Electrodeposited zinc oxide nanostructures with adsorbed natural dyes for photovoltaic applications

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We report on a cost-effective alternative synthetic method for creation of ZnO-based natural-dye sensitized solar cells (DSSC). ZnO arrays were electrodeposited on transparent fluorine doped tin oxide covered glass cathodes in aqueous electrolytes in three-electrode cell under potentiostatic conditions and under pulse plating modes with rectangular impulses of cathode potential. Then ZnO layers were dye-sensitized by a freshly prepared blackcurrant juice. The studies of structure by XRD-method, surface morphology by atomic force microscopy and optical properties by spectrophotometry have demonstrated the promise of ZnO arrays electrochemically grown in the rectangular pulse mode for creation of natural-dye sensitized DSSC.

Сообщается об экономически эффективном альтернативном методе синтеза оксида цинка для сенсибилизированных натуральными красителями солнечных элементов. Массивы ZnO осаждали электрохимически в трехэлектродной ячейке на стеклянные подложки, покрытые прозрачным электропроводным оксидом из легированного фтором диоксида олова, как в потенциостатическом режиме, так и в импульсных режимах с прямоугольными импульсами катодных потенциалов. Затем слои ZnO сенсибилизировали красителем из свежеприготовленного черносмородинового сока. Исследования структуры методом рентгеновской дифрактометрии, морфологии поверхности с помощью атомного силового микроскопа и оптических свойств спектрофотометрическим методом продемонстрировали перспективность электрохимически осажденных в прямоугольно-импульсном режиме массивов ZnO для создания DSSC на натуральных красителях.

1. Introduction

A dye-sensitized solar cell (DSSC) is a promising route toward solar energy conversion. The main idea is to simulate natural light harvesting procedures in photosynthesis by combining dye sensitizers with semiconductors [1]. The DSSC has advantages in both low-cost and high-efficiency in comparison with the more established technologies based on monocrystalline Si and nanocrystalline thin-film solar cells. Early DSSC designs involved transition metal coordinated compounds (e.g., ruthenium polypyridyl complexes) as sensitizers because of their strong visible absorption, long excitation lifetime, and efficient metal-to-ligand charge transfer. In spite of highly effectiveness, with current maximum efficiency of 11 %, the costly synthesis and undesired environmental impact of those prototypes call for cheaper, simpler, and

Table 1. Electrolytes and electrolysis regimes used for deposition of ZnO

Pattern number	Electrolyte	Deposition regime	Cathode potential (V)			Current density j (mA/cm^2)	Frequency f (Hz)	Duty cycle	Charge-area ratio q (C/cm^2)
			U	U_{off}	U_{on}				
P14	$7 \cdot 10^{-4}$ M ZnSO$_4$ 0.1 M KCl 0.001 M NaNO$_3$	Pulse	–	–0.9	–1.5	0.4	20	0.40	1.4
D15	0.05 M Zn(NO$_3$)$_2$	Potentiostatic	–1.1	–	–	1.1	–	–	4.0
P16	0.1 M NaNO$_3$	Pulse	–	–0.8	–1.4	0.8	20	0.40	2.9
P23		Pulse	–	–0.8	–1.4	–	6	0.42	2.8
P26		Pulse	–	–0.8	–1.4	–	5	0.40	3.2

safer dyes as alternatives. Natural pigments are freely available in plant leaves, flowers, and fruits and fulfill these requirements. Experimentally, natural-dye sensitized DSSC have reached an efficiency of 7.1 % and high stability by use porous titanium oxide ceramics as photoanode semiconductor material [1]. However, the further enhancement in power conversion efficiency is difficult, partly due to charge recombination and reduced electron transport rate through the nanocrystalline photoanodes. Efforts have been made and the enhancement of the charge transport has been demonstrated by using one dimensional (1D) zinc oxide (ZnO) nanostructures [2]. According to [3], electrodeposition of nanoporous ZnO films under potentiostatic condition from an aqueous zinc nitrate solution containing polyvinylpyrrolidone surfactant is a cost-effective alternative synthetic method for creation of ZnO-based DSSC which provides a conversion efficiency of 5.08 %. On the other hand, pulse electrodeposition when cathode potential is alternated swiftly between two different values favor the initiation of grain nuclei and greatly increases the number of grains per unit area resulting in finer grained deposit with better properties than conventionally potentiostatic plated coatings [4]. Moreover, the latter method does not require of organic additives that can contaminate ZnO layers and provides for successful growth of 1D ZnO nanostructures [5]. So, the goal of the present work is to investigate the possibility to use zinc oxide nanostructure layers electrodeposited under potentiostatic and pulse conditions for creation natural-dye sensitized DSSC.

2. Experimental

ZnO arrays were electrodeposited on transparent fluorine doped tin oxide (FTO) covered glass (Pilkington) cathodes in aqueous electrolytes contained ZnSO$_4$ or Zn(NO$_3$)$_2$, KCl and NaNO$_3$ (Table 1) in three-electrode cell with platinum counter-electrode and saturated Ag/AgCl reference electrode. Electrodeposition of each ZnO layer sample was carried out at 70°C under potentiostatic conditions (direct current regime D at constant cathode potential U) or under pulse plating modes with rectangular impulses of cathode potential (pulse regime P with more negative cathode potential U_{on} and less negative one U_{off}). All potential values in Table 1 are given versus saturated Ag/AgCl reference electrode. Pulse plating parameters were determined in accordance with [4]. A duty cycle was given by:

$$duty\ cycle = \frac{T_{on}}{T_{on} + T_{off}} = T_{on} \cdot f, \qquad (1)$$

where T_{on} is time at potential U_{on}; T_{off} is time at potential U_{off}; f is frequency, defined as the reciprocal of the cycle time T:

$$f = \frac{1}{T_{on} + T_{off}} = \frac{1}{T}. \qquad (2)$$

As such as at some frequencies we could not see current densities (j), so the electric charges passed during the electrolysis were determined by copper coulometer. Then, the ZnO layer patterns were dye-sensitized by immersion in a freshly prepared blackcurrant juice during 1 h. and by subsequent drying in air.

Table 2. Structure characteristics of the electrodeposited ZnO arrays

| Pattern number | Preferable orientation | | Lattice constant (Å) | | Average crystalline size t (nm) | Lattice strain $\Delta d/d \cdot 10^3$ |
	texture axis	texture factor P_i	a	c		
P14	<001>	1.51	3.245	5.215	exceeds 200	–
D15	<103>	1.75	3.257	5.221	80–180	0.3–1.1
P16	<001>	3.12	3.253	5.220	73–163	0.3–0.6
P23	<001>	3.65	3.258	5.215	73–150	0.1–0.8
P26	<001>	3.47	3.257	5.217	exceeds 200	–

Study of zinc oxide array surface morphology was performed by atomic force microscopy (AFM) by using "NanoLaboratoriya Integra Prima NT-MDT in a tapping mode. Phase composition and structure of the deposited films were determined by XRD-method using an X-ray diffractometer DRON-4M with CoK_α radiation according to θ–2θ-scheme. Preferable orientations of the films were researched by analytical treatment of X-ray diffractions by means of obtaining the texture factor P_i [6]:

$$P_i = \frac{(I_i/I_{0i}) \cdot N}{\sum_i I_i/I_{0i}}, \qquad (3)$$

where I_i — experimental intensity of maximum; I_{0i} — intensity of this line in accordance with JCPDS card; N — total number of X-ray reflections.

The values of angles φ between texture axis and surface normal have been calculated for all reflection planes and P_i values according to relation [6]:

$$\cos\varphi = \qquad (4)$$
$$= \frac{hh_i + kk_i + \frac{1}{2}(hk_i + h_ik) + \frac{3a^2}{4c^2}l_il}{\sqrt{h^2 + k^2 + hk + \frac{3a^2}{4c^2}l^2}\sqrt{h_i^2 + k_i^2 + h_ik_i + \frac{3a^2}{4c^2}l_i^2}}.$$

A shape of function $P_i = f(\varphi)$ allowed [6] to distinguish degree of texture perfection: the texture is perfect if P_i has large value and decreases rapidly with φ. Average crystalline sizes t (i. e. X-ray domains defined as volumes that diffract coherently) and lattice strains $\Delta d/d$ of the electrodeposited ZnO arrays were determined by Williamson-Hall formula for adherent deposits [7]. ZnO lattice characteristics a and c were calculated using the formula [6]:
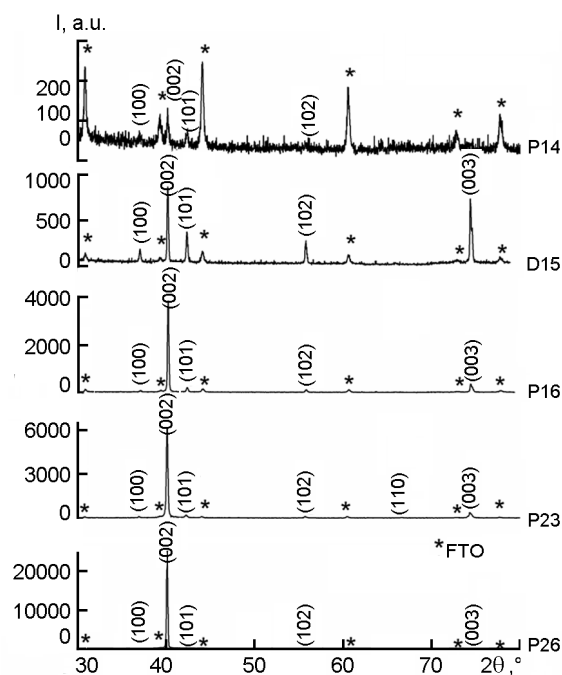

Fig. 1. XRD patterns of ZnO arrays (hexagonal structure of wurtzite ZnO) electrodeposited onto transparent conducting oxide coated glass substrates (* — FTO).

$$\frac{1}{d^2} = \frac{4}{3}\frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2}. \qquad (5)$$

The transmittance spectra of ZnO layers and dye-sensitized ZnO arrays were measured by double beam spectrophotometer SF-46 in the spectral range 350–700 nm, when the patterns ZnO/FTO/glass or ZnO+dye/FTO/glass were put into a working canal and FTO/glass one was placed in a reference canal.

3. Results and discussion

Investigation of structure of zinc oxide arrays electrodeposited in electrolytes and under regimes presented in Table 1 has shown (Fig. 1) that all diffraction peaks
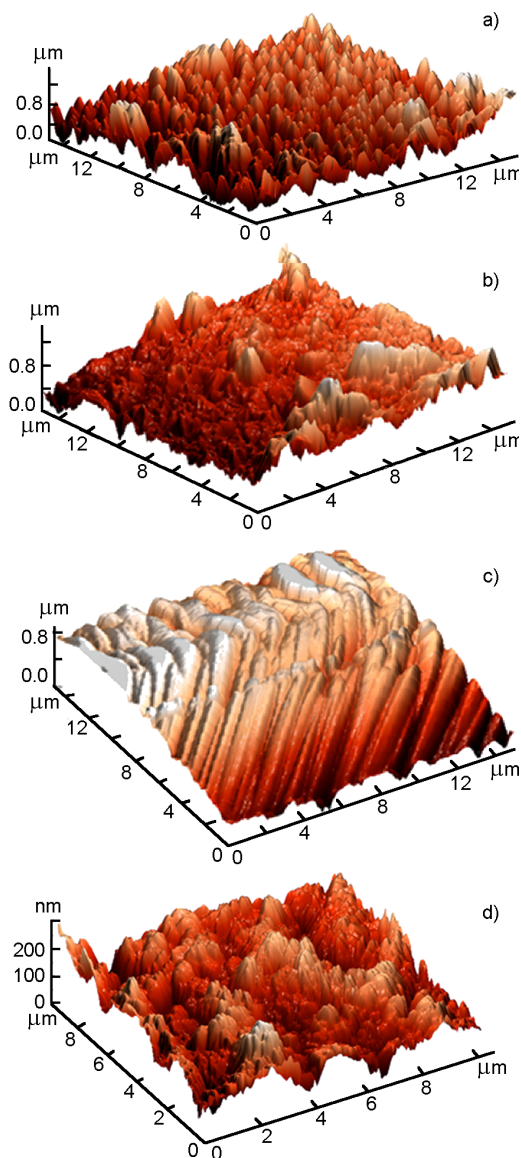
Fig. 2. AFM images of ZnO arrays: a — P14; b — D15; c — P16; d — P23.

Fig. 3. Transparencies (a); $[(-\ln T)\cdot h\nu]^2$ vs. $h\nu$ (b) and $\ln[-\ln T]$ vs. $h\nu$ (c) dependences for ZnO arrays.

match the hexagonal structure of wurtzite ZnO (with the exception of reflections assigned to FTO-glass substrates). Comparative analysis of XRD patterns of the electrodeposited ZnO layers has revealed that the intensity of ZnO diffraction peaks is in direct proportionality to concentration of NO_3^--ions in the electrolyte that allows us to conclude that thicknesses of ZnO layers grow when amounts of nitrates increase. Table 2 shows structure characteristics of ZnO layers. We can see that all electrodeposited ZnO arrays are nanostructured and characterized by little compressive stress or tension. Lattice constants a are near value for single crystal ZnO of hexagonal modification, but the electrodeposited ZnO grains
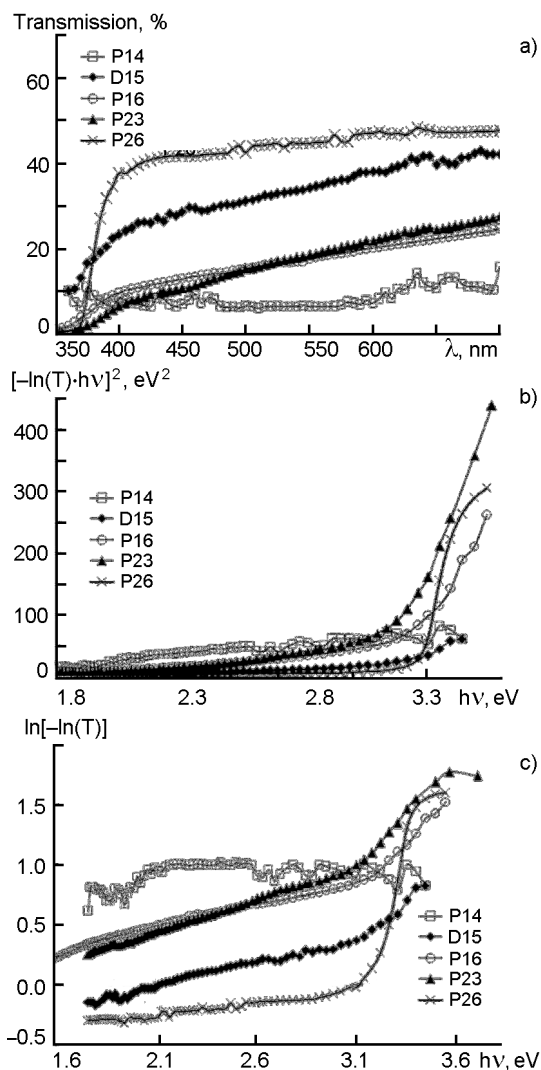
were elongated along c axis (according to JCPDS 36-1451, $a = 3.250$ Å, $c = 5.207$ Å). Comparison of preferable orientations has revealed that ZnO layer which had been pulse plated in the electrolyte with low concentration of nitrates (pattern P14) has crystallites with minor preferable orientation along axis <001>. There seems to be main reason for such structure that the polar (002) crystal plane of the ZnO is capped by Cl^--ions (from the KCl supporting electrolyte), which [8–9] redirects the growth of ZnO. Pattern D15 plated at direct current in NO_3^--enriched electrolyte has light preferable orientation along axis <103>, probably because of influence of cathode reaction of hydrogen evolution on the growing (002) plane that was noted ear-

lier [5]. Only patterns electrodeposited in electrolyte, which contains large concentration of NO_3^--ions at pulse plating conditions (P16, P23 and P26) have strong (002) preferable growth with orientation in the *c*-axis direction. AFM images (Fig. 2) demonstrate correlation between texture and shape of ZnO arrays: the pulse plated especially in nitrate enriched solution crystals with stronger texture <001> are elongated in the direction perpendicular to the substrate plane, so such patterns represent one dimensional zinc oxide nanostructures.

According to transmittance data (Fig. 3a), transparencies of ZnO arrays in the visible region are of 10–40 % and largely depends not on their thickness and the electric charge expended in the electrodeposition process, but to a much greater extent due to their diffuse scattering. As can be seen in Fig. 3a, the most highly diffuse scattering distorted the transmission spectrum of ZnO array P14 produced in a pulsed mode in the electrolyte with a low concentration of nitrates. Note, that since in the DSSC construction the light to the photosensitive dye goes through the glass with FTO and ZnO layers, to improve the efficiency of such solar cell it is desirable to have the greatest possible transparency of the zinc oxide array. Assuming ZnO to be typical direct band gap semiconductor the corresponding optical band gap has been estimated by zero-crossing of the rising edge of $[(-\ln T) \cdot h\nu]^2$ vs. $h\nu$ curve in accordance with [9] (Fig. 3b). All obtained band gap values E_g were near 3.2–3.3 eV, so they correspond to ZnO [2, 3, 9]. Research of dependencies $[(-\ln T) \cdot h\nu]^2$ vs. $h\nu$ has shown that the absorption edge is not sharp and increases exponentially with photon energy according to Urbach rule [10]. As far as Urbach energy E_o is a measure of disorder of the semiconductor structure, E_o values obtained in accordance with [11] by the graph $\ln[-\ln T]$ vs. $h\nu$ from slope of the curve near E_g (Fig. 3c) have revealed that the most disordered layer was D15 except of the array P14. On the contrary, ZnO array P26 has the highest ordering.

Absorption curves $A = -\lg(T)$ vs. wavelength for bare ZnO arrays and for sensitized by freshly prepared blackcurrant juice ZnO layers are presented in Fig. 4. We can see that P14 pattern (Fig. 4a) was destroyed during sensitization due to chemical interaction ZnO with the dye, either because of poor adhesion to the substrate. Electrodeposited in potentiostatic mode pattern D15
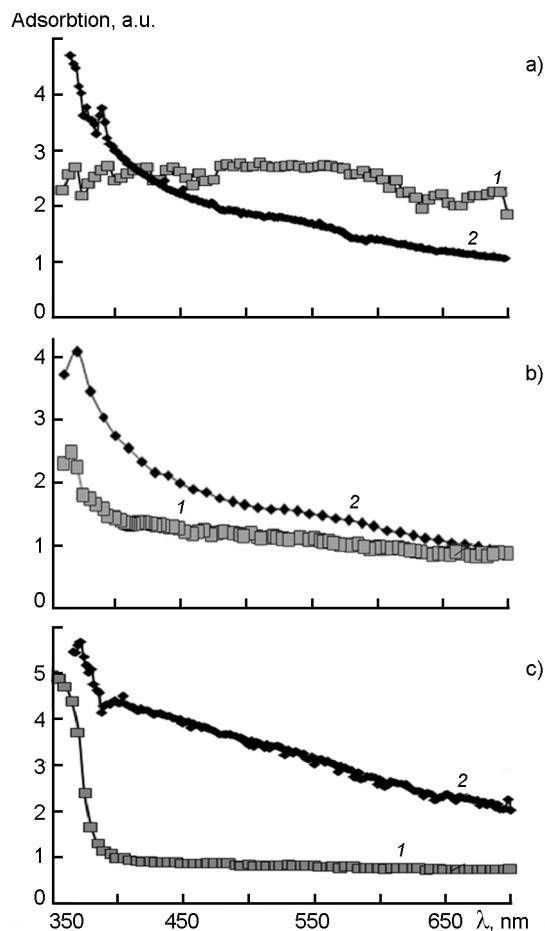

Fig. 4. Absorption vs. wavelength curves for bare ZnO arrays (*1*) and for sensitized by freshly prepared black currant juice ZnO layers (*2*): a — P14; b — D15; c — P26.

was characterized by weak absorption in the visible range (Fig. 4b). At the same time the most transparent and well-ordered pulse plated in the electrolyte with high concentration of nitrates zinc oxide array P26 (which was characterized by perfect texture <001>) has demonstrated after its dye-sensitization the best absorption of the visible light (Fig. 4c). That was commensurate or even greater than the data in the literature for obtained by different methods ZnO arrays with dyes based on ruthenium complexes [3, 12,13].

3. Conclusion

Thus, the studies of structure, surface morphology and optical properties have demonstrated the promise of ZnO arrays electrochemically grown in the rectangular pulse mode for creation of natural-dye sensitized solar cells.

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Електроосаджені наноструктури оксиду цинку з адсорбованим натуральним барвником для використання в фотовольтаіці

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Повідомляється про економічно ефективний альтернативний метод синтезу оксиду цинку для сенсибілізованих натуральними барвниками сонячних елементів (DSSC). Масиви ZnO виготовлено у трьохелектродній комірці методом електрохімічного осадження на вкритих прозорим електропровідним легованим фтором діоксидом олова скляних підкладках як у потенціостатичному режимі, так і в імпульсних режимах з прямокутними імпульсами катодних потенціалів. Після цього шари ZnO сенсибілізовано барвником із щойно виготовленого чорносмородинового соку. Дослідження структури методом рентгенівської дифрактометрії, морфології поверхні за допомогою атомного силового мікроскопа та оптичних властивостей спектрофотометричним методом продемонстрували перспективність електрохімічно осаджених у прямокутно-імпульсному режимі масивів ZnO для створення DSSC на натуральних барвниках.