

obtained for the cells prepared with the same sensitizer and electrolyte (I^-/I_3^-).[9,10] The photocurrent action spectrum of solid-state cell TiO_2|mercurochrome|natural pomegranate juice|CuI is shown in Figure 3 (curve c). Maximum IPCE of 58% was observed at 510 nm for the TiO_2|mercurochrome|pomegranate pigment|CuI cell. In addition, an enhancement of IPCE was observed in longer wavelengths compared to that of TiO_2|pomegranate pigment|CuI cells. The photocurrent action spectrum of the cell prepared by changing the order of dye deposition (i.e., TiO_2|pomegranate pigment|mercurochrome|CuI cell) is also shown as curve d (Figure 3). Higher resistant or unfavorable LUMO levels of dyes might be the reason for the observed decrease of photocurrent in TiO_2|pomegranate juice|mercurochrome|CuI cell.

The photovoltaic properties of TiO_2|dye|CuI type solar cells sensitized with mercurochrome, natural pomegranate juice, and their mixtures under different conditions are shown in Table 1.

Table 1. The maximum photocurrent and photovoltage obtained under illumination for different cell configurations, where V_{oc}, I_{sc} and V'_{oc}, I'_{SC} donate photovoltage and photocurrent under illumination with Xe lamp and tungsten filament bulb with a intensity of 100 mW cm^{-2} at the surface of the cell, respectively, MC: mercurochrome, PJ: pomegranate juice.

Cell configuration	V_{OC}/mV	I_{SC} /mA cm^{-2}	V'_{OC}/mV	I'_{SC} /mA cm^{-2}
TiO_2|MC|CuI	490	5.5	300	2.7
TiO_2|PJ|CuI	300	5	310	8
TiO_2|MC|PJ|CuI	370	6.5	370	10.8
TiO_2|PJ|MC|CuI	419.2	3.0	419	0.6

The anion–cation coupling of mercurochrome and pomegranate anthocyanin pigment seems to produce higher photocurrent than the pigments alone. As is observed, optimum performance occurs when pomegranate pigment in the outer dye. Anionic mercurochrome and cationic anthocyanin pigments could act as acceptor–donor pair and electron transfer is facilitated when pomegranate pigment is placed as the outer layer. Better matching of the absorption spectrum of pomegranate pigment with emission spectrum of the tungsten filament lamp is the reason for higher performance of the cell under illumination with tungstant filement lamp than Xe lamp under equal illumination conditions (100 mW cm^{-2}). A maximum conversion efficiency of 1% is observed for TiO_2|MC|PJ|CuI cell among the tested cells.

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