Int. J. Electrochem. Sci., 8 **(2013)** 8320 - 8328

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Curcumin Dye Extracted from *Curcuma longa* L. Used as Sensitizers for Efficient Dye-Sensitized Solar Cells

Hee-Je Kim[1], *Dong- Jo Kim*[1], *S.N. Karthick*[*,1], *K.V. Hemalatha*[1], *C. Justin Raj*[1,2], *Sunseong ok*[3], *Youngson choe*[3]

[1] School of Electrical Engineering, Pusan National University, Jangjeon, Geumjeong, Busan 609-735, Republic of Korea.
[2] Department of Chemistry, University of Dongguk-Seoul, Jung-gu, Seoul, 100-715, South Korea.
[3] Department of Chemical Engineering, Pusan National University, Jangjeon, Geumjeong, Busan 609-735, Republic of Korea.
[*]E-mail: snkarthick007@gmail.com

Received: 12 April 2013 / *Accepted:* 7 May 2013 / *Published:* 1 June 2013

The natural dye, curcumin, was extracted from *Curcuma longa* L. using a simple extraction technique. The dye was then used as a sensitizer in a dye-sensitized solar cell (DSSC) without further purification, and its characteristics were studied. The dye was treated with acetic, nitric and hydrochloric acid for stabilization and increasing the conversion efficiency. The current conversion efficiency was 0.60% for the acetic acid-treated curcumin dye, which was double that of the nitric and hydrochloric acids treated dyes. The short-circuit current (J_{sc}), open-circuit voltage (V_{oc}) and fill factor of the DSSCs made from the acetic acid treated dye were 1.6544 mA cm^{-2}, 0.5511 V and 0.6646 respectively. Therefore, the addition of acetic acid to the curcumin dye results in slightly higher conversion efficiency than the bare dye, whereas the conversion efficiency is suppressed when the dye is treated with nitric and hydrochloric acid. This paper briefly discusses the effects of naturally obtained curcumin dye on the performance in DSSCs.

Keywords: Natural dye, Curcumin, Dye-sensitized solar cell, Photocurrent conversion efficiency

1. INTRODUCTION

Over the past two decades, dye-sensitized solar cells (DSSCs) have attracted considerable attention as a replacement for conventional inorganic semiconductor photovoltaic devices because of the low fabrication costs. The DSSC is basically composed of a photoanode, a sensitizer, redox electrolyte and photocathode. The dyes are sensitizers that play a key role in light harvesting and in the conversion of solar energy to electrical energy. Dyes are referred to as “sensitizers” because the dye molecules in DSSCs “sensitize” wide-bandgap semiconductors to visible radiation. Gratzel and

O’Regan [1] first reported the performance of this cell in 1991 using ruthenium polypyridyl complexes as a sensitizer because of their intense charge transfer absorption in the visible range, increase in the excited lifetime of the electron, transfer of charge from dye to TiO_2 and effective anchorage of the dye to the TiO_2 surface [2]. Ruthenium polypyridyl complexes are anchored to nanocrystalline TiO_2 surfaces through carboxylic acid groups [1]. On the other hand, the long-term unavailability and high cost of Ru highlights the need to identify low-cost, efficient sensitizers. Natural dyes are well known for their high extinction coefficient, cheap and easy availability, nontoxic and renewable reservoir to materials for many applications. These types of dyes are promising alternative sensitizers for DSSCs because they are easy to prepare, widely available, cheap and eco-friendly. Accordingly, they have attracted the attention of the scientific community for use in dyeing textile fibers and photosensitized solar cells [3]. Thus natural sensitizers, such as anthocyanin, chlorophyll, carotenoid and xanthophyll pigments, have been used in DSSCs. These sensitizers were extracted from the flowers such as Blue pea (0.05%), Annatto (0.19%), Norbixin (0.13%), Spinach (0.13%), Frutus lyciia (0.17%), Lily (0.17%) [4-7]. The conversion efficiency was very poor with the cells sensitized with these natural extracts. So in order to improve the conversion efficiency the research is under progress on the extraction of various type of natural dye. In the present study yet another attempt was made to extract the dye from another natural resource namely Curcuma longa L. Interestingly, the use of curcumin-derived dyes as sensitizers in dye sensitized solar cells has not attracted significant research attention. Curcumin, which is derived from the ground rhizome of *Curcuma longa* L. (turmeric), has a long intense wavelength absorption range from 420-580 nm in the visible region [8]. In addition, curcumin is a promising material for use in solar cells owing to its high thermal and chemical stability, as well as its eco-friendliness and cost effectiveness.

In the present investigation, DSSCs were assembled using curcumin as a sensitizer extracted by solvent extraction from commercial turmeric, which is present at a concentration of 1.5–2.0 wt % [9]. The extracted curcumin was used as extracted without any purification in order to monitor the performance of the dye with minimal chemical procedure and simple extraction technique. The first important feature of curcumin is the presence of extended conjugation in its structure due to the aromatic and enol groups, which provide the basic long-wavelength absorption. A second prominent feature is the presence of methoxy and hydroxyl groups in the 3- and 4-positions, respectively, of the terminal phenyl groups, which results in a further bathochromic shift in the maximum (λ_{max}) absorption of this compound [9]. Curcumin molecules, however, are unstable in basic media and undergo rapid hydrolytic degradation with a half life of a few minutes accompanied by a strong decrease in the absorbance in the visible region. Therefore, curcumin was treated with acetic, nitric and hydrochloric acid to improve its stability, and increase its color intensity and conversion efficiency. Therefore, acid was added externally to the curcumin dye, and the current conversion efficiency was evaluated.

2. EXPERIMENTAL DETAILS

2.1 Preparation of dye sensitizer solutions

Curcumin was extracted from commercially purchased turmeric powder prepared from the ground rhizome of *Curcuma longa* L.. Approximately 0.25 g of the sample was dissolved in 50 mL of ethanol. After extraction, the solid residues were filtered out, and the clear solutions were used as prepared. Further purification of the extracts was avoided to achieve efficient sensitization using simple extraction procedures. The extractants were properly stored, protected from direct sunlight, and used further as sensitizers in DSSCs.

2.2 Solar-cell assembly

A fluorine-doped tin oxide (FTO) glass plate of 13 Ω/sq was used as a current collector. The FTO plate was first cleaned with acetone, ethanol and water for approximately 10 min each using an ultrasonic bath. A spacer was used to control the film thickness and provide uncoated areas for electrical contact. The doctor-blade technique was adapted to coat the TiO_2 paste (Ti-nanoxide T/SP, Solaronix) on the FTO plate. After coating, the TiO_2 films were air-dried for approximately 5 min to reduce the surface irregularities. The substrates were then annealed at 450°C in air for 30 min to facilitate interconnection of the TiO_2 nanoparticles and remove the organic loads present in the film. The film thickness was ~20 µm, and the active area of the TiO_2 electrodes used was 0.18 cm^2. After annealing, the TiO_2 film electrodes were cooled to 80 °C, and immersed in an extracted curcumin dye solution for 24 h. After dye adsorption, the film was cleaned with pure ethanol and dried with hot air. A Pt electrode was prepared using platinum paste (platisol T/SP, Solaronix). The paste was coated on the FTO glass plate using the doctor-blade technique and heated to 400 °C for 30 min. The dye-covered TiO_2 electrode and Pt counter electrode were assembled as a sandwich-type cell. One drop of Iodolyte AN-50 (Solaronix) electrolyte solution was injected into the cell through a hole at the back of the counter electrode. The hole was then sealed with hot-melt ionomer film (SX 1170, Solaronix) and covered with glass. Finally, the edge of each side of the FTO glass was cleaned and soldered (ultrasonic soldering system, Model-9200) with alloy #143 (Cerasolza) to achieve good electrical contact for the measurements.

2.3 Material characterization

Fourier transform infrared (FTIR, Perkin Elmer US/Spectrum GX) spectroscopy was performed using KBr pellets. The UV-Vis absorption spectra were recorded on a UV-VIS-NIR scanning spectrophotometer (Optizen-3220UV, MECASYS). The current-voltage characteristics were measured at one sun illumination (AM 1.5 G, 100 mW cm^{-2}) using a Keithley 2400 source measurement unit.

3. RESULTS AND DISCUSSION

3.1 Fourier transform infrared spectral analysis

Fig. 1 shows the IR spectra of curcumin. The spectrum of curcumin in the present study coincides with that reported by Zebib et al.,[10]. The broad band at 3341 cm^{-1} was assigned to the vibrations of the free hydroxyl-group of phenol (Ar-OH). The bands at 719, 815 and 962 cm^{-1} were attributed to the bending vibrations of the C-H bond of alkene groups ($RCH=CH_2$). An intense band at 1745 cm^{-1} assigned to the vibration of the carbonyl bond (C=O) accompanied by a small shoulder at 1712 cm^{-1} was attributed to the Keto-enol tautomerism of curcumin. The bands at 1463 and 1378 cm^{-1} corresponding to the vibrational mode of C−O elongation of the alcohol and phenol groups confirmed the extraction of curcumin from turmeric.

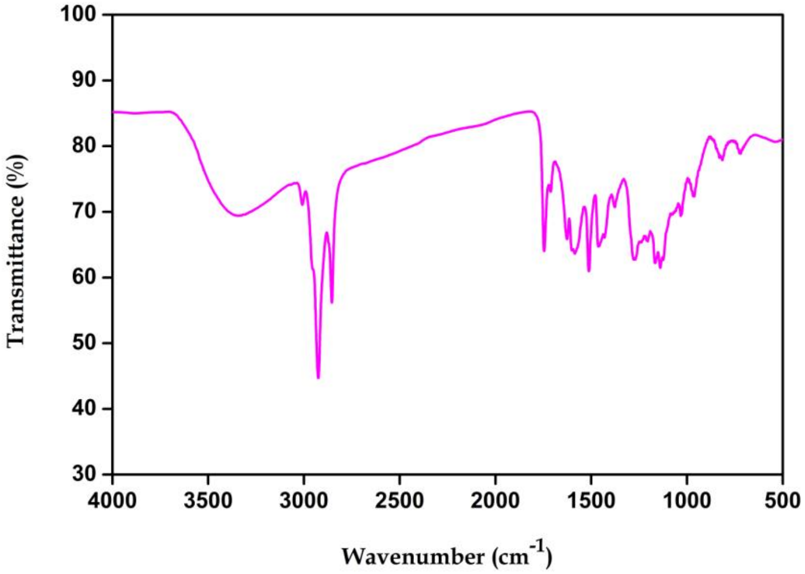


Figure 1. FT-IR spectrum of natural dye extracted from *Curcuma longa* L.

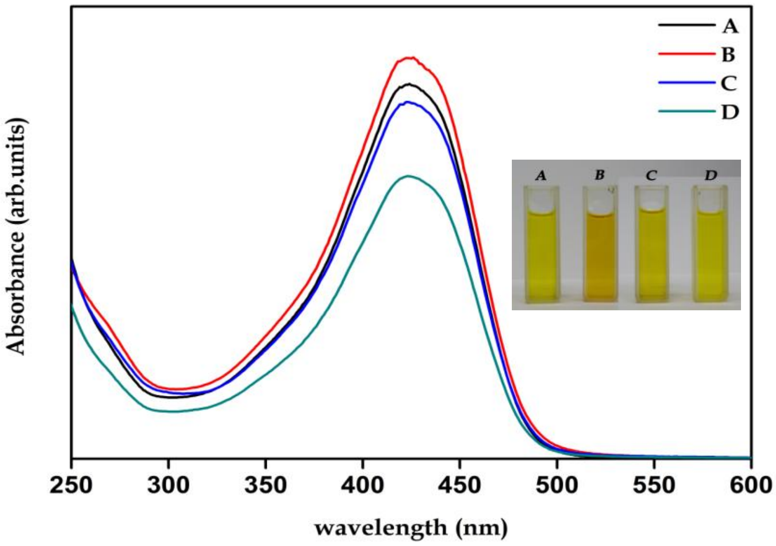


Figure 2. UV absorption spectra of natural dye solution extracted from *Curcuma longa* L. A - Curcumin; B – Curcumin treated with hydrochloric acid; C – Curcumin treated with nitric acid; D – Curcumin treated with acetic acid (Inset figure: Image of fresh dye solutions)

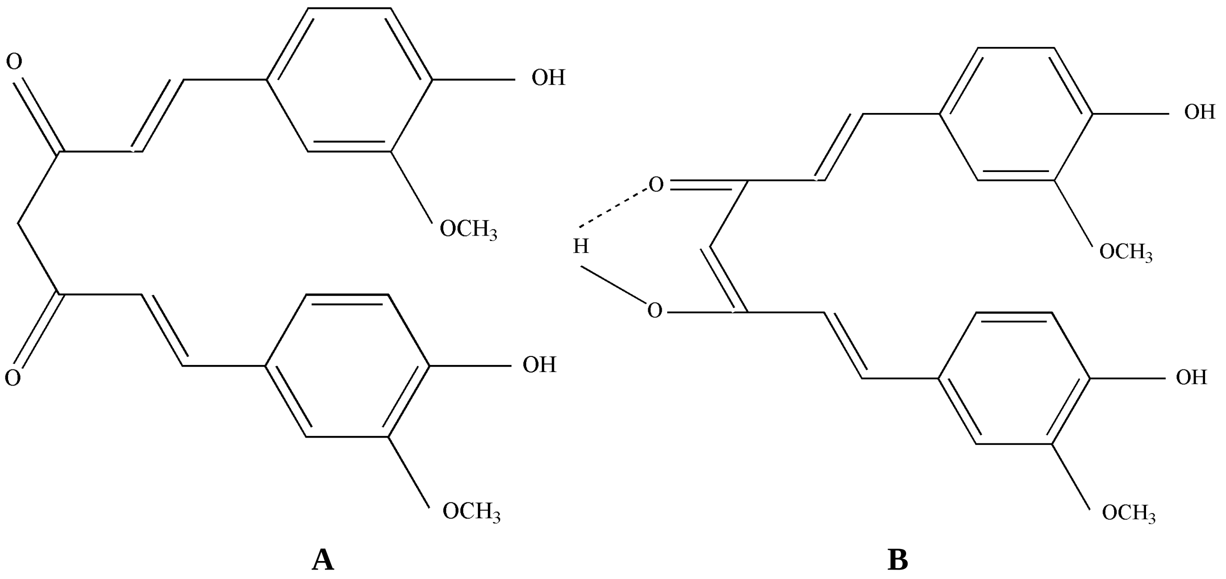


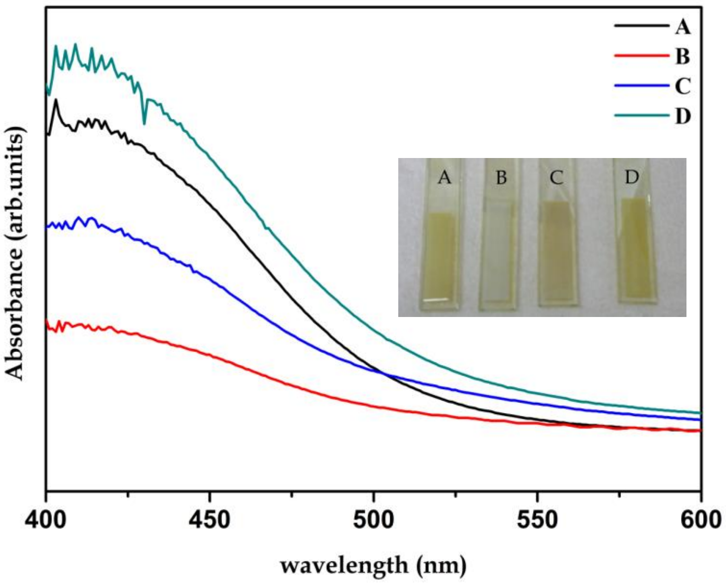
Figure 3. Structure of Curcumin a) Keto form and (b) Enol form

3.2 UV-Visible absorption spectroscopy

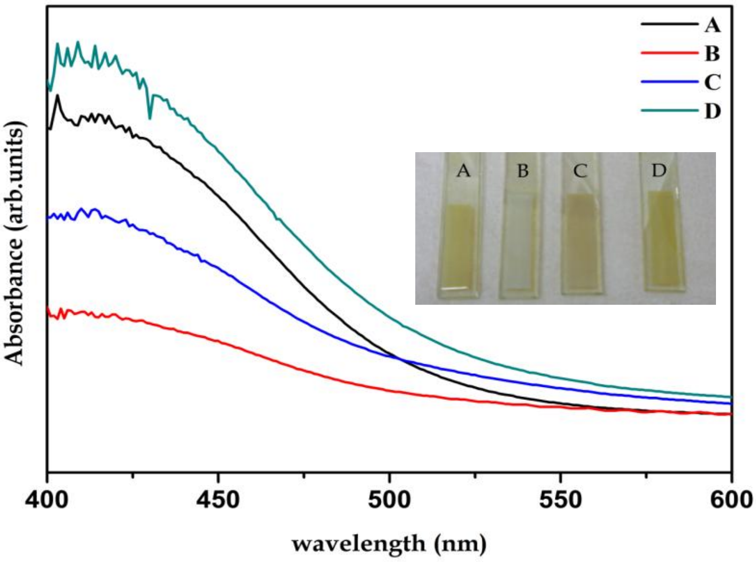
Fig. 2 shows the UV-Vis absorption spectrum of curcumin and curcumin treated with acids. Curcumin is a strongly solvent dependent and it posses broad UV absorption spectrum from 300 to 500 nm due to the presence of phenolic groups. Curcumin exists in an enol form. The presence of the diketone (Fig. 3a) moiety is responsible for the enol form (Fig. 3b) of curcumin with *trans* geometry both in the solid state and solution [11]. Therefore, in a planar geometry, enolization allows conjugation between the π electron systems of the two feruloyl chromophores through the central sp^2 hybridized carbon atom, resulting in light absorption in the visible range causing the yellow color [11]. The yellow colored curcumin dye extracted from the ethanolic solution showed an intense absorption band at 425 nm in polar solvents for all acid treatments. Electron excitation from the $\pi \rightarrow \pi^*$ transition is responsible for the absorption band in the visible range, not a $n \rightarrow \pi^*$ transition, which was proved by a theoretical study. The first excited state of curcumin was highly polar due to intramolecular charge transfer from the phenyl ring towards the carbonyl moiety [12].

In the absorption spectra of a fresh dye solution (Fig. 2), the absorption was high with the HCl-treated dye followed by the bare dye, HNO_3-treated and finally CH_3COOH treated dye. Curcumin was treated with acids because it is more stable under acidic conditions. Under basic conditions, the compound will degrade to trans-6-(4′-hydroxy-3′-methoxyphenyl)-2,4-dioxo-5-hexanal, ferulic acid, feruloylmethane and vanillin within a short period of time [13]. Therefore, the study was carried out with curcumin dye under acidic conditions to improve the stability of curcumin.

Fig. 4 shows the absorption spectra of TiO_2-adsorbed curcumin. A broad absorption peak in all samples indicates that the dye adsorbed well on the TiO_2 particle because the dye sensitizer increased the absorption of light by the TiO_2 nanoparticles in the visible range. The intensity of the spectra was high for the curcumin treated with CH_3COOH followed by the bare dye compared to HCl and HNO_3 treated dyes.



A



B

Figure 4. UV absorption spectra of TiO_2 adsorbed dye of *Curcuma longa* L. A – Curcumin; B – Curcumin treated with hydrochloric acid; C – Curcumin treated with nitric acid; D – Curcumin treated with acetic acid (Inset figure: Image of dye adsorbed TiO_2)

The controversy in the order of intensity with the fresh dye solution and TiO_2 adsorbed dye was attributed to an interaction of the acidified dye with the TiO_2 photoanode, HCl and HNO_3, being strong acids with high dissociation constants, in the sensitizers might etch the TiO_2 photoanode and create defect centers [14], which leads to a decrease in dye adsorption which ultimately reflects on light absorption by the sensitized TiO_2 nanoparticles in the visible range.

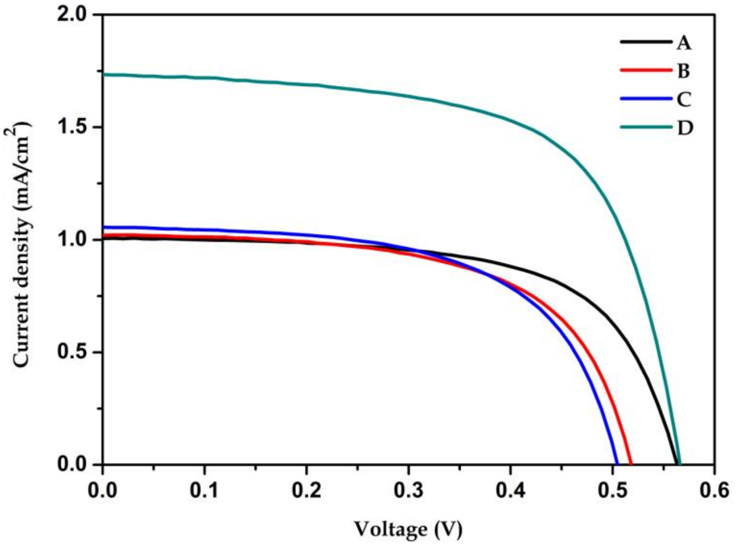


Figure 5. Photocurrent-voltage characteristics of the DSSC using the natural dye of *Curcuma longa* L. (A – Curcumin; B – Curcumin treated with hydrochloric acid; C – Curcumin treated with nitric acid; D – Curcumin treated with acetic acid)

Table 1. Characteristics of the dye sensitized solar cell fabricated using the curcumin dye of *Curcuma longa* L. with and without acid treatments.

Sample	Voc (V)	Jsc (mA/cm^2)	Fill Factor	Efficiency (%)
Curcumin	0.5632	1.0055	0.6399	0.36
Curcumin + HCl	0.5194	0.9003	0.6094	0.28
Curcumin + HNO_3	0.5046	0.9252	0.6055	0.28
Curcumin + CH_3COOH	0.5511	1.6544	0.6646	0.60

3.3 Current-voltage measurement for DSSC

Table 1 lists the conversion efficiencies of the DSSCs fabricated using curcumin extracted from the curcumin treated with acetic, nitric and hydrochloric acid and without acid. The efficiency of the acetic acid-treated dye was 0.60%, which is high compared to the untreated dye (0.36%), nitric and hydrochloric acid (0.28%) treated dyes. The efficiency was doubled with the acetic acid treatment. The open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor (*FF*) of the acetic acid treated dye was 0.551 V, 1.6544 mA cm^{-2} and 0.6646, respectively. The conversion efficiency of the DSSCs fabricated from the hydrochloric and nitric acid treated dye was 0.28%, the V_{oc} was 0.5194, 0.5045 V, J_{sc} was 0.9003, 0.9252 mA cm^{-2}, and *FF* was 0.6094, 0.6055, respectively (Fig. 5).

The J_{sc} was lower for the nitric and hydrochloric acid treated dyes because during coordination of the dye with the photoanode, the presence of these acids in the dye might modify the surface state of the porous film and create defect centers on the surface of TiO_2. These defects prevent the transfer of electrons to the TiO_2 grid from the excited state of the sensitized dye molecule, which reduces the electron transportation efficiency [14]. Sometimes, the presence of these acids in dyes can alter the size of the TiO_2 nanoparticle and reduce the surface area of TiO_2, which makes a smaller contact area between the particles, creating difficulty for the electrons to flow, and leading to a decrease in J_{sc}.

According to Sreekala et al. [15] a better photovoltaic performance was obtained when the curcumin dye was extracted with acetone as a solvent, they obtained an efficiency, open circuit voltage (V_{oc}), short circuit current density and fill factor of 0.63%, 0.43 V, 1.35 mA cm^{-2} and 0.517, respectively. In the present study, using ethanol as the extractant, the efficiency, V_{oc}, current density and fill factor was 0.36%, 0.56 V, 1.00 mA cm^{-2} and 0.6399, respectively. The efficiency was enhanced to 0.60% by the addition of acetic acid to the dye. This efficiency was similar to that reported by Sreekala et al. [15].

Sreekala et al. [15] reported a better DSSC performance by treating the TiO_2 photoanode with HCl before soaking in dye. On the other hand, in the present study, acids were added directly to the dye, which resulted poor performance compared to the bare dye. This is because in the acidified dye, the TiO_2 surfaces are affected by HCl, which strongly suppresses the adsorption of dye on the TiO_2 surface. The inset Figure in Fig. 4 clearly shows the adsorption of dye on the TiO_2 surface, which can be observed directly with the naked eye. The adsorption was stronger with the acetic acid-treated dye and bare dye than the nitric acid and HCl treated dye. Therefore, the efficiency obtained was also in the same sequence.

From the above results, most natural-dye-based DSSCs produce efficiencies of less than 1%. The main reasons for the low efficiencies of the natural dyes are the structure of the pigment, the anchoring group in the natural dye, and stability. The performance of the cells sensitized with the natural dye extracted from Dragon fruit (0.22%), Kerria japonica (0.22%), Rosa chinensis (0.29%), Begonia (0.24%), Tangerin peel (0.28%), Marigold (0.23%), China loropetal (0.27%), yellow rose (0.26%), Flowery knotweed (0.21%), and Ipomoea (0.27%) [16-19] showed much lower efficiencies than our pigments. Some of the natural dyes extract from Rose (0.38%), Petunia (0.32%) [18], Rosella (0.37%), Bixin (0.37%), Bougainvillea (0.36%), Rhododendron (0.33%) [20-23] provided similar efficiency to the dye in the present study.

4. CONCLUSION

DSSCs were assembled using natural dyes extracted from the ground rhizome of *Curcuma longa* L. as photosensitizers. The curcumin extracts used as a sensitizer after an acetic acid treatment produced the best photosensitized effect compared to the hydrochloric and nitric acid treatments. This was attributed to a better interaction between the acetic acid-treated dye and the TiO_2 surface. Therefore, the acetic acid-treated curcumin acts as an efficient sensitizer, whereas the nitric and hydrochloric acid treated curcumin etches the TiO_2 surface, leading to a decrease in current density

(J_{sc}). The DSSCs using acetic acid-treated curcumin under irradiation of AM 1.5 (100 mW cm^{-2}) simulated sunlight showed an energy conversion efficiency, J_{sc}, V_{oc} and FF of approximately 0.6%, 1.65 mA cm^{-2}, 0.55 V and 66%, respectively.

ACKNOWLEDGEMENT
This work was supported by the Mid-career Research Program through NRF grant funded by the MEST (No. 2011-0001295).

References

1. B.O. Regan, M. Grätzel, *Nature* 353 (1991) 737-739.
2. P. Luo, H. Niu, G. Zheng, X. Bai, M. Zhang, W. Wang, *Spectrochim Acta Part A.* 74 (2009) 936-942.
3. A. Mishra, S. Daswal, *Colloid Polym. Sci.* 285 (2007) 1109-1117.
4. K. Wongcharee, V. Meeyoo, S. Chavadej, *Sol. Energ. Mat. Sol. C.* 91 (2007) 566-571.
5. N.M. Gomez-Ortiz, I.A. Vazquez-Maldonado, A.R. Perez-Espadas, G.J. Mena-Rejon, J.A. Azamar-Barrios, G. Oskam, *Sol. Energ. Mat. Sol. C.* 94 (2009) 40-44.
6. H. Chang, H.M. Wu, T.L. Chen, K.D. Huang, C.S. Jwo, Y.J. Lo, *J. Alloy. Compd.* 495 (2010) 606-610.
7. H. Zhou, L. Wu, Y. Gao, T. Ma, *J. Photochem. Photobio. A.* 219 (2011) 188-194.
8. T. Ganesh, J.H. Kim, S.J. Yoon, S. Lee, W. Lee, R.S. Mane, J.W. Han, S.H. Han, *J. Appl. Phys.* 106 (2009) 084304-5.
9. J.V. Crivello, U. Bulut, *J. Polym. Sci. Part A Polym. Chem.* 43 (2005) 5217-5231.
10. B. Zebib, Z. Mouloungui, V. Noirot, *Bioinorg. Chem. Appli.* (2010) 292760.
11. F. Zsila, Z. Bikadi, M. Simonyi, *Biochem. Biophys. Res. Commun.* 301(2003) 776-782.
12. F. Zsila, Z. Bikadi, M. Simonyi, *Tetrahedron Asymmetry* 14 (2003) 2433-2444.
13. R.A. Sharma, A.J. Gescher, W.P. Steward, *Eur. J. Cancer.* 41 (2005) 1955-68.
14. S. Hao, J. Wu, Y. Huang, J. Lin, *Sol. energy* 76 (2004) 745-750.
15. C.O. Sreekala, I. Jinchu, K.S. Sreelatha, Y. Janu, N. Prasad, M. Kumar, A.K. Sadh, M.S. Roy, *IEEE J. Photovoltaics.* 2 (2012) 312-319.
16. R.A.M. Ali, N. Nayan, *Int J. Integrated Eng.* 2 (2010) 55-62.
17. K.V. Hemalatha, S.N. Karthick, C. Justin Raj, N.Y. Hong, S.K. Kim, H.J. Kim, *Spectrochim. Acta Part A* 96 (2012) 305-309.
18. H. Zhou, L. Wu, Y. Gao, T. Ma, *J. Photochem. Photobio. A.* 219 (2011) 188-194.
19. H. Chang, H.M. Wu, T.L. Chen, K.D. Huang, C.S. Jwo, Y.J. Lo, *J. Alloys Compd.* 495 (2010) 606-610.
20. K. Wongcharee, V. Meeyoo, S. Chavadej, *Sol. Energy Mater. Sol. Cells* 91 (2007) 566-571.
21. N.M. Gomez-Ortiz, I.A. Vazquez-Maldonado, A.R. Perez-Espadas, G.J. Mena-Rejon, J.A. Azamar-Barrios, G. Oskam, *Sol. Energy Mater. Sol. Cells* 94 (2009) 40-44.
22. G. Calogero, G.D. Marco, S. Cazzanti, S. Caramori, R. Argazzi, A.D. Carlo, C.A. Bignozzi, *Int. J. Mol. Sci.* 11 (2010) 254-267.
23. H.-J. Kim, Y.-T. Bin, S.N. Karthick, K.V. Hemalatha, C. Justin Raj, S.Venkatesan, Songyi Park, G. Vijayakumar, *Int. J. Electrochem. Sci.* 8 (2013) 6734-6743.