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Application of dyes extracted from *Alternanthera dentata* leaves and *Musa acuminata* bracts as natural sensitizers for dye-sensitized solar cells

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ABSTRACT

The natural dyes anthocyanin and chlorophyll were extracted from *Musa acuminata* bracts and *Alternanthera dentata* leaves, respectively. The dyes were then applied as sensitizers in TiO_2-based dye-sensitized solar cells (DSSCs). The ethanol extracts of the dyes had maximum absorbance. High dye yields were obtained under extraction temperatures of 70 to 80 °C, and the optimal extraction temperature was approximately 80 °C. Moreover, dye concentration sharply decreased under extraction temperatures that exceeded 80 °C. High dye concentrations were obtained using acidic extraction solutions, particularly those with a pH value of 4. The DSSC fabricated with anthocyanin from *M. acuminata* bracts had a conversion efficiency of 0.31%, short-circuit current (I_{sc}) of 0.9 mA/cm^2, open-circuit voltage (V_{oc}) of 0.58 V, and fill factor (*FF*) of 62.22%. The DSSC sensitized with chlorophyll from *A. dentata* leaves had a conversion efficiency of 0.13%, I_{sc} of 0.4 mA/cm^{-2}, V_{oc} of 0.54 V, and FF of 67.5%. The DSSC sensitized with anthocyanin from *M. acuminata* bracts had a maximum incident photon-to-current conversion efficiency of 42%, which was higher than that of the DSSC sensitized with chlorophyll from *A. dentata* leaves (23%). Anthocyanin from *M. acuminata* bracts exhibited the best photosensitization effects.

1. Introduction

The conversion of solar energy into electric energy by solar cells is a highly promising and environmentally friendly method for electric energy production [1]. In 1974, Melvin Calvin first proposed the use of photosynthesis in photoelectric conversion [2]. In the following years, solar cells have become an attractive topic in fundamental and applied research on energy production. In 1991, Grätzel and his co-workers successfully developed a novel solar cell: dye-sensitized solar cell (DSSC) or Grätzel cell [3]. DSSC is a third-generation photovoltaic device that converts visible light into electricity on the basis of sensitized wide band-gap semi-conductors [4]. DSSCs are potential alternatives to p–n junction photovoltaic devices given their inexpensive starting material, which is usually silicon, environmental friendliness, and facile fabrication process. The emergence of DSSCs that are based on conducting polymers and nanocrystals has challenged the dominance of inorganic solid-state junction devices [5,6]. A DSSC is composed of a nanocrystalline semiconductor electrode with a wide band gap, adsorbed dye, an electrolyte containing redox-coupled iodide/triiodide ions (I^-/I_3^-), and a counter-electrode [7,8]. Oxides with wide band gaps, such as ZnO [9], Nb_2O_5, SnO_2 [10], and TiO_2 have been successfully used as photoanodes [11]. TiO_2, in particular, is widely used as a photoanode. The use of sintered mesoporous TiO_2 increased the efficiency of DSSC from 1% to 7% and established DSSC technology [12]. Anatase TiO_2 has considerably better photocatalytic activity than rutile and brookite TiO_2 polymorphs [13].

The performance of DSSCs mainly depends on the dye utilized as a sensitizer. The light-harvesting range of the dye should extend from the visible to near-infrared regions. In addition, the presence of ═O or —OH groups that anchor the dye to the TiO_2 surface is an important parameter that determines the efficiency of a DSSC sensitizer [14]. Several organic, inorganic, and hybrid compounds, such as fluorescent dyes, xanthene, platinum complexes, and phthalocyanine, have been used as sensitizers. Transition-metal coordination compounds, such as ruthenium polypyridyl complexes, have been successfully used as effective DSSC sensitizers with maximum conversion efficiencies of 11%–12% that result from their highly efficient metal-to-ligand electron transfer and intensive electron-transfer absorption throughout the entire visible light range [15]. However, the preparation of noble-metal sensitizers is based on multi-step procedures. Moreover, noble metals are very rare and expensive. By contrast, metal-free organic dyes are not only

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inexpensive and easy to synthesize but also exhibit conversion efficiencies of as high as 9.8% [16]. For example, the efficiency of indoline dye D205 is 9.5% [17] and that of C217 is 9.8%; these conversion efficiencies are highly promising considering that ruthenium complexes have a conversion efficiency of 11.1% [18]. However, organic dyes are less efficient and stable than metal organic dyes. Two major recombination processes give rise to the low efficiency of organic dyes: (1) electron capture by oxidized redox couples in the TiO_2 conduction band; and (2) back electron transfer, which hinders electron injection from the excited dye to the TiO_2 conduction band [19]. In nature, the colors of flowers, fruits, roots, and leaves vary from red to purple. These colors are conferred by dyes that can be extracted and used as sensitizers for DSSCs. Natural dye-sensitized solar cells fabricated using natural plant dyes are receiving increased research interest because of the following advantages of natural plant dyes over synthetic ones: simple extraction with cheap, cost-effective organic solvents; ubiquity; full biodegradability; and environmentally-friendly fabrication [20]. Plant pigmentation results from the interaction between the electronic structures of the pigment with sunlight; this interaction changes the wavelengths that are reflected or transmitted by plant tissues [21]. The specific color perceived relies on the visual abilities of the observer. Natural dyes can be described on the basis of (1) maximum absorbance wavelength (λ_{max}) and (2) color perceived by humans [3]. The natural dyes anthocyanins [22,23], chlorophylls [24,25], carotenoids [26,27], and flavonoids [28,29] have been used as sensitizers in DSSCs.

In this study, natural dyes extracted from *A. dentata* leaves and *M. acuminata* bracts were used to prepare natural sensitizers for DSSC fabrication. The effect of solvent, temperature and pH on natural extract yield was investigated. The presence of chlorophyll and anthocyanin in the extracts of *A. dentata* and *M. acuminata* respectively and their functional groups were determined using UV–Vis absorption spectroscopy and Fourier-Transform Infrared Spectroscopy (FTIR). Using scanning electron microscope (SEM) and X-Ray Diffraction (XRD), the optical properties of TiO_2 thin film of sensitizers were studied. In Addition, the inhibition of crystallinity of TiO_2 particles was investigated by the Energy Disperse X-ray (EDX) analysis. DSSCs were fabricated using extracted dyes as photosensitizers and the performance of natural photosensitizers of these cells were evaluated. The main parameters of solar cell are short circuit current (I_{SC}), open circuit voltage (V_{OC}), fill factor (*FF*), energy conversion efficiency (η) and maximum power point (P_{max}) were determined.

2. Materials and Experiments

2.1. Materials

Scientific classification of plants			
Kingdom:	Plantae	Kingdom:	Plantae
Order:	Zingiberales	Order:	Caryophyllales
Family:	Musaceae	Family:	Amaranthaceae
Genus:	*Musa*	*Genus*:	*Alternanthera*
Species:	*M. acuminata*	*Species*:	*A. dentata*
Common name:	Banana, Bananito	Common name:	Purple knight
Part used:	Bracts	Part used:	Leaves

Musa acuminata is a species of wild banana that is native to Southeast Asia, India, and northern Australia. Banana plants are not woody plants but giant herbs with a growth rate of 3–6 m/year. Banana inflorescences grow horizontally or obliquely from the trunk. Every banana blossom develops into a small fruit that is covered with small dark red leaves (bracts) [30]. *Alternanthera dentata* is a species of flowering herbaceous perennial plant that is native to South America and is particularly popular in China and Malaysia. This plant is approximately 30–40 cm tall and 60–90 cm wide. The leaves are simple, blade-like in morphology, and can grow to lengths of approximately 2.5–7.5 cm or longer when grown in watery places. The leaves are green or deep purple in color. *A. dentata* is a tropical foliage plant that thrives under high heat. Under hot conditions, its color deepens and becomes richer [31].

2.2. Experimental

2.2.1. Preparation of Natural Dye Sensitizers

Fresh *M. acuminata* bracts and *A. dentata* leaves were washed with water prior to extraction and oven-dried at 45 °C for 24 h. The dried organs were crushed into fine powder using a grinder (Mulry function Disintegrator SY-04). Plant materials were stored in a dry, dark place at room temperature for later use. The exact structures of the extracted dyes were not subjected to characterization because this study aimed to use plant-available dyes without any further isolation or purification.

2.2.2. Preparation of DSSCs

TiO_2 porous film was fabricated by mixing 3.0 g TiO_2 powder (titanium oxide nanopowder, TiO_2, anatase, 99.5%, 15 nm, supplied by US Research Nanomaterials, Inc.) with 6 ml of 0.1 M nitric acid in a mortar and pestle. Nitric acid was added to enhance the dispersion of TiO_2 particles. The mixture was ground for 30 min to a milky white paint-like solution. Then, 3 ml of polyethylene glycol (PEG, MW 10,000, supplied by SIGMA-ALDRICH) was added to the solution with stirring. PEG was added to create a porous structure in the TiO_2 film. The porous structure would maximize dye adsorption on the TiO_2 surface and minimize crack formation during high-temperature sintering [32–36]. Finally, several drops of Triton X-100 (Triton X-100 for electrophoresis, supplied by SIGMA- ALDRICH) were added to the mixture to facilitate the adhesion of TiO_2 particles to the transparent conductive oxide (TCO) glass substrate [26]. After the addition of Triton, the mixture was ground carefully and slowly to avoid bubbling and foaming.

To prepare the anode of the DSSC, conductive glass with the dimensions of 3 cm × 2.5 cm was soaked in acetone and then sonicated for 15 min (using ULTRA sonik, NEY, 208H). The slide was then wiped with ethanol on a tissue to remove any oils, impurities, and fingerprints and then dried using a hair dryer. The FTO glass was taped down with transparent tape (Scotch, Magic™ Tape) with its conductive side facing up. Multimeter (SANWA, YX360TRF) probes were used to measure resistance across two points on the glass surface. Transparent tape was used as a spacer to control the thickness of the TiO_2 film. A clean glass rod was used to spread TiO_2 paste as evenly as possible onto an area of approximately 1 cm^2 on the conductive face of the FTO substrate. The glass slide was then sintered at 500 °C for 30 min in a furnace (*Lenton Thermal Design*, England) to solidify TiO_2 on conducting glass substrate. After cooling TiO_2 at 100 °C, the FTO directly immersed in the dye solution extracted from plant species for 24 h in dark condition at room temperature to adsorb the dye properly on the TiO_2 surface. The FTO/TiO_2/dye electrode was rinsed with isopropyl alcohol to remove the non-adsorbed dye and the excess water from the porous TiO_2 and subsequently dried using nitrogen gas. Pt was deposited on the FTO as a counter electrode. Pt was deposited by dropping a Pt paste on the FTO-glass substrate and spread it with a glass rod sliding over the glass surface. The glass slide was sintered at 450 °C for 30 min in a furnace to solidify Pt on conducting glass substrate. Currently, Pt is the best material to make efficient devices technically.

2.2.3. Cell Assembly

The dry porous TiO_2 film electrode was placed face up, and the conductive side of the catalyst-coated counter-electrode was placed on the TiO_2 film and sealed. A DSSC was assembled by injecting liquid electrolyte into the space between the TiO_2 electrode (photoanode) and counter-electrode (cathode) through a hole in the counter-electrode to prevent the electrolyte from leaking out (Fig. 1).

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