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PRELIMINARY STUDY OF NATURAL PIGMENTS PHOTOCHEMICAL PROPERTIES OF *Curcuma longa L.* AND *Lawsonia inermis L.* AS TiO_2 PHOTOELECTRODE SENSITIZER

(Kajian Awal Sifat Fotokimia Bahan Warna Semulajadi *Curcuma longa L.* dan *Lawsonia inermis L.* Sebagai Pemeka Fotoelektrod TiO_2)

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Abstract

Curcumin and lawsone dyes extracted from turmeric (*Curcuma longa L.*) and henna (*Lawsonia inermis L.*) are used to investigate their possibility as photosensitizers on a TiO_2 photoelectrode, respectively. The natural dyes undergo simple cold extraction techniques without further purification. The photochemical properties are studied by FT-IR spectroscopy and UV-Vis spectrophotometer. The FTIR spectra revealed that the presence of hydroxyl and carbonyl functional groups in both dyes indicated the presence of important characteristics in a sensitizer to graft on to TiO_2 photoelectrode. The broad range of absorption peak wavelength obtained in this work shows that curcumin and lawsone are promising candidates for efficient sensitizers in dye-sensitized solar cells (DSSC). The maximum absorption peak attributed for curcumin and lawsone are 425 nm and 673 nm. The optical bandgaps calculated are 2.48 eV and 1.77 eV, respectively. The findings indicated the potential of naturally obtained dyes to act as photosensitizers in DSSC.

Keywords: curcumin, lawsone, natural photosensitizer, DSSC, optical band gap

Abstrak

Kurkumin dan lawson adalah pigmen pewarna yang diekstrak daripada kunyit (*Curcuma longa L.*) dan inai (*Lawsonia inermis L.*) digunakan untuk mengkaji kebarangkalian sebagai pemeka cahaya pada TiO_2 fotoelektrod. Pewarna semula jadi ini diekstrak menggunakan teknik rendaman sejuk tanpa penulenan lanjut. Sifat fotokimia dikaji menggunakan spektroskopi FT-IR dan spektrofotometer UV-Vis. Spektrum FTIR mendedahkan bahawa kehadiran kumpulan berfungsi hidroksil dan karbonil dalam kedua-dua pewarna menunjukkan kehadiran ciri-ciri penting dalam pemeka untuk melekat pada TiO_2 fotoelektrod. Lebar luas puncak penyerapan gelombang yang diperolehi dalam kajian ini menunjukkan kurkumin dan lawson adalah pigmen pewarna yang berpotensi untuk menjadi pemeka yang berkesan dalam DSSC. Puncak penyerapan maksimum untuk kurkumin dan lawson adalah 425 nm dan 673 nm. Jurang jalur optik dikira masing-masing adalah 2.48 eV dan 1.77 eV. Dapatan kajian menunjukkan potensi pewarna yang diperolehi secara semulajadi untuk bertindak sebagai pemeka cahaya dalam DSSC.

Kata kunci: kurkumin, lawson, pemeka cahaya semulajadi, DSSC, jurang jalur optik

Introduction

A dye sensitizer layer serves as the solar energy absorber in dye-sensitized solar cells (DSSC) that absorbs solar photons, thus transforming solar energy into electricity. Since the electrons and holes in the dye layer have a very little mobility, this layer must be very thin for the charge carriers to reach the membranes within their lifetime [1]. The examination of numerous dyes with a variety of chromophoric ligands has indicated that the main factor in optimization of solar photon harvesting is the significant light absorption in the ultraviolet (UV)-visible (VIS) - near infrared (NIR) region. There is a large volume of published studies stating that the ideal sensitizer should absorb all light below a threshold wavelength of about 920 nm. During the past 30 years much more information has become available on different types of dyes, which have been studied extensively for DSSC application. A number of studies have found that dyes can be classified into two main types-organic dyes and inorganic dyes-according to their structure [2]. Organic dyes include natural organic dyes such as coumarin [3, 4], perylene [5, 6] and synthetic dyes. While, inorganic complexes dyes include metal complexes, such as polypyridyl complexes of transition metals, metalloporphyrins, metallo-phathalocyanines and inorganic quantum dots, which high thermal stability and chemical stability have compared to organic dyes [7-10].

Molecular engineering of the interface is important to obtain high harvesting photons. Among the factors that influence the harvesting of photons is the position of the dye's energy levels in the ground and excited states. Previous studies have revealed that dyes should be firmly grafted to the semiconductor oxide surface, in order to permit efficient injection of charges to the conduction band with a quantum yield of unity, while also permitting quantitative regeneration of the dye by redox mediators [11, 12]. The presence of suitable anchoring groups in the dyes also plays an important role in promoting the efficient coupling of the dye's excited state with the acceptor levels of the oxide [12]. Finally, it should possess an adequate chemical stability in its oxidized form to sustain redox turnovers under illumination, corresponding to about 20 years of exposure to natural light [11]. Numerous studies have focused on developing efficient dyes, and over the last 20 years, ruthenium complexes have had a lot of attention because of their great performance amongst thousands of the dyes [13, 14]. In this study, natural dye pigment is our interest as our main aim is finding a solution for cheap energy and an eco-friendly source of sensitizer. Two types of natural dyes were extracted: henna (*Lawsonia inermis L.*) leaves: and turmeric (*Curcuma longa L.*) roots. Henna's colouring properties are due to lawsone (2-hydroxy-1,4-naphthoquinone) [15], while curcumin, also known as (1E,6E)-1,7-bis (4-hydroxy-3-methoxyphenyl)-1,6-heptadiane-3,5-dione is the active substance in turmeric that can be exist in at least in two tautomeric forms, keto and enol [16]. These extracted dyes were used to investigate their potential as a sensitizer.

Materials and Methods

Materials

The fresh henna (*Lawsonia inermis L.*) leaves were harvested in a rural area of Malacca, Malaysia, and turmeric (*Curcuma longa L.*) roots were bought from a local market in Kuala Lumpur, Malaysia. Methanol purchased from J. T. Baker, USA, was used as a solvent, fluorine-doped conducting tin oxide (FTO) glasses (~15 Ω sq^{-1}) by Solaronix, Switzerland were used as the conductive glass plates, and TiO_2 paste purchased from Dyesol, United State was used as the photoelectrode.

Cold Extraction Method of Natural Dye Sensitizer

All extraction procedures were carried out under dimmer conditions and glassware containing dyes were covered with aluminium foil to minimize photo-oxidation. The dye pigments were extracted by grinding 30g of cleaned and dried samples with absolute methanol in a 1:10 w/v ratio, and left overnight at room temperature. The mixtures were then centrifuged for 15 minutes at 8000 rpm to separate the solid content of the samples. The residual solids were filtered off and the filtrate was then concentrated using a rotary evaporator. The crude extract was stored in a refrigerator (4℃) until used. The presence of curcumin and lawsone was confirmed by FT-IR spectroscopy.

Preparation of Sensitized-TiO_2 Photoelectrode

The TiO_2 paste was coated using Doctor Blade's method on pre-cleaned FTO glasses [17]. Electrodes were then sintered at 500℃ for 30 minutes. After they cooled down, the TiO_2 electrodes were dipped in the extracted curcumin and lawsone for 24 hours. The electrodes were then rinsed with absolute methanol and dried with nitrogen gas. The absorption spectrum was analysed using a UV-visible absorption spectroscope (model: Shimadzu UV-1800, Japan).

Results and Discussion

FTIR Analysis

Figure 1 illustrates the FTIR spectra of curcumin and lawsone, extracted from turmeric roots and henna leaves, respectively. The obtained spectrum of curcumin corresponds to that reported previously by Kim et al. [18]. The broad band obtained at 3334 cm^{-1} was allocated to the stretching vibration of the free hydroxyl-group of phenol (Ar–OH). The sharp band at 2974 cm^{-1} was attributed to the sp^2 C–H bond stretching. The conjugate of carbonyl bond (C=O) with two aromatic rings was accompanied by a small shoulder at 1651 cm^{-1}. The band at 750 cm^{-1} corresponded to *ortho* (1,2), substituted out of the phase of hydroxyl and $O–CH_3$ bond at the aromatic ring. The sharp bands at 1044 and 1087 cm^{-1} were assigned to the C–O stretch of phenyl alkyl ether that confirmed the molecular structure of curcumin extracted from turmeric. The IR spectra of lawsone showed the characteristic of the bending vibration of the C–H bond at 1000 cm^{-1}. The broad band at 3309 cm^{-1} was allocated to the stretching vibration of H-bonded hydroxyl of phenol. The small and sharp peak at 2953 cm^{-1} was assigned as an aliphatic and aromatic C–H group. Meanwhile, a small shoulder band at 1655 cm^{-1} was attributed to the stretching vibration of a carbonyl bond (C=O), and peaks at 1403 and 1438 cm^{-1} were attributed to the C=C of the naphthalene ring. These characteristics coincide with the molecular structure of lawsone pigment [19]. The presence of hydroxyl and carbonyl groups in curcumin and lawsone molecules proved the interaction between TiO_2 and dyes as a functional group capable of chelating with Ti(IV) sites on the TiO_2 surface [20],which will contribute to the photoelectric conversion efficiency of the device [21]

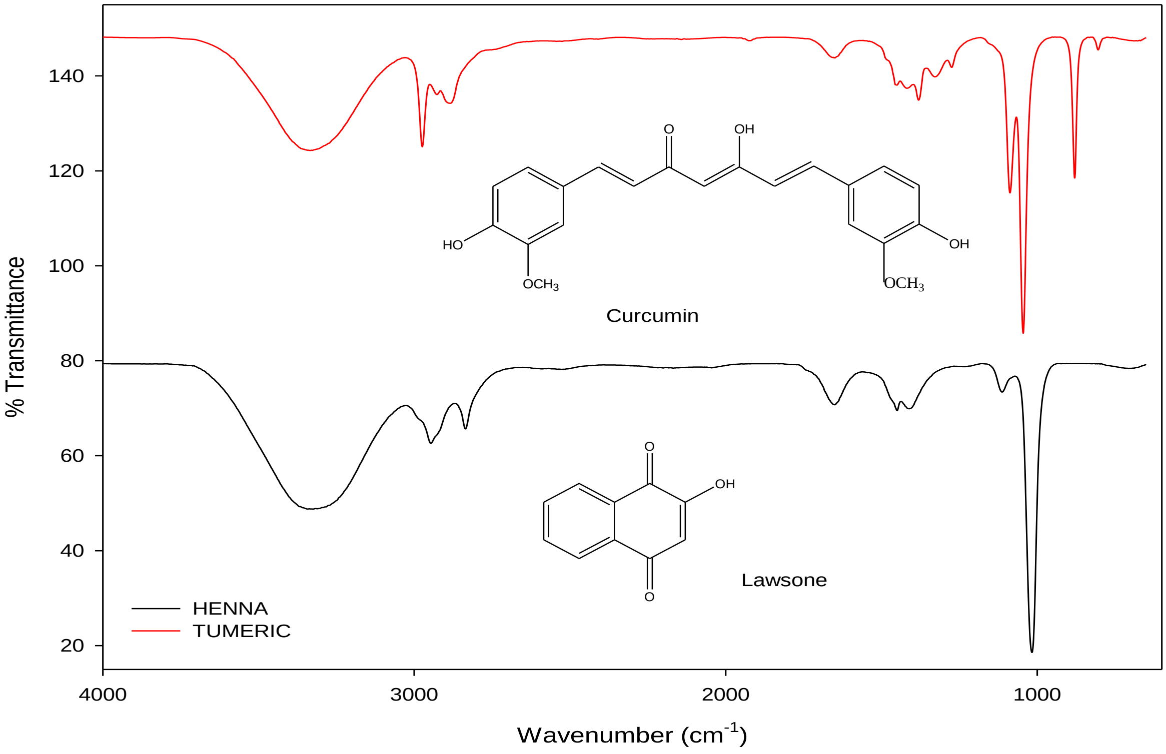

Figure 1. FTIR analysis of turmeric (*Curcuma longa*) and henna (*Lawsonia inermis*) crude extract

UV-Vis Analysis

A sensitizer is considered effective if it has the ability to absorb light over a broad range of wavelengths, from ultra-violet-visible to near-infrared [22]. From a previous study, the absorption spectrum of pure TiO_2 shows that nanoparticles of TiO_2 are only capable of absorbing photons in nearby regions [23]. This is the reason why a light sensitizer is needed to enhance the light absorption intensity of aTiO_2 photoelectrode and increase the absorption into a broader range. Therefore, the sensitizer needs to be chemically and/or physically grafted onto the surfaces of TiO_2 to make it possible to be a light harvester in DSSC. Fig. 2 exhibits the UV-Vis absorption spectrum of pure TiO_2, curcumin, and curcumin sensitized on the TiO_2 photoelectrode, while Fig. 3 presents the spectrum for lawsone, lawsone treated on TiO_2, as well as pure TiO_2. As seen from the curves of the spectrum, the maximum absorption peak (λ_{max}) of curcumin is at the wavelength 425 nm and the maximum peak for lawsone is at wavelength 673 nm. This clearly shows the different absorption properties possessed by these two pigments in the wavelength range 400-700 nm, as result of their transition energy. This absorption initiates from electron excitation upon photon exposure. The π-π^* transitions involved for the absorption band in visible light generally reflect the intensity of each absorption peak. The UV-Vis absorption spectrum for curcumin treated on TiO_2 shows a broad peak at the wavelength 400 nm to 450 nm, while the absorption spectrum for lawsone treated on TiO_2 shows a broad peak at the wavelength 665 nm to 675 nm. Owing to adsorption on the TiO_2 of all pigments, the absorption band shifts to higher energy in the visible range. The broad range also indicates that the dye pigment is stained well on the TiO_2 nanoparticles. This broadening can lead to the ability of dye pigment to harvest photons in a broader spectrum of solar energy, which eventually produces a higher photocurrent [24].

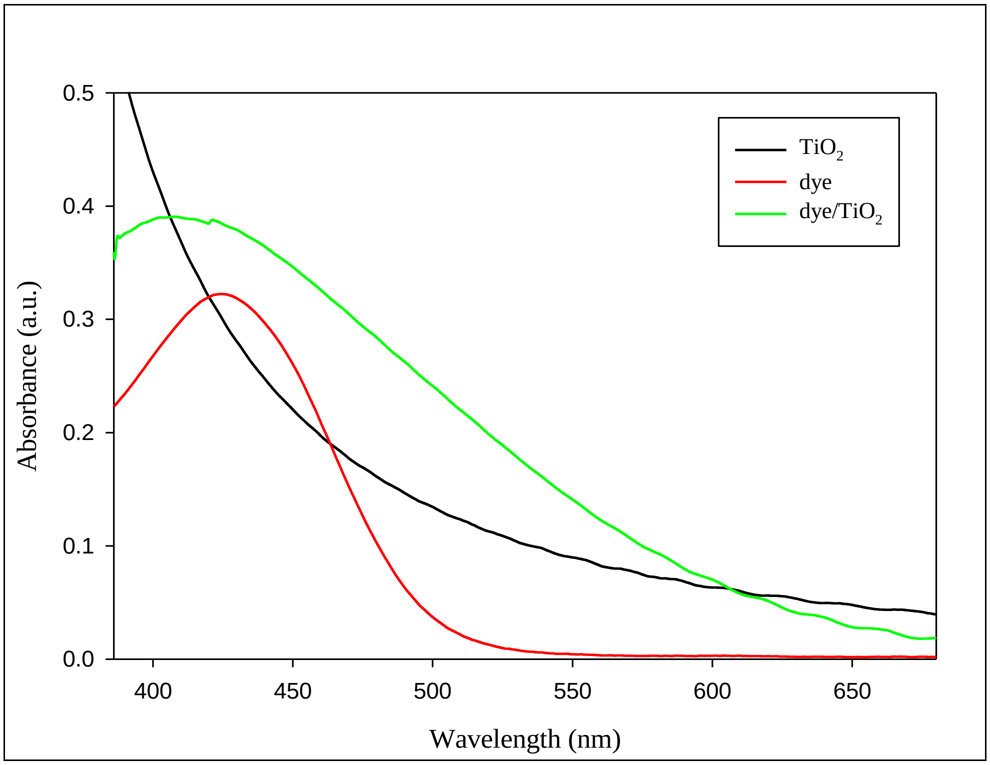

Figure 2. UV-Vis absorption spectra of turmeric (*Curcuma longa*) roots treated in methanol

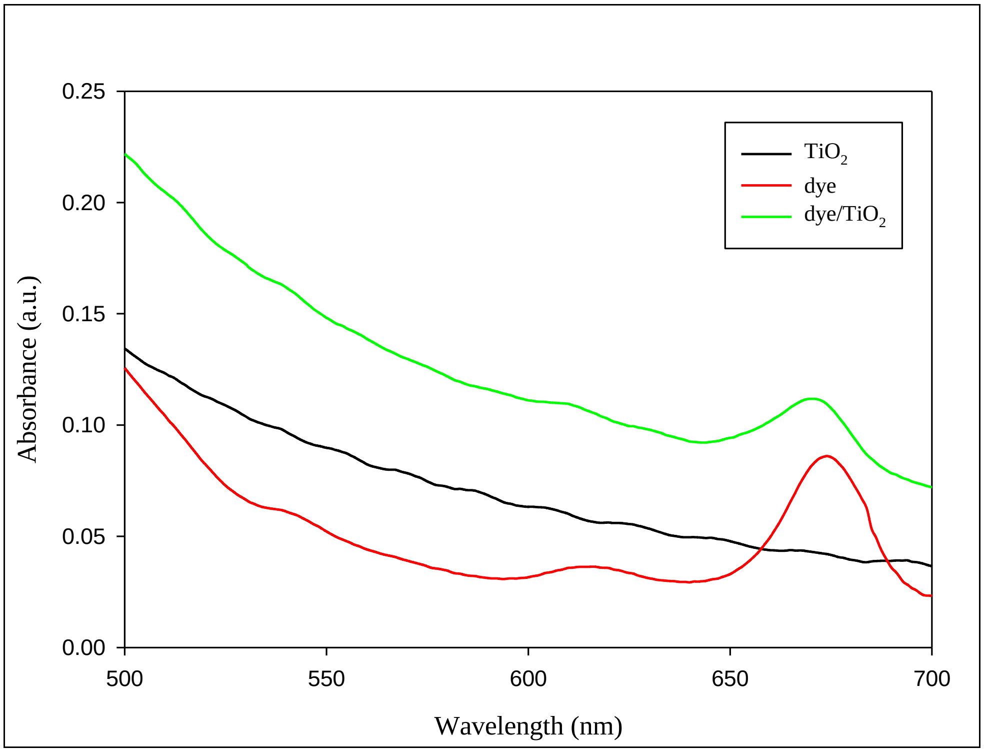

Figure 3. UV-Vis absorption spectra of henna (*Lawsonia inermis*) leaves treated in methanol

From the cut-off wavelength of the absorption spectrum, obtained in Figs. 2 and 3, the optical bandgap can be calculated by using relation E_g (eV)=1240/λ (wavelength in nm) [25]. The cut-off wavelength of the TiO_2 absorption spectrum was obtained at 351 nm, thus the value of the optical bandgap of TiO_2 nanoparticles was found to be 3.53 eV. This value may vary from other studies, as it is related to the change in particle size [24]. The cut-off wavelengths for curcumin and lawsone are 500 nm and 700 nm, respectively. The optical bandgap obtained in this work for curcumin is 2.48 eV and for lawsone is 1.77 eV as indicates in Table 1. These results suggest that the value of the absorption wavelength is smaller with the increase in bandgap. Another important characteristic of an efficient sensitizer is to ensure the electronic excited state lies above the conduction band-edge (CB) of TiO_2 [22]. Moreover, the electrons from the lower unoccupied molecular orbital (LUMO) level are easier to be injected into the CB of TiO_2 if the LUMO level of the dye pigments is more positive than that of the CB level. As the position of the LUMO level is related to the bandgap it is important to verify the value of the bandgap for the sensitizer.

Table 1. UV-Vis absorption and band gap value of dye pigments and TiO_2 stained dye pigments

Dye Pigment	**Absorbance Peak (nm)**	**Band Gap (eV)**
Curcumin	425	2.48
Curcumin/TiO_2	400-450	-
Lawsone	673	1.77
Lawsone/TiO_2	665-675	-

Conclusion

The photochemical properties of natural dye with two types of pigments, which curcumin extracted from turmeric rhizome (*Curcuma longa L.*) and lawsone extracted from henna (*Lawsonia inermis L.*) were determined by using FTIR spectroscopy and a UV-Vis spectrophotometer. All the peaks from the FTIR spectra show the existence of a functional group existings in the chemical structure of the pigments. The presence of hydroxyl and carbonyl groups is important, as these are functional groups which initiate strongly the attachment of sensitizer on to the surface of a TiO_2 electrode. It was shown that both pigments have a broad range of absorption wavelengths in the UV visible and near-infrared regions, which are between 380 nm and 500 nm for curcumin, and between 650 nm and 700 nm for lawsone. Moreover, it is confirmed that dye structures attach well to the TiO_2 because the absorption band of the UV spectra shifted to higher energy, compared to the absorption peak of the dye pigment itself. Further study is needed to calculate the position of the LUMO and the higher occupied molecular orbital (HOMO) levels of the dye pigments from the optical bandgap obtained in this study.

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