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Optical properties of TiO_2 electrodes sensitized by Red Cabbage dye for application in Dye-Sensitized Solar Cells

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ABSTRACT

The dye-sensitized solar cell (DSSC) is a third-generation photovoltaic device that holds great promise for the economic conversion of solar energy into electrical energy. TiO_2 layers have been deposited by the spin-coating technique based on excess of a TiO_2 solution on glass substrates heated to a fixed temperature of 80°C. The objective of the present study is the study of the effect of dye on the optical properties of these layers. For this, we used UV-Visible spectroscopy for optical characterizations. UV-Visible transmission spectra confirm that it is possible to obtain good transparent TiO_2 films with a 68 to 87 % transmittance in the visible. The maximum absorption of anthocyanin changes in the visible range when the pH of the solution varies between 3 and 12.

Introduction

Dye-sensitized solar cells (DSCCs) has been known as apromising photovoltaic device to achieve moderate efficiency at ultra-low cost (O'Regan and Grätzel, 1991) [1]. The use of large surface area semiconductor materials in DSCC is necessary to provide sufficient light absorption with only one adsorbed mono-layer of dye. For the working electrode in DSCC, multidisciplinary research of semiconductor clusters witnessed a huge and exceptional growth particularly concerning TiO_2 as a promising material [2]. Many factors can affect semiconductor efficiency such as light intensity, material band gap, surface area, charge carrier density, and photoelectron separation efficiency [3–6].

Several methods of elaboration have been carried out to obtain thin nanostructured films, generally by high temperature techniques or methods in phase vacuum vapour, physical and chemical vapour deposition [7].

Spin coating method has several advantages compared to other techniques: easy control of the morphology and thickness the of the film, simplicity, low equipment cost and possibility of making large-area thin films [8].

The absorption of light photon in DSSC occurs in the dye molecule layer. The dye molecules (sensitizers) collect photons and produce the excited electrons (S^*) from the highest occupied molecular orbital in the ground state to the lowest unoccupied molecular orbital (LUMO) in the excited state [9]. Red cabbage (*Brassica oleracea L.*) has a bioactive substance such as anthocyanines, flavonols, and glucosinolates having a positive impact on human health. Red cabbage anthocyanins are currently used to color various beverages, candies, dry mixed concentrates, chewing gums, sauces and yoghurts [10]. Red cabbage is one of the sources of anthocyanins for coloration of food since its anthocyanins are unique, exhibiting colour over a very broad pH range. Anthocyanins, as natural colorants, are widely used in the food industry as an alternative to synthetic colorants. However, anthocyanins from other sources including grape skin, black currant and elderberry have a remark- able degree of colour at pH < 4 [11]. Anthocyanin extracted from red cabbage can have a multitude of colours ranging from red to yellow to violet according to the pH [12]. Their use is not limited to acidic foodstuffs but can be extended to neutral products as well. Hence they have potential to provide a natural alternative to synthetic colorants. On the other hand, red cabbage has been used as a sensitizer in dye-sensitized solar cell (DSSC).

A good dispersion of dye molecules on an oxide surface could improve the efficiency of a DSSC. Therefore, it is meaningful to investigate the influence of solvents and pH on the solubility of natural dyes for DSSC performance. However, systematic studies on the influence of the solvents and pH change on the adsorption and electrochemical properties of natural dyes

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have not yet been investigated so far for the enhancement of the photovoltaic performance of DSSCs.

In this work, we report on the study of the properties of TiO_2 thin films elaborated with spin-coating method and the effect pf pH on absorption spectra of red cabbage dye.

Experimental

TiO_2 thin films were prepared by spin-coating method onto indium doped tin oxide (ITO, 25Ω/sq) glass coated substrates. The ITO substrates were ultrasound cleaned sequentially with acetone, ethanol and distilled water. The preparation of TiO_2 solution was likewise described in previous works [13].

The solutions containing the TiO_2 were deposited at 2500 rpm for 30 s. After each coating, the films were preheated at 100°C for 10 min. Finally,

Red cabbage was purchased from one of the Ouargla market (Algeria). Before extract the dye, the red cabbage was cleaned with drinking water and distilled water. Red cabbage dye was extract with distilled water at 80°C for 2h. The solution pH of red cabbage extract was adjusted by adding HCl acid or NaOH base.

The TiO_2 electrodes are sensitized by immersing the films in each dye solution for 4 hours. After immersion, the films are rinsed with acetone to remove the unabsorbed dye from the porous layers and then dried.

The UV-Vis transmittance spectra were recorded with a Shimadzu UV-1800 spectrophotometer.

Results and discussions

Fig. Ia show the UV-Visible transmission spectra of undoped TiO_2 films obtained with different thicknesses 3 layers, 5 layers, 10 layers and 15 layers. As can be seen in this figure, the presence of a region of high transparency located between 300 and 800 nm, the value of the transmission is of the order of 68 to 87% in the visible with a maximum value obtained at 3 layers of TiO_2. The films of with 5 layers show a good transparency in the visible, associated with a very good homogeneity of the deposits. It is observed that the transmittance decreases with the increase of the thickness of the layers (15 layers). these results prove that the Spin coating technique is suitable for obtaining a good optical quality TiO_2 thin films.

The Tauc plots shown in Fig. Ib were performed using the transmission data obtained from each sample [14–16]. The intercepts of these plots with y=0 axis lead an estimation of the optical bandgap energy (Eg) of the corresponding sample. As we know, E_g is related to the absorption coefficient (α) as following:

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g)$$

where A is a constant and hυ is the photon energy. The values of E_g obtained for the TiO_2 layers are between 3.20 and 3.40 eV. These performances are very interesting for making TiO_2 as attractive material for application in DSSCs.

For dye extract, in the first place, a mass of red cabbage leaves is cleaned with distilled water and then cut into pieces to extract the anthocyanin. As the manufacturing processes must be easily applicable on an industrial scale, on the other hand the cost of extraction and production must be taken into consideration. We chose distilled water as a solvent to extract the pigment. The red cabbage is heated to between 70 and 80°C until the leaves lose their violet colour. The solution is then filtered and the resulting anthocyanin is cooled to room temperature.

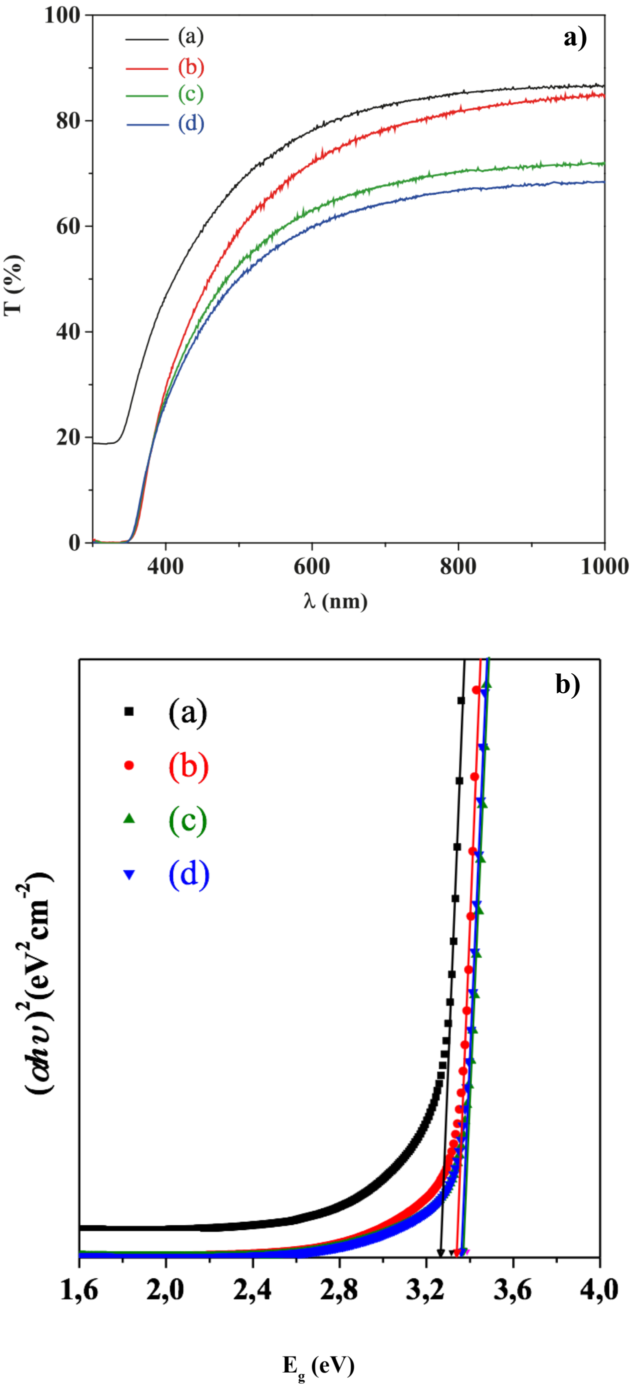

Fig. 1. UV-Vis and Tauc plots of undoped TiO_2 on ITO : (a) 3 layers, (b), 5 layers (c), 10 layers and (d) 15 layers.

In order to we examined the influence of pH on proprieties of dye. The solution pH of red cabbage was adjusted by adding hydrochloric acid or sodium hydroxide. The colour of anthocyanin changes immediately due to the change in molecular structure. The different colours obtained with the pH variation are presented in Fig. 2a.

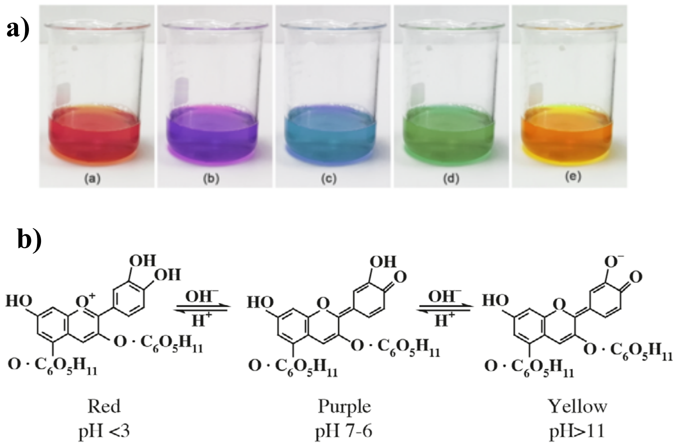

Fig. 2. a) The different colours of anthocyanin solution obtained by varying the pH from the acid medium (left) to the basic (right). b) Effect du pH sur la structure moléculaire [17].

Fig. 2b shows the change in molecular structure as a function of pH values. The change in pH increases the number of conjugated double bonds in the molecule lowers the energy level, resulting in the absorption of photons at a higher wavelength [12].

In acidic solution, Aglycone core can exist as a positively charged oxonium ion (flavylium cation). The oxonium ion results in an extended conjugation of double bonds through three rings of the aglycone moiety, which helps in the absorption of photons in the visible spectra.

In basic pH, the flavylium cation can exist in equilibrium with a quinoidal form. The addition of a base disrupts the conjugation of double bonds between the second and third rings and results in the absorption of photons in the UV range rather than in the visible range.

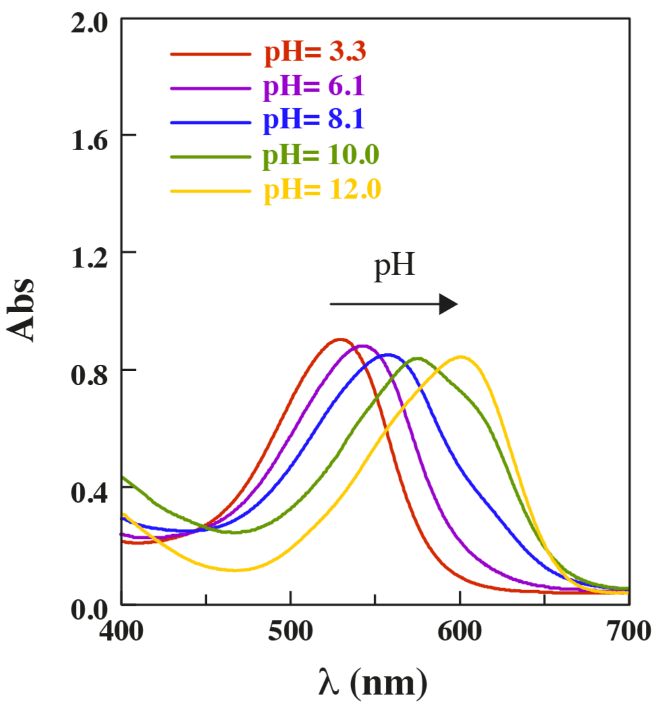

Fig. 3. The absorbance of red cabbage in different pH.

Fig. 3 shows the UV-visible spectra of anthocyanin with different pH. The absorption peak that characterizes anthocyanin is at about 570 nm. The maximum absorption of anthocyanin changes in the visible range between 540 and 610 nm when the pH of the solution varies between 3 and 12. This peak shifted to red in the case of a basic medium and towards the blue in the case of an acid medium. This is due to the color change of the anthocyanin solution, and hence the molecular structure of the anthocyanin.

Dye is the key element of DSSCs. It must have the widest possible absorption spectrum of light and have excellent stability. These dyes used for producing the cells are natural organic dyes. They are less expensive. For the elaboration of the photoanodes, the TiO2 electrodes are immersed in the dye solution.

To test the effect of anthocyanin on the adsorption of TiO_2 in the visible, the TiO_2 elecrode is immersed in the pigment for a period of 4 hours. Fig. 4.a shows photoanodes based on TiO_2 sensitized with anthocyanin at different pH. According to the UV-vis spectra in Fig. 4b, TiO_2 absorbs in the UV and the visible. The pigmentation with anthocyanin improved the visible absorption of TiO_2. The peak absorption peaks become narrow and shift to red. When complexing with metal ions, the spectrum shifts to lower energy levels. The adsorption of anthocyanin on the surface of TiO_2 is a rapid chemical reaction that is the result of the alcoholic protonic bonds that condense with the hydroxyl groups of TiO_2.

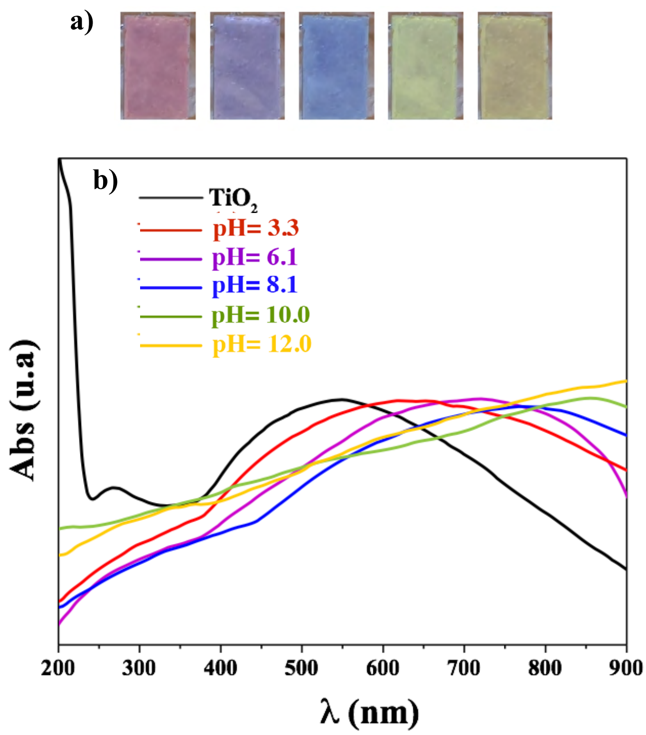

Fig. 4. a) TiO_2 photoanodes sensitized with anthocyanin at different pH. b) Uv-visible spectrum of TiO_2 and TiO_2 layers sensitized with pigment at different pH.

Conclusion

Adsorption characteristics of red cabbage dye and TiO_2 thin films were systematically investigated over a wide range of pH. TiO_2 films with good transparency, and homogeneity were successfully elaborated with spin coating method. Presence of a region of high transparency located between 300 and 800 nm of obtained TiO_2. The transmittance decreases with increasing layer thickness. Their optical gap obtained for the TiO_2 layers are between 3.20 and 3.40 eV. The

UV-visible spectrum of anthocyanin with different pH shows that the absorption peak that characterizes the anthocyanin is at about 570 nm. The maximum absorption of anthocyanin changes in the visible range between 540 and 610 nm when the pH of the solution varies between 3 and 12. This peak shifted to red in the case of a basic medium and towards the blue in the case of an acid medium.

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Conflicts of interest

Authors declare no conflict of interests.

Notes

The authors declare no competing financial interest.

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