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Photovoltaic properties of cd-based ionic liquid crystals with semiconductor nanoparticles

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ABSTRACT

The photovoltaic effect in pure cadmium-alkanoate matrices and in their nanocomposites with semiconductor CdS nanoparticles (NPs) was revealed and investigated. The main mechanism of the phenomenon is the Dember effect, in which the internal field of non-equilibrium charge carriers is formed due to a significant difference in the mobility of positive and negative charges. NPs synthesized in the matrix lead to a significant increase in the concentration of the photo-generated electrons and thus to an increase in the photo-electro-driving force in the material. The magnitude and kinetics of the photocurrent for nanocomposites substantially depend on the content of only a small amount (2 – 4 mol. %) of NPs.

KEYWORDS

CdS quantum dots; ionic liquid crystals; nanocomposite; nanoparticles; photoconductivity

1. Introduction

At the moment, liquid crystals (LCs) are mainly used for the fabrication of displays. Research and new developments in electronic devices indicate that LC displays can be substantially replaced by organic electrolysis displays, since they do not require back-lighting and can be flexible. Therefore, an important scientific task at the present stage of scientific research is the expansion of the functional capabilities of the LCs from point of view of their utilization in several new application fields other than display technologies.

Solar cells can be considered as one of the most promising areas for using LCs. Starting with one of the first papers [1], a considerable attention of researchers was attracted to the solar cells, in which LCs were used. In addition, not only pure LCs [2], but also LCs with porphyrin [3, 4] were investigated. It should be noted, that photovoltaic properties of LCs with polymers or LC polymers [5–14] are studied most intensively. However, in such studies, there were no found materials with parameters, which can be close to parameters of the best organic solar cells.

From the analysis of literature, one can conclude that at present, discotic LC materials are the most promising for the production of solar cells [15–18]. However, they also

have the worst parameters compared to those, demonstrated by the best samples of organic solar cells.

As one of the possible ways to increase the efficiency of the solar cells on the basis of LCs can be considered heterojunctions [19, 20] where one of the layers is the LC. However, in such structures, high parameters of photovoltaic energy conversion have not been obtained yet. In the case of heterostructures, the use of a LC as a luminescent solar concentrator can be regarded as a promising direction [21].

From the above discussed, it can be concluded that, in principle, LCs can be considered as one of promising materials that should be investigated in order to assess the possibility of their use in photovoltaic converters. To reach this, it is not enough just to improve the parameters already investigated before the LCs, and expand the range of research on new materials. The new approaches, such as introduction of nanoparticles in to a matrix, have to be considered.

In this article, we report on the first study of the photovoltaic properties of new materials: metal alkanooates nanocomposites with CdS semiconductor nanoparticles (NPs). The metal alkanooates belong to ionic liquid crystals (ILC), they have common formula $(C_nH_{2n}+COO^-)_k^{-1}Me^{+k}$, where Me is a mono- ($k=1$), di- ($k=2$), or trivalent ($k=3$) metal cation, and combine simple chemical structures and a versatility of condensed states of matter they exhibit. The thermotropic LC phase of these materials is formed in the temperature range 98–180 °C, where they have a layered structure of smectic A. In this phase, different types of NPs can be synthesized through chemical reactions, thereby creating various of nanocomposites of metal alkanooates. The structural and electrical properties of such materials were studied [22–25]. In [22] we show that susceptible to the action of light is metal ions of thermotropic ILC matrix. In addition, we also showed that photosensitivity can be changed in the nanocomposites by adding different types of nanoparticles NPs. The aim of this work is to study the photovoltaic properties of cadmium octanoate nanocomposites with CdS NPs.

2. Materials and methods

The cadmium octanoate matrix (abbreviation CdC₈) have the chemical formula $Cd^{+2}(C_7H_{15}COO)^{-2}$. These materials at room temperature exist as a polycrystalline powder. When heated to temperatures of 98–180 °C, metal-alkanoates move to a smectic mesophase, where they can be used as nanoreactors for the chemical synthesis of different types of NPs. After synthesis in the mesophase, the nanocomposite is cooled to room temperature. When slowly cooling, polycrystalline powder of nanocomposites is obtained, when rapidly cooled to room temperature an anisotropic glass is formed which has the same multilayer structure as smectic (A) one with built-in NPs in the matrix.

Advantages of the method of synthesizing NPs in the matrices of metal-alkanoates are as follows:

- The chemical reactions are performed in one stage, and they are simple;
- NPs have a small dispersion in size, the NPs is arranged in the smectic layers of nanocomposites of metal-alkanoates and have a substantially spherical shape;

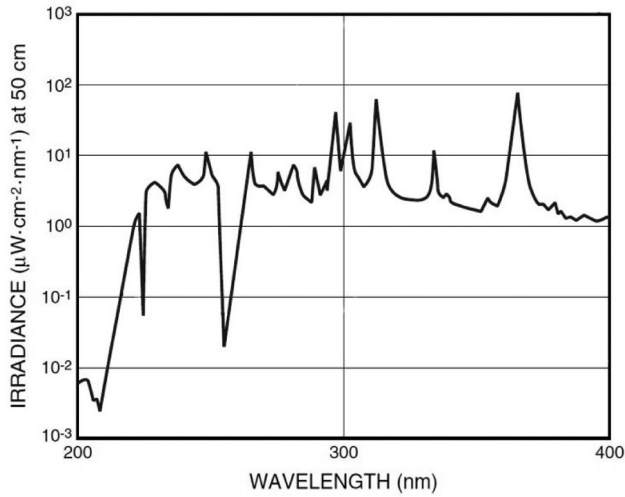


Figure 1. Spectrum of the lamp measured at a distance of 50 cm.

- It is possible to obtain a high concentration of NPs in the material up to 8 mol. %;
- For nanocomposites metal-alkanoates with metallic NPs, it is not necessary to use additional reagents for transformation and stabilization, since the smectic matrix performs both these functions simultaneously;
- There is no aggregation of NPs, since they are stabilized by a smectic matrix;
- Nanocomposites are stable for a long time (years).

We investigate pure matrix CdC_8 and nanocomposites $\text{CdC}_8:\text{CdS}$ with NPs concentration of 2 mol.% and 4 mol.%. The size of CdS NPs was in the range 1.7–3.5 nm, with an average diameter of ~ 2.7 nm [25]. The preparation of the samples and the used equipment were the same as in the case of the investigation of photoconductivity of samples of nanocomposites of metal-alkanoates [22].

All studied samples in the "sandwich" cells had the same thickness of $50 \mu\text{m}$, and the area of the illuminated surface of the samples was 1×1 cm. The smectic layers of the investigated samples were oriented parallel to the substrates. The sign of the potential on the illuminated electrode was positive.

To determine the photovoltaic properties of the samples, we used a high-precision Keithley T 2635B source-meter and the ultraviolet light source Hamamatsu 200 series L7212 with a lamp of type L7212-02 from 240 to 400 nm (Fig. 1).

The samples were placed at a distance of 40 cm from the UV light source so that the heat did not affect the experiment. The radiation power of the lamp at the location of samples at a distance of 40 cm from the source of illumination was $0.73 \text{ mW}/\text{cm}^2$, measured by Thorlabs PM100D power meter with Thorlabs S401C sensor. The dynamics of the photovoltaic response (short circuit current) was recorded on the technique "time trace", the duration of the light pulse was 5 s.

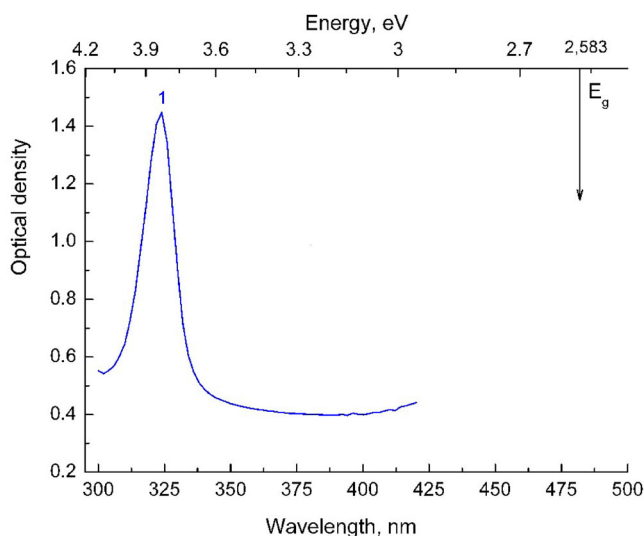


Figure 2. Absorption spectrum of CdS NPs in nanocomposite materials CdC₈:CdS. The arrow indicates the band gap energy of the CdS bulk crystal.

3. Influence of NPs on absorption spectra of CdC₈

The absorption spectrum of nanocomposites was measured in an anisotropic glass-like phase using the automated spectral complex of KSVU-6 (LOMO). Absorption spectra of investigated nanocomposites are presented in Fig. 2. It should be noted that the pure matrices of cadmium octanoate CdC₈ without NPs do not absorb light in the visible range of the spectrum.

The absorption spectrum of the nanocomposite CdC₈:CdS has a narrow band with a maximum $\lambda = 323$ nm (3.8 eV). These absorption bands are due to the excitation of localized excitons in CdS NPs; they are shifted to the UV range relative to the forbidden energy band of the bulk crystal CdS ($E_g = 2.583$ eV, shown by arrow in Fig. 2). As can be seen from Fig. 2, the absorption band have relatively high intensity and is narrow (half the bandwidth is about 10 nm).

This indicates a small size dispersion of CdS NPs synthesized in the smectic meso-phase of CdC₈.

The absorption spectra of the pure matrix CdC₈ and the nanocomposites CdC₈:CdS of different concentrations of NPs are shown in Fig. 3.

By comparing absorption spectra with the radiation spectrum of a lamp (see Fig. 1), it is important to emphasize that the radiation spectrum of a lamp falls at the energies corresponding to the edge of the absorption spectrum of the pure matrix CdC₈ and the maximum absorption of semiconducting CdS NPs. In this case, the absorption occurs mostly not near the electrode, through which the sample is excited by light, but in the sample volume.

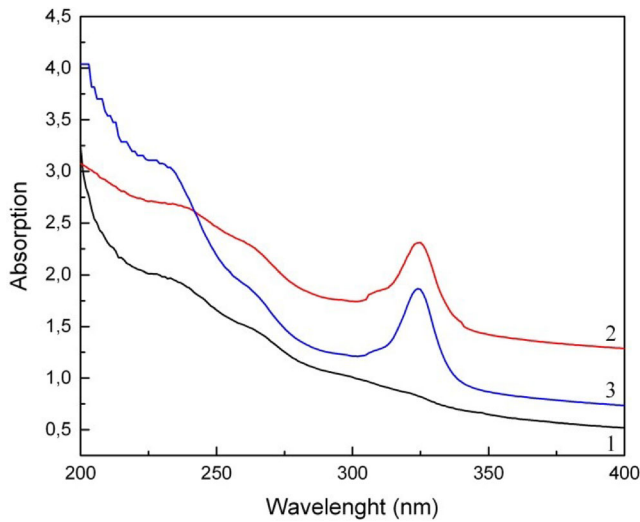


Figure 3. Absorption spectrum of the pure matrix CdC_8 (1), and nanocomposites $\text{CdC}_8:\text{CdS}$ (2 mol %) (2) and $\text{CdC}_8:\text{CdS}$ (4 mol %) (3).

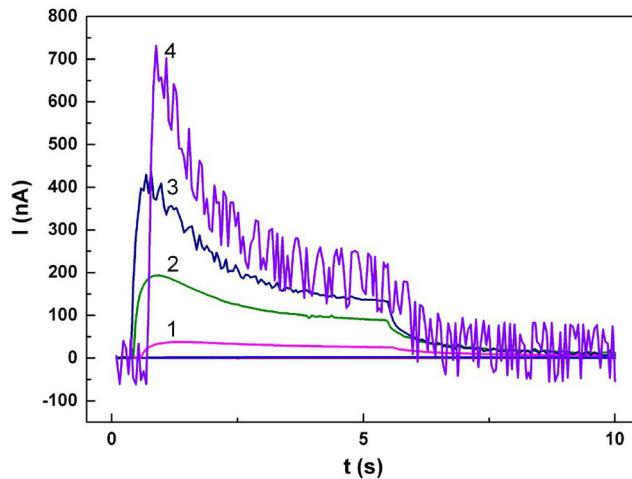


Figure 4. The short circuit kinetics of the current change in the sample of pure CdC_8 as a result of switching on and turning off the light at temperatures T : 1 - 70°C , 2 - 90°C , 3 - 110°C , 4 - 130°C and 5 - 150°C .

4. Photovoltaic properties of CdC_8 without NPs

From the analysis of the temperature dependence of the photovoltaic response of pure CdC_8 , it follows that the measured short-circuit current exceeds the noise signal at temperatures above 90°C . The fact reflects, that the temperature is higher than the transition temperature from the solid phase to the LC state.

Fig. 4 shows the kinetics of the current short circuit of the sample CdC_8 as a result of turning on and turning off the light measured at different temperatures. The results of studying the shortcircuit current dynamics demonstrate that there are two

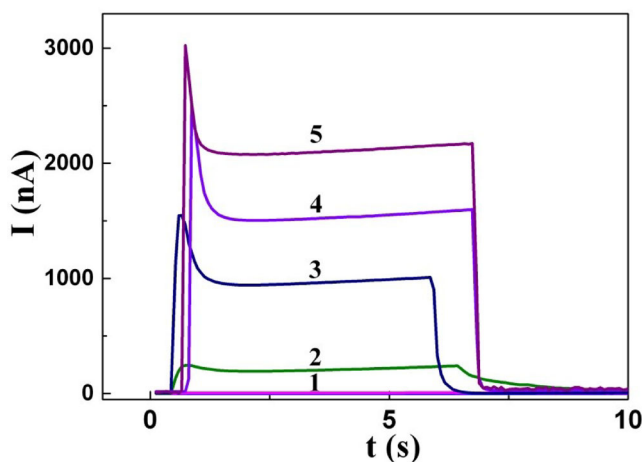


Figure 5. Kinetics of short circuit current of sample Cd₈:CdS (4 mol. %) as a result of switching on and switching off the light at temperatures T: 1 - 70°C, 2 - 90°C, 3 - 110°C, 4 - 130°C and 5- 150°C.

components: fast when the light is turned on and slow when the light is switching off. With an increase in temperature to 150 °C, the fast component of short-circuit current increases sharply, and the slow component increases significantly less. Therefore, the ratio of the fast component of the short-circuit current to the slow is increasing.

The significant dependence of the short-circuit current on temperature and the correlation of the changes in the photovoltaic response with the temperatures of the phase transitions in ILCs allow to claim that the photovoltaic response is mostly determined by processes in the volume of the ILC.

5. Influence of CdS NPs on photovoltaic properties of cadmium octanoate

For the nanocomposites of Cd₈:CdS, we investigated the effect on photovoltaic properties of CdS NPs with two different concentrations (2 and 4 mol. %). Fig. 5 shows the kinetics of *I* magnitude for a sample of Cd₈:CdS (4 mol %) when the light is turned on and turned off. We can distinguish the following features.

First, in the case of samples Cd₈:CdS (4 mol.%) there is no fast component of *I* magnitude in contrast to the fast component observed in Fig. 4.

Secondly, the time of decreasing *I*, when the light is turned off for samples Cd₈:CdS (4 mol.%), is much larger than the time for samples for pure matrix Cd₈.

Thirdly, the most important difference between the data given in Fig. 4 and in Fig. 5 is considerably larger short-circuit current in Cd₈:CdS (4 mol.%) compared to the value of the current for the sample Cd₈. From the comparison of these peculiarities, it follows that under the same conditions of excitation of samples by light, the current of short-circuit in samples with CdS NPs was more than 10 times larger compared to the value of the current for samples of pure Cd₈ matrix.

An analysis of the short-circuit current kinetics of samples Cd₈:CdS (2 mol.%) CdS has shown that it is close to the kinetics of samples pure Cd₈. From the abovementioned results, an important conclusion can be made: the value of current depends

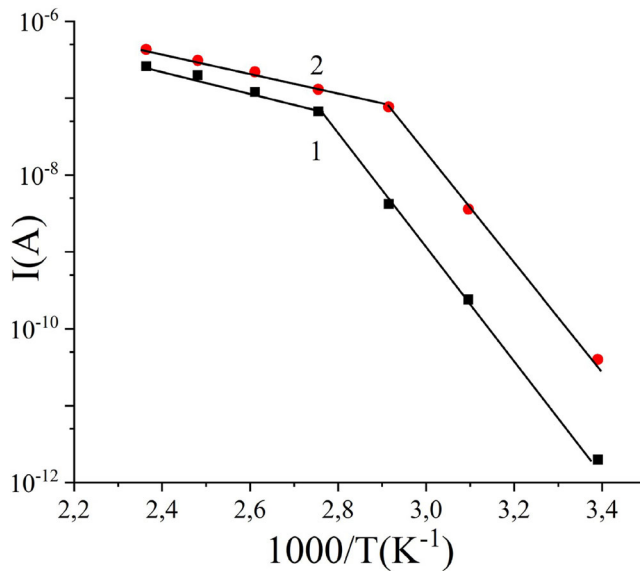


Figure 6. Temperature dependence of short-circuit current obtained for the nanocomposites with different concentration of CdS NPs: (1) 2 mol. % CdS and (2) 4 mol. % CdS.

essentially on temperature. Therefore, it was important to analyze the temperature dependence of the value of current I . From Figs. 4 and 5, we see that the fast component of the current quantity obtained at each of temperatures after the switching on the light does not reach the stationary value. We decided to analyze the temperature dependence and take the value of the short-circuit current at the moment of switching off the light, taking into account that the pulse duration of the sample illumination was approximately the same.

The temperature dependences of the short-circuit current for the CdC₈ matrix with two concentrations of CdS NPs in the coordinates $\lg I$ ($1/T$) is shown in Fig. 6. From these results, it can be seen that there are two different behaviors for the LC phase and the solid-state phase. The inclination of the lines determines the activation energy of charge carriers occur when illuminated by light. A more significant difference in the magnitude of the short-circuit current is observed in the solid phase than in the LC one. At the same time, the curves for both concentration are close in the LC phase. The activation energy of the short-circuit current of CdC₈:CdS (2 mol.%) and CdC₈:CdS (4 mol.% CdS) samples in the LC phase is slightly different. Thus, we can conclude that in the LC phase and in the solid phase, different carriers excited by light and affect the short-circuit current.

From the last regularity a very important conclusion can be made concerning to the establishment of the mechanism of the photovoltaic effect. The magnitude and kinetics of the photovoltaic effect in the CdC₈ matrix essentially depend on the nature and content of a relatively small (4 mol. %) number of NPs.

6. Discussion of photovoltaic results

In the study of photovoltaic properties of certain specimens, the conditions for obtaining the maximum efficiency of energy conversion have to be considered at the initial

stage. To reach this, an internal electric field in the sample has to be increased. This can be done in various ways: Schottky's barrier, p-n transition, heterostructures, etc. When we fabricated the samples of the cadmium octanoate and its nanocomposites, we did not create such internal electric fields. Therefore, by analyzing the results obtained, it was important for us to establish which mechanism in the samples under study is responsible for the photovoltaic effect.

By analyzing the spectra of absorption of samples, the spectrum of the radiation of the lamp (see the [Section 1](#) of the experimental results), we have shown that the samples were irradiated with weakly absorbing light. The fact reflects that the light has sufficient intensity of penetrating practically the entire thickness of the sample. This allows us to state that the photovoltaic effect arises in the volume of the samples. This conclusion is confirmed by the significant dependence of the value of the short-circuit current on the phase of SLC, including the concentration of NPs in the ILC nanocomposites.

Based on the analysis of published data on various types of photovoltaic effects, we came to the conclusion that in the investigated samples the main component of the photoelectric effect is the Dember effect [26, 27]. ILCs of metal alkanoates have high ionic conductivity. Carrier excitation in ILCs obeys the Arrhenius law, whence the activation energy is quite small, comparable to the value of kT , both in the LC phase and in the solid state phase [22–24].

The main reason for the occurrence of the photoelectric Dember effect is a significant difference in the magnitude of the mobility of positive charges (metal ions) and negative charges (electrons). Estimations performed in [26], show that the maximum value of the electromotive force for the Dember effect can be equal to 0.5 V. This value is sufficient to provide a short-circuit current that was recorded in our experiments. In nanocomposites with CdS NPs, an additional contribution to photoconductivity can be made by photogenerated electrons in CdS with their subsequent injection into the ILC matrix. The differences in the magnitude of the short-circuit current shown in [Fig. 6](#) can be well explained on the basis of the found mechanism of the photoelectric effect.

In addition, semiconductor quantum dots can strongly affect the excitation of the photovoltaic potential [28]. For Dember effect in semiconductors, as shown in [26], the electromotive force E can be determined as follows:

$$E = G_0 \frac{k_B T}{e} \frac{\mu_n - \mu_p}{n\mu_n - p\mu_p} \frac{1}{\sqrt{D/\tau + s}} \quad (1)$$

where G_0 is the surface density of photons, k_B is the Boltzmann's constant, T is the absolute temperature, e is the charge of the electron, μ_n and μ_p is the mobility of negative and positive charges, respectively; n and p is the concentration of negative and positive charges, respectively; D is the diffusion coefficient charges, τ is the lifetime of charge carriers and s is the magnitude of the surface recombination of charge carriers. But in order to confirm this contribution of CdS NPs to the photovoltaic effect, we should provide additional experiments with voltage measurements in idle mode.

7. Conclusion

The photovoltaic effect was obtained for the first time in ionic liquid crystals of metal alkanoates, as well as in their nanocomposites with CdS NPs. Photovoltaic effect is

revealed both in the pure matrix and in the nanocomposites with semiconductor NPs, in the "sandwich" cells in the illumination of the samples perpendicular to the cation-anion layers by a lamp, which emits the light in a wide range of wavelengths at the ultra-wavelength range. The photovoltaic effect arises due to the photo-ionized ions by resonant absorption of both the cadmium-alkanoate matrix and the NPs ultraviolet light over a wide range, with subsequent charge separation during ion movement along the cation-anion layers.

The main mechanism of the photovoltaic effect is the Dember effect, which arises due to the significant difference in the magnitude of the mobility of positive and negative charges (ions and electrons in our case), where the internal field of unbalanced charge carriers is result of the motion of ions and charge carriers. This occurs mainly due to electron diffusion in the sample volume. NPs synthesized in the matrix and embedded in the cation-anion layers lead to a significant increase in the concentration of photo-ionized electrons and thereby increase the photo-electro-driving force in the material.

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