ENHANCED PERFORMANCE OF BIXIN-SENSITIZED TiO₂ SOLAR CELLS WITH ACTIVATED KAOLINITE

Ayong Hiendro, Ferry Hadary, Winda Rahmalia, Nelly Wahyuni, Tanjungpura University

Abstract

The development of a natural dye sensitizer for solar cell applications has attracted much attention because of its inherent advantages, such as inexpensive, simple preparation, easily available resources, and being environmentally friendly. However, the main problems associated with dye-sensitized solar cells (DSCs) are low photostability and low efficiency. In this study, an alternative method for improving DSC performance using activated kaolinite was evaluated. Pure bixin extracted from achiote seeds (*bixa orellana l.*) was immobilized on the activated kaolinite. Kaolinite-bixin was synthesized and used as a sensitizer in nanocrystalline titanium-dioxide-based DSCs. Experimental results showed that kaolinite-bixin is better than pure bixin in ultraviolet-visible (UV-Vis) light absorption, photostability, and photoelectric conversion efficiency. In this case, the titanium dioxide (TiO₂) kaolinite-bixin sensitized solar cells yielded conversion efficiencies up to 1.01%.

Introduction

Organic dyes from natural extracts have been applied in DSCs [1-11]. These natural dyes were obtained by purification from fruits, flowers, and leaves of plants. Thus far, these natural dye sensitizers can provide photoelectric conversion efficiencies of 0.05% to 2.09% [1-11].

Wongcharee et al. [1] reported conversion efficiencies of DSCs with rosella, blue pea, and mixed extracts as 0.37%, 0.05%, and 0.15%, respectively. Fernando & Senadeera [2] used natural anthocyanins extracted from hibiscus surattensis, sisbania geandiflora scarlet, hibiscus rosasinensis, nerium oleander, ixora macrothyrsa, and rhododendron arboretum zeylanicum for DSCs. The best conversion efficiency was 1.14%, and it was achieved by using hibiscus surattensis extract as a sensitizer. Using rose bengal extract resulted in a conversion efficiency of 2.09% [3]. Red sicilian orange and eggplant peel extracts yielded conversion efficiencies of 0.66% [4]. Luo et al. [5] used canna indica l., salvia splendens, cowberry, and solanum nigrums l. extracts as photosensitizers and achieved conversion efficiencies of 0.29%, 0.26%, 0.13%, and 0.31%, respectively. Calogero et al. [6] reported a conversion efficiency of 1.70% using red turnip extract and 1.26% when using wild sicilian prickly pear fruit extract as a sensitizer. Gomez-Ortiz et al. [7] used bixin extracted from achiote seeds as a sensitizer and reported their best results in efficiencies up to 0.53%. Chang & Lo [8] used pomegranate leaf and mulberry fruit extracts as sensitizers. They reported conversion efficiencies of pomegranate leaf, mulberry, and mixed extracts of 0.597%, 0.548, and 0.722%, respectively. Bazargan et al. [9] reported a conversion efficiency of DSCs with pomegranate extract of 1.50%. Zhou et al. [10] used 20 natural extracts in their studies with the highest conversion efficiency of 1.17% obtained with mangosteen pericarp extract as a sensitizer. Other researchers used bougainvillea extract and achieved a conversion efficiency of 0.48% [11].

The results obtained with natural extracts have shown a successful conversion of visible light into electricity in DSCs. However, DSCs with natural extract dye sensitizers have low photoelectric conversion efficiencies. In this study, bixin extracted from achiote seeds was utilized as a photosensitizer in DSCs. Bixin has conjugated double-bond molecules, which give it the ability to capture solar energy. Bixin has a great ability to absorb UV-Vis light spectra. However, the conjugated structures cause the pigment molecules to degrade quickly from the UV radiation.

An alternative method for enhancing the bixin performance by immobilizing it on a solid matrix was proposed in this study. Kaolinite, a clay mineral, was used as a host material to improve the absorption, photostability, and electron transfer of the pure bixin and, hence, increase the photoelectric conversion efficiencies of the bixin-sensitized TiO₂ solar cells. Kaolinite has interlayer regions that can be intercalated by both polar and nonpolar organic molecules. In this manner, kaolinite gives the advantage as a bearer to protect bixin molecules from degradation.

Extraction of Bixin

Achiote seeds (100g) were dissolved in acetone and acidified with ascorbic acid. Ascorbic acid assists in preventing oxidation of the pigment. Calcium carbonate (CaCO₃) as a neutralizing agent was also added to the mixture. Afterward, the mixture was stirred by a magnetic stirrer. The residue obtained by filtration was then re-extracted in acetone and partitioned with diethyl ether. The ether layer was collected, added to anhydrous sodium sulfate (Na₂SO₄), and dried un-

der N$_2$ gas. Afterward, column chromatography was performed on the silica gel-60 (stationary-phase) using n-hexane/acetone (2/1, v/v) as a mobile phase. Each fraction was collected into bottles and then dried under N$_2$ gas.

Preparation and Activation of Kaolinite

The kaolinite sample was washed with distilled water 3 times. Subsequently, it was centrifuged at 2000 rpm for 15 minutes. The wet kaolinite was then dried at a temperature of 80°C. The dried kaolinite was crushed into a fine powder and finally screened using a 100-mesh sieve (149 microns). Kaolinite powder (50g) obtained from the preparation process was prepared. Next, 400ml of hydrochloric acid (HCl-8M) was added, stirred and refluxed for 24 hours. The resulting kaolinite was then filtered and washed with distilled water until neutral.

Immobilization of Bixin on Kaolinite

The bixin solution (50ml) was mixed with 0.97 mmol/l of acetone. Activated kaolinite was then added piecemeal to the solution and stirred for 24 hours. Three different masses of kaolinite were immobilized: 1g (KBx1), 2g (KBx2), and 3g (KBx3). The products were then dried with N$_2$ gas. The immobilization process of bixin was conducted under illumination with red light in a dark room. The final results were characterized by IR spectroscopy and a UV-Vis spectrophotometer.

Preparation of Solar Cells

A polymer gel electrolyte was prepared by dissolving 7g of polyethylene glycol (PEG) in 25ml of chloroform. Several drops of a potassium iodide (KI) solution were added to the gel. The mixture was then stirred gently at a temperature of 80°C until a homogeneous gel was obtained. A TiO$_2$ electrode was prepared by adding 7g of TiO$_2$ powder to 7ml of acetylacetone until a paste was formed. Two drops of Triton X-100 were added to the titanium paste. The titanium paste was then coated on a transparent conductive oxide (TCO) glass substrate, dried in air, and heated at 130°C for 25 minutes. The TiO$_2$ on the TCO glass substrate (working electrode) was immersed in the kaolinite-bixin (KBx1, KBx2, or KBx3) suspension for 24 hours. A drop of electrolyte solution was added on the TiO2/TCO, and then the carbon counter electrode was placed on top of the working electrode.

Electrical Measurements

The photovoltaic properties of the DSCs are short-circuit current density (J_{sc}, mA/cm^2), open-circuit voltage (V_{oc}, mV), fill factor (FF), and photoelectric conversion efficiency (h, %). The conversion efficiency of DSCs at an irradiation intensity of P_{in} (mW/cm^2) is

$$\eta = \frac{J_{sc}.V_{oc}.FF}{P_{in}} x 100\% \tag{1}$$

where

$$FF = \frac{J_m.V_m}{J_{sc}.V_{sc}} \tag{2}$$

The maximum power point current density (J_m, mA/cm^2) and voltage (V_m, mV) are determined from the maximum power point of the DSCs current-voltage curve.

Identification of Activated Kaolinite and Kaolinite-Bixin

Kaolinite activation in hydrochloric acid (HCl) aims to enlarge the interlayer region of kaolinite. The X-ray diffraction (XRD) patterns of kaolinite before and after activating (see Figure 1) shows that there is a decrease in the intensity at angles of 2q = 12° and 2q = 25°. The treatment reduced the peak intensities down to 249 counts. This indicates that the acidity process has removed aluminum hydroxide (Al$_2$O$_3$) from the layer (dealumination). The dealumination does not only expand the interlayer region but also increase the percentage of silicon dioxide (SiO$_2$) in the kaolinite. Silicon dioxide (SiO$_2$) is identified by the intensities between 47 and 1743 counts. Table 1 presents the percentage compositions of prepared and activated kaolinite. It was observed that the silica-alumina mol ratio of kaolinite increases from 1.96 to 2.21 after the dealumination.

Impregnating the activated kaolinite into bixin contributes greatly to the bixin. The advantage of the large interlayer region is that it gives kaolinite a greater ability to trap more bixin molecules during the immobilization process. Moreover, silicon in the kaolinite layer can act as a semiconductor and improve the electron transfer of TiO$_2$ in solar cells.

Bixin molecules can form complexes with kaolinite molecules due to hydrogen bonding between the hydroxyl group (-OH) of bixin and the silicate group (-SiO) of kaolinite. Another hydrogen bonding that may occur is between the carbonyl group (C=O) of bixin and the hydroxyl group (-OH) of kaolinite.
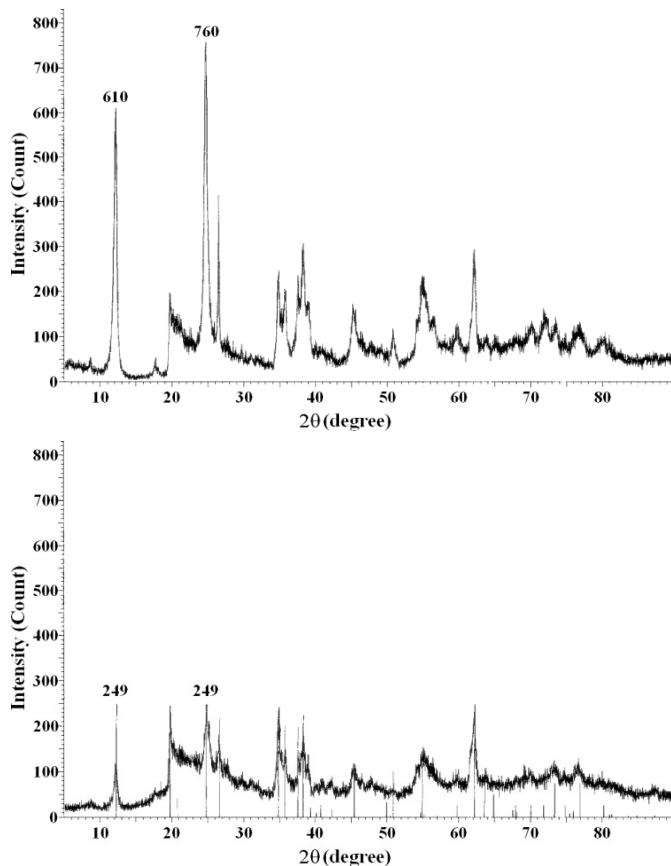
Figure 1. XRD Patterns of Kaolinite and Activated Kaolinite

Table 1. Percentage Composition of Prepared and Activated Kaolinite

	Prepared Kaolinit	Activated Kaolinite
SiO_2 (%)	60.56	62.64
Al_2O_3 (%)	30.88	28.31
Fe_2O_3 (%)	1.06	0.65
K_2O (%)	0.02	0.01
Na_2O (%)	0.03	0.01
MgO (%)	2.15	1.98
TiO_2 (%)	0.01	0.01
Si/Al	1.96	2.21

An infrared (IR) absorption spectrum of bixin shows certain characteristic absorption bands (as seen in Figure 2). A broad absorption band at $3410cm^{-1}$ indicates the presence of –OH stretching of the hydroxyl group. The band of absorption at $1745cm^{-1}$ indicates the presence of C=O. The bands at $1612cm^{-1}$ and $2924cm^{-1}$ were assigned to C=C and C-H, respectively.

The infrared absorption spectra of kaolinite-bixin (KBx1, KBx2, KBx3, in Figure 2) show two absorption peaks; the first near $1600cm^{-1}$, which was associated with C=O, and the second near $1700cm^{-1}$ which was attributed to C=C. Furthermore, the spectra also show broad absorption bands at $3400cm^{-1}$, which indicate the presence of the hydroxyl group (-OH). These specific absorption bands do not appear in the IR spectra of kaolinite and activated kaolinite. The IR absorption spectra of KBx1, KBx2, and KBx3 indicate that bixin molecules have successfully entered the interlayer region of kaolinite through the impregnation process.
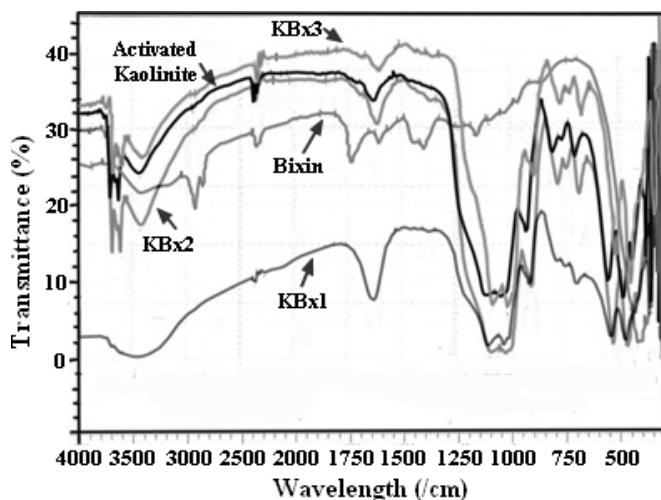

Figure 2. Infrared Absorption Spectra of Bixin, Activated Kaolinite, and Kaolinite-Bixin (KBx1, KBx2, KBx3)

UV-Vis Absorption

From the UV-Vis absorption spectra (as seen in Figure 3), it was found that the maximum absorbance peak of bixin decreases dramatically to less than 3% after 12 hours. Kaolinite-bixin received the same treatment as bixin and still had the maximum absorbance peak of 30% after 12 hours (as seen in Figure 4). It is clear that activated kaolinite can improve the photostability of bixin. Kaolinite-bixin showed better light absorption and higher photostability than pure bixin.

Photovoltaic Properties

A typical current-voltage curve for a kaolinite-bixin sensitized solar cell prepared with TiO_2 is shown in Figure 5. The measurements were taken in sunlight with an irradiation intensity of $55mW/cm^2$, resulting in a short-circuit cur-

rent of 1.3mA/cm^2, an open-circuit voltage of 0.7V, and a fill factor of 0.61. The overall energy conversion efficiency of 1.01% was obtained, which was much higher than that obtained with pure bixin [7]. The conversion efficiency of bixin-kaolinite sensitized solar cells was higher than that of pure bixin sensitized solar cells. This was due to better light absorption of kaolinite-bixin compared to pure bixin. Moreover, kaolinite provides strong interaction between TiO$_2$ and bixin, and this leads to better electron transfer in the solar cell.
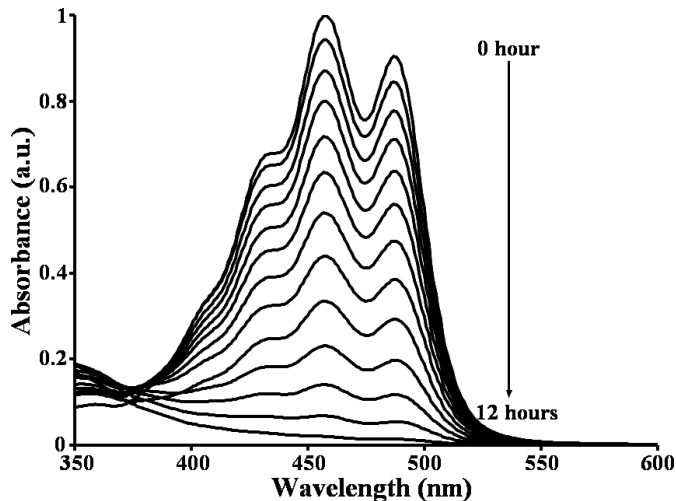

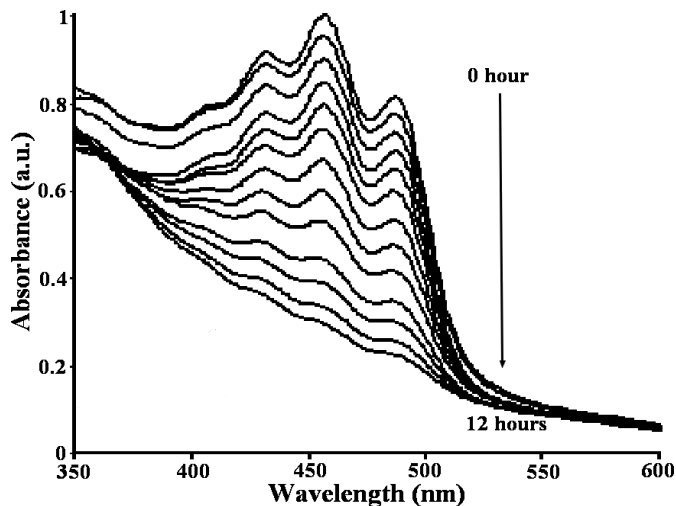**Figure 3. UV-Vis Absorbance of Bixin: 0 to 12 Hours**

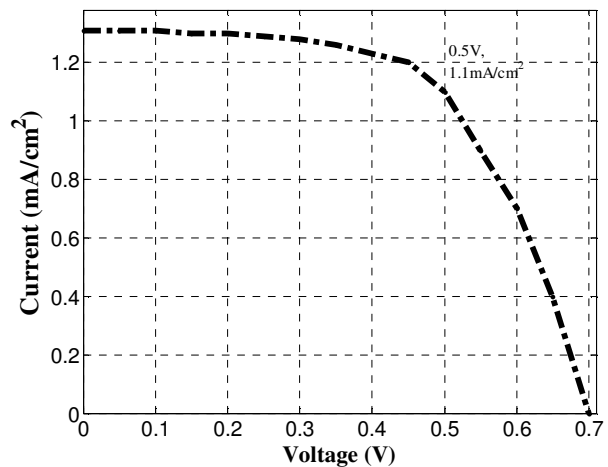**Figure 4. UV-Vis Absorbance of Kaolinite-Bixin: 0 to 12 Hours**

Figure 5. Current-Voltage Curve for a DSC with TiO$_2$ and Kaolinite-Bixin in Sunlight Irradiation Intensity of 55mW/cm^2

Conclusion

Natural dye sensitizers used in DSCs give low photoelectric conversion efficiencies. An alternative technique for improving efficiencies is by impregnating activated kaolinite into the pure natural dye. In this study, activated kaolinite was impregnated into pure bixin. Experimental results showed that activated kaolinite enhances the photostability and light absorption characteristics of the DSCs based on TiO$_2$ and bixin as sensitizers. Kaolinite-bixin gave higher photoelectric energy efficiency than pure bixin in the DSCs.

Acknowledgements

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Biographies

AYONG HIENDRO is a Senior Lecturer at Tanjungpura University (UNTAN), Pontianak, Indonesia. He earned his B.Eng. degree from Tanjungpura University and M. Eng. (Electrical Engineering) from Institut Teknologi Bandung (ITB), Bandung, Indonesia. He is currently teaching at Department of Electrical Engineering, Tanjungpura University. His interest is in energy conversion. He may be reached at ayongh2000@ieee.org

FERRY HADARY is an Assistant Professor of Control Systems at Tanjungpura University (UNTAN), Pontianak, Indonesia. He earned his B.Eng. degree from Tanjungpura University, M. Eng. from Tokyo Institute of Technology, Japan, and Dr. Eng. from Kyushu Institute of Technology, Japan. He is currently teaching at Department of Electrical Engineering, Tanjungpura University. His interests are in control systems, robotics, new and renewable energy. He may be reached at ferryhadary@engineering.untan.ac.id

WINDA RAHMALIA is an Assistant Professor of Chemistry at Tanjungpura University (UNTAN), Pontianak, Indonesia. She earned her B.S. degree from Tanjungpura University and M. Si. (Natural Science for Pigments and Chlorophyll) from Christian University of Satya Wacana, Indonesia. She is currently teaching at Department of Chemistry, Tanjungpura University. Her interests are in pigments as light harvesting and renewable energy conversion and storage systems. She may be reached at winda_rahmalia@mipa.untan.ac.id

NELLY WAHYUNI is an Assistant Professor of Chemistry at Tanjungpura University (UNTAN), Pontianak, Indonesia. She earned her B.S. degree and M. Si. (Natural Science for Inorganic Chemistry) from Gadjah Mada University (UGM), Indonesia. She is currently teaching at Department of Chemistry, Tanjungpura University. Her interests are in inorganic materials especially clay materials for adsorbent, catalysts and host materials. She may be reached at nelly_kimiauntan@mipa.untan.ac.id