Photostability testing for coumarin-153 doped ZnO thin films prepared with spin-coating technique

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Abstract. The main aim behind the present study is solar cells of increased efficiency and low cost per unit of power generation, specifically dye-sensitized cells. Their first component is semiconducting ZnO commonly used to build photovoltaics, which absorbs sunlight in the ultraviolet region. The second component, the dye coumarin-153 that absorbs in a lower-energy spectral region, enhances the light harvesting. We study the optical absorbance and fluorescence for the combination of coumarin-153 with ZnO nanoparticles, which are prepared in sol-gel films formed using a simple spin-coating technique for creating a stable photovoltaic.

Keywords: semiconductors, dyes, solar cells, spin coating, thin films.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been discovered as long ago as in 1991 [1–3]. Owing to their high efficiency, low cost and easy manufacturing process, they have remained a subject of numerous studies as an alternative to silicone photovoltaics. DSSC is composed of a metal oxide film, a photosensitive dye, an electrolyte-hole transporter and a counter electrode. In this system, the sensitizer, usually a dye, plays a vital role. Since the metal oxides absorb only in the ultraviolet part of the spectrum, the main function of the dye is to absorb light in the visible and near-infrared spectral ranges [2, 3].

There is a great need in alternatives to ruthenium-based dyes, which is caused by a high cost of rare metals, as well as complicated processes of synthesis and purification of the mentioned dyes [2, 4]. On the other hand, organic dyes could be easily synthesized, or even simply extracted from plants. Their structural modification is feasible with a simple synthesis process, thus enabling one to tune the positions and the intensities of charge-transfer transitions. Moreover, the organic dyes have higher molar extinction coefficients, if compared with the ruthenium-based dyes [2, 5].

Among the organic metal-free dyes, the common system is donor–π-bridge–acceptor (D-π-A). It ensures both efficient transport and separation of charges. The electron donor affects the molecular energy levels and so the absorption spectrum of the molecules. Another role of the electron-donor component is to modify geometric structure of the molecule and, in this way, to provide the more efficient charge transfer. A red shift of the absorption is achieved with a π-conjugated component of the dye molecule, which influences so called HOMO/LUMO energy levels [1, 6].

Many metal-free organic dyes have demonstrated very promising results in photovoltaic applications. These are derivatives of coumarin, triphenylamine, carbazole, and indoline [2, 4, 6]. In particular, coumarin-153 is a derivative of coumarin, with additional electron-donor and electron-acceptor groups. The electron-donor group lowers significantly the $S_{\pi\pi*}$ and $T_{\pi\pi*}$ energies, while the electron-acceptor group shifts the peaks of optical fluorescence and absorption to longer wavelengths. Therefore the absorption peak of coumarin-153 is shifted towards 430 nm, while the same peak for coumarin is known to be located at 365 nm as [7].

There are two aspects stipulating the present work (see Refs. [7–9]). First, ZnO is a material often used for solar cells because of its good basic optical properties. Second, coumarin-153 has revealed very promising results in photovoltaic applications when being combined with TiO_2. It would be interesting to verify its combination with ZnO. As a consequence, below we report about their efficient combination, which is used to enhance the efficiency and stability of sunlight absorption of ZnO.

2. Experimental

For making sol-gel ZnO/coumarin-153 films, polymethymethacrylate (PMMA) was dissolved in dichloromethane (DCM). Ethanol solution of coumarin-153 (0.01 mol/dm^3) was added, followed by 50 weight % ZnO solution. We prepared different amounts of the components, as presented in Table 1. ZnO films were made with ethanol instead of coumarin-153 ethanol solution (see Table 2). Finally, coumarin-153 films were made by mixing PMMA with coumarin-153 ethanol solution, pure ethanol and DCM, as shown in Table 3. All the mixtures were sonicated in an ultrasonic bath for 30 min, in order to make homogeneous solutions.

Table 1. Components of our sol-gel ZnO/coumarin-153 films.

PMMA, gm	Coumarin-153, μL	ZnO solution, μL	DCM, μL
0.2	400	117.5	482.5
0.2	400	129.5	470.5
0.2	400	141	459

Table 2. Components of our ZnO films.

PMMA, gm	Ethanol, μL	ZnO solution, μL	DCM, μL
0.2	400	117.5	482.5
0.2	400	129.5	470.5
0.2	400	141	459

Table 3. Components of our coumarin-153 films.

PMMA, gm	Coumarin-153, μL	Ethanol, μL	DCM, μL
0.2	400	100	500

After drying the samples prepared as described above, we measured the optical absorbance and fluorescence of our films using the apparatus introduced in Fig. 1 and Fig. 2. White light from a tungsten lamp shown in Fig. 1 was incident onto a sample placed into a cuvette holder. The absorbance was detected with a standard spectrophotometer. High-power LEDs, with the excitation wavelength 398 nm, sent ultraviolet light onto a sample placed in another holder (see Fig. 2). Then the fluorescence spectra were detected with the same spectrophotometer. As a reference for the

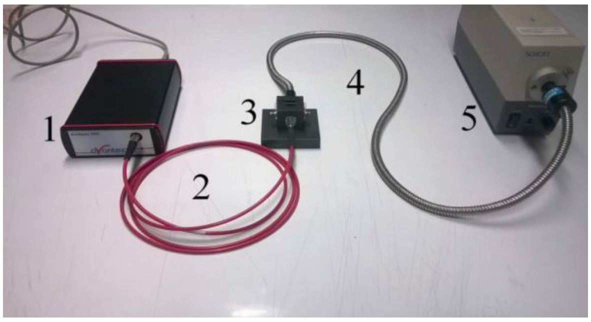

Fig. 1. Equipment used for measuring optical absorbance: 1 – spectrophotometer, 2 and 4 – optical cables, 3 – sample holder, and 5 – tungsten light source.

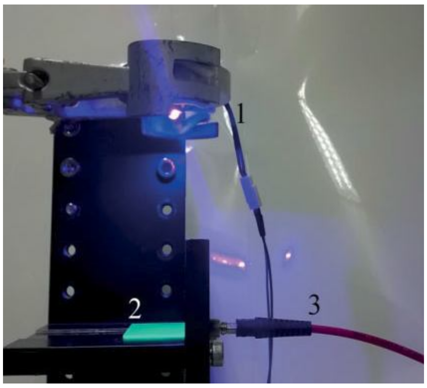

Fig. 2. Equipment used for measuring optical fluorescence: 1 – UVB light source, 2 – sample, and 3 – optical cable connected with spectrophotometer.

absorbance, a film was made by dissolving 0.2 gm PMMA in 500 μL DCM and 500 μL ethanol. To examine stability characteristics of our films, we exposed them to ultraviolet (UVB) radiation for 180 min. The conclusions about the stability were derived by measuring and comparing the fluorescence signals at pre-determined times (20, 50, 80, 110, 140 and 180 min).

3. Results and discussion

ZnO is a semiconducting material commonly used in photovoltaic techniques. It has the bandgap of about 3.37 eV, which means absorption of light in the ultraviolet range. For ensuring more economical ways of acquiring energy, the efficiency of this material needs to be enhanced, e.g. with the aid of dye-sensitization. A dye with lower bandgap energy would absorb light at lower frequencies, thus transferring electrons into the conductive band of ZnO. In this way much higher light utilizations are usually reached [1, 7, 10]. Below our main results aimed at solving this problem will be elucidated, which are based on coumarin-153.

Fig. 3 illustrates the appearance of our coumarin-153, ZnO and mixed coumarin-153/ZnO films, whereas Fig. 4 shows the absorbance of different amounts of ZnO mixed with 4×10^{-3} mol/dm^3 of coumarin-153. The first peak located at 370 nm originates from ZnO and the second one, at 420 nm, belongs to coumarin-153. One can see that the total absorbance becomes higher with increasing ZnO amount.

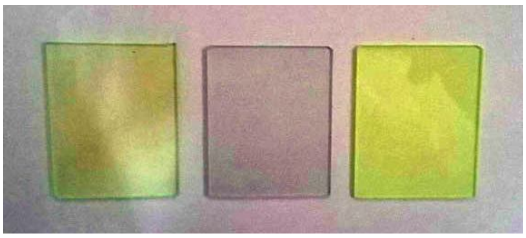

Fig. 3. Appearance of our coumarin-153 (left), ZnO (middle) and coumarin-153/ZnO films (right).

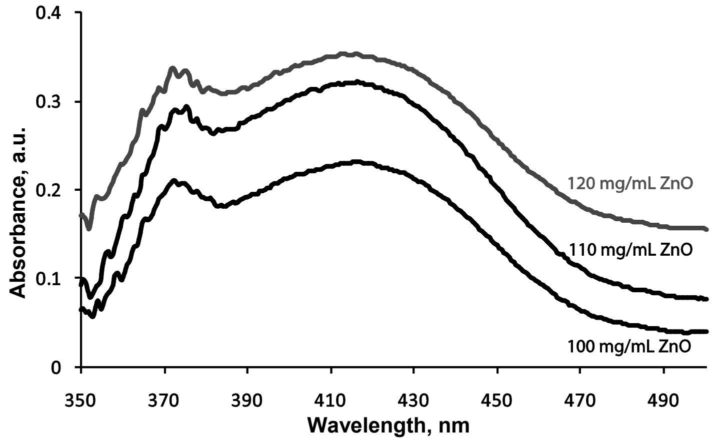

Fig. 4. Absorbance spectra of coumarin-153 mixed with different amounts of ZnO.

Fig. 5 represents the fluorescence of different amounts of ZnO mixed with 4×10^{-3} mol/dm^3 coumarin-153. Our data shows that the fluorescence intensity is proportional to the amount of ZnO, which is to be expected.

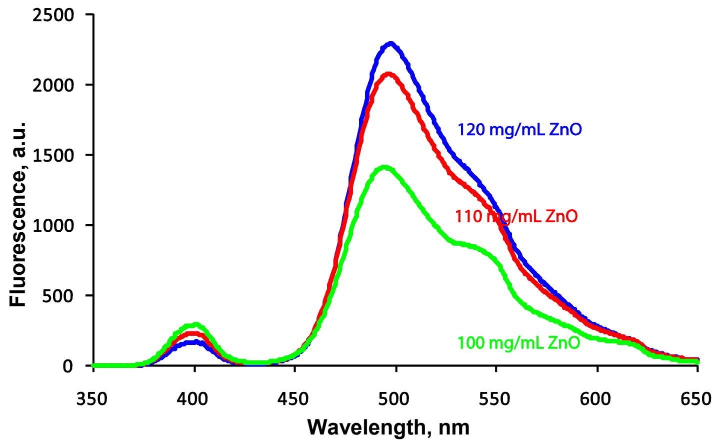

Fig. 5. Fluorescence spectra of coumarin-153 mixed with different amounts of ZnO.

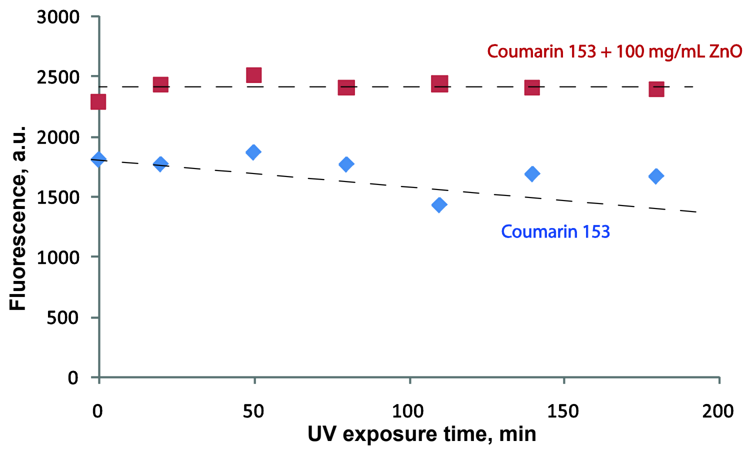

Fig. 6. Fluorescence of our films exposed to UVB irradiation as a function of exposition.

The data shown in Fig. 6 illustrates the fluorescence of our films as a function of UVB exposition time. The photostability of pure coumarin-153 films, with no ZnO included, decreases with increasing ultraviolet radiation time. We have performed the same measurements using several samples produced with the same method. In all the cases the fluorescence of pure coumarin-153 decreases notably with increasing exposure time. Coumarin-153 shows lower photostability than coumarin-153 mixed with 100 mg/mL ZnO (a reference sample). In other words, the stability of the coumarin-153/ZnO system is efficiently enhanced. Hence, the present study demonstrates that coumarin-153 doping of ZnO is suitable for building long-lasting photovoltaics.

4. Conclusion

The present study reports the effect of coumarin-153 doping upon the photovoltaic properties of ZnO. With the goal of creating efficient and stable photovoltaics, we have investigated the effect of adding coumarin-153 to the ZnO films, which have been prepared using a very simple method of spin coating. Higher total absorbance of the mixture indicates that coumarin-153 has an important role in light-harvesting. Here the dye absorbs the light in the lower-frequency region, transferring its electrons to the conductive band of ZnO and enhancing in this manner the semiconductive activity of ZnO. The measurements of optical fluorescence of the films as a function of ultraviolet (UVB) irradiation exposition have revealed that the dye-sensitizing positively influences the stability of the mixture, when compared with the organic dye alone which is essentially unstable under the UVB irradiation.

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Анотація. *Основна мета цього дослідження полягає у підвищенні ефективності та зменшенні вартості виробленої електроенергії сонячними батареями в розрахунку на кількість, наприклад, сенсибілізованих барвником комірок. Першою компонентою цих комірок був напівпровідниковий ZnO, який здебільшого використовується для створення сонячних батарей і поглинає сонячне світло в ультрафіолетовій області спектра. Другою компонентою був барвник кумарин-153, який поглинає в спектральної області з нижчою енергією. В цій роботі ми вивчали поглинання і флуоресценцію комбінації кумарину-153 з наночастинками ZnO, які виготовлялись соль-гель методом у вигляді плівок, сформованих за допомогою техніки ротаційного нанесення для створення стійкого фотоелектричного відгуку.*