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Fabrication and performance studies of TiO_2 and Porphyrin Heterojunction based organic photodetector

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Organic photodetector of TiO_2/Porphyrin has been fabricated and its performance has been tested in dark and under various illumination of light intensity from 20 to 100 $mWcm^{-2}$. Four samples of porphyrin films have been used in the device, namely 1, 3, 5 and 7 times spin coating. TiO_2 films were deposited onto ITO covered glass substrate by controlled hydrolysis technique assisted with spin coating technique. Then porphyrin film was deposited on TiO_2 using spin coating technique. The films of TiO_2/porphyrin has absorbance maximum at 660 nm, which is in the red region. An aluminium electrode was prepared on top of porphyrin films by electron beam evaporation technique. The device shows rectification behaviour in the dark and shows photosensitization effect under illumination of visible lights. The device with 3 times spin coating of porphyrin shows the highest J_{sc} of 1.02 μAcm^{-2} and V_{oc} of 520 mV.

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1. Introduction

The growth of works toward organic electronic devices motivated by their flexibility, luminescence in the visible range, large covered area and ease of fabrication, has led to the successful realization of light-emitting diodes [1-2], transistors [3-4] and phototransistors [5]. Concerning light-detecting devices, research and industrial interests have focused on photovoltaic cells [6-7], with a very few attempts toward photodetectors [8-9].

The potential applications of porphyrins in the design of functional materials, sensors, catalysts, and sieves are well documented [10-11]. The rich photochemistry and redox chemistry is readily modulated by both the nature of the substituents on the macrocycle and of the metallo derivatives. Porphyrins are a ubiquitous class of naturally occurring molecules involved in a wide variety of important biological processes ranging from oxygen transport to photosynthesis and from catalysis to pigmentation changes. The common feature of all these molecules is the basic structure of the macrocycle, which consists of four pyrrolic subunits bridged by four (meso) carbon atoms. This macrocycle is an aromatic system, the size of which is perfect to bind almost all metal ions and, indeed, a number of metals (e.g. Mg, Fe, Zn, Cu, Ni, and Co) can be inserted in the center of the macrocycle to form metallo-porphyrins (Fig.1).

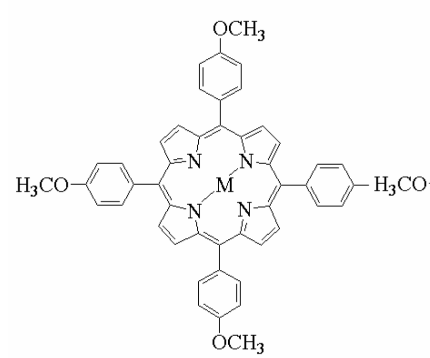

Fig. 1. Molecular structure of metallo-porphyrins

Metallo-porphyrins structure that has Mg metal ion has similarity with Chloropyll-A structure. It has been used as the organic semiconductor material and as a dye sensitizer. For example, it has been used as the material for making OLED [12], dye sensitizer in solar cells [13-14], TNT gases sensors [15].

Semiconductor materials such as TiO_2 have been widely used as photocatalysts for solar energy conversion [16] and for the photodegradation of organic pollutants [17]. However, solar energy reaching the surface of the earth and available to excite TiO_2 is relatively small and artificial UV light sources are more expensive. Therefore, recent efforts have been focused on exploring means to utilize effectively the cheaper visible light [18]. Sensitization processes resulting from photoexcitation of dye molecules bound to semiconductor nanoparticles are of great importance [19].

Gratzel et al. reported the mechanism of photosensitization of nanocrystalline TiO_2 solar cells by chlorophyll derivatives chlorine and copper chlorophyllin [20]. The mechanism of photoinduced electron transfer between the photoexited state of chlorophyll derivatives and nanocrystalline TiO2, the photoelectrochemical properties of chlorophyll derivatives immobilized on nanocrystalline TiO_2 and the photocurrent and photovoltage transient were reported. However, the properties of dye-sensitized solar cell using visible light sensitization of TiO_2 film by chlorine have not yet been clarified. To develop highly photosensitizing conversion device using dye-sensitized based on the visible light sensitization of TiO_2 film by porphyrin it is necessary to investigate the detailed characteristic of the dye-sensitized cell using porphyrin immobilized on TiO_2 film. In this work, the structure of organic photodetector devices made of porphyrin combined with a film of TiO_2. Porphyrin film that has been isolated from spirulina microalgae used for materials sensititizer as electron donor and accepted by the TiO_2 film as acceptor. Porphyrin was coated onto the film (ITO/TIO_2) by spin coating technique. The films were characterized using ultraviolet-visible (UV-Vis) spectrophotometer to investigate their optical absorption. The photosensitizer parameters such as short circuit current density *(J_{sc})*, and open circuit voltage *(V_{oc})* were investigated.

2. Material and methods

Titanium(IV) 2-propoxide, $Ti(OC_2H_5)_4$, was purchased from Aldrich. The doubly distilled deionized water was used for preparing the solutions. All measurements were performed at room temperature. TiO_2 nanoparticles were prepared by controlled hydrolysis of $(Ti\ (OC_2H_5)_4$ in ethyl alcohol [21]. A 0.0596 gram potassium chloride was mixed with 5 ml deionized water. A 0.085 ml $(Ti(OC_2H_5)_4$ was added dropwise into 5 ml ethyl alcohol and mixed using a magnetic stirrer. As a result, transparent solution was obtained.

Porphyrin was isolated from the spirulina microalgaes that were freshly harvested from a local farming in Jepara, Central Java, Indonesia by solvent extraction using acetone as a solvent. The ITO substrates was subjected to a routine chemical cleaning using acetone, 2-propanol and distilled water in sequence in an ultrasonic bath. The TiO_2 layer was deposited onto ITO substrate by spin coating technique. Then, the porphyrin was coated onto the film (ITO/TIO_2) by the same technique using porphyrin solution in acetone. The films were characterized using ultraviolet-visible (UV-Vis) spectrophotometer to investigate the optical absorption within a wavelength region from 300 nm to 800 nm. An organic photodetector device of ITO/TiO_2/Porphyrin/Al was fabricated by using spin coating technique. Aluminium electrode was prepared on the films by electron beam evaporation technique.

The current–voltage characteristic in dark at room temperature was obtained using a 238 Keithley high voltage source. The performance under dark and illumination was performed to study the photosensitizing effect in the device. The device was illuminated by a visible light from tungsten light source. The tungsten light source was calibrated by adjusting the light intensity or by adjusting the distance from the cell to the source so that the intensity in the range of 20 to 100 $mWcm^{-2}$ was obtained. The current-voltage of the device under illumination was recorded using a Keithley high voltage source model 238 and a personal computer. The operational temperature was 25-27^oC and 40 % of humidity. The intensity was controlled by solar power meter and temperature was measured by thermocouple. The illuminated cell area was 0.09 cm^2. The photosensitizing parameters of short circuit current density *(J_{sc})* and open circuit voltage *(V_{oc})* were obtained from the intersection axis of current and voltage from the current-voltage curve under dark and illumination, respectively. Fig. 2 shows the structure of an organic photodetector of ITO/TiO_2/Porphyrin /Al.

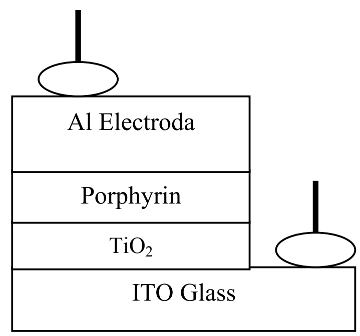

Fig. 2. The structure of an organic solar cell of ITO/TiO_2/ Porphyrin/Al

3. Results and discussion

Fig. 3 shows the absorption spectra of bare TiO_2 film and TiO_2 film coated with various porphyrin layers. The porphyrin films were prepared by 1, 3, 5 or 7 rounds of spin coating. It was found that the bare TiO_2 film shows the highest absorption under irradiation of light at 400 nm. In the visible range, the absorption decreases with the increasing wavelength. This result is in a good agreement with the optical behaviour of TiO_2 film prepared by plasma and ion beam assisted methods [22]. Also, the absorption peak for bare TiO_2 film was seen at the wavelength of 400 nm. Meanwhile, the films of TiO_2 coated with 1, 3, 5 or 7 rounds of spin coating of porphyrin have the absorption peak at 660 nm. The spectra indicated that the porphyrin layers were successfully grown on the top of TiO_2 film. The film of TiO_2 coated by 3 times spin coating has the highest absorbance.

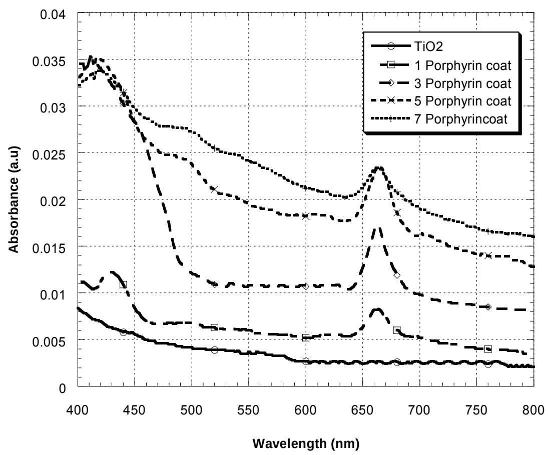

Fig. 3. Optical absorption spectra of (a) uncoated TiO_2 film, (b) TiO_2 coated by various layers of porphyrin

The current-voltage behaviour of the films under dark and under illumination was then studied. Fig. 4 shows the current-voltage curve of the device at different level of porphyrin coating. The dc voltages of -3V to 3 V were applied. Fig. 4 (a) shows the current-voltage curve of device prepared by one time spin coating of porphyrin in the dark condition at room temperature and under illumination with various light intensity from 20 to 100 $mWcm^{-2}$ increasing by 20 $mWcm^{-2}$. The current voltage curve was monitored using a PC.

The film with 1 time porphyrin spin coating does not show photosensitizing effect under illumination from 20 to 60 $mWcm^{-2}$. There is a shift of curve at about $3x10^{-9}$ A under illumination at 80 and 100 $mWcm^{-2}$. Fig. 4 (b-d) shows the current-voltage curve for the films with 3, 5 and 7 round of spin coating of porphyrin in the dark and under various light intensities from 20 mWm^{-2} to 100 $mWcm^{-2}$ at room temperature. They all show photosensitizing effect. The current-voltage curve for the film prepared by 3 time spin coating of porphyrin gives the highest current ($3.91x10^{-7}$ A) under illumination of 100 $mWcm^{-2}$. The calculated current density of J_{sc} was $4.34x10^{-6}$ Acm^{-2} and the open circuit voltage V_{oc} was 522 mV, respectively. [23]

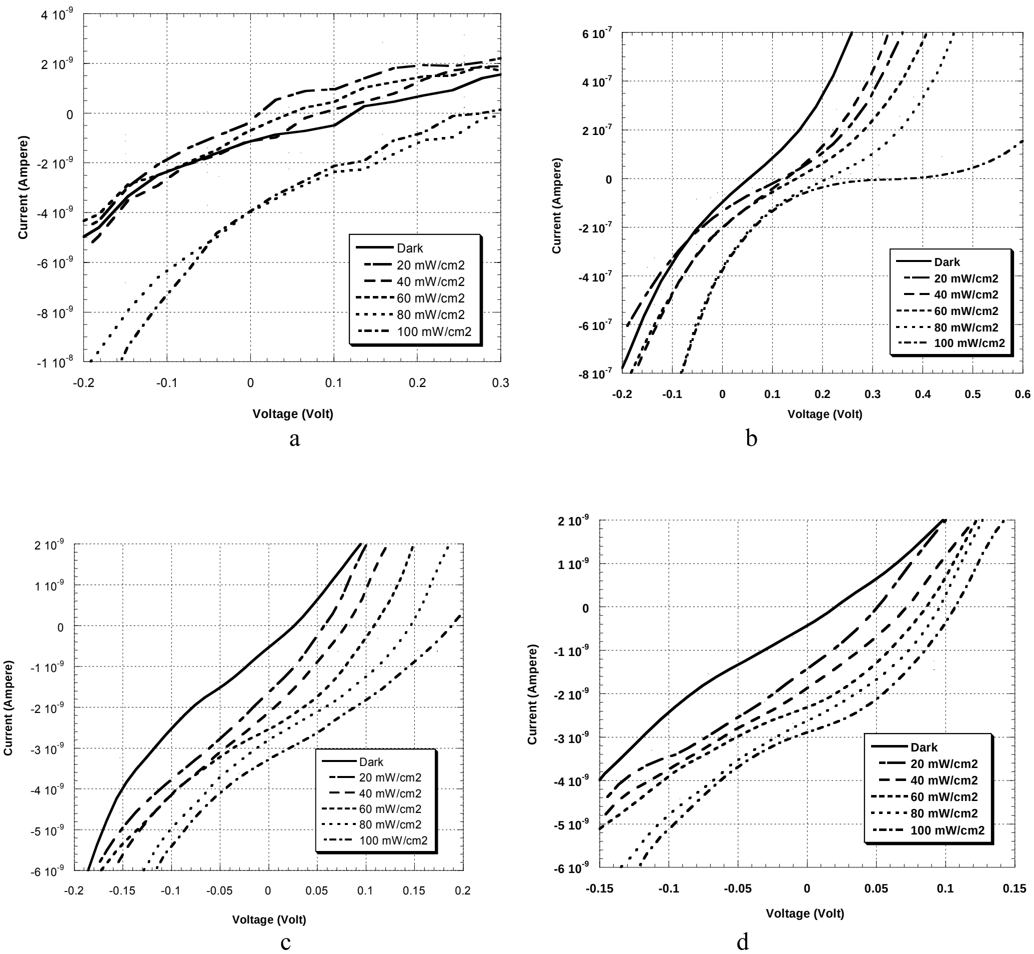

Fig. 4. The current–voltage curves of the films with porphyrin layers (a) 1 layers , (b) 3 layers , (c) 5 layers, (d)7 layers.

The difference in current density among the films obtained by 1, 3, 5, or 7 times spin coating of porphyrin was small. The organic compound of porphyrin deposited onto the TiO_2 film does not seem significantly to affect the rectification property. In general, the films give small variation in current density in the range of 0.40 – 4.3 μAcm^{-2}. Poor interfacial contact may cause a high internal resistance in the devices that eventually leads to a small current across the films. This indicates that the current flow towards the aluminum counter electrode is larger than that towards the ITO electrode.

Table 1. Photosensitizing effect of devices for different porphyrin layers coated on TiO_2

Device	**Size**	**Light Intensity (mW/cm^2)**	**I (A)**	**Isc (A/cm^2)**	**Voc (Volt)**
1 spin coating	(3x3) mm^2	Dark	1.36E-10	1.51E-09	0.060
		100	3.66E-09	4.07E-08	0.466
3 spin coating	(3x3) mm^2	Dark	4.19E-08	4.66E-07	0.088
		100	3.91E-07	4.34E-06	0.522
5 spin coating	(3x3) mm^2	Dark	6.98E-10	7.76E-09	0.030
		100	3.36E-09	3.73E-08	0.214
7 spin coating	(3x3) mm^2	Dark	6.87E-10	7.64E-09	0.010
		100	2.82E-09	3.13E-08	0.112

Table 1 show that the largest J_{sc} of 4.34 $\mu A/cm^2$ and V_{oc} of 522 mV were obtained for the film prepared by 3 times spin coating of porphyrin. On the other hand, the lowest J_{sc} of 1.5 nA/cm^2 and V_{oc} of 60 mV were obtained from the films produced by 1, 5 or 7 spin coating. High open-circuit voltage and small short-current density lead to the low conversion efficiency. The value of V_{oc} is comparable to those obtained from the cell developed previously [24-25]. In addition, the J_{sc} is comparable to that obtained from the non-dye sensitized solid state cell developed earlier [14], in which the J_{sc} was 5.0 $\mu A/cm^2$. The device also shows the rectification property in the dark and shows the photosensitizing effect under illumination. The excited porphyrin molecule under illumination of visible lights acts as an organic photosensitizer.

4. Conclusions

We have prepared and tested a photodetector based on TiO_2/porphyrin compound in dark and under illumination of visible light from 20 to 100 $mWcm^{-2}$. The films of TiO_2/porphyrin have the absorption peak at 660 nm. The film obtained by 3 times spin coating of porphyrin has absorbance maximum at 660 nm. This film shows rectification effect in the dark and photosensitizing effect under illumination with J_{sc} of 1.02 μAcm^{-2} and V_{oc} of 522 mV, respectively. This film is expected to give a good current-voltage performance when it is applied as photodetector in many applications.

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