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PHOTOCURRENT VARIATION OF DYE COATED TITANIUM DIOXIDE LIQUID JUNCTION PHOTOCELLS

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Abstract

Low cost liquid junction photocell with methyl violet or N3 dye coated Titanium Dioxide (TiO$_2$) films consist of TiO$_2$ nanoparticles was fabricated using a platinum plate as the secondary electrode. I-V characteristic curves of this cell filed with KI/I$_2$ electrolyte were investigated. Maximum photocurrent and photo-voltage could be obtained for a cell with dye coating time of 12 hours for both dyes. The separation between platinum electrode and the TiO$_2$ film of the photocell was 1mm at this optimum photocurrent and photo-voltage. The thickness of TiO$_2$ film was varied to obtain the maximum efficiency, and the efficiency could be optimized at the film thickness of 0.6 mm. Photocurrent and photo-voltage obtained for N3 dye were 0.05mA/cm^{2}and 0.02 V, respectively. While the photocurrent obtained with N3 dye was higher than that obtained with methyl violet dye, the photo-voltage measured with methyl violet dye is higher than that measured with N3 dye.

Keywords: Photocells, dye coated films, photocurrent, TiO$_2$

1. Introduction:

Titanium dioxide (TiO$_2$) with band gap of 3.0-3.5ev finds potential applications in photoanodes [1], solar cells, sensors, photocatalysts [2] and photovoltaic field. Due to this high band gap, n-type TiO$_2$ absorbs the ultraviolet part of solar spectrum similar to ZnO. The band gaps of anatase and rutile phases of TiO$_2$ are 3.2 and 3.0eV, respectively. The optical absorption of TiO$_2$-based systems to the visible-light region can be improved by doping with various transition metal cations [3]. Because of their thermal and chemical stability and optical properties, TiO$_2$ is extensively used in optical thin film devices. Thin films of TiO$_2$ are suitable for applications such as antireflection coating [4], multi-layer optical coatings [5] and optical wave guides [6]. TiO$_2$ films have been synthesized using many different methods such as sol-gel process [7], metal organic chemical vapor deposition [8] and ion-assisted deposition [9]. Because TiO$_2$ material is hard and chemically resistant, transparent in the visible and near-IR range and has a high refractive index, it is useful for some interference applications. Since TiO$_2$ is inexpensive compared with other semiconductors employed in solar cells, researchers are keen to study the photovoltaic properties of TiO$_2$.

Many oxide semiconductors such as ZnO and CuO are used in photovoltaic applications. Because of large band gap of ZnO, ZnO liquid junction photocells consist of sputtered ZnO thin films provide a high photo-voltage. This photo-voltage of these ZnO [10] thin films depends on the sputtering pressure and deposition temperature. On the other hand, photocurrent of CuO thin films measured in liquid junction photocell is large due to the small band gap of CuO compared with that of ZnO. The photocurrent of these CuO [11] thin films also increases with substrate temperature and substrate pressure. Although the thin films synthesized using sputtering in a high vacuum is highly pure, the sputtering method is considered to be expensive. In this paper, TiO$_2$ films synthesized using a low cost method will be explained.

2. Experimental:

TiO$_2$ nanoparticles with high purity were grinded well to make a uniform sample of fine nanoparticles. These nanoparticles were mixed with ethyl alcohol to prepare a paste. A layer of this paste was uniformly applied on the conductive surface of well cleaned conductive glass plates. Within one hour, the alcohol of this sample evaporated. Then the TiO$_2$ film sample was annealed in air in an oven at 450 ^{0}C for 30 minutes to crystallize the TiO$_2$ phase and to make the film adhesive to conductive glass substrate. After the sample cooled down in the oven, the sample was taken out for dye treatments and measurements. Samples with area of 1cmx1cm were prepared for the measurements. But the thicknesses of the samples were varied from 0.2mm to 2mm in order to investigate the effect thickness on photocurrent and photo-voltage. Then the samples were immersed in methyl violet or N3 dye solutions and left for dye coating for 1-24 hours. Commercially available low cost methyl violet and N3 dye were used for this project.

Then the photocell was prepared using this dye coated TiO$_2$ film sample and a platinum electrode. A platinum plate with same area as TiO$_2$ film sample was used as the platinum electrode. The separation between platinum plate and TiO$_2$ film of this photocell was varied in the range of 0.5-2.3mm in order to obtain optimum efficiency. Then well sealed photocell was filled with KI/I$_2$ solution. KI/I$_2$ solution with 0.01M/0.0001M concentration and redox couple I$_3^-$/I$^-$ was used as the electrolyte in this liquid junction photocell. The variation of photocurrent of the cell at different applied voltages was measured by means of computerized Keithly 236 source measurement unit, and a lamp calibrated similar to solar spectrum was used to illuminate the photocell. The photocell was illuminated from the side of conductive glass for these I-V characteristic measurements. The Raman spectrums were performed to investigate the structure of these samples using Raman system R-3000 spectrometer with wavelength 532nm.

3. Results and discussion:

Because optimum photovoltaic properties could be obtained for TiO$_2$ films with thickness of 0.6mm, all the films explained in this report is 0.6mm thick. The I-V characteristic curve of TiO$_2$ film coated with N3 dye for 12 hours is given in figure 1. The area of all the samples given in this report is 1cm^2. The maximum efficiency could be observed for the coating period of 12 hours. The optimum photocurrent and photo-voltage of the photocell could be measured when the separation between the TiO$_2$ film and platinum plate is 1mm. The separation between the TiO$_2$ film and the platinum electrode was 1mm for the photocell given in figure 1. The center part of I-V characteristic curve was enlarged in order to measure the photocurrent and photo-voltage, and that I-V curve is shown in figure 2. While the photocurrent has been defined as the difference between the current with light and without light, the photo-voltage has been defined as the difference between voltage with light and without light. The minus signs of photocurrent or photo-voltage have been disregarded. The photocurrent at V=0 is 0.05mA/cm^2, and the photo-voltage at I=0 is 0.02 V. The power corresponding to this current and voltage is 0.001mW/cm^2. In all the graphs, the dashed and solid lines indicate dark and light I-V curves, respectively. A bulb calibrated similar to solar spectrum was used for all the measurements.
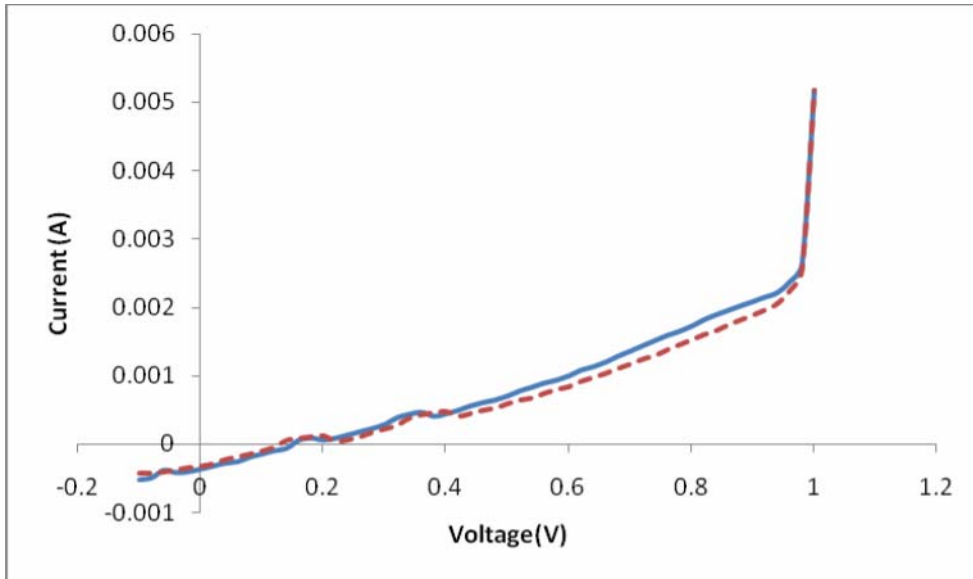
Figure1. Dark (dash line) and light (solid line) I-V characteristic curves of TiO_2 film coated with N3 dye for 12 hours.
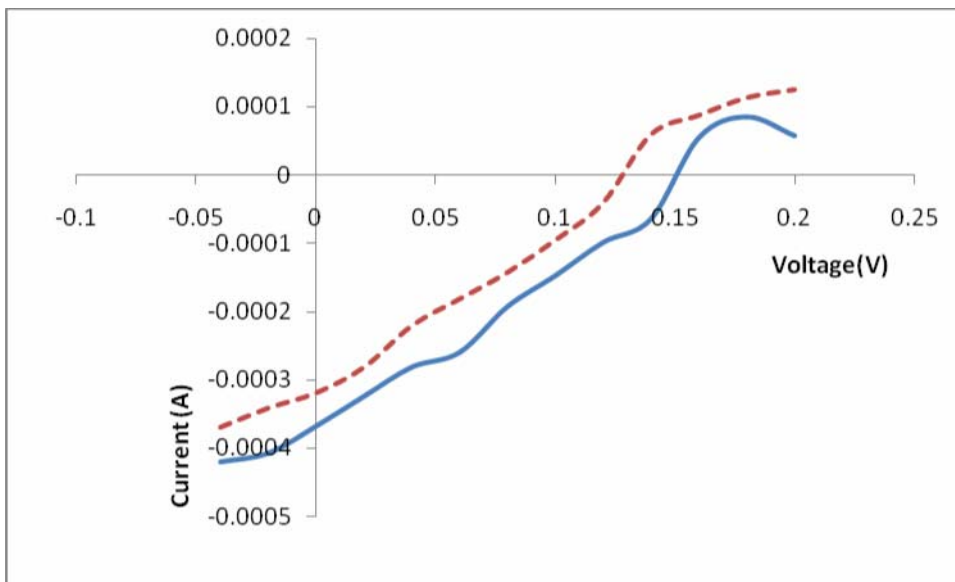

Figure2. Center part of I-V characteristic curves of TiO_2 film coated with N3 dye for 12 hours given in figure 1.

I-V characteristic curve of TiO_2 sample coated with N3 dye for 4 hours is given in figure 3. The photocurrent at V=0 is $0.011mA/cm^2$, and the photo-voltage at I=0 is 0.005 V. I-V characteristic curve of TiO_2 sample coated with N3 dye for 24 hours is shown in figure 4. The photocurrent at V=0 is $0.02mA/cm^2$, and the photo-voltage at I=0 is 0.015 V. These photocurrent and photo-voltage are considerably smaller compared with those of the sample coated with N3 dye for 12 hours. The separation between two electrodes of photocell was kept at 1mm in order to maintain the maximum

efficiency as explained in previous paragraph. Dye has been coated on TiO_2 films to enhance the light absorption. The thickness of coated dye layer increases with dye coating time. When the dye coating time is very small, the sample does not absorb enough light. When the dye coating time is too high, the dye layer reduce the intensity of light reaching TiO_2 sample. Therefore, the power becomes optimum at an intermediate value of dye coating time.
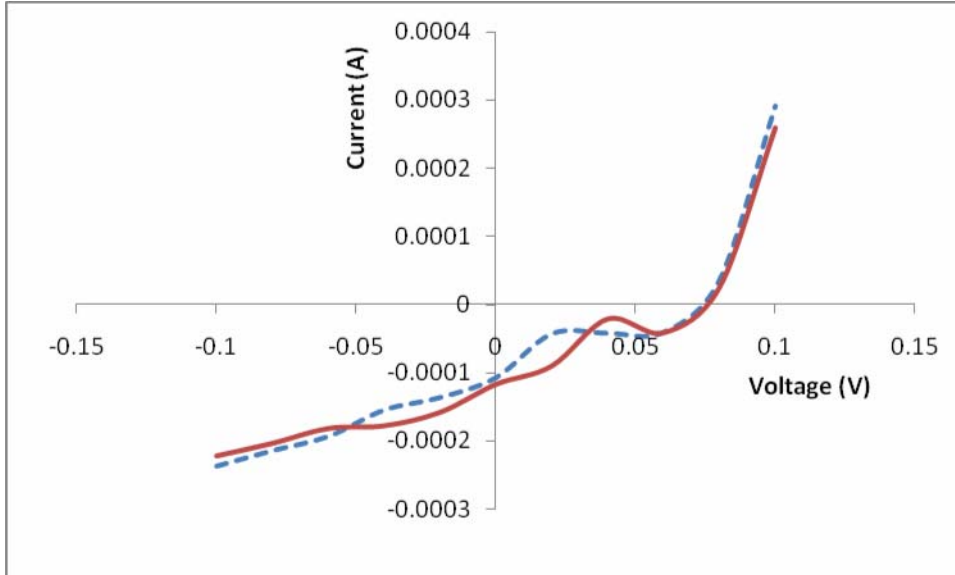

Figure3. Dark (dash line) and light (solid line) I-V characteristic curves of TiO_2 sample coated with N3 dye for 4 hours.
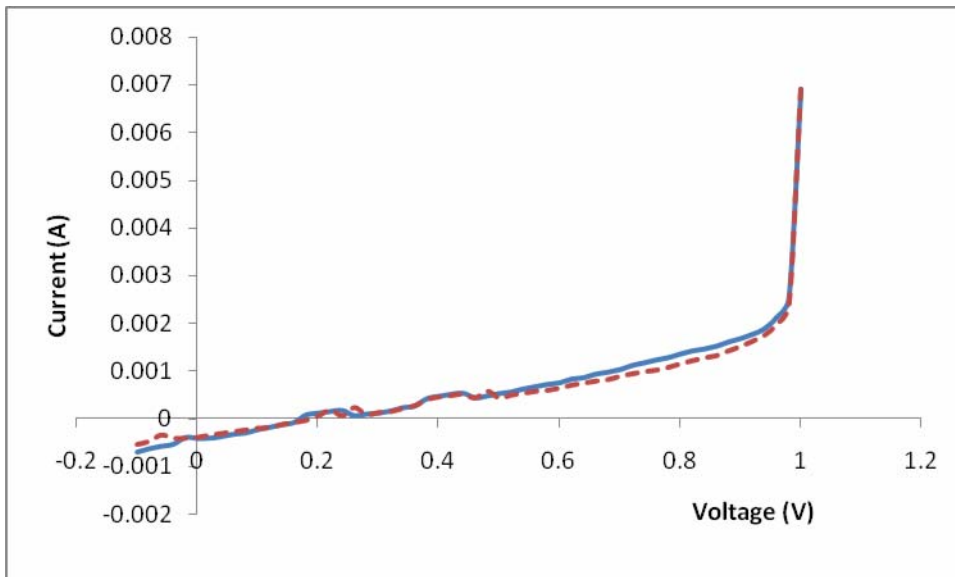

Figure4. Dark (dash line) and light (solid line) I-V characteristic curves of TiO_2 sample coated with N3 dye for 24 hours.

I-V characteristic curve of TiO_2 thin film immersed in methyl violet dye for 12 hours is given in figure 5. The photocurrent at V=0 is $0.006mA/cm^2$, and the photo-voltage at I=0 is 0.08 V. Although the photocurrent in this case is smaller than that of N3 dye coated TiO_2 film, the photo-voltage in this

case is higher than that of N3 dye coated TiO_2 film. The power related to this voltage and current is $0.00048mW/cm^2$. However, the power of methyl violet dye coated TiO_2 film is almost half of that of N3 dye coated TiO_2 film. Similar to N3 dye coated TiO_2 films, the optimum efficiency could be obtained for the methyl violet dye coating time of 12 hours. The separation between TiO_2 film and platinum electrode is 1mm in this case, and the maximum photocurrent and photo-voltage could be observed at this separation. I-V characteristic curve of TiO_2 sample coated with methyl violet dye for 4 hours is given in figure 6 to imply that the photocurrent and photo-voltage in this case is less than that of 12 hour case. The dashed and solid lines indicate the dark and light curves, respectively. The Raman spectroscopy of a TiO_2 film sample without any dye coating is given in figure 7. All the peaks appeared in this spectrum belongs to rutile phase of TiO_2, indicating the formation of single phase of rutile TiO_2[12].
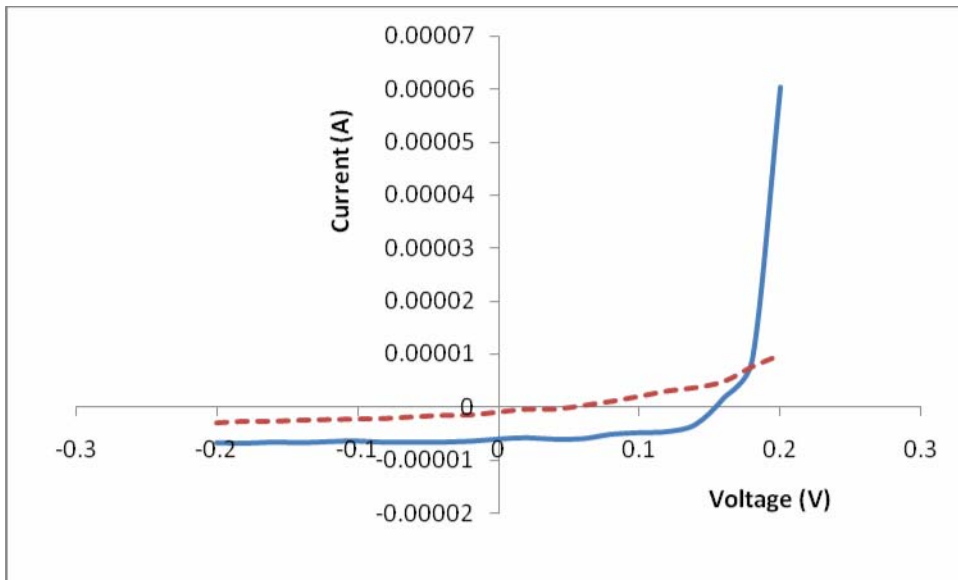

Figure5. Dark (dash line) and light (solid line) I-V characteristic curves of TiO_2 thin film immersed in methyl violet dye for 12 hours.
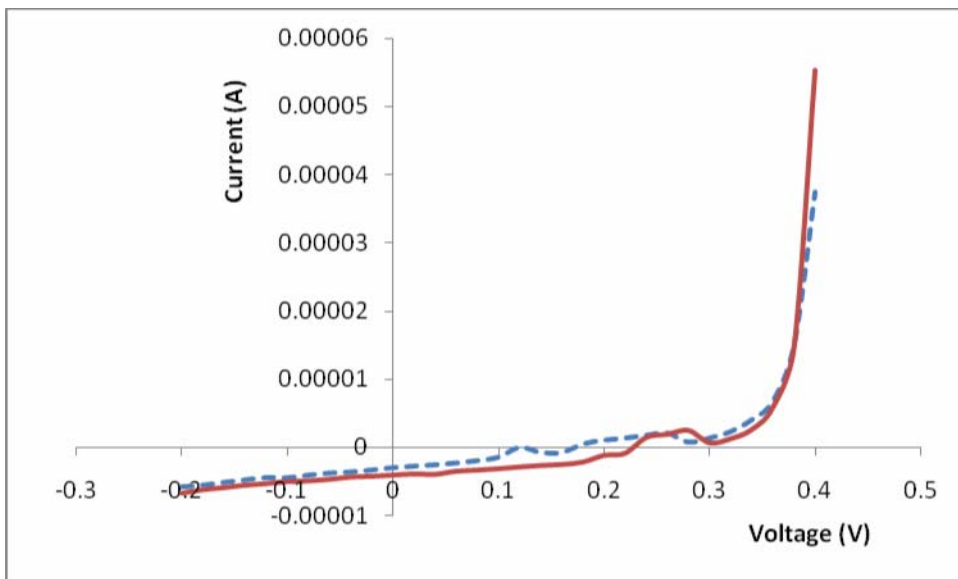
Figure6. Dark (dash line) and light (solid line) I-V characteristic curves of TiO_2 sample coated with methyl violet dye for 4 hours.
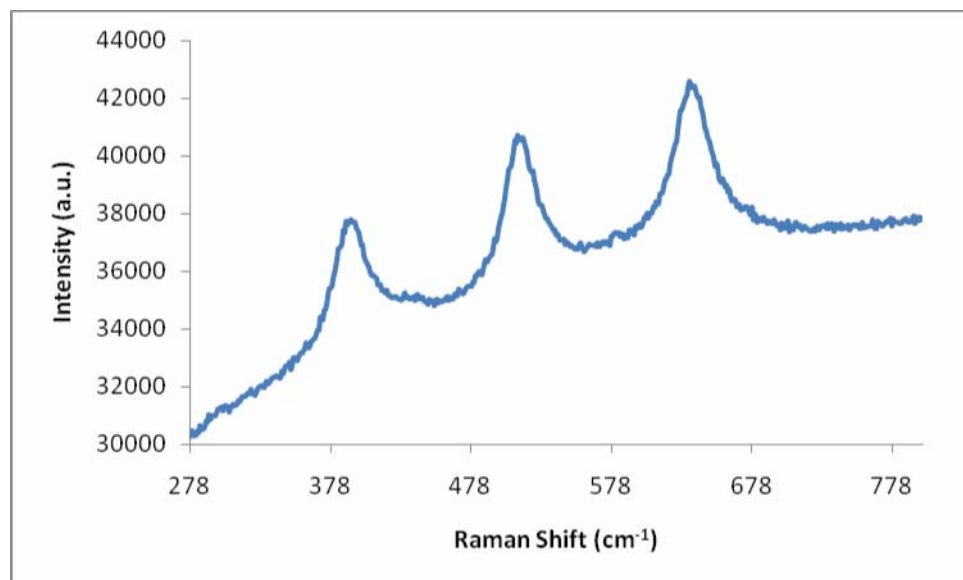

Figure7. Raman spectroscopy of TiO_2 film sample without any dye coating.

4. Conclusion:

According to Raman spectrums, single phase of rutile TiO_2 could be formed. Films immersed in methyl violet and N3 dye for 12 hours provide the optimum efficiency. Also TiO_2 films with thickness of 0.6mm were prepared, and the separation between platinum electrode and the TiO_2 film of well sealed photocell was kept at 1mm to obtain maximum photocurrent and photo-voltage. According to I-V characteristic curves, the optimum photocurrent and photo-voltage of TiO_2 film coated with N3 dye for 12 hours were $0.05mA/cm^2$ and 0.02 V, respectively. While the film does not absorb enough light at less dye coating time, the dye layer reduces the light intensity reaching the TiO_2 sample at high dye coating time. Therefore, optimum power could be obtained at an intermediate value of dye coating time. The optimum photocurrent and photo-voltage obtained for TiO_2 film coated with methyl violet dye for 12 hours were $0.006mA/cm^2$ and 0.08 V, respectively. Although a higher photocurrent could be obtained with N3 dye, a higher photo-voltage could be obtained with methyl violet dye. The photocurrents and photo-voltages measured at other conditions were smaller than this photocurrent and photo-voltage for both dyes. Although a higher photocurrent and photo-voltage could be obtained for TiO_2 films prepared using expensive methods, the experimental method explained here is an inexpensive method. Therefore, the photocurrent and photo-voltage obtained here were reasonably higher for this kind of low cost preparation method of TiO_2 films.

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