TEXTILE BASED DYE-SENSITIZED SOLAR CELLS WITH NATURAL DYES

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ABSTRACT

Natural dyes extracted from hibiscus petals, elderberries and mallow flowers were investigated in dye-sensitized solar cells. Two approaches were followed: 1. Hybrid glass/fabric cells with titanium dioxide on glass as working electrode and a textile counter electrode; 2. hybrid fabric/glass cells with zinc oxide as working electrode on textile and a glass counter electrode. The zinc oxide layer on cotton was prepared by electroless deposition whereas the titanium dioxide coated glass electrodes were obtained directly from the manufacturer. In both cases the redox couple consisted of iodine / triiodide and the counter electrode was based on an electrically conductive fabric.

Key Words: RENEWABLE ENERGY, MULTILAYER STUCTURE, ZINC OXIDE, LIGHT HARVESTING

1. INTRODUCTION

The worldwide energy demand is increasing while resources of fossil fuel are limited [1]. In addition, their production has negative impact on the environment, and the carbon dioxide release due to combustion is immense. With the Paris Agreement the United Nations agreed to limit global warming. Therefore, the energy production from renewable and sustainable resources is favored and must be developed further.

Dye-sensitized solar cells (DSSCs) can be produced at low costs and without special equipment. They are also known as Grätzel cells named after their inventor, Michael Grätzel [2]. Compared to conventional silicon-based solar cells, DSSCs can be produced under ambient conditions with non-toxic materials. An advantage of DSSCs is their behavior under diffuse light conditions. The efficiency is much higher than for conventional silicon cells. The principle built-up of the multi-layer structured DSSC is shown in Figure 1.

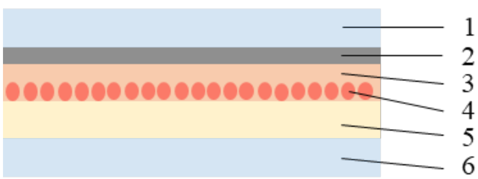

Figure 1. Principle built-up of a DSSC: 1 – counter electrode, 2 – catalyst layer, 3 – electrolyte, 4 –dye molecules adsorbed on semiconductor, 5 – semiconductor, 6 – transparent working electrode

The transparent working electrode (6) is covered by a semiconductor (5), usually titanium dioxide or zinc oxide. Because of the high sintering temperature of titanium dioxide it cannot be used in solar cells with a textile working electrode. However, hybrid fabric-glass cells were fabricated with titanium dioxide as semiconducting layer.

A monomolecular dye layer (4) is adsorbed on the semiconductor. In high-efficient DSSCs ruthenium complexes are used despite their toxicity. Also natural dyes like anthocyanins can be used [3]. Anthocyanins can be extracted from a number of plant parts like petals or fruits, most prominent anthocyanins are the glycosides of delphinidin and cyanidin, which absorb light at 535 nm and 525 nm, respectively [4].
An electrolyte is sandwiched between the two electrodes (4). Traditionally, the electrolyte consists of a mixture of iodine and potassium iodide solution, also known as Lugol's solution. The catalyst (2) between electrolyte and counter electrode enhances the transportation of the electrons from electrode to electrolyte.

2. EXPERIMENTAL

2.1 Materials

Dried natural products (hibiscus petals, elderberries and mallow flowers; see Figure 2) were obtained from naturix24.de (Dransfeld, Germany). All used glass slides with deposited fluorine-doped tin oxide (FTO) and titanium dioxide, respectively, were purchased from ManSolar (Petten, The Netherlands). Gelatin 707 was sponsored from InovisCoat GmbH (Monheim am Rhein, Germany). Iodine, potassium iodide and all chemicals for the electroless deposition of zinc oxide were purchased from Sigma-Aldrich (Taufkirchen, Germany). PEDOT:PSS dispersion Clevios S V4 was obtained from Heraeus (Leverkusen, Germany) and all Tubicoat dispersions were from CHT R. Beitlich (Tübingen, Germany). Fabrics used were a cotton plain weave fabric and a plain weave polyester fabric, which was pre-coated with a polyurethane layer to prevent capillary forces. A copper plated polyester (PES) taffeta fabric from LessEMF (Latham, NY, USA) was used as an alternative for the counter electrode.

2.2 Extraction of Dyes

20.0 g dried hibiscus flowers were crushed in a mortar with a pistil and then immersed in a solution of 160 ml water and 40 ml ethanol for extraction. 2 ml concentrated hydrochloric acid were added for pH adjustment. The solution was kept still for 24 hours in the dark at room temperature. The solid content was filtered off and washed with a mixture of ethanol and water (volume 1:4) until the solvent was colorless after washing. All collected solutions were merged and boiled down to 100 ml using a rotating evaporator (40 °C at 20 mbar). The pH-value was adjusted to 1 using concentrated hydrochloric acid. The procedure for extracting anthocyanin dyes from dried mallow flowers and elderberries was the same.

2.3 Preparation of Gelled Electrolyte

14.0 g powdered gelatin were swelled in 17.2 ml deionized water for 10 minutes at room temperature. 4.00 g (24.1 mmol) potassium iodide and 2.00 g (7.9 mmol) iodine were separately mixed in 20.0 ml deionized water. The swelled gelatin was removed from water, melted at 50 °C and poured under stirring into the iodine-triiodide-solution. 6.00 ml glycerol were added as wetting agent. The solution was allowed to cool down and gel. It was stored in the dark at 8 °C and was stable for at least 28 days. Prior to further use it was heated up to 50 °C.

2.4 Conductive coatings on fabrics

All electrically conductive coatings were applied with a 50 µm roller bar. For the textile working electrode a cotton fabric was coated with PEDOT:PSS. Counter electrode materials were also PES fabrics coated with PEDOT:PSS or Tubicoat ELH, which is a dispersion containing carbon .

2.5 Electroless deposition of zinc oxide

Zinc oxide was electroless deposited on PEDOT:PSS coated cotton fabrics. The fabrics were sensitized in a two-step procedure. First, they were immersed for 30 minutes in a hydrochloric acid solution of 1 g/l chloride and after carefully rinsing with deionized water they were immersed in a hydrochloric acid solution containing 0.1 g/l palladium chloride for 10 minutes. After careful rinsing and drying, the fabrics were immersed in a solution of zinc chloride and dimethylamino borane. The reaction took place in a laboratory microwave oven between 80 and 120 °C during 10 to 30 minutes.

2.6 Assembly of DSSCs and testing of their electrical properties

2.6.1 Cells with textile counter electrodes
Titanium dioxide coated FTO glass slides were immersed in dye solution for 24 h unless stated otherwise. After removing from the dye solution they were carefully washed with deionized water. The molten gelatin electrolyte was dripped carefully on the dyed slide and put together with a conductively coated fabric. The photosensitive area of all samples was 6 cm².

2.6.2 Cells with textile working electrodes
Cotton fabrics with electroless deposited zinc oxide were immersed in dye solution for 24 h and carefully washed with deionized water in a petri dish. Droplets of molten gelatin electrolyte were put onto the counter glass electrode, which was coated with a thin graphite layer. Before gelling, the solar cell was assembled by putting both electrodes together. Like the cells with textile counter electrodes, the photosensitive area was 6 cm².

2.6.3 Testing of electrical properties
The electrodes were connected to two multimeters to measure the short-circuit current (J_{sc}) and the open-circuit voltage (V_{oc}) under irradiation with an 800 W halogen lamp.

3. RESULTS AND DISCUSSION

3.1 General investigations

Firstly, the pH-dependency of the dye was investigated with glass cells. UV/Vis-spectroscopy indicated that light absorption of extracted anthocyanin solution increases in the range of 520-540 nm with lower pH values. Correspondingly, best results were obtained when the working electrodes were dyed at a pH value between 0 and 1. Also the dyeing time was investigated. The properties of the cells improved with the dyeing time. They reached the top after 24 hours.

3.2 Cells with textile counter electrodes

All results of these cells are given in Table 1. Figure 2 shows a cell with a textile counter electrode with hibiscus extract. The counter electrode was a PES fabric coated with Tubicoat ELH. The samples show an open circuit voltage between 405 and 511 mV. The short-circuit current strongly correlates with the used counter electrode material and the dye source. Best results are obtained with the copper plated fabric for which currents of approx. 150 µA could be obtained. Also samples with a Tubicoat ELH counter electrode show a current above 100 µA. Cells with PEDOT:PSS counter electrodes showed lower currents compared to the above. Generally, the obtained current correlates with the surface resistance of the used counter electrode material. With a decreasing resistance the current increases.

Table 1. Electrical properties of freshly prepared DSSCs with textile counter electrodes

Dye extracted from	Counter electrode	V_{OC} [mV]	J_{SC} [µA]
Hibiscus	Tubicoat ELH	500	114
	PEDOT:PSS	511	80
	Copper fabric	475	155
Mallow flower	Tubicoat ELH	481	98
	PEDOT:PSS	426	79
	Copper fabric	491	142
Elderberries	Tubicoat ELH	405	104
	PEDOT:PSS	413	81
	Copper fabric	491	147

It must also be taken in account that the catalyst layer is missing on the Tubicoat ELH samples. But it was presumed that this electrode material acts as both, electrode and catalyst.
The best dye in all cases was the hibiscus extract. The other dyes resulted in lower short-circuit currents. With the other counter electrode materials, also lower short circuit currents are obtained.

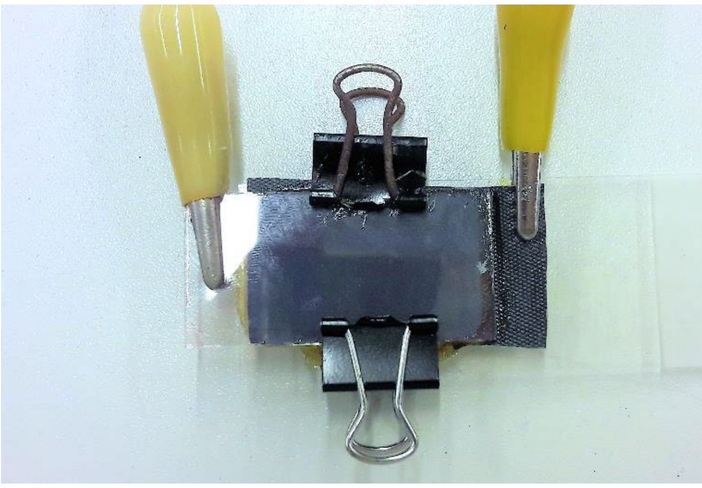

Figure 2. Hybrid glass/textile dye sensitized solar cell with hibiscus dye and Tubicoat ELH polyester fabric as counter electrode

A degradation of the PEDOT:PSS coating and the copper fabric is observed. Both electrodes oxidize when they are brought in contact with the electrolyte. The obtained voltage and current decrease rapidly for the copper plated fabric. Even the PEDOT:PSS is degraded, only a slight decrease of current production was observed for these cells. No degradation of the Tubicoat ELH counter electrode was detected.

3.3 Cells with textile working electrode

Titanium dioxide must be annealed at high temperature of more than 400 °C, which is not possible with most textile fibers. Therefore titanium dioxide was replaced by zinc oxide, which is also a common material in dye sensitized solar cells [5]. The microstructure of the deposited zinc oxide depends on the reaction conditions. After 20 minutes at 120 °C, crystalline needles in the range of few micrometers are formed, whereas at lower temperatures smaller rods and structures are formed (see Figure 3). With all of these materials solar cells were fabricated. The samples which were prepared at a temperature below 120 °C did not show any activity.

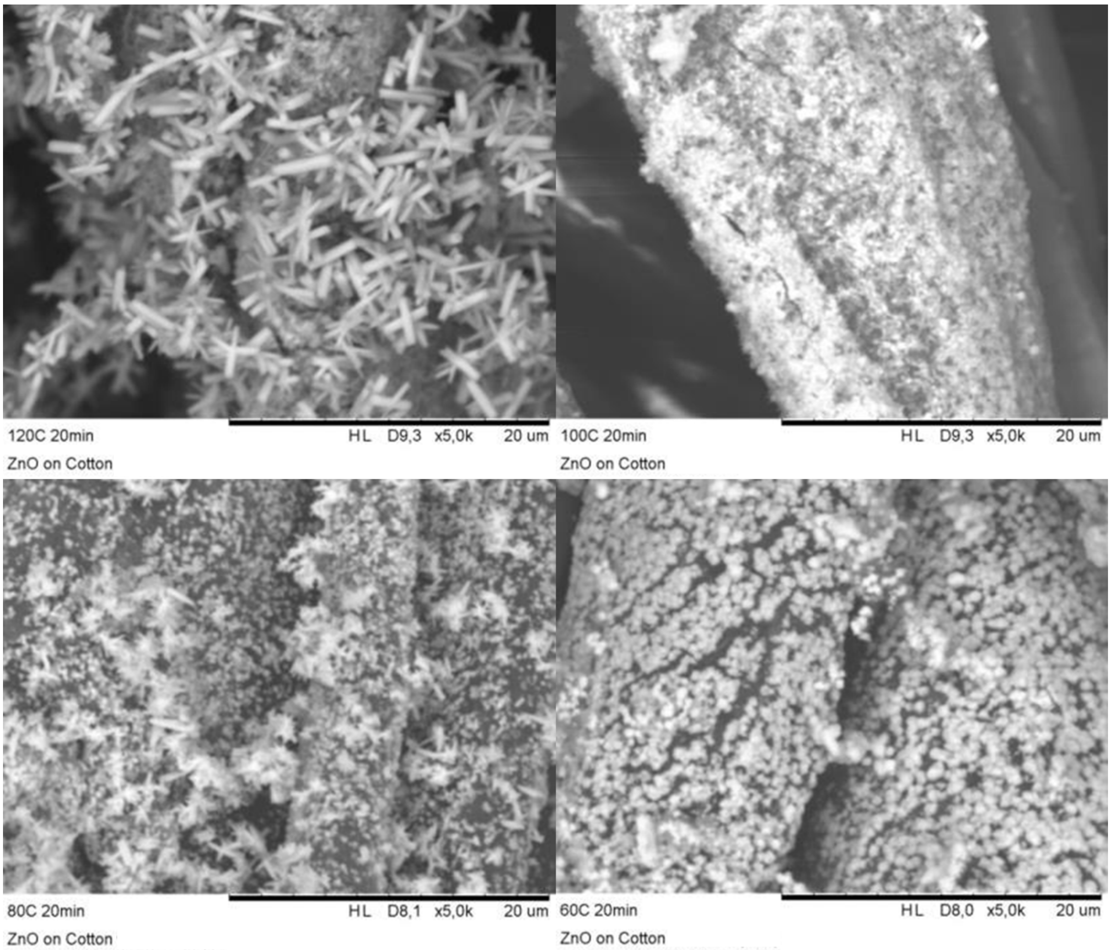

Figure 3. SEM image of electroless deposited zinc oxide on PEDOT:PSS coated cotton fabric prepared at different temperatures in a microwave oven

In contrast to glass based working electrodes, zinc oxide is deposited on both sides of the fabric. The dye is adsorbed not only from the semiconducting material but also soaked up by the fabric. Also with zinc oxide, the hibiscus extract was the best dye tested for achieving high short circuit currents. Results are given in Table 2. The current production was 25 µA for all dyes. The obtained voltage with the fabric-based working electrode was lower, only around 272 to 350 mV. While literature shows that the voltage of zinc oxide cells is generally lower, the main reason here is the substrate.

Table 2. Electrical properties of DSSCs with textile working electrode

Dye extracted from	Counter electrode	V_{OC} [mV]	J_{SC} [µA]
Hibiscus	Tubicoat ELH	350	25
Mallow flower	Tubicoat ELH	272	25
Elderberries	Tubicoat ELH	285	25

4. CONCLUSION AND OUTLOOK

Textile DSSCs were successfully fabricated using either a textile working or counter electrode. Zinc oxide seems to be a promising alternative to titanium dioxide for preparing textile based working electrodes. The open circuit voltages measured for different dyes in these cells indicate either a different increase of the Fermi level in the semiconductor due to excited dye states, or different ratios for the rate of the electron injection into the semiconductor and the competing processes like electron recombination with the oxidized dye or the electrolyte. The latter process may also be influenced by the remaining free semiconductor surface.
However, in the experiments using textile counter electrodes such conclusions are ambiguous, since a possible overpotential at the counter electrodes contributes to the open circuit voltage. This is of importance, because the catalyst on the copper and PEDOT:PSS types had to be applied manually and individually for each cell. So only the samples containing Tubicoat can be compared, which shows similar results as in the cells using textile working electrodes. Nevertheless, Tubicoat ELH coated electrodes result in cells of similar performance than PEDOT:PSS coatings or copper fabrics, which renders this substance promising to omit the additional catalyst application.

5. ACKNOWLEDGEMENT

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