Synthesis of Triphenylamine Trisazo Dye and Study of its Uses in Dye Sensitized Solar Cells

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ABSTRACT

A new triazo dye was synthesized from tri(p-aminophenyl)amine and 2 hydroxy-3-napthoic acid and explored the possibilities of its uses in dye sensitized solar cells for the first time. The photocells were able to generate reasonably high photocurrent in the presence of the electron donating ionic liquids in the electrolyte composed of redox couple I₃⁻/I⁻. Cells fabricated by sensitizing TiO₂ generated a short-circuit photocurrent of ~ 3.5 mA cm⁻², an open-circuit photovoltage of ~ 500 mV with a total power conversion efficiency of ~ 1 % under simulated full sunlight of 100 mW cm⁻² (Air Mass 1.5).

1. INTRODUCTION

With the advent of the highly efficient “Gratzel cell”, dye sensitization of wide band gap semiconductors has become a rapidly expanding solar-light conversion system with potential practical applications [1]. In these devices, upon absorption of light, the dye adsorbed on the surface of the semiconductor injects and electron into the conduction band of the semiconductor. The oxidized dye molecule is then regenerated by accepting an electron from a reducing agent present in the electrolyte of the cell. In this context, the best performing sensitizers were carboxyl group-bearing Ru complexes such as cis-

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dithiocyanatobis (4,4′, -dicarboxy-2-2′bipyridine)ruthenium (II) giving photovoltaic energy conversion efficiencies, as high as 10% at AM 1.5 standard solar spectrum (100 mW cm\(^{-2}\)). Consequently, there has been increasing interest in studying of these dyes [1-6]. However the high cost of RuCl₃ and the difficulties of synthesizing Ru (II) polypyridine complexes limit the practical application of these cells at the present time. Therefore, some pure organic dyes with rich photophysical properties are expected to be promising sensitizers for nanocrystalline solar cells in view of their character of less cost and easy tailoring. In this context, Azo dyes and pigments have attracted considerable attention in recent times since they represent not only the largest chemical class in the colour index but also the largest class of the dyes used in the industry and the analytical chemistry [11-14]. In addition, they are also widely investigated for xerographic photoreceptor application as charge generation materials. The synthetic pathways for Azo compounds, by the classic azotization and coupling reaction, are relatively simple [11]. In this communication we report for the first time synthesis of a new triazo dye from tri(p-aminophenyl) amine and 2-hydroxy – 3- napthoic acid and explored the possibilities of use in photovoltaic devices (PVD).

2. EXPERIMENTAL

2.1 Synthesis of dye

Scheme 1 shows the synthetic procedures of the triazo dye. Tri(4-nitrophenyl)amine (3 mmol) (Aldrich) and 6 M HCl (30 ml) were mixed in a 100 ml three neck flask equipped with a mechanical stir and refluxed for 24 hours. Zinc powder (1g) was added slowly to the reaction vessel and refluxing was continued for another one hour. The solution was then cooled down to room temperature and filtered. The filtrate was then diluted with water, adjusted to pH= 12 and extracted with CH₂Cl₂. The solvent was removed in vacuum to give a purple solid. The resulting tris(4- aminophenyl) amine was stirred in 18% HCl, for 1 hour and cooled down to 0- 5 °C. Then NaNO₂ was added drop wise while keeping the solution at 0- 5 °C and filtered the solution. The solution was then precipitated by adding fluoroboric acid, (0.1M) and collected by filtration. The resulting tetrazolium salt was dissolved in DMF at 0-5 °C and a solution of 2-hydroxy-3-napthoic acid in DMF was added. The solution pH was then adjusted to 11 by adding aqueous solution of NaOH.
slowly. After the addition was completed, the solution was stirred at room temperature for 4 h and then diluted with distilled water. Then the pH of the solution was adjusted to 4 by adding 10% HCl. The precipitated crude powder was filtered off, isolated by filtration, washed with water and recrystallized from ethanol and dried under vacuum, giving purple solid product Triphenylamine trisazo (TPTA) dye (yield: 41%). Formation of TPTA was confirmed by $^1$H NMR (JEOL EX-270, 270 MHz).

2.2 Fabrication of solar devices

In the fabrication of dye sensitized solar devices (DSCs) containing semiconducting nanocrystalline TiO$_2$ films with various thickness, the TiO$_2$ paste purchased from “Solaronix” (Solaronix Nanooxide T, Switzerland) was coated by the “doctor blade” method on pre-cleaned fluorine doped conducting tin oxide (FTO) glasses (Nippon Sheet glass, 10-12 Ohm sq$^{-1}$) and sintered at 500 °C for 1 hour. The thickness of the films on FTO substrates were determined by a Dektak profilometer (Veeco, Dektack 3).

The dye TPTA ($5 \times 10^{-4}$ mol l$^{-1}$) was then dissolved in dried dimethyl sulfoxide (DMSO) and the above semiconducting films were dipped in the dye solution for 60 min at 80 °C. After the dye adsorption films were washed with dried ethanol and dried under N$_2$. DSCs were constructed by introducing the redox electrolyte consisting of 1-methyl 3-n-
hexylimidazolium iodide (HMImI) (0.5M), I₂ (0.05M), 0.40 M LiI and (0.5 M) tert-butylypyridine in a mixture of acetonitrile and ethylene carbonate (6:4 v/v) between the TPTA coated electrodes and a Pt coated counter electrode as shown in the Figure 1. Photoenergy conversion efficiency was evaluated using standard solar irradiation of 100 mW cm⁻² (AM1.5) with a solar simulator (YSS-50A, Yamashita Denso) and a computer controlled voltage current sourcemeter (R6246, Advantest) at 25 °C. The dependence of the short-circuit photocurrent on the incident light intensity was examined by controlling the intensity using an optical lens and neutral density filters. The effectiveness of a cell to convert light of various wavelengths into electrical current was measured as the incident photon to current conversion efficiency (IPCE) defined as the number of electrons generated by light per number of photons incident on the cell as formulated by IPCE % = 1240 J_sc / λ W_i, where J_sc is the short circuit current density (µA cm⁻²), λ, the excitation wavelength (nm) and W_i, is the photon flux (W m⁻²) using a commercial setup for IPCE measurement (PV-25DYE, JASCO). All measured IPCE values were not corrected for the loss of incident light due to the absorption and reflection by the conducting glass support. The optical absorption spectrum of TPTA in DMSO was measured with JASCO (V-570) UV-Visible spectrophotometer. The oxidation potential of the polymer in DMSO was measured in a standard-three-electrode-one-compartment cell using Ag/AgCl in saturated KCl solution, Pt and glassy carbon electrodes as reference, counter and working electrodes respectively.

![Figure 1: Schematic diagram of construction of photcells with TPTA and I⁺/I⁻ electrolyte.](image-url)
3. RESULTS AND DISCUSSION

The UV-vis absorption spectrum of TPTA dye in DMF and absorbed on a TiO$_2$ film (2.3 µm Thick) are shown in figure 2 (a) and (b) respectively. In DMF solution (curve (a)), the dye shows a peak at 520 nm (absorptivity = 9.5x $10^4$ l mol$^{-1}$ cm$^{-1}$) and a shoulder peak around 545 nm. The threshold wavelength of the spectrum is around 620 nm, which is desirable for the light harvesting of corresponding dye sensitized solar cells. When each dye molecule was anchored on TiO$_2$ film via three carboxylic acid groups, the absorption band became broaden and the peak is blue shifted, indicating that the dye on the TiO$_2$ film degraded under illumination. It is observed that the colour of the dye on TiO$_2$ film turned from red to yellow under illumination in the absence of electrolyte. Generally it is proved that excited state of azo dyes can inject electrons to TiO$_2$ particles within a few Pico seconds to form the oxidation state [11,12], which can be degraded to give corresponding aromatic amines in the absence of donors such as I$^-$/I$_3^-$ in a electrolyte. Figure 2 (c) shows the spectrum of incident photon to current conversion efficiencies (IPCE) obtained from the nanocrystalline TiO$_2$ solar cells sensitized by TPTA dye. The IPCE performances were mainly observed in the 400-600 nm ranges and the photocurrent action spectra resembled well with the absorption spectrum of TPTA, indicating that photocurrent is generated by the electron injection from the excited TPTA molecules into the conduction band of the semiconductor TiO$_2$. Therefore, photon energies in the visible light around 400-600 nm can be converted to current with a maximum of ~ 30 % around 550 nm, which is better than those of solid organic photovoltaic solar cells and comparable to those of solar cells sensitized with perylene derivatives [7], merocyanin dyes and pthalocyanine derivatives [15]. Further, the red shift of the action spectra with the optical absorption spectrum is an indication for the chemical attachment of TPTA to the semiconductor.

The dark and the photo current-voltage curves obtained for the cells sensitized with TPTA are shown in the figure 3. While curve (a) illustrates the dark current behavior of the cell, the curve (b) depicts the photoresponses of the cell under the illumination of 100 mW cm$^{-2}$ (A.M. 1.5, 1 sun). The average thickness of the TiO$_2$ photoelectrode was ~ 6.5 µm. As depicted by the curve (a) it is clear that back current is low, suggesting that the low interfacial recombination of photo injected electrons with the oxidized half of the redox couple I$^-$/I$_3^-$.
Figure 2: UV-Visible absorption spectrum of TPTA in (a) DMSO and (b) on TiO₂ electrode. (c) IPCE spectrum of TiO₂/TPTA/Electrolyte.

Figure 3: Current-voltage characteristics of the cell TiO₂/TPTA/Electrolyte under (a) dark and (b) illuminated conditions.

Under the illumination of 1 sun the cell generated 3.5 mA cm⁻² of short circuit photocurrent density with, 500 mV of open circuit voltage. The average fill factor and the
light to electron conversion efficiency of the cell were 0.55 and ~ 1% respectively. The stability of the dye was tested with unsealed cell and the results showed that there was a little variation for the performances of the cell under illumination. The long-term stability will be carried out for the sealed cells.

4. CONCLUSION

In conclusion, a new triazo dye was synthesized by tri(p-aminophenyl)amine and 2-hydroxy-3-napthoic acid and the photo-to-electron properties were studied for the resulting dye sensitized cells for the first time. The results showed that the dye could easily be degraded on TiO$_2$ film under illumination in the absence of donors. However the cell with I$^-$/I$_3^-$ electrolyte becomes quiet stable and generated considerable and comparable photocurrent with the previously reported dyes.

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