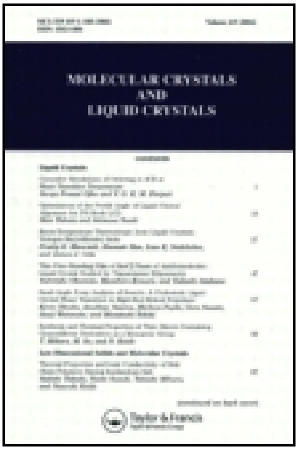

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Photovoltaic Effects in Composites of V_2O_5 Xerogel with Polymethine Dye

L. I. Fenenko [a] , A. A. Ishchenko [a] , A. B. Verbitsky [c] & Ya. I. Vertsimakha [c]

[a] Institute of Semiconductor Physics of NASU, Kyiv, Ukraine

[b] Institute of Organic Chemistry of NASU, Kyiv, Ukraine

[c] Institute of Physics of NASU, Kyiv, Ukraine

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L. I. Fenenko
Institute of Semiconductor Physics of NASU, Kyiv, Ukraine

A. A. Ishchenko
Institute of Organic Chemistry of NASU, Kyiv, Ukraine

A. B. Verbitsky
Ya. I. Vertsimakha
Institute of Physics of NASU, Kyiv, Ukraine

Photovoltaic properties of composites from V_2O_5 *xerogel and aqua soluble indocyanine green polymethine dye with different ratios of components have been investigated. The formation of a photovoltage in a wide spectral range (from 400 to 950 nm) is found. The maximal photosensitivity is observed in the 600–900 nm range and increases with the dye concentration. The spectral dependences of photosensitivity of the composites studied are compared with the spectral dependences of developed plastic solar cells based on conductive polymers with organic and inorganic photoconductors. Ways to enhance the photosensitivity of the studied composites in the short-wavelength spectral region are discussed.*

Keywords: photovoltaics; polymethine dye; vanadium pentoxide; xerogel

INTRODUCTION

Gels of complex metal oxides, in particular those of V_2O_5, are perspective materials for the use as a component of multilayered or composite structures for different photonic applications because of their good conductivity and the possibility to change their electronic properties by the nanosized effect.

Address correspondence to Ya. I. Vertsimakha, Institute of Physics of NASU, Prosp. Nauki 46, Kyiv 03028, Ukraine. Tel.: 380442650912, Fax: 380442651589, E-mail: yavertsi@iop.kiev.ua

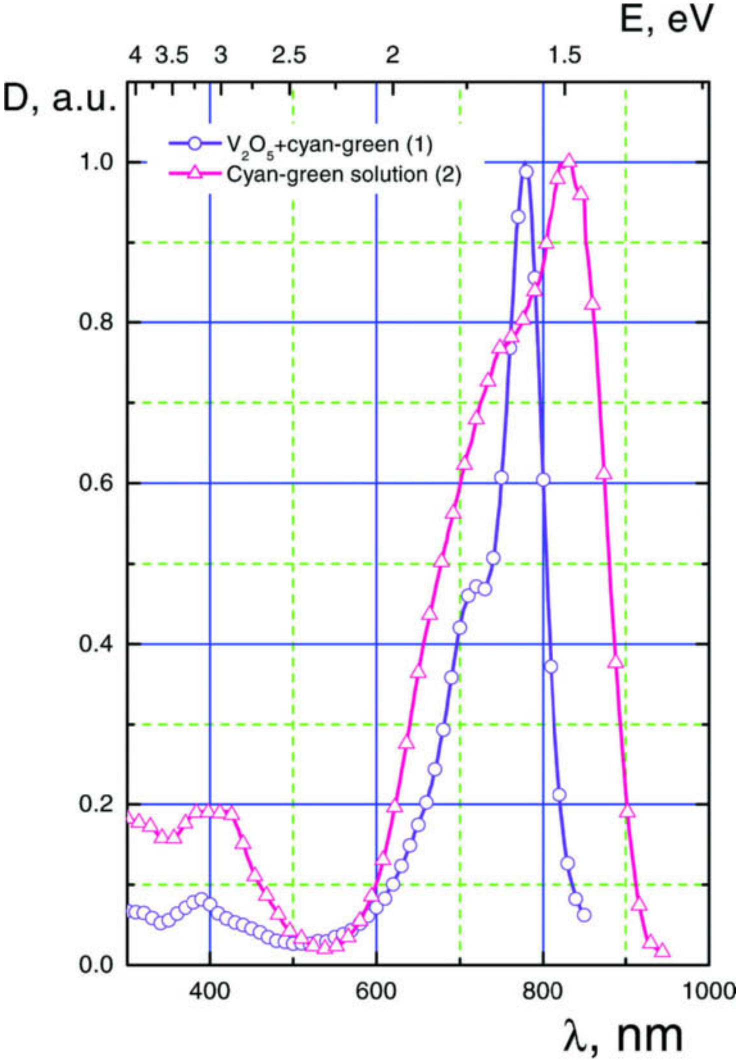

FIGURE 1 Spectral dependences of optical density of V_2O_5 + cyan-green composite films (dye concentration of 44 w.%) (curve 1) and an aqueous solution of dye (concentration 10^{-5} g/l) (curve 2).

According to [1], gels of $V_2O_5 \times nH_2O$ are hydrates of polyvanadium acid, in which the molecules of oxide layers are connected by the layers of water molecules. A part of water can be dried at 300 K, and $V_2O_5 \times 1.6\ H_2O$ xerogel with the 11.55 Å interlayer distance is formed. It is

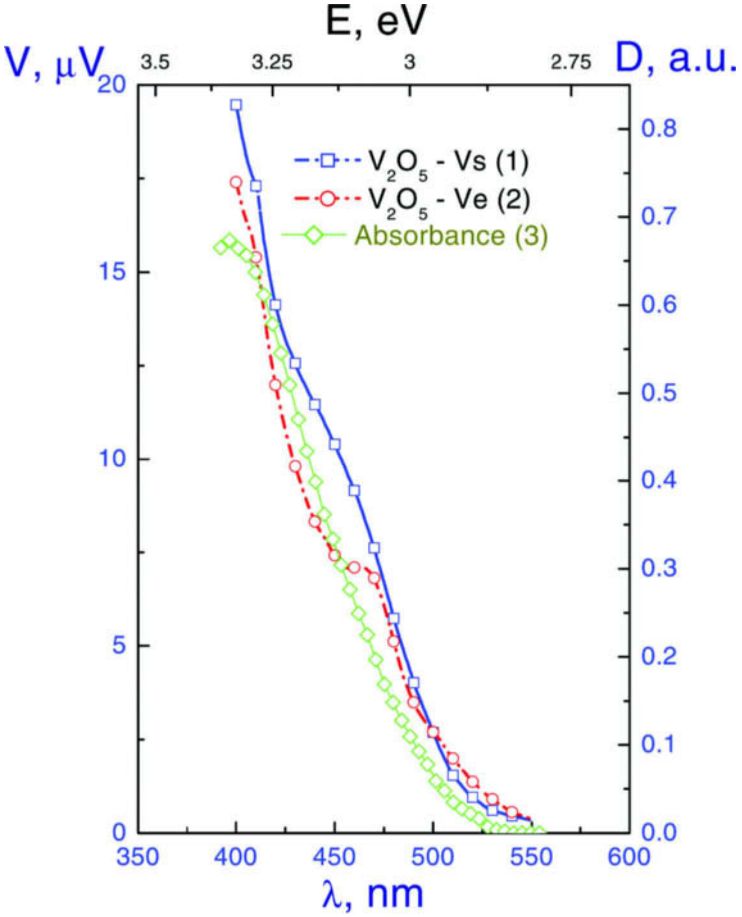

FIGURE 2 Photovoltage under different sides illumination (1, 2) and absorption (3) of V_2O_5 films.

stated by electronic microscopy [1,2] that this xerogel consists of flat strips of ~1000 Å in length, 100 Å in width, and 10 Å in thickness.

The conductivity of $V_2O_5 \cdot nH_2O$ is $\approx 10^{-2}$ $Ohm^{-1} \times cm^{-1}$, which is by 4 orders greater than the conductivity of vacuum deposited films of V_2O_5 [3]. In such films of xerogel, one observes a small photosensitivity in the UV region. However, their absorption and photosensitivity in the visible and near IR-regions are very low (irrespectively of the method of their production). Therefore, they cannot be used for transformation of solar light.

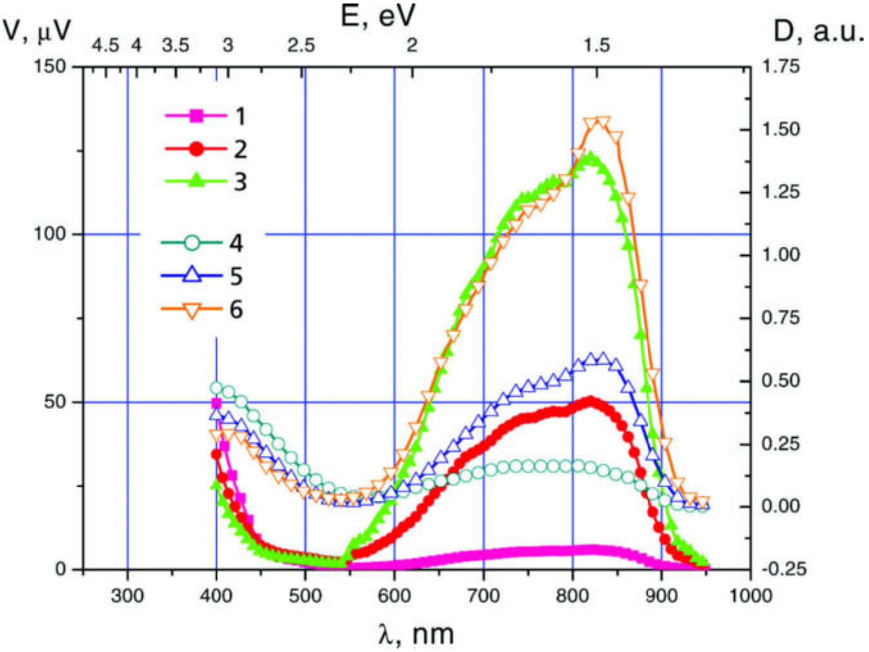

FIGURE 3 Spectral dependences of optical density D (1, 2, 3) and photovoltage V_s (4, 5, 6) V_2O_5 + cyan-green composite films with different concentrations of dye: 20 w.% (1,4), 34% (2, 5), and 44% (3, 6).

The purpose of the present work was to develop composites of V_2O_5 xerogel with organic dyes photosensitive in the 550–950 nm range and to examine them for the presence of photosensitivity. Since xerogel films are deposited from an aqueous solution, we selected indocyanine-green dye for this aim [4,5] which has good solubility in water and maximal absorption near 800 nm.

MAIN RESULTS

In the visible and near IR-regions, the absorption spectrum of films of indocyanine green/V_2O_5 composites consists of two wide asymmetric bands with maxima at 832 and 402 nm (Fig. 1, curve 1). The short-wave half-widths of IR-absorption bands in the films of composites are greater than the long-wave ones, and the ratio of half-widths increases up to 5 with the concentration of dye.

The comparison of the absorption spectra of the composite and the aqueous solution of dye (Fig. 1, curve 2) has shown that, at the

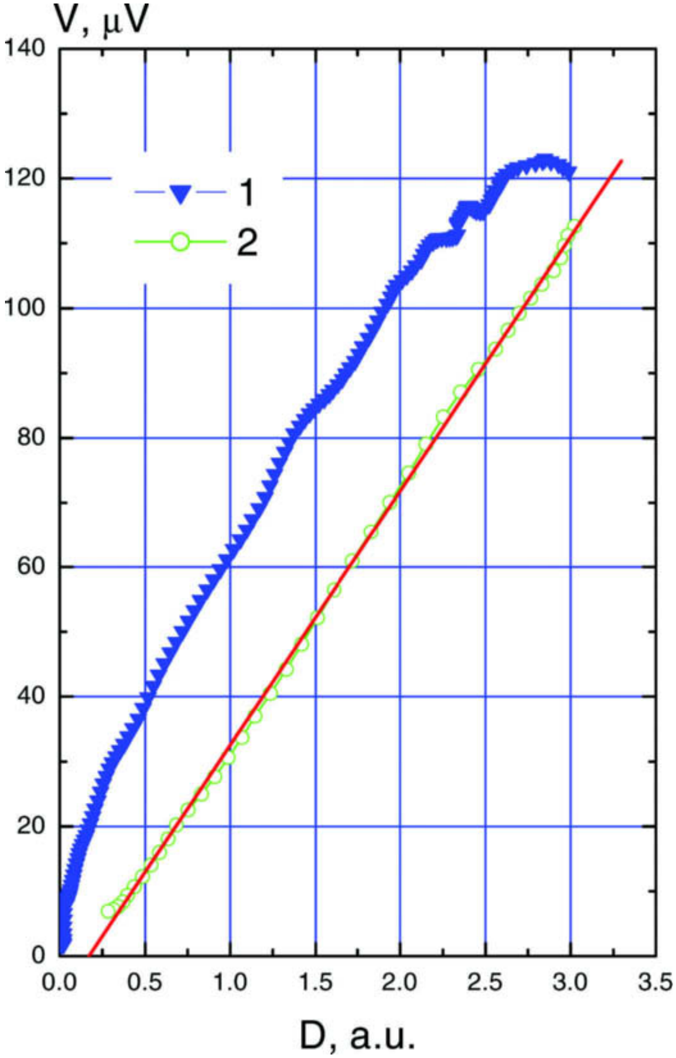

FIGURE 4 Dependences of surface photovoltage V_s on optical density D for V_2O_5 + cyan-green composite films in the range 830–890 nm, where the absorption of dye molecules predominates, (1) and in the range 550–830 nm, where there is the absorption of aggregates and complexes V_2O_5–dye (2).

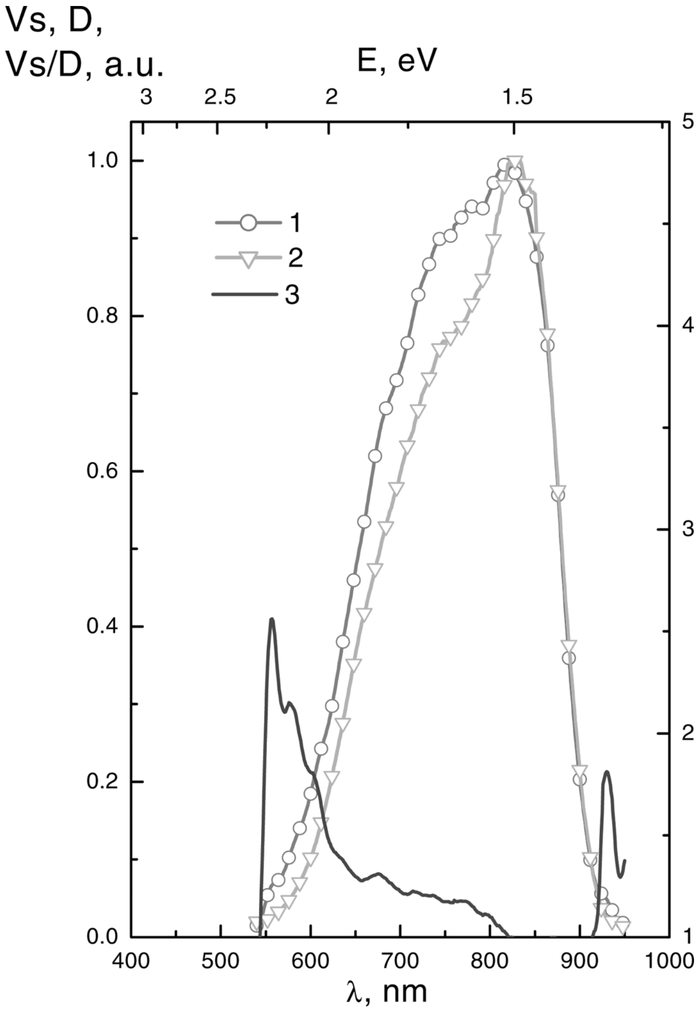

FIGURE 5 Normalized values of V_s per equal number of light quanta (1), optical density D (2), and their ratio V_s/D (3) for a composite film V_2O_5 with the 44%-concentration of dye.

transition from the solution to the composite, there is the 0.1-eV shift of the maxima of absorption bands to the side of smaller energies. This testifies to a weak interaction of dye molecules and xerogel ($\Delta E/E >> 7\%$).

The absorption and photosensitivity of vanadium pentoxide composite are shown in Figure 2. The analysis of the IR-band shape has

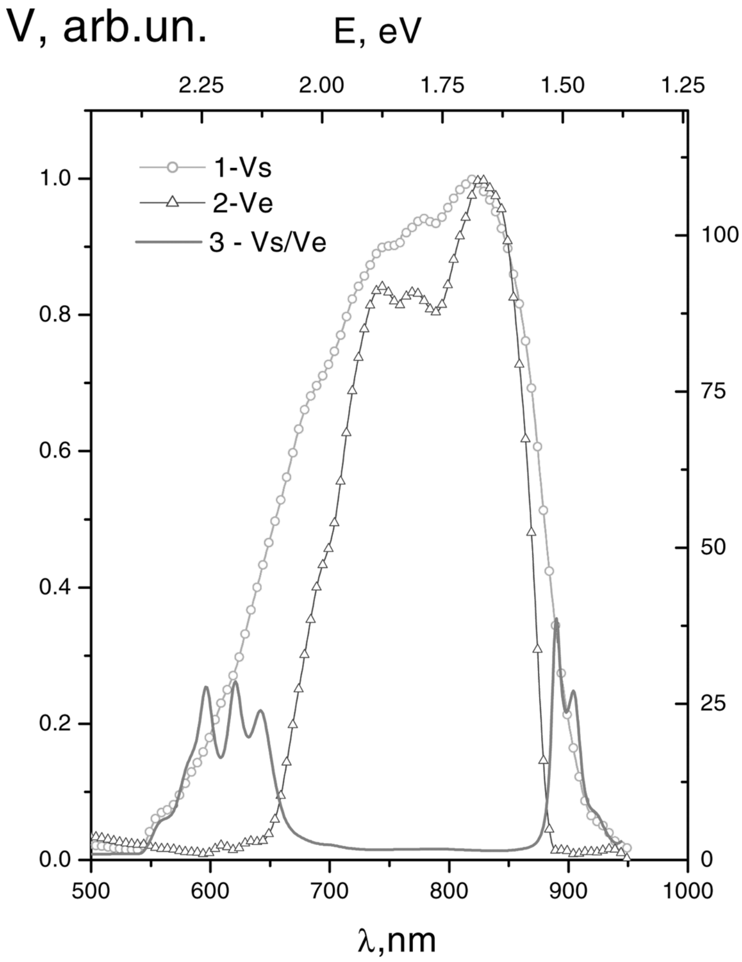

FIGURE 6 Spectral dependences of photovoltage under illumination of the free surface side V_s (1) and via SnO_2V_e (2) electrode and their ratio for composite V_2O_5 + dye films with 44% of cyan-green.

shown that it can be described with the 2% accuracy by two Gaussian components with the 0.05 eV width and maxima at 1.59 and 1.73 eV. Thus, the intensity of the Gaussian component with a maximum at 1.73 eV is approximately twice smaller than the intensity of the band with a maximum at 1.59 eV. Thus, the IR-absorption band is caused by the electronic transition at 1.53 eV with the intramolecular vibronic transition at 0.14 eV. The contribution of transitions with a participation of several intramolecular oscillations is insignificant (<2%).

The absorbance of dye in the aqueous solution near the second electronic transition with a maximum at 3.18 eV is almost by one order smaller than that near the first electronic transition. In the films of sensibilized composites, the intensity of absorption at the second electronic transition increases approximately twice. But this increase is essentially defined by the absorption of V_2O_5 particles, which is confirmed by our measurements of the absorption spectra of nonsensibilized films of xerogel (Fig. 2).

In the region of 520–950 nm, the optical density and surface photovoltage V_s (and, therefore, photosensitivity) are increased in composite films with increase in the concentration of dye (Fig. 3). It should be noted that the asymmetry of the IR-band in the spectra of V_s for all the composites is greater than that of the absorption bands due to the increase of V^* in the region of 550–750 nm, where several weak bends on the spectral dependence of V_s are observed.

This becomes obvious if we plot V_s vs optical density D for the short (520–830 nm) and long wavelength (830–890 nm) regions (with the respect to the absorption maximum) (see Fig. 4). It can be seen that the long wavelength part is well described by the classical linear dependence $V_s(D)$, except for the region of weak absorption with $D < 0.3$ (curve 1). Under same conditions, the short wavelength part of $V_s(D)$ is more strong and nonlinear (with several shoulders). This means that, only in the 830–890 nm range, the quantum yield of the photogeneration of charge carriers is constant, and, in the 520–720 and 900–950 nm regions, it is greater and depends on the wavelength of absorbed light.

The presence of a significant absorption for composite films in the 520–700 nm (1.8–2.4 eV) region, where there is practically no molecular absorption of dye in a solution, can be formally explained by the amplification of transitions with the participation of several intermolecular oscillations. But, in this case, the reason for the probability to increase in the composite for such a transition is unclear and it is difficult to explain correctly the rise of V_s in this region.

Therefore, we propose to explain the presence of this absorption and photosensitivity (V_s) in the 520–700 nm region by the formation of several types of aggregates with the energies in the 1.7–2.2 eV range in the studied composites. The formation of aggregates is characteristic of this class of dyes [5]. In this case, great V_s values in this region and the manifestation of shoulders evidence for that the efficiency of the photogeneration of charge carriers for aggregates is greater than that for isolated molecules of dye.

In such a case, the energy of most photosensitive aggregates can be estimated by the V_s/D dependence (Fig. 5, curve 3). It is seen that

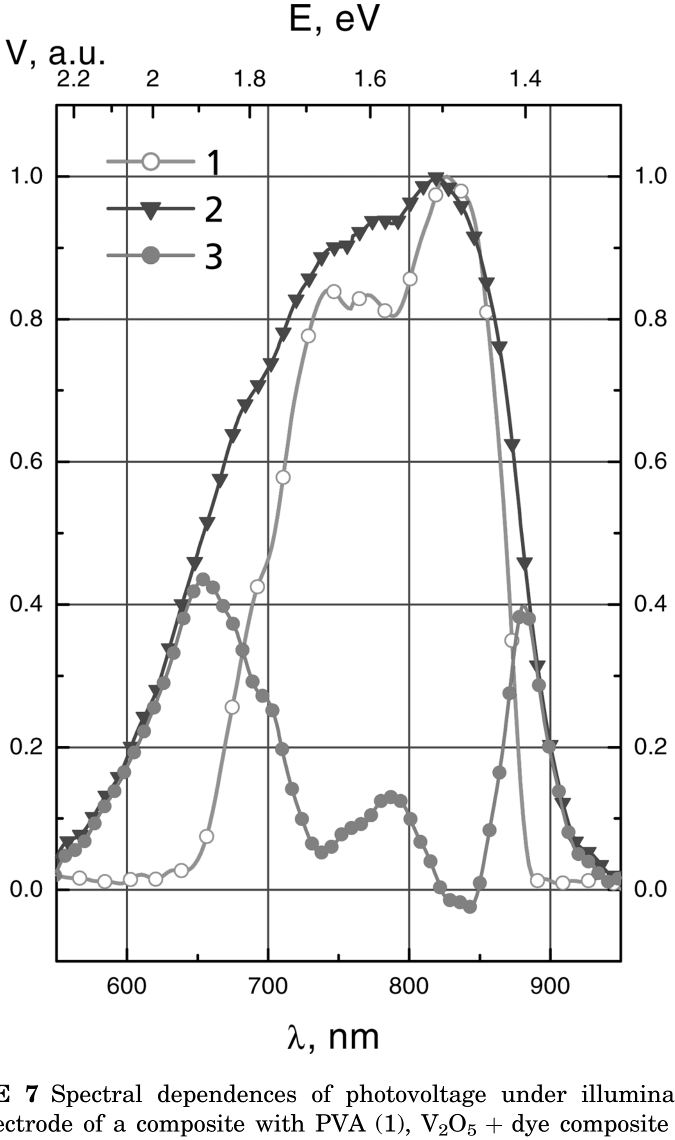

FIGURE 7 Spectral dependences of photovoltage under illumination via SnO_2 electrode of a composite with PVA (1), V_2O_5 + dye composite (2), and their ratio (3) for composite films with 44% of cyan-green.

most photosensitive is aggregate A1 with the 2.2-eV energy. The presence of shoulders on this dependence in the 1.7–2.0 eV region testifies to the formation of about 3 aggregates, whose photosensitivity decreases with decrease in their energy. However, it is impossible to

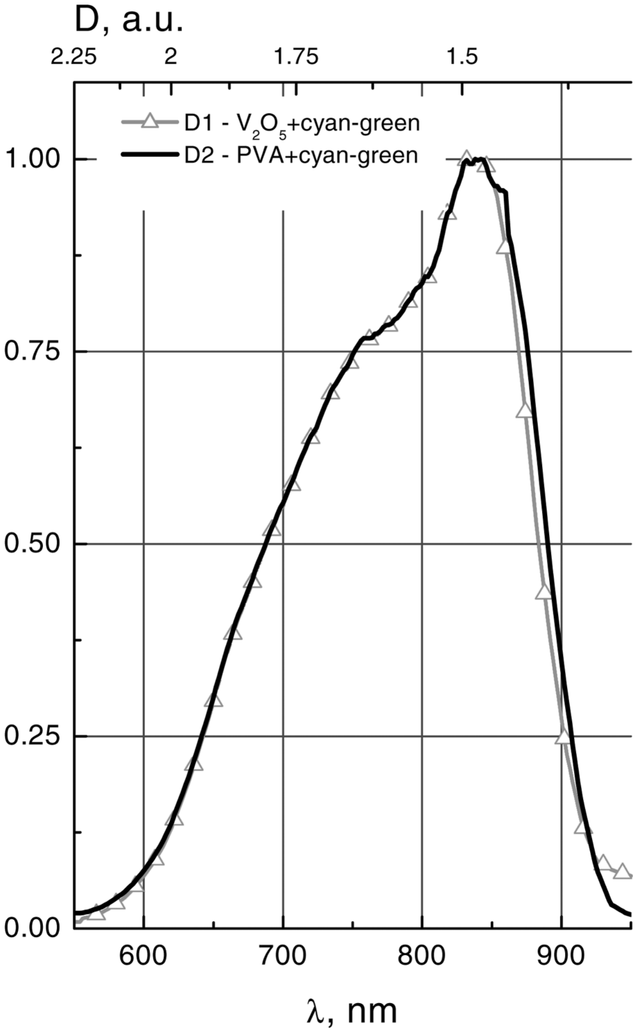

FIGURE 8 Spectral dependences of optical density D of a composite with PVA (1), V_2O_5 + dye composite (2) for samples with 44% of cyan-green.

estimate their energies from this dependence. The smallest photosensitivity is observed for A**5** aggregate with the 1.83–1.85 eV energy.

In addition, in the long-wavelength region, a photosensitive center with an energy of about 1.34 eV is also observed. Since its energy is less by 0.15 eV than the first electronic transition energy, it is most

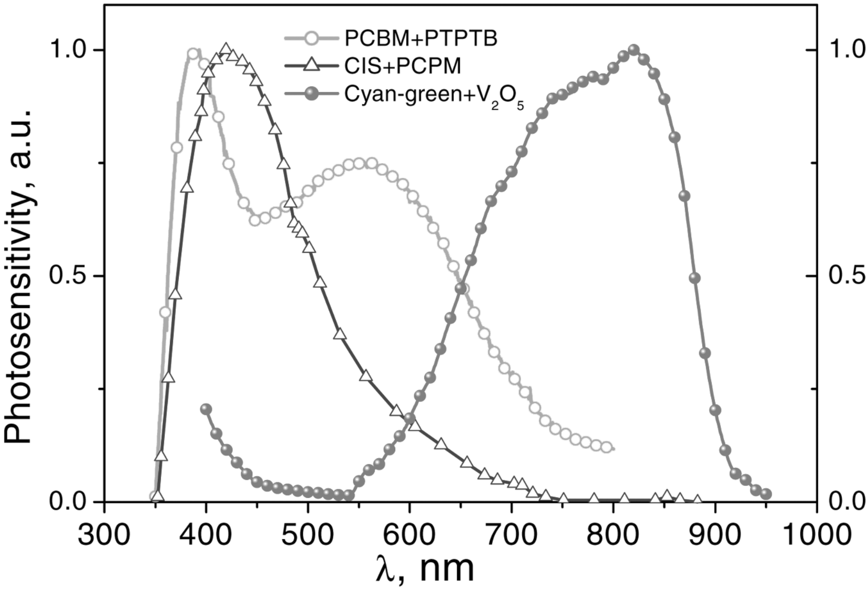

FIGURE 9 Spectral dependences of photosensitivity of a cyan-green composite sample and recently developed layers for plastic solar cells.

likely caused by the formation of a weakly bounded complex from molecules of dye and xerogel.

The measurements of the photovoltage under illumination of different sides have shown that, for all the studied samples, the photovoltage under illumination from the SnO_2-electrode side (V_e) is smaller by 30–40% than V_s and the shape of curves sufficiently differs in the region of displaying the above-mentioned aggregates (Fig. 6).

This means that some of the found aggregates and complexes can be formed both in the bulk of a composite film and mainly at its free surface. To determine the energies of aggregates and complexes which are localized mainly at the free surface, the spectral dependence of V_s/V_e is plotted (Fig. 6, curve 3). It can be seen that A2–A4 aggregates with energies 2.08, 2.00, and 1.93 eV and the complex with an energy of 1.39 eV are localized at the free surface. Probably, owing to their localization in a narrow near-surface area, they are manifested more clearly on the spectral dependence of V_s/V_e (Fig. 6) than on that of V_s/D (Fig. 5).

The relative contribution of a particular type of the aggregate of the studied dye should strongly depend on a material of the second component. To check this, we prepared the films of indocyanine green composites with polyvinylalcohol (PVA) and measured their optical and photovoltaic properties. The obtained V spectral dependences (at irradiating through a SnO_2-electrode) of composites of dye with xerogel and the water-soluble polymer (PVA) are shown in Figure 7. From the comparison of their spectral dependences, it becomes obvious that the relative contribution of the aggregates with energies 1.9–2.2 eV in V for polymer composites is more than that of the aggregates with xerogel. It can be conditioned by a greater probability of the formation of the aggregates in polymer composites (by the greater concentration) and/or by a greater efficiency of the photogeneration of charge carriers by these aggregates. From the comparison of spectra of the optical density of composite films shown in Figure 8, it is seen that their spectra practically coincide, i.e. the relative ratios of these aggregates in xerogel and polymer are practically the same. Hence, in the composites of dye with PVA, the efficiency of the photogeneration of charge carriers by the 1.93–2.0 eV energy aggregates is greater than that by the aggregates with xerogel.

The comparison of the V spectral dependence of the obtained aggregates with the spectral dependence of recently designed plastic solar devices based on the composites of conductive polymeric compounds with C_{60} [6] or CIS [7] (Fig. 9) shows that the composites studied by us absorb more effectively in the near IR part of solar radiation where the sunlight intensity is greater and less effectively in the short-wavelength part of the visible range (450–550 nm).

The obtained data allow us to hope that the use of water-soluble PPV revealing the considerable absorption and photosensitivity in the 400–550 nm region or of polyoxometalate with smaller band gap and greater photosensitivity instead of xerogel V_2O_5 will lead to an increase in the photosensitivity of composites in the short- wavelength part of the visible range and the development of polymeric composites photosensitive in the wide (400–850 nm) region of solar radiation.

CONCLUSIONS

1. The possibility of the preparation of V_2O_5 xerogel composites with water-soluble polymethine dye photosensitive in a wide spectral range (400–950 nm) has been confirmed experimentally. The photosensitivity maxima of the obtained composites are shifted to the region of a greater intensity of solar radiation, which is a necessary requirement for the development of solar devices on their base.
2. It is shown that the wider spectral region of the composites as compared to the absorption spectra of a water solution of dye is caused by the formation of a few types of aggregates of dye and complexes

of molecules of dye and xerogel which generate charge carriers more effectively than isolated molecules of dye.

3. One of the shortages of these composites is their insufficient photosensitivity in the 450–550-nm spectral range. This is caused mainly by the insufficient photosensitivity of vanadium oxide xerogel particles. The derived preliminary data for the composite of this dye with PVA allow us to assume that, to enhance the photosensitivity in the short- wavelength region, it is necessary to produce the components of this dye with water-soluble PPV or with polyoxometalates possessing the lesser width of the gap and the greater photosensitivity than the V_2O_5 composites.

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