Spectroscopic evidences of synergistic co-sensitization in dye-sensitized solar cells via experimentation of mixture design

Chien-Hsin Yang*, Pei-Yu Chen, Wen-Janq Chen, Tzong-Liu Wang, Yeong-Tarng Shieh

Department of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung 811, Taiwan

ABSTRACT

A systematic analysis for mixed dyes of D131, D149, and N3 ternary components on performance of dye-sensitized solar cells (DSSCs) has been performed. Using an experimental design of mixture, empirical models are fitted and plotted as contour diagrams, which facilitate revealing the synergistic/antagonistic effects between these mixed dyes. Dye co-sensitization effects in DSSCs are proved by the photo-physic properties, efficiency of the DSSC devices, and kinetic parameters of photo-electron transfer. The performance of DSSCs is significantly affected by the composition of dyes. The optimal efficiency (ca. 9.5%) of these mixed-dye DSSCs exists at the composition of 1/2 D149–1/2 N3. This composition appears to help conveying the charge transfer from the excited dye molecules to the conduction band of TiO_2, leading to a higher efficiency of the assembled devices. Supplementary study of the electrochemical impedance are in support of enhancing charge transfer of TiO_2 (e^-) with the co-sensitized dyes.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been extensively investigated for the areas of designing more efficient dyes and electron mediators [1], fabricating better nanostructured films [2], and more deeply understanding the interfacial charge-transfer process [2–4]. In a DSSC device, light is absorbed by the dye anchored on the TiO_2 surface and then electrons from the excited dye inject into the conduction band of the TiO_2, generating electric current, while the ground state of the dye is regenerated by the redox mediator to give efficient charge separation [5]. Thus, the dye in DSSCs is essential for efficient light harvesting and electron generation/transfer. Because the electrons injected into the TiO_2 nanoparticles are surrounded by high concentrations of cations from the electrolyte, there is no significant electric field present in the TiO_2 film. As a result, the transport of injected electrons to the collector electrode occurs by diffusion. To obtain high conversion efficiencies, it is required that the photogenerated electrons diffuse into the oxide film with minimal losses to interfacial recombination [2–4]. The electron diffusion coefficients (D_{eff}) and electron lifetime (τ) provide information about the distribution of electron states and rate constant of charge transfer [6]. Electrochemical impedance spectroscopy (EIS) [7,8] is a useful technique that has been employed to get some kinetic parameters occurring in the DSSC.

The typical Ru complex sensitizers, such as N3 (cis-bis(isothiocyanato)-bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II)) and N719 (cis-bis(isothiocyanato)-bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) bis-tetra-n-butylammonium), have been demonstrated photoconversion efficiency up to 11% under AM 1.5 irradiation [9], which is grafted onto the semiconductor through anchoring groups, e.g. carboxylate that bind strongly to the oxide by coordination of surface titanium ions. Owing to the cost of rare metals and the difficulty of purification of the ruthenium dyes, organic dyes are synthesized to be an alternative as they are relatively feasible [10–15]. Among these dyes, the indoline dye has demonstrated the promising high efficiency of 9% [14,15] with significant different absorption spectra and adsorption termini as compared to N3. Therefore, it is predicted that a mixture of the multiple dyes would enlarge a strong sensitized range, whereas the electron transfer of the multiple dyes can work mutually. A design of the organic sensitizer is generally to link the electron donor and the electron acceptor. And, the TiO_2 surface anchoring group, such as carboxylate, is integrated at the acceptor end. With light irradiation, these dipolar molecules induce intramolecular charge transfer from the donor to the acceptor, and then the electron is injected into the TiO_2 via the anchoring group. An ideal sensitizer needs to possess a sufficiently high LUMO energy level for efficient electron injection into the TiO_2 and a sufficiently low HOMO energy level for efficient regeneration of the oxidized state, the absorption band ranging from the visible region to near-IR as well as enough spatial separation between the positive charge density on the dye and the electron injection. Compared with Ru complexes, organic sensitizer dyes generally have larger molar

* Corresponding author. Tel.: +886 7 5919420; fax: +886 75919277.
E-mail address: yangch@nuk.edu.tw (C.-H. Yang).

extinction coefficients and can in many case be prepared more readily and economically, which therefore demonstrate promising potential in DSSC applications. Consequently, the simultaneous adsorption on TiO₂ electrodes of the various dyes with different absorption wavelengths, which was utilized to broaden the absorption spectrum [16].

We try to investigate the effects of mixed complex/organic co-sensitizers for the applications in solar cells. Mixture design strategy is based on statistical analysis, where a limited number of experiments are used to study the multi-component system. The experimental region can be represented by a regular simplex, and since the sum of the component proportions is unity, this region is a triangle. The experimental region is explored at a point of composition corresponding to an ordered arrangement [17]. The mixture design method assumes that the performance of the DSSCs is a function of its dye components (D131, D149, N3). This relationship can be expressed as

$$\psi = f(x_1, x_2, x_3)$$

where the variable x_i represents the molar proportions of D131 (x_1), D149 (x_2) and N3 (x_3), respectively, in the mixed dyes.

In this work, we report the mixed effects of D131, D149, and N3 ternary dyes in DSSCs. The mixed dyes were characterized by a variety of spectroscopic techniques. A forward stepwise regression procedure was employed to achieve a statistically significant regression equation. The regression model was then plotted as a property-against-composition contour diagram on a computer program, which facilitated straightforward interpretations of the properties of binary and ternary components. Ideally, this method will shed an insight into the dependence of performances of dye composition.

2. Experimental

2.1. General information

The chemical structures of D131 (Mitsubishi Paper Mills Co.), D149 (Mitsubishi Paper Mills Co.), and N3 (Solaronix) dyes are shown in Scheme 1, and these dyes were used as received.

2.2. TiO₂ mesoporous electrode

The hydrothermal processed TiO₂ colloid was synthesized. In brief, 3 g TiO₂ nanoparticles (P25, Degussa AG, Germany, a mixture of ca. 30% rutile and 70% anatase) were dispersed in 100 mL 10 mol l⁻¹ NaOH and heated to 130 °C in autoclave for 1 day. The precipitate was then re-dispersed in 100 mL 1 mol l⁻¹ HNO₃. This suspension was subsequently subjected to autoclaving at 240 °C for 12 h to give the TiO₂ colloid. The TiO₂ specimens were baked at 450 °C in air for 30 min. The Raman spectra of TiO₂ nanoparticles, revealed that there existed a pure anatase phase corresponding to the wavenumbers of 150, 400, 517, and 638 cm⁻¹. X-ray diffraction (XRD) patterns of the titanate-derived TiO₂ also proved a pure anatase phase. The average crystal size was calculated, according to Scherrer's equation, to be approximately 20 nm. The solution of TiO₂ colloid was mixed with polyethylene glycol (PEG-2000) (Fluka) to form a viscous TiO₂ dispersion at a ratio of 0.15 of PEG/TiO₂, which was spin-coated onto a fluorine-doped tin oxide (FTO)-coated glass (10 Ω/□, Hartford) to form a TiO₂ film of 0.25 cm². The TiO₂ film was controlled at a desired thickness (optimal at ca. 8 μm). The film was dried in air at 120 °C for 30 min and calcined at 450 °C for 30 min.
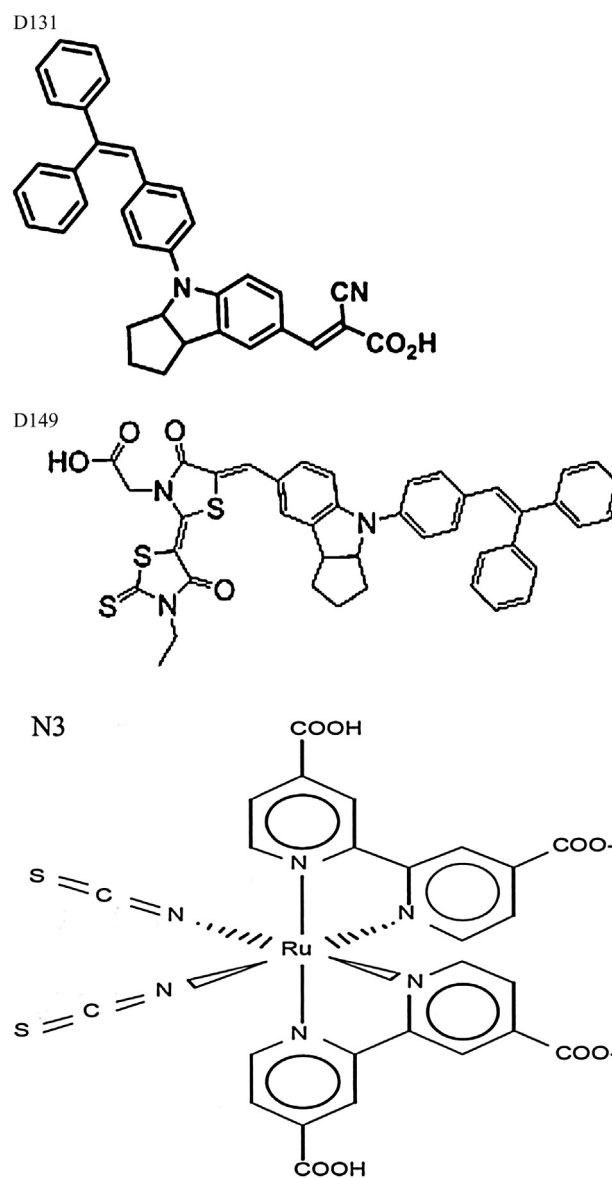
Scheme 1. Chemical structures of dyes.

2.3. Assembly and characterization of DSSCs

TiO₂-coated FTO electrodes were heated at 100 °C. The dye-loaded anodes were prepared by dipping the above TiO₂-coated FTO electrodes into the mixed dye ethanol solutions (5×10^{-4} mol l⁻¹ of total concentration) at varying feed ratios, the design matrix of dye composition is listed in Table 1. The counter electrode of platinum was coated onto an FTO glass by spin-coated processes. The dye-loaded anode and a Pt counter electrode were sealed together with a sealing material, SX1170 (Solaronix), around the TiO₂ active area of 0.25 cm². The electrolyte contained 0.6 mol l⁻¹ 1-propyl-2,3-dimethylimidazolium iodide (DMPII), 0.1 mol l⁻¹ lithium iodide, 0.05 mol l⁻¹ iodine, and 0.5 mol l⁻¹ 4-tert-butylpyridine (TBP) in 3-methoxypropionitrile (MPN).

2.4. Measurements

Absorption spectra were obtained with a Perkin-Elmer Lambda 25 UV-visible spectrophotometer. The thickness of TiO₂ films was determined by an α-step instrument (Surfocorder TE 2400M,