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DSSCs based on ZnO photoelectrodes sensitized with natural dyes extracted from the bark of Brazil and Taray

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We report the extraction of natural dyes from Brazil and Taray bark, the impregnation of these dyes in thin films of ZnO synthesized via sol-gel method and deposited by Doctor Blade and finally the fabrication of dye sensitized solar cells (DSSC). The ZnO/dyes structures were characterized using UV-Visible and infrared spectroscopy. The analysis of the infrared spectra shows that the semiconductors impregnated with the extracted dyes exhibit the characteristic of dye anchorage in ZnO. The photovoltaic performance and efficiency of the assembled DSSCs was evaluated.

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1. Introduction

Dye-sensitized solar cells invented by O'Regan and Grätzel [1], is attracted attention because of the simple manufacturing processes, environmentally friendly, good cell performance and low fabrication cost. The DSSCs are composed of a transparent conducting photoanode (FTO or ITO) coated with a nanocrystalline semiconductor (n-ZnO, n-SnO2 or n-TiO_2), dye photosensitizer, a liquid redox electrolyte and finally transparent conductive oxide (TCO) glass coated by a thin film of platinum or carbon as a counter-electrode. In the DSSC, synthetic or natural resource dyes are used as sensitizers. The sensitizer dyes generate electrons and holes under illumination. The generated electrons are transferred to the conduction band of the acceptor semiconductor metal oxide, while holes are transferred to the electrolyte.

The most efficient dyes for DSSCs are based on ruthenium polypyridyl complexes, which are related to a high absorption coefficient across the entire visible spectrum and the efficient injection of electrons into the ZnO conduction band. However, the ruthenium polypyridyl complex contains a heavy metal of relatively high cost and the synthetic routes are complicated with low yields [2].

The use of natural dyes in the manufacture of DSSCs has proven to be an alternative source of energy production, as it does not contain rare, toxic and inorganic metals or inorganic metal ions. Researchers have tried to identify plants and fruits that produce dyes to evaluate their compatibility as sensitizers in solar cells. Several reports discussing DSSC assembly using natural dyes such as cyanin, anthocyanin, tannin, chlorophyll, bethalains, carotenoids, etc., as sensitizer have appeared in recent times [3]. Natural dyes containing anthocyanin [4,5,6] and their derivatives show broad absorption band in the visible spectrum ascribed to charge transfer transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [7]. It is a non-toxic naturally occurring pigment, soluble in water, found in fruits, vegetables, flowers, and other plant tissues and responsible for a wide range of colors [8].

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The objective of this work is the extraction of natural dyes from Brazil and Taray bark, the impregnation of these dyes in ZnO-based photoanodes, the manufacture of solar cells sensitized with these dyes, as well as the evaluation of their photovoltaic behavior. The ZnO nanoparticles were synthesized via sol-gel and deposited by the Doctor-Blade method. In addition, DSSCs were manufactured using nano-sized zinc oxide as photoanodes; the photoanodes were then sensitized with the dyes. The ZnO/dyes structures were characterized by UV-Visible and FTIR to identify the light absorption behavior, the existence of anchor groups of the extracted dyes. These structures have been characterized and the photovoltaic performance of the DSSC is reported.

2. Experimental

For the extraction of the natural dyes, 6.75 g of the bark of Brazil and 6.75 g of the bark of Taray were used. Each of these materials were poured separately into 50 ml of ethanol, for one day. Finally, the dyes were stored in dark containers to avoid light and thus prevent degradation.

In the deposition of ZnO thin films, powders previously synthesized by the sol-gel method were used [9]. The process of preparing the ZnO ink was as follows: 0.6 g of ZnO powder, 0.12 g of polyethylene glycol, 60 μl of deionized water and 1890 μl of ethanol were measured. These chemicals were mixed and placed in constant agitation for 24 hours. Thin films of ZnO were deposited by the Doctor-Blade technique on previously washed glass substrates. The deposit of the ZnO ink was done in an area of 1.0 x 0.5 cm delimited with a 3 *mm* thick tape. The ZnO films were dried for 10 minutes. Finally, the films were heat treated at a temperature of 450 °C for 30 minutes to seal the film to the substrate.

The ZnO thin films were immersed in a solution containing 50 mL ethanol and each of the dyes (6.75 g of Brazil bark and 6.75 g of Taray bark) for three hours. To improve the adsorption of the dye, the substrates were sintered at 80°C and immersed in the dyes after sintering, subsequently were then taken out and rinsed with ethanol to remove excess dye, finally they were placed on an inclined surface for drying.

The fabrication of the DSSCs were performed as follows: The cathode was prepared by coating clean FTO with H_2PtCl_6 platinum solution and heat treated at 400°C for 30 min. The electrodes were fixed with thermoplastic frames, then were placed on top of each other and placed in the oven at 215°C to achieve sealing. The injected electrolyte solution consists of 1.59 g of DMPII, 0.134 g of LiI, 0.118 g of GuSCN and 0.127 g of I_2, dissolved in 0.732 mL of 4-tertbutylpyridine, later a solution of 8.5 mL added acetonitrile and 1.5 mL of valeronitrile, the mixture is dispersed for 15 minutes. The electrolyte solution is injected through the holes of the counter electrode. Finally, holes were sealed and a coat of silver paint was applied to improve contact with measuring devices.

2.1. Characterizations

The optical transmittance and absorbance were measured in the spectral range of 280-800 nm, using a Shimadzu UV-VIS-NIR double beam spectrophotometer. The absorption coefficient and band gap were determined. The Fourier Transform Infra-red (FTIR) spectra were measured by FTIR 7800 Spectrometer in the wave number range 4500-1000 cm^{-1} with a maximum resolution of 0.5 cm^{-1}. Current–voltage measurements on the fabricated DSSC were performed with a Kiethley Source meter under simulated white light source (100 mW/ cm^2).

3. Results and discussion

3.1. Optical properties

Transmittance and the plot $(\alpha h\nu)^2$ vs $h\nu$ is shown in Figure 1. The optical absorption coefficient (α) of the ZnO films at different wavelengths was calculated from the optical transmittance, the value of the energy gap was estimated by extrapolation of a straight line to the axis of the photon energy, assuming that $\alpha = 0$ according to the equation [10]:

$$\alpha = A\,\frac{(h\nu - E_g)^n}{h\nu}$$

where A is a constant, $h\nu$ is the photon energy and E_g is the band gap. In this equation the values of n depend on the nature of the transitions; n is 1/2 and 3/2 for allowed and forbidden direct transitions respectively, and n is 2 and 3 for allowed and forbidden indirect transitions.

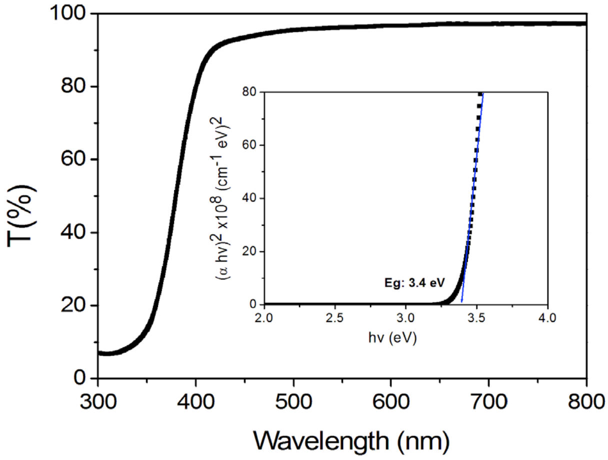

Fig. 1. Transmittance and plot $(\alpha h\nu)^2$ *vs hv of ZnO.*

Band gap of the ZnO film was found with a value for direct transitions of 3.4 *eV*. Band gap is similar to those reported in the literature which are 3.37-3.57 eV [11].

Figure 2 shows the UV-Vis spectra of the bark of Brazil tree and Taray tree dyes impregnated in the ZnO semiconductors thin films, also shows the absorption spectra of pure ZnO thin film, the measures scanning was of 800 to 280 nm in the spectrum wavelength. It can be observed that the films absorb at ~300-330 nm wavelength, indicating that the films are in the UV-visible.

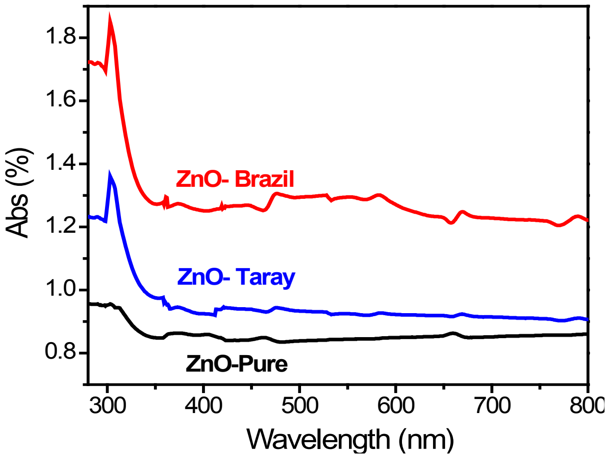

Fig. 2. UV-Vis absorption spectra of different dyes deposited on ZnO thin films.

The spectrum of figure 2 shows a broad absorption peak at 305 nm which is possible due to the surface plasmon absorption of ZnO nanoparticles and the influence of the dye pigment. The surface plasmon absorption phenomenon occurs due to the collective oscillation of free conduction band electrons when electromagnetic radiation strikes them [12, 13]. As we can see from figure 2, the dye from Brazil bark had de highest absorbance in the range of 280-800 nm. The lowest absorbance occurs for bark of Taray dye.

3.2. FTIR spectrum analysis

Figure 3 shows the IR absorption spectra of ZnO and dyes in ZnO, the functional groups are showed inside of figure, a shift of bands is observed due to sensitization of the dyes.

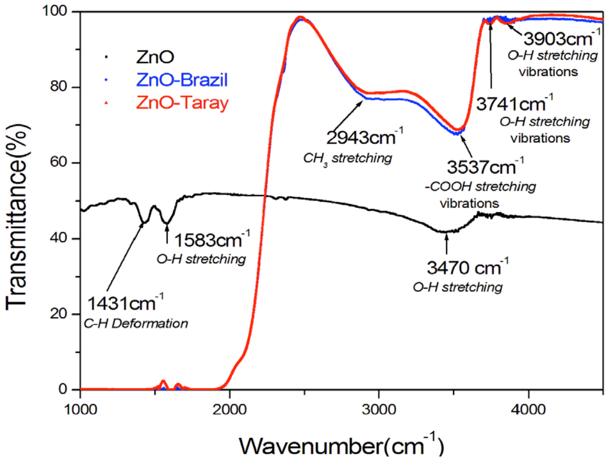

Fig. 3. FTIR spectra of ZnO and dyes sensitized ZnO and identification of functional groups from FTIR spectra.

The O-H species observed on ZnO nanoparticles are identified as follows: 1583 cm^{-1} and 3470 cm^{-1}. Assigned to the O-H stretching mode of hydroxyl group [14].

FTIR spectroscopy was used to identify the functional groups of the synthesized dyes on ZnO and to verify whether anchoring occurs. The spectra of the dyes sensitized in ZnO showed the same IR bands positioned at 2943 cm^{-1}, 3537 cm^{-1}, 3741 cm^{-1} and 3903 cm^{-1} were obtained from the functional groups region 2000-4000 cm^{-1} of the spectrum corresponding to the methyl and carboxylic acids groups. Associated O-H hydrogen absorption appears in the 3600-3200 cm^{-1} range as a broad and intense band.

3.3. Photovoltaic performance of the DSSCs

The photovoltaic characteristics of the fabricated DSSCs were obtained using a simulated sun light (1.5 AM—irradiated power density equal to 1000Wm^{-2}) with halogen light source.-The J-V characteristics of the ZnO layers with dyes were evaluated and the results were compared, these are shown in the Figure 4. From the J-V characteristics, the photovoltaic performance parameters, namely the open circuit voltage (Voc), the short circuit current density (Jsc), the fill factor (FF) and power conversion efficiency (η) of the fabricated DSSCs were determined.

The overall solar to electrical energy conversion efficiency η for a solar cell is given by the photocurrent density measured at short circuit (J_{sc}), the open circuit photovoltage (V_{oc}), the fill factor of the cell (FF) and the intensity of the incident light (P_{in}) as described by the following expression [15]:

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}}$$

The fill factor can have values between 0 and less than 1 and is defined by the ratio of the maximum power (P_{max}) of the solar cell per unit area divided by the V_{oc} and J_{sc} according to the following equation:

$$FF = \frac{P_{max}}{J_{sc} V_{oc}}$$

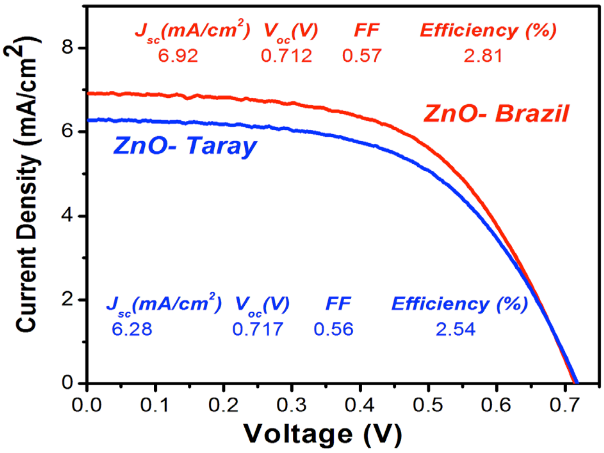

Fig. 4. J-V characteristics of DSSCs on the natural dyes. Photovoltaics parameters of the cells.

It can be observed that the variation in the performance of DSSCs measured in the case of the cells with dyes are minimal. The conversion efficiencies DSSCs were of η=2.81 and 2.54% for Brazilian bark and Taray bark, respectively. The maximum conversion efficiency of 2.81% corresponds to the cell with bark of Brazil dye, the high efficiency can also be explained by the increase in adsorption due to the increase in the number of dye molecules adsorbed on the ZnO surface. The efficiency values of the DSSCs were found to be quite similar and in some cases better compared to studies of ZnO nanoparticle structures reported in the literature [16]. The current density value was found relatively low, the most important parameter that determines the overall efficiency limit of the system is the photocurrent. Various factors such as a small roughness factor, reflection or scattering in the photoanode, low injection efficiency, charge collection efficiency can cause a relatively low photocurrent [17]. It´s also observed that V_{oc} values are similar in all cases, this is because the open circuit voltage value is mainly determined by the difference between the Fermi energy level of the ZnO photoanodes.

4. Conclusions

In this paper, the ZnO nanoparticles were successfully prepared by the sol-gel method and deposited by Doctor Blade on to glass substrates. The FTIR spectroscopy showed that there is a bond between the sensitizer and the surface of the semiconductor by the carboxyl groups present in its structure because they have interactions with the hydroxyl groups of the semiconductors allowing a transfer of electrons. Photovoltaic performances of DSSCs with different dyes have been compared. We found that the best efficiency (η=2.81 for Brazil bark) is due to a significant increase in the absorption of dye molecules onto the surface of ZnO.

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