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Natural Dye Sensitized Solar Cells

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More than 20 kinds of dyes extracted from natural matters such as plants, bacteria and insects were used to sensitize the nanocrystalline TiO_2 and ZnO electrodes. Both kinds of electrodes were nicely colored by the natural dyes. All of the dyes exhibited photosensitization in the photoelectrochemical measurement on the cells using the colored semiconductor films, although their efficiency varied for each dye and also by the semiconductor/dye combinations. For TiO_2/dye cells, red cabbage color was the best, achieving 25% of incident photon to current conversion efficiency (IPCE) and 41% of the absorbed photon to current efficiencies (APCE) around the absorption maximum of the adsorbed dye, under monochromatic light illumination. Under 1 sun illumination, 4.7 mA/cm^2 of a short-circuit photocurrent (I_{sc}), 0.525 V of an open-circuit photovoltage (V_{oc}), and 61% of a fill factor (*F.F.*) were obtained, yielding an overall light-to-electricity conversion efficiency (η) of 1.51%. For ZnO/dye cells, Gardenia blue was the best, although the same dye was one of the poorest on TiO_2. This cell exhibited IPCE, APCE, I_{sc}, V_{oc}, *F.F.* and η of 3.2%, 6.7%, 0.97 mA/cm^2, 0.286 V, 45% and 0.13%, respectively. These results shows that natural dyes are cheap and nontoxic alternatives as photosensitizers for solar cell applications.

Key Words: Natural Dye, Food Colorant, Porous Electrode, Dye-Sensitization, Solar Cell

1. INTRODUCTION

Increasing attention has been paid to dye-sensitized solar cells (DSCs) in recent years since the group of Grätzel achieved strikingly high efficiencies using nanocrystalline porous TiO_2 electrodes to which polypyridine Ru complex is adsorbed [1,2]. Aside from its cost effectiveness, the wide choice of semiconductor/dye combinations is a technological merit of DSCs. Besides TiO_2 [1,2], other oxide semiconductors with wide band gap, such as ZnO [3], SnO_2 [4], Nb_2O_5 [5], WO_3 [5], In_2O_3 [5], have also been studied. Meanwhile, many kinds of organic dyes with effective light absorption within visible range have been actively studied as low cost alternatives to Ru complexes which are efficient as sensitizer but are costly because they contain rare metal Ru [6]. Some of the recent studies have revealed a high incident photon to electron conversion efficiency (IPCE) [7] or a high solar to electric power conversion efficiency [8] comparable to the systems employing Ru complexes, suggesting high capabilities of organic dyes which can be synthesized in large quantities with low cost. Besides such synthetic dyes, several natural dyes have also been tested as unique alternatives [9-11]. Natural dyes are extracted from colored natural matters such as flowers, fruits, vegetables and many other parts of plants body as well as other living beings such as bacteria and insects. They are abundant in nature and recycled (regenerated) naturally. They are also non-toxic and perfectly bio compatible. In fact, many of the natural dyes are used as safe food colorants today. Natural dyes can therefore be the greenest alternative photosensitizers for DSCs. In the present study, we have explored possibilities of natural dyes for application in DSCs. 15 kinds of natural dye extracts used as food colorants and 7 other kinds directly extracted from foods have been tested. Nanocrystalline porous TiO_2 and ZnO films have been employed as the electrodes to be sensitized, because they are most frequently used in the studies of DSCs. Although the natural dyes are not pure, being mixtures of several dyes and containing many other chemical substances, they allowed good coloration of semiconductor films and demonstrated rather promising efficiencies as photosensitizers.

2. EXPERIMENTAL

Nanocrystalline TiO_2 electrode was prepared by following the procedure reported in literature [1,2]: Colloidal TiO_2 suspension was prepared by hydrolysis of titanium isopropoxide (97%, Aldrich Chemical Co.) in a pH=1 aqueous solution under vigorous stirring at 80°C. The resultant suspension was autoclaved at 220 °C and condensed by a rotary evaporator and dispersed ultrasonically. After addition of carbowax (M-20,000), the colloidal TiO_2 suspension was spread on a F-doped SnO_2 (FTO) conducting glass (10Ω/sq.), followed by a sintering at 450 °C for 30min in air. TiO_2 thin film prepared consisted of anatase particles with average size of 15nm.

Nanocrystalline ZnO electrode was prepared by the following method: 1.5g commercial ZnO powder (20nm), 1.5g $ZnAc{\cdot}2H_2O$, 0.1ml acetic acid and 10 ml ethanol were ground in an agate mortar for about 40 min. to get viscous paste, then coated on a FTO glass. After dried in air for half hour it was sintered at 450°C for 30min. The film thickness of two types of electrodes was 8μm determined by a surface profilometer.

22 kinds of natural dyes tested as sensitizers are listed in Table 1. Natural dye extracts sold for industrial purpose as food colorants (i-xiv) were generous gift from San-Ei Gen F.F.I., Inc. Spirulina dye (xv) was kindly offered from Dainippon Ink & Chemicals, Inc. Food samples (xvi-xxii) were simply crashed in a mortar and their fresh juice or extract to water were used.

Table 1 List of the natural dyes used and photoelectrochemical properties of TiO_2/natural dye cells.

	Dye	Dye content (%)	Additives[a] (%)	λ_{max}[b] (nm)	λ_{thd}[b] (nm)	LHE[c] (%)	IPCE[c] (%)	APCE[c] (%)	I_{sc} (mA/cm^2)	V_{oc} (V)	*F.F.* (%)	η (%)
(i)	Red cabbage	36	CA(2), GS(62)	547(571)	647(707)	61	25	41	4.70	0.525	61	1.51
(ii)	Cochineal	80	DX(20)	492(480)	582(702)	39	—	—	6.00	0.397	52	1.24
(iii)	Purple sweet patato	43	CA(7), DX(50)	535(574)	626(630)	41	—	—	5.68	0.393	51	1.13
(iv)	Curcumin	100	—	427(485)	507(621)	58	16	28	5.35	0.410	50	1.10
(v)	Kaoliang	76	SC(0.8), DX(23.2)	497(495)	588(607)	37	19	51	3.64	0.452	61	1.00
(vi)	Gardenia yellow	60	DX(40)	441(438)	512(520)	34	15	44	3.20	0.570	49	0.90
(vii)	Carthamus yellow	40	DX(60)	406(432)	481(650)	29	11	38	1.90	0.465	68	0.60
(viii)	Beet red	80	SA(8), SMP(1), DX(11)	539(494)	626(620)	—	—	—	2.90	0.400	38	0.44
(ix)	Monascus	50	DX(50)	491(529)	607(630)	31	—	—	1.58	0.396	53	0.33
(x)	Annatto	10	LA(90)	455(438)	538(608)	—	—	—	2.45	0.294	38	0.27
(xi)	Gardenia blue	90	LA(10)	597(600)	683(720)	44	1.5	3.4	1.33	0.387	45	0.23
(xii)	Lac	100	—	478(498)	588(636)	—	—	—	1.56	0.349	39	0.21
(xiii)	Cacao	90	DX(10)	446(570)	600(750)	32	1.3	4.1	1.17	0.312	44	0.16
(xiv)	Tamarind	90	DX(10)	447(570)	623(757)	36	2.7	7.5	1.36	0.280	42	0.16
(xv)	Spirulina	66	—	616(666)	680(750)	—	—	—	0.89	0.363	40	0.13
(xvi)	Strawberry	—	—	(534)	(707)	—	—	—	2.86	0.405	53	0.61
(xvii)	Blueberry	—	—	(590)	(742)	—	—	—	4.29	0.360	34	0.52
(xviii)	Coffee	—	—	(442)	(690)	—	—	—	2.55	0.409	39	0.41
(xix)	Grape	—	—	(550)	(692)	—	—	—	1.81	0.427	43	0.33
(xx)	Green tea	—	—	(445)	(660)	—	—	—	0.98	0.412	47	0.19
(xxi)	Lemon	—	—	(606)	(750)	—	—	—	1.41	0.416	29	0.17
(xxii)	Orange	—	—	(608)	(748)	—	—	—	1.02	0.412	31	0.13

[a]; CA = citric acid, GS = glutinous starch syrup, DX = dextrin, SC = sodium carbonate, SA = sodium L-ascorbate, SMP = sodium metaphosphate, Their contents are indicated in parenthesis. [b]; Measured for aqueous solutions of natural dyes except for (iv) for which ethanol was used as solvent. In parenthesis are the values for the same dyes adsorbed on TiO_2 films. [c]; Measured at λ_{max} of adsorbed dyes.

Dye adsorption on the semiconductor electrodes has been carried out by soaking them while they are still warm (about 80 °C) after sintering into 1% aqueous solutions of the food colorants and keeping overnight or by refluxing for 1 hour. Ethanolic solution was used for Crucumin (iv) due to its limited solubility to water.

A Pt sputtered FTO glass counter electrode was attached in face to face to a dye modified semiconductor film photoelectrode by a thermally fused adhesive film spacer (ca. 80 μm) to configure a photocell. Electrolyte solution made by dissolving 0.5 M KI and 0.03 M I_2 in ethylene carbonate / acetonitrile (4:1 by volume) was introduced to the gap between the two electrodes by capillary action. A white light (100 mW/cm^2) generated by a 500 W Xe lamp equipped with an IR cut and a 420 nm long pass filters was shined from the side of the photoelectrodes for the measurements of *I-V* characteristics. Monochromatic light illumination was used for the measurements of photoaction spectra by IPCE scale. Intensity of incident light was measured by an EPPLEY thermopile. Since the purity, molecular weight and molar absorptivity of the dyes used in this study are uncertain, the degree of film coloration has been compared by light harvesting efficiency (LHE) which is defined as the proportion of photons absorbed by the dyes over incident photons. The determination of LHE allows comparison of the system efficiency by internal quantum efficiency (APCE), as IPCE is simply related to APCE by

$$IPCE = APCE \times LHE \quad (1)$$

Since TiO_2 electrodes were highly transparent with a transmittance as high as 95%, LHE was determined from the transmission spectra measured on a Hitachi U-3500 spectrophotometer by neglecting reflected and scattered light. On the other hand, ZnO was highly scattering. LHE in this case was determined from diffuse reflection spectra measured on a Hitachi U-4000 spectrophotometer, as one can neglect transmitted light.

3. RESULTS AND DISCUSSION

Although exact molecular structures of the natural dyes are unknown often being mixtures of several kinds of dye molecules with uncertain compositions, most of the dyes are soluble to protic solvents such as water and alcohol owing to the presence of COOR, COOH or OH groups in their framework (Fig. 1). These chemical groups are expected to form chemical bond to the surface of oxide semiconductors for attachment of the dye molecules. The food colorants contain additives for stabilization of the dye molecules as indicated in Table1. These additives, especially organic acids, can also be adsorbed on the surface of metal oxide semiconductors. Nevertheless, both TiO_2 and ZnO films could be nicely colored by all of the dyes, suggesting higher affinity of dye molecules to the semiconductor surfaces than the additives. The films were nicely colored even by the direct extracts from the food samples, for which dye content should be fairly low and many kinds of chemicals other than dyes should be present.

The color of dyes often changed after adsorption on semiconductors from that of the dye solutions, probably due to formation of ordered aggregates which causes specific intermolecular electronic interactions between the dye chromphores. The color of adsorbed dyes was

also different between TiO_2 and ZnO. An example of the color change is shown for Cohineal dye (ii) in Fig. 2. The aqueous solution of (ii) is red having an absorption maximum at 492 nm. The color of TiO_2 film turns into brownish red after adsorption of (ii). The absorption peak is significantly broadened and the maximum is slightly blue shifted to 480 nm. When the same dye was adsorbed on ZnO, it became purple. The absorption range is clearly red shifted to show a characteristic spectrum having two maxima at 547 and 588 nm. Cohineal is a kind of anthraquinone dye having a rod-like π-system. The observed red shift suggests formation of dye J-aggregates in which head to tail electronic interaction of dye chromophores becomes dominant. The absorption peak wavelength (λ_{max}) and the absorption threshold (λ_{thd}) below which photon absorption arises both for solutions and as adsorbed on TiO_2 (Table 1) or ZnO (Table 2) are listed also for other dyes. The longer λ_{thd} is, the higher portion of solar radiation can potentially be harvested. However, the photon harvesting efficiency also depends on the degree of coloration. The degree of coloration can be seen from the LHE values read from the transmission (TiO_2) and reflection (ZnO) spectra at the absorption maximum (Tables 1 and 2). By average, dye adsorbed ZnO had a deeper color than the dye modified TiO_2 as noticed from the higher values of LHE. Although no precise measurement was carried out, the color of dyes appeared rather stable after adsorption on semiconductor surfaces.

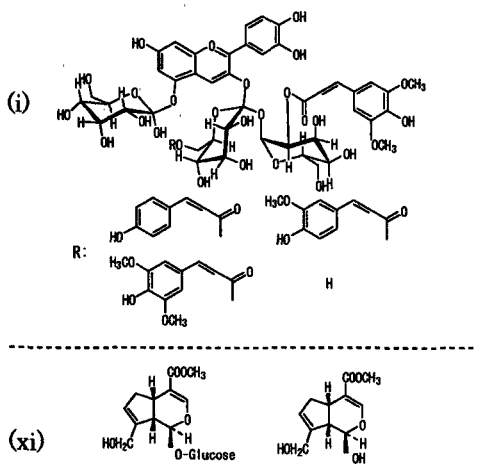

Fig. 1 Structures of dyes (i) and (xi).

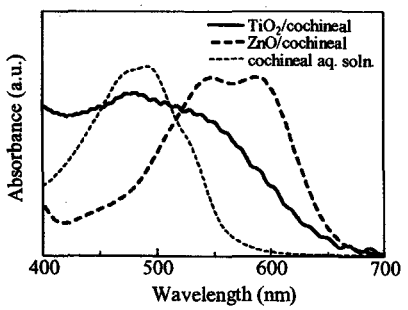

Fig. 2 Absorption spectra of (ii) Cochineal dye as aqueous solution, as adsorbed on TiO_2 and ZnO.

Table 2 Photoelectrochemical properties of ZnO/natural dye cells.

Dye	λ_{max}* (nm)	λ_{thd}* (nm)	LHE (%)	IPCE (%)	APCE (%)	I_{sc} (mA/cm^2)	V_{oc} (mV)	*F.F.* (%)	η (%)
(i)	592	701	54	—	—	0.55	286	31	0.050
(ii)	588	700	40	—	—	0.049	38	—	—
(iii)	523	649	46	—	—	0.12	170	33	0.0068
(iv)	433	601	52	3.0	5.8	0.92	273	28	0.070
(v)	430	615	43	—	—	0.47	282	33	0.051
(vi)	433	500	27	0.9	3.3	0.29	307	63	0.057
(vii)	429	550	31	—	—	0.69	353	43	0.10
(viii)	493	621	46	—	—	0.12	136	29	0.014
(ix)	523	648	44	—	—	0.69	323	51	0.11
(x)	437	608	28	—	—	0.64	285	41	0.075
(xi)	596	692	48	3.2	6.7	0.97	286	45	0.13
(xii)	543	730	50	—	—	0.22	276	32	0.019
(xiii)	459	650	41	0.6	1.5	0.19	254	29	0.014
(xiv)	458	800	13	1.0	7.7	0.17	153	31	0.0081
(xv)	632	734	34	—	—	0.26	299	39	0.030
(xviii)	530	700	51	—	—	0.55	149	27	0.022

*: Measured for the dyes adsorbed on ZnO. Dyes were adsorbed from aqueous solutions except for (i) and (iv) for which ethanolic solutions were used.

However, there was a tendency that dyes (viii)(ix)(xi) (xvi) and (xix) were bleached after storage of the samples for about a month even in the dark, while dyes (ii) – (vi) (xii)(xiii)(xvii)(xviii)(xx) did not change the color at all. The stability of the rest was in between above two groups. The stability of the photocells showed a similar trend to that of color bleaching.

Sandwich type photocells were fabricated using the dye-modified semiconductor film electrodes for photoelectrochemical measurements. White light illumination at an intensity equivalent to 1 sun generated electrical outputs from all of the cells. Since UV portion of Xe lamp was cut by a filter, the observed photoresponse cannot arise from photon absorption by TiO_2 or ZnO, but is a clear proof of photosensitization by the natural dyes. The short circuit photocurrent (I_{sc}), open circuit photovoltage (V_{oc}), fill factor (*F.F.*) and light to electric power conversion efficiency (η) were determined from the measured *I-V* curves and are listed for each TiO_2/dye (Table 1) and ZnO/dye (Table 2) cells. Incident monochromatic photon to current conversion efficiency (IPCE) has also been measured at the absorption maximum of the adsorbed dye. Absorbed photon to current conversion efficiency (APCE) which indicates internal quantum efficiency of the cells was derived by dividing the IPCE values by LHE at the same wavelength. These values are also listed in Tables 1 and 2. The highest power conversion efficiency was obtained by the combination of TiO_2 and red cabbage (i) dye, achieving I_{sc}, V_{oc}, *F.F.*, η, IPCE and APCE of 4.70 mA/cm^2, 0.525 V, 61%, 1.51%, 25% and 41%, respectively (Fig. 3). This is a quite high efficiency on considering the fact that eosinY, a pure synthetic organic dye typically used as a photosensitizer, achieved only η = 1.3% in combination with nanocrystalline TiO_2 [12]. Besides (i), Cohineal dye (ii) exhibited the highest I_{sc} of 6.00 mA/cm^2, while the highest V_{oc} of 0.570 V was attained by Gardenia yellow (vi). One can also notice

that (vi) and Kaoliang dye (v) exhibit higher APCE values than (i) indicating that the lower η should mainly be attributed to the lower LHE. Further improvement of conversion efficiencies is therefore expected by increasing LHE through optimization of film thickness and the adsorption procedure. It is interesting to note that direct use of food samples was also quite effective in combination with TiO_2. Strawberry (xvi) was the most efficient sensitizer achieving η = 0.61%.

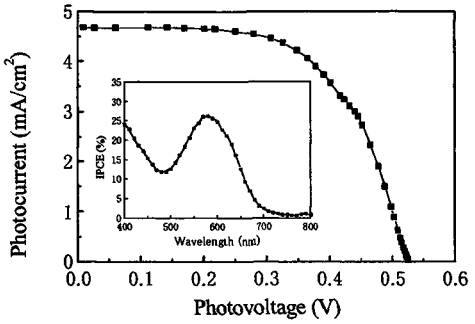

Fig. 3 Photocurrent – voltage characteristics and photocurrent action spectrum (the inset) of TiO_2/Red cabbage (i) cell.

By average, ZnO/dye cells gave poorer efficiencies than TiO_2/dye cells (Table 2). The difference may be attributed to the less efficient electron injection from excited dyes to the conduction band of ZnO and/or the higher recombination of the injected electron and oxidized dye as compared to the case with TiO_2. However, it is interesting to note that the order of the efficiencies for the dyes is totally different from that with TiO_2. The highest η of 0.13% was obtained for Gardenia blue (xi) with ZnO. The next was Monascus dye (ix) (η = 0.11%). Both of them were not very well performing in combination with TiO_2. On the other hand, Cochineal dye (ii) which was one of the best sensitizers for TiO_2 was found to be extremely poor on ZnO. Dye (ii) was found to give very different absorption spectra on TiO_2 and ZnO (Fig. 2). It is likely that ordered packing of (ii) on ZnO surface in J-aggregate form enhances self quenching of dye excited states and significantly reduces its activity as photosensitizer. Since the position of conduction band is almost the same for anatase TiO_2 and ZnO (ca. -0.4 V vs. NHE), matching of energy levels with those of dye excited states cannot account for the observed differences of efficiencies. They may arise from the differences in the intermolecular electronic interaction occurring as a consequence of surface dye aggregation as well as the electronic interaction between electron orbital of adsorbed dye and conduction band of semiconductors which should be influenced by the nature of chemical bonds between them. This conversely means that we have good possibilities to find better sensitizers from extremely wide choice of natural dyes, depending on the kind of semiconductors to be used as electrodes. Since high efficiencies have been reported for natural dye sensitized cells employing aqueous redox electrolyte solution [9], dramatic improvements of the cell efficiencies are expected also by this approach.

It has been shown through the present study that various kinds of natural dyes can be used as good photosensitizers for DSCs. The highest advantage of natural dyes is their low cost, low toxicity and high recyclability. It has also been shown that they do not need to be pure. Neither the impurities added to the food colorants nor those of raw natural matters hindered coloration of the semiconductor films, indicating a self-purification during the process of chemical adsorption of dyes on semiconductor surfaces. Application of natural dyes as photosensitizers is therefore very promising even when we intend large scale production of DSCs.

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