Agata ZDYB[1*] and Stanisław KRAWCZYK[2]

NATURAL FLAVONOIDS AS POTENTIAL PHOTOSENSITIZERS FOR DYE-SENSITIZED SOLAR CELLS

NATURALNE FLAWONOIDY JAKO POTENCJALNE FOTOSENSYBILIZATORY DO ZASTOSOWAŃ W BARWNIKOWYCH OGNIWACH SŁONECZNYCH

Abstract: Natural flavonoids quercetin, morin, fisetin and luteolin were studied as potential photosensitizers for dye-sensitized solar cells (DSSC). Spectroscopic methods were used to investigate the formation of dye/TiO_2 nanoparticles assemblies and the development of their absorption spectra. The results show that the flavonoids adsorb well on TiO_2 nanoparticles and this process causes the shift of absorption spectra from the near UV into the visible range of solar light. The mode of binding of the dye molecules on TiO_2 surface is analyzed by comparison of spectral absorption properties and with the use of structural differences introduced by fisetin and luteolin for discrimination between several possibilities.

Keywords: dye-sensitized solar cell, DSSC, sensitizer, flavonoid, TiO_2, nanoparticles

Introduction

The growing energy demand forces us to develop new environmentally friendly technologies for exploitation of renewable sources. Photovoltaic solar cells are a valuable alternative for diminishing fossil fuels [1, 2]. As a result of intensive development of issues related to photovoltaics, it is possible to distinguish four generations of solar cells. The first one includes conventional cells using silicon p-n junction, which have definitely dominated photovoltaic market due to their highest energetic efficiency of over 20 %. In spite of widely conducted research on improving of this type of cells, this parameter has been increased only slightly in a long time period. The second generation based on thin-film solar cells using various materials such as amorphous Si, CdS/CdTe and CIGS gained an increasing popularity. Their most characteristic features are 10-20 % efficiency, lower price and very good effects of recycling. Among many new solar technologies, dye-sensitized solar cells (DSSC) belonging to third generation of solar cells offer significant advantages:

[1] Faculty of Environmental Engineering, Lublin University of Technology, ul. Nadbystrzycka 40B, 20-618 Lublin, Poland, phone +48 81 538 47 47, fax +48 81 538 47 00
[2] Institute of Physics, Maria Curie-Skłodowska University, pl. M. Curie-Skłodowskiej 1, 20-031 Lublin, Poland, phone +48 81 537 62 53, fax +48 81 537 61 91, email: skraw@hektor.umcs.lublin.pl
* Corresponding author: a.zdyb@pollub.pl

low price, flexibility, colorfulness, low weight, good performance in diffuse light and efficiency of 11.3 % [3-6].

Typically dye sensitized cell, that is a photoelectrochemical device, consists of the illuminated electrode covered by titanium dioxide nanoparticles with dye sensitizer adsorbed on them, the electrolyte and counter electrode [7-9]. High porosity of TiO_2 layer allows a dye to be adsorbed not only on the external surface but also inside the layer, which increases the amount of dye serving as an absorber of light energy. The role of the dye molecules is to make wide bandgap semiconductor (3.2 eV) indirectly sensitive to the visible light where the maximum intensity of sunlight occurs by absorbing the photons and transferring the electrons from the excited dye molecule into the conduction band of the TiO_2 electrode (anode) - a process that is fundamental for DSSC performance [10-12]. The next step closing the light-driven electrochemical cycle is the transport of electrons from a counter-electrode (cathode) through an electrolyte, which reduces the oxidized dye molecules.

In recent years, many studies were focused on searching and development of new dye compounds that can be useful in DSSC [13]. A promising solution is application of natural dyes extractable from easily available plants, which can be cheap and environmentally friendly [14]. This kind of dyes occurring in higher plants are flavonoids belonging to polyphenol group of compounds and well known for their antioxidant and anti-inflammatory properties.
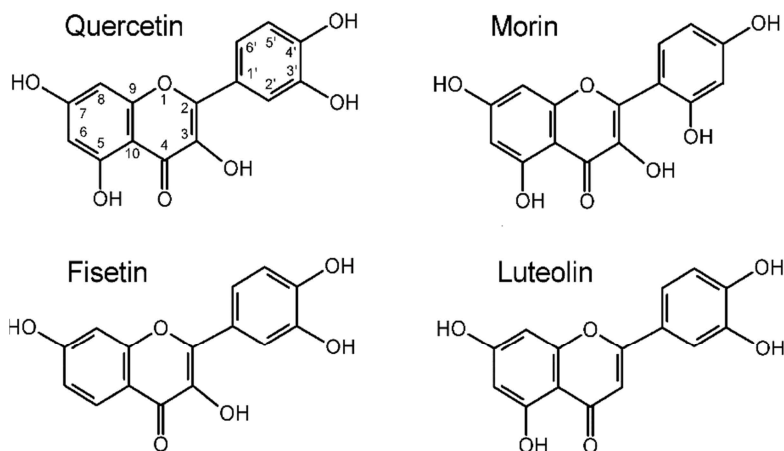

Fig. 1. Scheme of investigated flavonoids

Our previous results have shown a substantial shift of the absorption spectra of morin and quercetin, adsorbed on TiO_2 nanoparticles, from the near UV by ~5500 and 6500 cm^{-1} (0.68 and 0.81 eV) for morin and quercetin, respectively, into the blue-green region of the spectrum [15, 16]. These observations, together with Stark effect spectroscopy data, point to the strong interaction of adsorbed dye with surface titanium atoms, which may contribute to an effective electron transfer in flavonoid-based DSSC. However, the infrared absorption and Raman spectra indicated different modes of binding to TiO_2 through the dissociated 3-hydroxy and the 4-keto groups for morin and through dissociated 3'4'-hydroxy groups in

the case of quercetin. The dense vibrational spectra, as well as the quantum chemical computations, provide only indirect arguments for making a definite assignment of dye binding modes. Thus, in this work the binding modes of flavonoids are examined by comparing the electronic spectra of four flavonoids whose molecules shown in Figure 1 differ in the 2' or 3' positions of the hydroxy groups (morin and quercetin) and in the absence of either the 5-OH (fisetin) or 3-OH (luteolin) groups. We investigated the adsorption of flavonoids on colloidal TiO_2 nanoparticles and on commercially available, ready-to-use TiO_2 electrodes. The detailed results for morin and quercetin may be found in previously published work [15, 16]; here we concentrate mainly on the interaction of fisetin and luteolin with TiO_2.

Methods

Flavonoid dyes and other chemicals were purchased from Sigma-Aldrich. Titanium dioxide nanoparticles were obtained as 100 mM ethanolic colloidal solution by hydrolysis of titanium isopropoxide with addition of 0.2 % of acetic acid [17]. Glass electrodes covered by conductive, mesoporous TiO_2 paste for use in DSSC were bought from Dyesol company. Absorption spectra were measured by using Shimadzu UV-160A spectrophotometer. Fluorescence measurement was performed with Shimadzu RF5001 spectrofluorimeter.

Results

Free form of fisetin in ethanolic solution exhibits absorption maximum at 365 nm (Fig. 2). The process of fisetin adsorption on TiO_2 nanoparticles evolves in time and is completed after about 1 hour. The gradual disappearance of absorption band at 365 nm is accompanied by increasing intensity of the 425 nm band which then slowly broadens and shifts to longer wavelengths, that is towards the red. The fully developed absorption maximum of fisetin adsorbed on TiO_2 is finally observed at 442 nm. Isosbestic point at 385 nm which is well defined at the beginning is then slightly shifted due to the appearance of the second form of adsorbed fisetin absorbing at 442 nm.

Luteolin in free form exhibits only one absorption band at 350 nm. Addition of TiO_2 colloidal solution results in the decay of this band and in the growth of a new band centered on 415 nm (Fig. 3). The adsorption is completed after 1 hour and absorption spectra show one adsorbed form of luteolin.

The adsorption process of investigated flavonoids on commercial, ready to use electrodes covered by titanium dioxide mesoporous paste was performed by dipping the electrode in the dye solutions with equal dye concentrations for a short period of time. Then, the electrode was rinsed with pure solvent, microscope cover glass was applied and the absorption spectrum recorded. Absorption spectra of fisetin and luteolin adsorbed on the electrodes together with analogous data obtained for two previously investigated flavonoids - morin and quercetin are depicted in Figure 4. As can be seen, the adsorption proceeded equally intensely and quickly for all compounds except for morin. The comparison of the results reveals that adsorption of fisetin, luteolin and quercetin proceeds with a similar rate. Morin adsorbs on TiO_2 with the rate at least twice smaller leading to absorbance more than two times lower than for other investigated compounds.
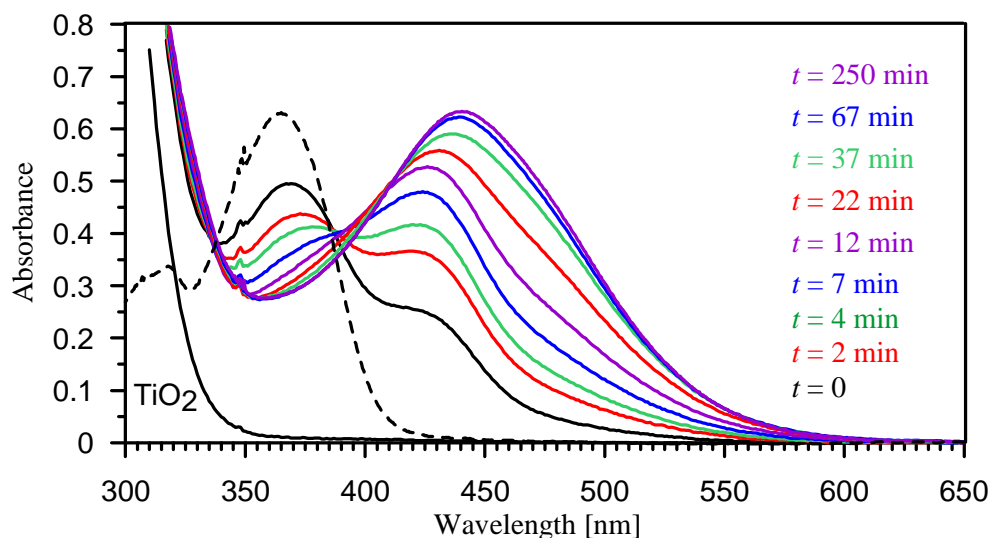
Fig. 2. The development of absorption spectra of fisetin adsorbed on TiO_2 nanoparticles in time; free fisetin in the absence of TiO_2 - dotted line. Fisetin concentration amounts to $2.5 \cdot 10^{-5}$ M/dm^3
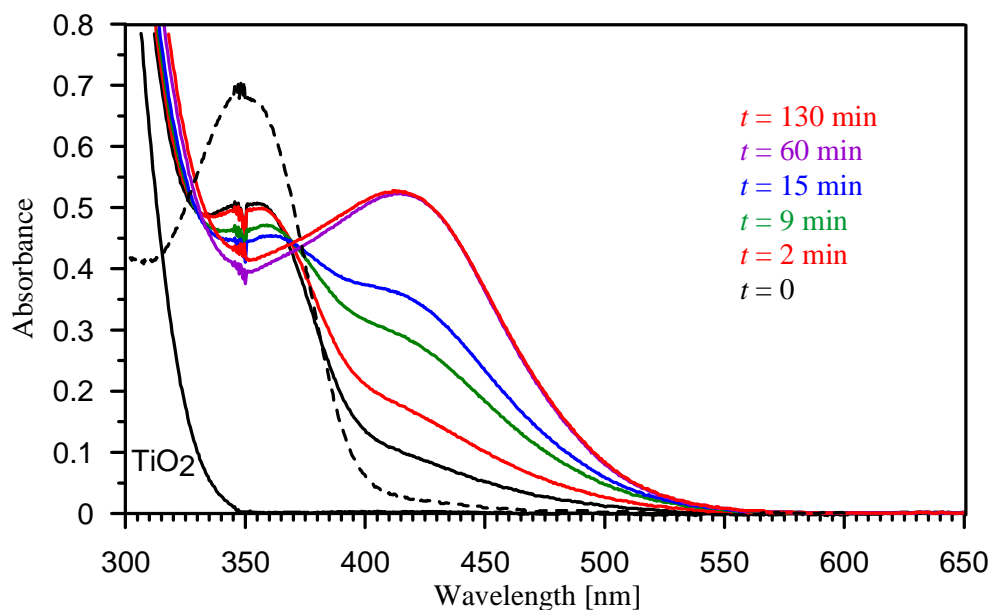

Fig. 3. The time development of absorption spectra of luteolin solution in the presence of a constant concentration of TiO_2 nanoparticles. Free luteolin in the absence of TiO_2 - dotted line. Luteolin concentration equals $2.5 \cdot 10^{-5}$ M/dm^3

Fluorescence measurement for fisetin shown in Figure 5 was possible to be performed since fisetin, contrary to other flavonoids, is fluorescent in free form. This feature, which

distinguishes fisetin among other investigated flavonoids [18] is caused by the lack of the 5-hydroxy group in its molecular structure. There are two forms of fisetin represented by the two fluorescence bands at 470 and 530 nm in Figure 5. The first one represents the normal molecule structure and the other one is from a tautomer resulting from the excited state internal proton transfer (ESIPT) from the 3-OH group to 4-keto oxygen [19].
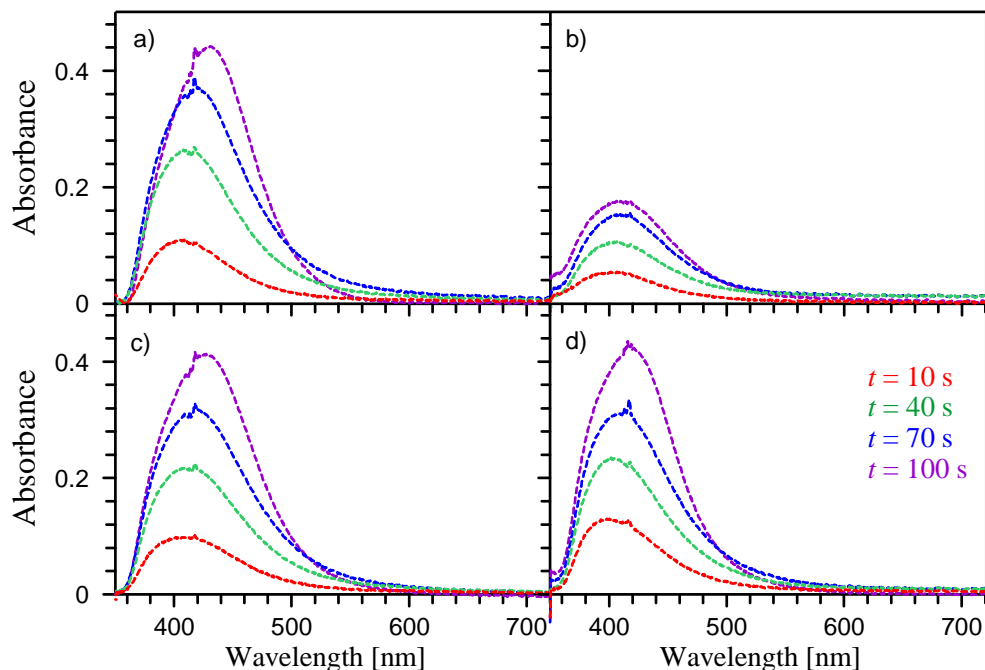

Fig. 4. Absorption spectra of flavonoids adsorbed on ready to use TiO_2 electrode: a) quercetin/TiO_2, b) morin/TiO_2, c) fisetin/TiO_2, d) luteolin/TiO_2. The presented curves are obtained after subtraction of clean electrode absorption from the measured data. The concentration of dyes in ethanolic solutions was equal to 0.3 mM. Below 350 nm the absorption of glass and titanium dioxide occurs

Addition of TiO_2 causes a decrease of both fluorescence bands, proportional to the amount of TiO_2, with similar time dependence as in absorption spectra (Fig. 2). This fluorescence quenching effect of TiO_2 strongly points to the effective electron transfer process from the excited dye molecule to TiO_2 nanoparticle. Here, this process leads to dissipation of the electronic excitation energy into heat through charge recombination, but in the DSSC where the injected electron is withdrawn into the electrode, it can constitute the basis for conversion of light energy into electrical energy.
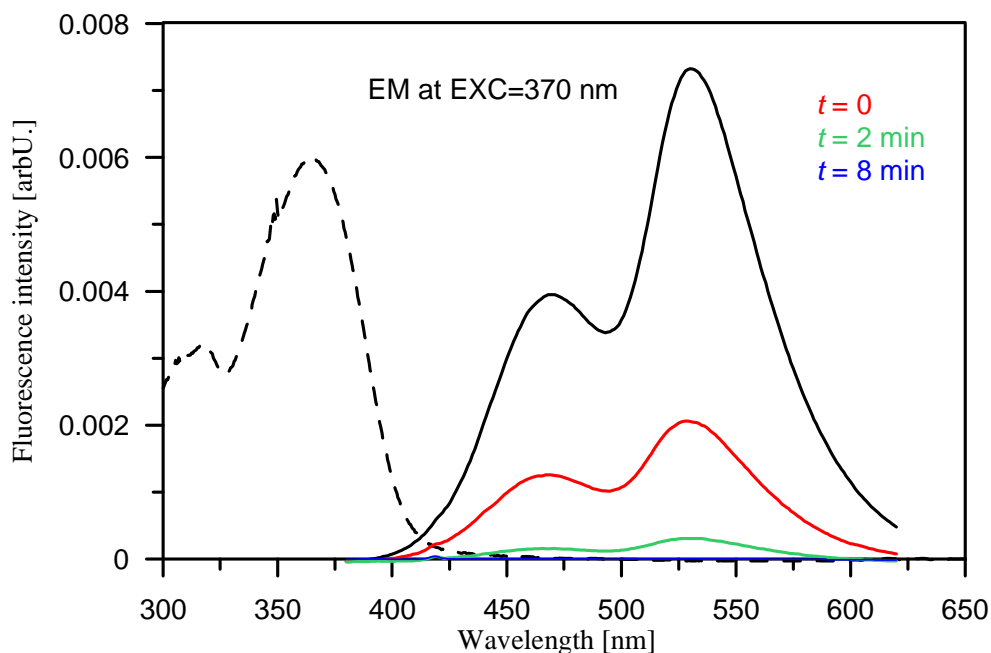
Fig. 5. The quenching of fluorescence of fisetin adsorbed on TiO_2 in time. Fluorescence of free fisetin - black solid line. Absorption of free fisetin - black dotted line. Fisetin concentration equals $1 \cdot 10^{-5}$ M/dm^3

Discussion

Adsorption of fisetin and luteolin on TiO_2 nanoparticles or commercial electrodes covered by TiO_2 paste leads to the development of new, broad absorption band in the range of about 350-500 nm. This feature of the investigated flavonoids is an evidence of their usefulness in dye-sensitized solar cells. However, in literature there is little information on the attempts of application of fisetin or luteolin in DSSC [20, 21].

The development of fisetin/TiO_2 absorption spectra in time reveals two absorbing forms: first at 425 nm and after some time at 442 nm, contrary to luteolin/TiO_2 which absorbs in one form. These observations can be interpreted basing on the analysis of the binding site of studied flavonoids molecules with TiO_2. Inspection of Figure 4 indicates that the dye adsorption is not sensitive to the presence or absence of the 5-hydroxy group (fisetin vs. other dyes) or the 3-OH group (luteolin vs. other dyes), and instead clearly distinguishes morin with its widely spaced 2'-hydroxy and 4'-hydroxy groups. These data directly indicate that the interaction of flavonoids with the surface of TiO_2 involves the formation of two chelating bonds between the dissociated hydroxy groups of the flavonoid and the positively charged titanium atom in TiO_2. The structural differences unable such bonding of morin; however, it is also capable to adsorb on TiO_2, although weaker. This can be explained by a weaker binding at the 3-hydroxy-4-keto groups, probably also in a dissociative mode at 3-hydroxy. This observation is analogous to the binding of luteolin, which lacks the 3-OH group, with Pb^{2+} and Al^{3+} ions in ethanolic solution (unpublished data). In both cases, the binding constant was an order of magnitude smaller than for other

flavonoids, suggesting the main mode of binding involving the 3-hydroxy group. The prevailing mode of binding of flavonoids with TiO_2 through the 3',4'-dihydroxy group is thus dissimilar to their interaction with metal ions in solution, and the difference may stem from the coordinative unsaturation of the Ti surface atom which is in unclear degree of oxidation.

Summary and conclusions

Adsorption of flavonoids on TiO_2 nanoparticles or commercial TiO_2 electrodes leads to the development of a new, broad absorption band extending to about 550 nm, here illustrated by the data for fisetin and luteolin. This feature of the investigated flavonoids is an evidence of their usefulness in dye-sensitized solar cells. Our study covers a gap in the literature data, where little information on the application of flavonoids in DSSC can be found. The investigated flavonoids readily adsorb on TiO_2 nanoparticles in both colloidal solution and on ready-to-use electrodes. The obtained assemblies are stable, resistant against desorption and absorb in the broad range of visible light which make them good candidates for sensitizers in dye-sensitized solar cells. Their ability to inject electrons into the conduction band of TiO_2 is directly demonstrated by the quenching of fisetin fluorescence when adsorbed to TiO_2. The comparative study of flavonoid adsorption on TiO_2 and spectral properties in this state enabled to confirm the main mode of binding between the flavonoids and TiO_2 through the 3',4'-dihydroxy group. This statement includes an exception for morin which binding involves the 3-OH-4-keto groups. This difference makes the comparison of morin with other flavonoids an interesting case with a possible output gaining our knowledge of molecular mechanisms underlying the basic processes of electron transfer from the excited dye to TiO_2 electrode in DSSCs.

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