Kinetic study of carminic acid and santalin natural dyes in dye-sensitized solar cells

Su Htike Aung[a,b], Yan Hao[a], Than Zaw Oo[b], Gerrit Boschloo[a,*]

[a] Department of Chemistry, Ångström Laboratory, Uppsala University, Box 523, 75120 Uppsala, Sweden
[b] Department of Physics, Materials Sciences Research Laboratory, Mandalay University, Myanmar

ABSTRACT

The performance of natural dyes in dye-sensitized solar cells is usually worse than that of purpose-built organic dyes. Here, we set out to investigate the underlying origins. Two natural dyes, carminic acid and santalin, were selected as potential sensitizers for dye-sensitized solar cells. They were compared to a state-of-the-art organic sensitizer, LEG4, in devices using relatively thin ($5\,\mu$m), transparent mesoporous TiO_2 electrodes and iodide/triiodide redox electrolyte in the low-volatile solvent 3-methoxypropionitrile. All dyes adsorbed well onto mesoporous TiO_2 electrodes, giving it bright red colors. The power conversion efficiency of the natural dyes, about 0.5%, was poor compared to that of LEG4 under identical conditions (5.6%), due to both lower open circuit potentials and photocurrent densities.

The origin of low efficiencies was investigated using a wide range of experimental techniques, such as (spectro)electrochemistry, ns-laser transient absorption spectroscopy and transient photocurrent and photovoltage measurements. The kinetics for regeneration of the oxidized natural dyes by iodide was found to about ten times slower than that of LEG4. This is probably due to the lower driving force for this reaction. Significant electron recombination to oxidized dye molecules and possibly poor electron injection efficiency caused the poor performance of the two natural dyes in dye-sensitized solar cells. In addition, for carminic acid electron injection into the conduction band of TiO_2 appears to be poor.

© 2016 Published by Elsevier B.V.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention because of their potential as a low cost renewable energy source [1,2]. Although their power conversion efficiencies are lower than that of conventional silicon solar cells, but they have some unique and attractive features, such as their variation in color, where almost any color is possible, (semi-) transparency, and low-tech fabrication. In these solar cells dye molecules are responsible for light harvesting, while electron transport takes place in the TiO_2 film onto which the dyes are attached. Hole transport is taken care of by a liquid redox electrolyte. Here, we focus on organic dye sensitizer molecules that are at the heart of dye sensitized solar cells. Sensitizers utilized in DSSC can be divided into two main types: metal complex dyes and organic dyes. Metal complex dyes are mostly based on ruthenium, which is a rare, expensive and toxic heavy metal. Ru-dyes usually have a long-lived excited states, rather low extinction coefficients and broad

absorption spectra [2]. Organic dyes are usually characterized by a narrower absorption spectrum and larger extinction coefficients and shorter excited state lifetime. The synthetic routes of organic dyes can be complex, which increases their cost. A large variety of organic dyes occurs in nature, and these can be potentially used to make very low-cost DSSC.

Many attempts have been made to use natural dyes as sensitizers in DSSC: anthocyanins [3], chlorophylls [4] and its derivatives [5], carotenoids [6], betanin [7] and other molecules that were extracted from fruits, flowers and leaves have been investigated [8–11]. Among the highest reported power conversion efficiencies (PCE) of natural dye-sensitized solar cells are that of betanin from beetroot of 2.7% [7] and that of a chlorophyll from a seaweed of 4.6% [4].

Despite the promising results, the performance of most natural dyes is much worse than that of purpose-built organic dyes in dye-sensitized solar cells. There are, however, few studies that focus on the reason for their poor photovoltaic performance. In this study, we investigate two natural dyes: carminic acid (CA), that is extracted from cochenical insects and santalin (SA), extracted from red sandal wood. There have been a few DSSC investigations on these dyes [12,13], but detailed solar cell studies, energy level
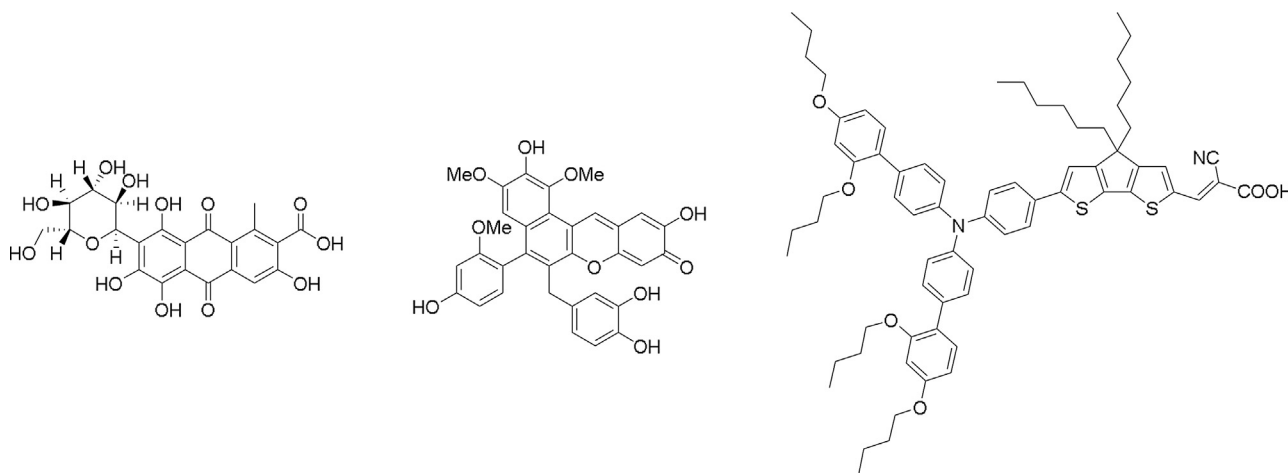

Fig. 1. Molecular structures of carminic acid (left), santalin A (middle) and LEG4 (right).

studies and kinetics studies are lacking. The molecular structures of these dyes are shown in Fig. 1. For comparison, a state of the art organic dye, LEG4 [14,15], is also investigated. Here we will take a detailed look at the DSSC performance of the two natural dyes, by studying optical and electrochemical properties, and electron transfer kinetics in DSSCs. The effect of two additives, 3-phenyl-propionic acid (PPA) [16] and chenodeoxycholic acid (cheno) [17], was also studied.

2. Experimental

Red sandalwood (Pterocarpus santalinus) contains two main pigments: santalin A (5,7-dihydroxy-6-methoxy-1,2,3,4-tetrahy-droanthracene-9, 10-dione) and santalin B, the corresponding 6-(4-hydroxy-3-methoxybenzyl) derivative [18]. Here a simple procedure was used to extract santalin: red sandalwood powder (Abbey Botanicals) was soaked in deionized water for one hour and then extracted with toluene (purity $\geq$ 99. 5%) using a separating funnel. The toluene fraction, containing most of the santalin, was separated and dried in a rotary evaporator. The orange-red colored solid was soluble in ethanol and is assumed to contain both santalin A and B. It was used in the dye bath without further purification. The UV–vis spectrum (Fig. 2b) shows three peaks at 446 nm, 473 nm and 505 nm, that can be assigned to santalin (santalin A and B have identical spectra) [18]. Carminic acid was purchased from Sigma-Aldrich and LEG4 from Dyenamo. The chemical structures of these three dyes are shown in Fig. 1.

2.1. Device fabrication

Fluorine-doped tin oxide (FTO) glass substrates (TEC8, Pilking-ton) were cleaned together in an ultrasonic cleaner with detergent, DI water, ethanol and acetone. Each step was taken for 1 h. Transparent nanostructured TiO_2 films were prepared with an area of 0.25 cm^2 by screen printing method with the colloidal TiO_2 paste (Dyesol DSL 18 NRT). Different film thicknesses were obtained by depositing layer by layer. The film thickness was measured by surface profilometer (Veeco Dektak 3). The films were sintered at 450 °C in air inside an oven and left overnight to be cool down. The TiO_2 films were treated by immersing in a 40 mM $TiCl_4$ solution at 70 °C for 30 min h that leading surface roughness to improve dye uptake as well as efficiency. After $TiCl_4$ treatment, the electrodes were heated in again to 450 °C. After the electrodes were cooled down to 90 °C, they were immersed in dye baths containing either 0.2 mM LEG4, 5 mM carminic acid (CA) or ∼5 mM santalin (SA) in ethanol and left overnight. In some cases, phenylpropionic acid (PPA) or chenodeoxycholic acid (cheno) was added in the dye bath. The films were rinsed in ethanol to remove excess dyes and dried in air. Platinized counter electrodes were prepared by depositing 10 μl per cm^2 5 mM H_2PtCl_6 solution in ethanol followed by heating at 400 °C for 2 h. A 30 μm thick thermoplastic Surlyn frame was used assemble photoanode and counter electrode together with hot press sealing machine (Heptachroma). An electrolyte solution was introduced through the predrilled hole in the counter electrode in the vacuum chamber and then the cell was sealed with thermoplastic Surlyn cover and a glass cover by using hot gun. Unless noted otherwise, the electrolyte was composed of 0.5 M lithium iodide (LiI), 0.05 M iodine (I_2) and 0.5 M 4-tert-butylpyr-idine (TBP) in 3-methoxyproprionitrile (MPN) (all from Sigma-Aldrich). Finally, the silver paint was put on the edges of counter and working electrodes.

2.2. UV–vis spectroscopy

The UV–vis spectrophotometer (HR-2000 Ocean Optics fibers optics spectrophotometer) was used to characterize the absorption properties of dye solutions and sensitized TiO_2 films. For the measurements of dye solutions, a normal quartz cuvette (1 cm path length) was used.

2.3. Electrochemistry

Cyclic voltammetry measurements were performed using a CH instruments 660 potentiostat with three-electrode setup. A stainless steel rod was used as counter electrode and an Ag/AgCl electrode in saturated LiCl in ethanol as reference electrode, calibrated against ferrocene. The supporting electrolyte solution was 0.1 M LiTFSI in acetonitrile. For dye in solution, glassy carbon electrode was used as the working electrode, while for the measurements of adsorbed dye, the dye adsorbed on mesoporous SnO_2:Sb films on FTO substrates were used as the working electrodes. At the same time absorption spectrum could be monitor using an Ocean Optics 2000 spectrometer. Transparent Sb: SnO_2 films were prepared by doctor blading method, using a slight modification of published method [19]. Briefly, 10 g of SnO_2:Sb colloid (Alfa) was stirred with 0.75 g polyethyleneglycol (MW 20 000) for an hour, then 2 ml of ethanol was added. This gives a viscous paste that was left overnight. The paste was diluted with