김일성종합대학학보
(자연과학)
주체103(2014)년 제60권 제6호

JOURNAL OF KIM IL SUNG UNIVERSITY
(NATURAL SCIENCE)
Vol. 60 No. 6 JUCHE 103(2014).

Photoelectrochemical Characteristics of the Photosensitizer N719 (Cis-dithiocyanato bis (4, 4'-dicarboxy-2, 2'-bipyridine) ruthenium(II) tetrabutylamonium Complex)

Ryu Kwon Il

The great leader Kim Jong Il said:

"The scientists and technicians in this sector must step up research work to develop compound semiconductors and precision porcelain materials, essential for the electronics industry, and to industrialize their production, and push ahead with research into developing new materials such as superconducting materials and metal plastic composite materials as well as materials that can substitute for what are not available in our country, in a far-sighted way."

The photosensitizer N719 is attracting attention for its capacity for generating photocurrent in a more effective way than N719. [4] N719, a complex that has substituted tetrabutylamonium for carboxyl acid, the fourth position of pyridine of N3, functions as an electron donor for excited electrons to flow better through the TiO_2 film with scarboxyl acid group of other pyridine (Fig. 1).

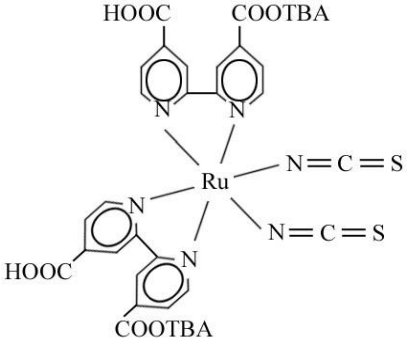

Fig. 1. The structure of photosensitizer N719

In general, the bipyridine group as electron receptor coordinated with metal determines energy level of LUMO while the thiocyan group as donor determinates energy level of HOMO. The higher level of LUMO of the photosensitizer N719 than that of N3 leads to higher voltage and photocurrent.

We synthesized the photosensitizer N719 and examined its photoelectrochemical characteristics.

2. Material and Method

Used here were methanol (AG), tetrabutylammonium hydroxide and dymethylformamide (CG).

The photosensitizer N3 as a precourse is synthesized on my own.

The confirmation of the product of N3 and N719 was done by the method of KBr indicator using an infrared spectrophotometer (FT-IR 8101 Shimadzu) and the visible spectrum of the product was measured by autographic recording spectrophotometer (Hitachi EPS-3T).

The synthesis of N719 is as follows.

30mg of the photosensitizer N3 was dissolved in 50mL of pure methanol, into which 0.026mL (10%) of tetrabutylammonium hydroxide was added to be reacted at the constant temperature for 2 hours. After that, the product was recrystallized with diethyl ether, filtered and again elutriated with diethyl ether and dried.

The photoelectrochemical characteristics were measured by the following method.

First, conductive transparent glass electrode which was elutriated with acetone was taped on both ends and it was coated with nano TiO_2 paste by doctor blade method and sintered for 30 min at 450℃. This nano TiO_2 electrode was cooled to about 80℃ and immersed in dye solution (6×10^{-3}mol/L) and left overnight.

Next, the solution of hexachloroplatinic acid was coated on the same area of the conductive transparent glass electrode and sintered at 450～500℃ to make a counter electrode (platonic catalytic electrode). These two electrodes were put in contact with each other (sandwiched) and in between was injected electrolyte (0.5 mol/L KI, 0.05mol/L I_2 0.025 TBP in 50mL $\gamma-$ butylroractone) with a capillary tube and the open circuit voltage and closed circuit current under sunlight was measured.

2. Results and Consideration

2.1. Synthesis of photosensitizer N719

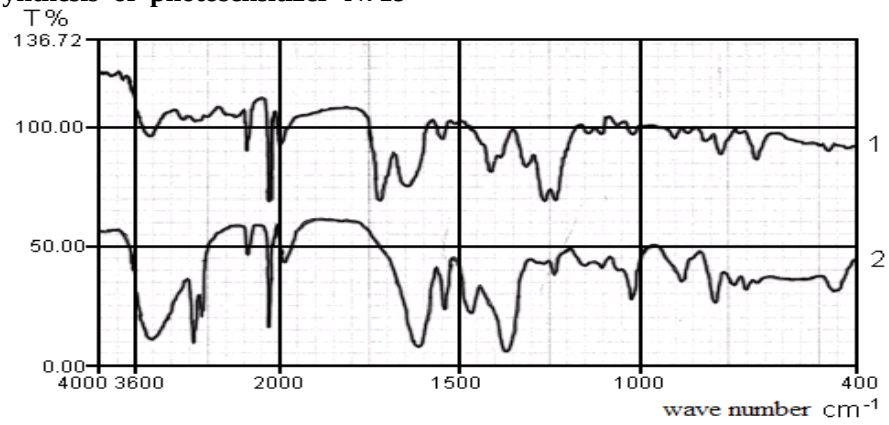

Fig. 2. IR spectrum of synthesized N719.

As shown in Fig. 2, specific absorption band of bipyridine group appeared in region at 1 200～1 650 cm^{-1} and vibration band of thiocyan group at 2 186 cm^{-1}, vibration band of tert butyl group of tetrabutylammonium hydroxide at 2 800～3 100 cm^{-1}.

N3 and N719 were dissolved in the solution of dimethylformamide and their visible spectrum was measured. N3 saw its maximum absorption at the points of 396 nm and 520 nm whereas in the case of N719 it was at 398 nm and 515～530nm.

This result conforms to that of previous study [3]. This indicates that the synthesized material is surely photosensitizer N719.

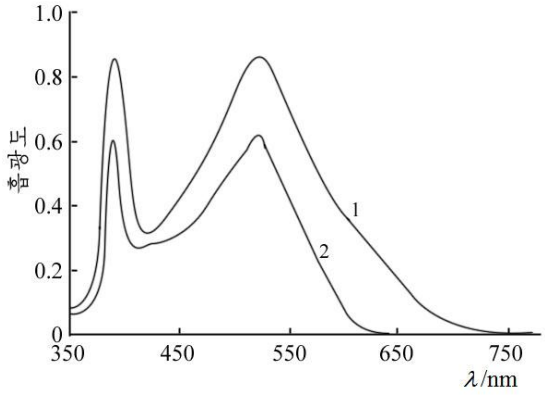

Fig. 3. Vis-spectrum of the photosensitizer N719
1－N719, 2－N3

Photoelectrochemical characteristics of N719

Nano TiO_2 made in the same way as above was left in the photosensitizers N3 and N719 overnight to make a battery and its photoelectrochemical characteristics were measured.

Table 1 shows the results of measuring Voc and Jsc in the nanoTiO_2 film prepared by two methods.

As shown in table 1, in high luminous intensity, Jsc of N719 as 2.40 mA/cm^2 is higher than that of N3. But, in nanoTiO_2 film made by using P25, Voc and Jsc of N719 is higher than those of N3 (table 2).

Table 1. Photoelectrochemical characteristics of N719 at nanoTiO_2 film with titanium butoxide

Luminous intensity/lx	N3		N719	
	V_{OC}/V	J_{SC}/(mA·cm^{-2})	V_{OC}/V	J_{SC}/(mA·cm^{-2})
6 000	0.539	0.350	0.534	0.210
18 000	0.589	0.800	0.590	0.430
36 000	0.630	1.250	0.620	1.300
60 000	0.663	1.500	0.660	1.800
65 000	0.685	1.800	0.670	2.400

Contrast: N3

Table 2. Photoelectrochemical characteristics of N719 in nanoTiO_2 film that used P25

Luminous intensity/lx	N3		N719	
	V_{OC}/V	J_{SC}/(mA·cm^{-2})	V_{OC}/V	J_{SC}/(mA·cm^{-2})
6 000	0.547	0.300	0.600	0.280
18 000	0.588	0.600	0.620	0.570
36 000	0.617	1.130	0.650	1.140
60 000	0.629	2.000	0.680	1.870
65 000	0.660	2.430	0.710	2.850

The above result shows that characteristics of photosensitizer change according to the way of making the nanoTiO_2 film. This is because the difference in the particle sizes of the photosensitizers N3 and N719 leads to variations in the amount of the dye that couples with the particles of nano TiO_2 depending on how nano TiO_2 is made..

After that, the TiO_2 film that was made using titanium butoxide and P25 was immersed in 0.2mol/L $TiCl_4$ aqueous solution, treated for 1 hour in 70℃. The electrode was again left in the dye solution overnight and elutriated with ethanol.

This electrode was used to make an electric cell and to examine the characteristics of

photosensitizers (table 3 and 4).

Table 3. Voc and Jsc of N719 at nanoTiO_2 electrode after-treated by aqueous solution of $TiCl_4$

luminous intensity/lx	N3		N719	
	V_{OC}/V	J_{SC}/(mA·cm^{-2})	V_{OC}/V	J_{SC}/(mA·cm^{-2})
6 000	0.558	0.800	0.540	0.400
18 000	0.565	1.700	0.560	1.700
36 000	0.605	2.400	0.600	2.200
60 000	0.630	3.200	0.620	3.400
65 000	0.660	3.700	0.652	4.500

NanoTiO_2 electrode with titanium butoxide

As shown in table 3, as in nanoTiO_2 film using titanium butoxide (not after being treated with $TiCl_4$ aqueous solution), Jsc of N719 increased in high luminous intensity but its Voc decreased compared to N3. But both Voc and Jsc of N719 increased in the case of nanoTiO_2 film made with P25 (table 4). This may be attributed to the fact that the source material with which to make nanoTiO_2 film causes the differences in the size of particles that together make a film as well as the size of air pores and as the result decreases the amount of dye absorption.

Table 4. Voc and Jsc of N719 in nanoTiO_2 film After being treated by aqueous solution of $TiCl_4$

Luminous intensity/lx	N3		N719	
	V_{OC}/V	J_{SC}/(mA·cm^{-2})	V_{OC}/V	J_{SC}/(mA·cm^{-2})
6 000	0.524	0.900	0.580	0.600
18 000	0.562	1.300	0.598	1.250
36 000	0.601	2.100	0.627	2.300
60 000	0.620	4.070	0.650	4.890
65 000	0.656	4.660	0.680	5.700

NanoTiO_2 electrode with P25

Conclusion

The maximum absorption of the photosensitizer N719 is 398nm and 515～530 nm.

The Jsc of photosensitizer N719 increases but Voc decreases in nano-TiO_2 film made by using titanbutocide. In case of the film made with P25, both Voc and Jsc of N719 increase.

The film treated by $TiCl_4$ aqueous solution enhances the photoelectrochemical characteristic of photosensitizer N719.

References

[1] 김일성종합대학학보(자연과학), 53, 11, 145, 주체96(2007).

[2] 김일성종합대학학보(자연과학), 53, 12, 96, 주체96(2007).

[3] M. K. Nazeeruddin et al.; J. Am. Chem. Soc., 115, 6382, 1993.

[4] 荒川榕則; 表面技術, 55, 12, 887, 2004.