Optik 158 (2018) 469–476

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Original research article

Application of paper industry waste materials containing TiO_2 for dye-sensitized solar cells fabrication

Maciej Zalas[a,b,c,*], Anna Cynarzewska[d]

[a] Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89B, 61-614 Poznań, Poland
[b] Department of Chemistry, University of Milan, Via Golgi 19, Milano 20133, Italy
[c] SmartMatLab Centre, Via Golgi 19, Milano 20133, Italy
[d] Paper Mill "Malta-Decor" Sp. z o.o., Wołkowyska 32, 61-132 Poznań, Poland

ARTICLE INFO

Article history:
Received 23 November 2017
Accepted 23 December 2017

Keywords:
Dye-sensitized solar cells
Solar energy
Paper industry
TiO_2
Waste material
Waste reclamation

ABSTRACT

A series of dye-sensitized solar cells have been constructed using titania-rich paper industry waste materials. The cells obtained were able to produce solar electricity, but with relatively poor photon-to-current efficiencies reaching only 0.47% and short circuit photocurrent densities up to 1.14 mA × cm^{-2}, but reasonable fill factors and very good open circuit photovoltage reaching 67% and 719 mV, respectively. The titania-rich waste samples were prepared by removal of water and post-production organic residues and well characterized with XRD, XRF, FT-IR, SEM, TEM, EDS and UV–vis techniques. This paper presents an alternative solution for green energy production and conversion of pollutants to useful materials.

1. Introduction

When in 1972 Fujishima and Honda discovered the phenomenon of photocatalytic water splitting over the titania electrodes [1], enormous potential to apply TiO_2 in such areas as photocatalysis, photovoltaics, photo and/or electrochromics and sensor construction was recognized [2]. Almost two decades after the Fujishima and Honda's discovery, O'Regan and Grätzel have presented the first highly efficient dye sensitized solar cell (DSSC) [3]. The device made by O'Regan and Grätzel is based on a mesoporous titania electrode sensitized with a ruthenium dye to convert energy of incident light to electricity with efficiencies about 7–8 %. In short, the DSSC device is made of two conductive glass electrodes [4–11]. The first electrode is a transparent photoanode, which consist of conducting oxide glass substrate coated with a thin mesoporous layer of nanocrystalline semiconducting oxide with a wide band gap (mostly TiO_2). The surface of the semiconductor is modified with a monolayer of chemisorbed dye molecules. The second electrode, the counter electrode, is made of conducting oxide glass coated with an ultrathin layer of platinum. The electrolyte containing redox medium (usually I^-/I_3^- couple) is injected between these two electrodes to transfer charge between them. The main attention has been focused on enhancing the photon-to-current efficiency and time stability of the DSSCs. The initial types of DSSCs based on a combination of mesoporous titania sensitized with ruthenium sensitizers cooperating with iodine-based electrolytes permitted the efficiencies up to 11.9%, but the devices of this kind have never surpassed the efficiency level of 12%. Further application of the new type of organic donor-π-acceptor dyes based on porphyrin with cobalt-based redox mediators permitted obtaining efficiencies

* Corresponding author at: Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89B, 61-614 Poznań, Poland.
E-mail address: maciej.zalas@amu.edu.pl (M. Zalas).

https://doi.org/10.1016/j.ijleo.2017.12.125
0030-4026/

over 13% and still has much potential of development [12]. Photoanode materials design and modification also have had high impact on DSSCs efficiency improvement. Various types of semiconductors e.g. TiO_2, ZnO, Nb_2O_5, WO_3, $SrTiO_3$, have been used as anode materials, but the one used in most efficient devices is TiO_2 [13].

Because titanium dioxide is relatively chemically inert and environmental friendly, it has been also widely used in industry as a pigment, in sunscreens, paints, ointments, toothpaste etc. since the beginning of the 20th century, when its commercial production began [2]. About 12% of global TiO_2 production is consumed by paper industry [14]. Both rutile and anatase forms of titanium dioxide are applied for paper production. The most important property determining wide application of TiO_2 in paper production is its high refractive index which endows manufactured product with high opacity. The higher refractive index of rutile (2.7), in comparison with anatase (2.45) [15], rather than their prices (rutile is more expensive than anatase) makes the former more widely applied in paper industry. The application of rutile is also responsible for higher light-resistance of produced paper due to the lower photocatalytic activity of this titania polymorph, but both forms are applied in photoenergetic processes [16]. Kang et al. have synthesized columnar-structured rutile TiO_2 layers using radio-frequency magnetron sputtering technique and applied them as working electrodes in DSSC [17]. The obtained photon-to-current overall conversion efficiency of rutile-based cells was 2.4%, while for anatase-based devices produced with the same procedure it was 1.78%. The better performance of rutile-based devices is caused by the growth of rutile films in specific direction in the (110) plane causing a decrease in the grain size and, in consequence, in improvement in dye adsorption which contributes to the enhancement of the photocurrent. Much better performance of rutile-based DSSCs has been obtained by Yu et al. [18] when three-dimensional rutile-nanorod-based network structure directly grown on FTO glass was used as working DSSC electrodes. The efficiency up to 6.31% was obtained thanks to a combination of light scattering effect with high dye loading due to large surface area. Single-crystal rutile nanorods have been also investigated by the group of Gu [19]. These authors have compared the overall photoconversion efficiency of the DSSC devices based on rutile nanorods arrays synthesized on the FTO substrates and post-synthetically treated by annealing at various temperatures from the range of 200–600 °C. They have found that the array treated at 500 °C gives the most efficient DSSC (η = 4.42%) which is a result of increase in the light harvesting, the enhanced electric contact and decrease in the recombination effect between injected electrons and redox species of the electrolyte.

Paper industry, as every other one, generates some number of waste which contains also titanium dioxide. To the best of our knowledge, no attempt has been made to use such wastes to prepare DSSC devices. The utilization of paper industry waste materials as a source of electrode material for DSSC to produce “green energy” seems to be attractive from both economic and environmental points of view. That is why we decided to make and characterize a series of DSSCs using paper industry waste materials containing rutile TiO_2. The chemical composition of electrode materials and the pre-applicative treatment procedure of waste materials were also developed. Photovoltaic properties of the cells obtained were determined and compared with those of the cells based on raw TiO_2 materials used in the paper manufacturing process.

2. Experimental

All chemicals were in analytical grade and were used as received without any additional purification. The paper industry waste materials, in the form of a wet pulp, were collected from “Malta Decor” paper factory’s production facility in Rudawa, Poland, after production of 5 types different white or low-stained papers. The freshly collected samples of the wastes from these five processes were dried at 353 K in air overnight. Each residue obtained was milled in a Mixer/Mill 8000M ball mill (SPEX Sample Preparation) equipped with a zirconia ceramic grinding set for 1 h. Soft white-greyish powders were obtained after calcination in air at 723 K for 2 h and labelled as T1, T2, T3, T4 and T5 to correspond to these five processes.

The procedure used for preparation of titania electrodes was similar to those described elsewhere [20] and was as follows: 3 mL titanium tetraisopropoxide (Aldrich) were added to 13.5 mL of ethylene glycol (Chempur) magnetically stirred at 333 K. The mixture, after addition 12.6 g of citric acid monohydrate (POCh), was heated upon stirring at 363 K, until clear. The 13.5 mL of transparent sol obtained was mixed with 5.6 g of T1-T5 samples by grinding in agate mortar for 1 h. The viscous titania paste obtained was spread on fluorine doped tin oxide (FTO) conductive glass substrate (Solaronix) using “doctor blade” technique and sintered in air at 723 K for 2 h. To prepare working electrodes for DSSCs, titania electrodes were immersed in 10^{-5} M solution of N3 dye (Solaronix) in absolute ethanol at 278 K overnight. After dye adsorption, the electrodes were washed with absolute ethanol and dried in hot air stream. A platinum film coated FTO was used as a counter electrode. The typical cell was assembled using a 25 μm thick, hot-melted, ionomeric foil (Solaronix) as a sealant and a spacer between the electrodes and the electrolyte (a mixture of 0.6 M 1-propyl-3-methyl-imidazolium iodide (Aldrich), 0.03 M iodine (POCh), 0.1 M guanidine thiocyanate (Fluka) and 0.5 M 4-tert-butylpiridine (Aldrich) in acetonitrile (Merck)) were injected through two holes predrilled in the counter electrode. The final sealing was realized with the use of hot melted sealant and a microscope cover slide. The typical active area of the obtained DSSC was approximately 0.125 cm^2. The obtained cells were labeled according to the T1-T5 samples used to obtain working electrodes. For each configuration three cells were prepared and photoelectric measurements were repeated five times for every cell prepared, and the results presented are for the best ones. The reference DSSCs made with the use of each of 5 different titania raw materials were also prepared using a similar procedure and labelled as RM1, RM2, RM3, RM4 and RM5.

The photovoltaic characteristics of the cells were measured using a Sun 2000 class A Solar Simulator (Abet Technologies) equipped with an AM 1.5 G filter, with the light intensity adjusted at 1000 W m^{-2} using a silicon reference cell (ReRa Systems). The J-V curves were recorded on a Keithley 2400 SourceMeter (Keithley). The diffuse reflectance UV–vis spectra