

UDC 621

## PHOTOELECTROCHEMICAL SYSTEM BASED ON SEMICONDUCTOR NANOMATERIALS AND GRAPHENE STRUCTURES FOR SOLAR HYDROGEN PRODUCTION

G.Ya.Kolbasov, I.A.Rusetskii, I.A.Slobodyanyuk, M.O.Danilov

V.I.Vernadski Institute of General and Inorganic Chemistry of the Ukrainian NAS,  
Palladina Ave., 32-34, 03680 Kyiv 142, Ukraine, e-mail: g\_kolbasov@inbox.ru

*The photo-electrochemical processes on epitaxial films of n-GaAs and polycrystalline films CdSe after modifying their surface by nano-sized particles of CdS, Zn, Pt, graphene oxide and Nb<sub>2</sub>O<sub>5</sub> have been studied. It revealed that the modification of the electrode causes increase in their photosensitivity, which comes from reduced rates of surface recombination and photocathode reactions that take place with the participation of surface electronic states. As cathodes for the hydrogen production there were used the nano-composites based on multiwalled carbon nanotubes and reduced graphene oxide. Materials analyzed are rather promising to be used as electrodes for electrochemical cells in solar hydrogen production.*

**Keywords:** GaAs, CdSe, nanostructures, graphene oxide, reduced graphene oxide, solar hydrogen production.

### Introduction

Development of renewable energy sources is one of the most challenging scientific and technical problems of our time. In this respect, an emphasis is laid on the use of solar energy by means of semiconductor solar cell converters. Currently developed are photo-electrochemical solar energy converters to accumulate hydrogen without the gas generation phase [1, 2]. Success in using these devices is dependent on the technology of producing low-cost and effective semiconductor and electro-catalytic materials. Principal factor in the production of these is the development of methods of their synthesis, which ensure high durability and reliability of solar energy electrochemical converters. An important aspect of these systems is to increase the efficiency of photo-conversion. One of the ways to attain this goal is the

modification and nano-structuring of semiconductors to prevent the recombination of charge carriers and thus enhance their catalytic properties.

With the advent of the new nanocarbon material – graphene, a lot of papers have been published to identify their use as a base material for anode and cathode in the photo-electrochemical cells [3-5].

The aim of the work is to examine photo-electrochemical properties of GaAs and CdSe composite films with the nanostructured surface that contain graphene oxide (GO) and make it possible to determine the applicability of these films and cathode materials based on graphene structures in the photo-electrochemical system for the hydrogen production.

### Experimental results and discussion

We are engaged in studying epitaxial films of n-GaAs, ~ 1 microns thick, which are chemically deposited on a single crystal GaAs-substrate, as well as electrodes on the basis of polycrystalline CdSe. Composite photo-electrodes based on photosensitive CdSe film

were obtained by applying an aqueous dispersion of mechanical CdSe powder in the polyethylene glycol of CdCl<sub>2</sub> solution (2 mass % of CdCl<sub>2</sub>) and 0.19-2.42 mass % of graphene oxide (by weight of CdSe) on the Ti substrate with preformed layer of TiO<sub>2</sub> nanotubes. Note

that TiO<sub>2</sub> nanotubes were obtained through the use of anodic potentiostatic polarization of the titanium foil in F<sup>-</sup> ions-containing [6, 7] electrolyte. Photo-electrodes were annealed in air at 530 °C for 1 hour to prevent the possible destruction of the material [6, 8]. The surface of the electrodes was studied by means of Auger spectrometer 09-I-OC-10-005, mass spectrometer IMS4f and electron microscopes JSM 6700F and JEM-100 CXII.

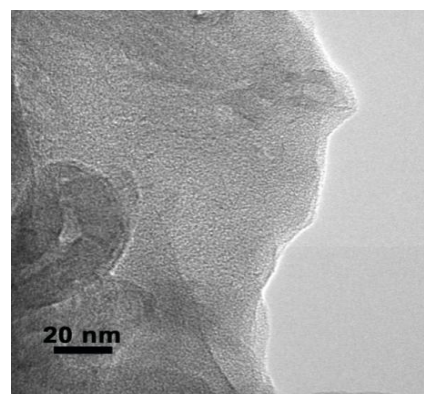
To examine the current-voltage characteristics, potentiostat-galvanostat P-8S (Elins, Russia) has been used. The electrode potential has been measured with respect to silver chloride reference electrode. Spectral dependences of photocurrent have been measured on a quartz cell that included an MDR-2 mono-chromator, and as a light source there was used a xenon lamp (DKSSH-500) with stabilized discharge current. The xenon lamp with power incident light  $P = (16 \div 50) \text{ mW} / \text{cm}^2$  was used to illuminate photo-electrode effect. Values of  $P$  have been established with help of photodiode head PD300 - UV and the display NOVA II (Ophir-Spiricon). Pulsed nitrogen laser LGI-21 ( $\lambda = 0.337 \text{ micron}$ ,  $P_i = 1300 \text{ W} / \text{cm}^2$ ,  $\tau_i = 15 \text{ ns}$ ) has been used to study the relaxation kinetics of the photo-EMF. The time resolution of the measurement setup made up 50 ns. As electrolyte, we used an aqueous solution of KOH and Na<sub>2</sub>S containing 1 mol / L of each component.

The electrodes have been modified by treatment in the solutions containing Zn<sup>2+</sup> ions. The presence of Zn on the surface was determined through the use of mass - spectrometry and by means of Auger spectroscopy; Zn concentration on the surface constituted about  $\sim 10^{13} \text{ atoms} / \text{cm}^2$ . Results of electron-microscopic analysis showed that at the resolution of  $\sim 2 \text{ nm}$  which took place during the experiment, the Zn metal nanoparticles were not observed; this may indicate that the nanoparticles have sizes, at least, 2 nm. It should be noted that similar conclusions were made by authors of [9], who carried out studies into the effect of modifying TiO<sub>2</sub> electrode by platinum on photo-catalysis; in this case the nanoparticles were not observed due to their extremely small size. We

performed deposition of CdS nanoparticles on GaAs during the formation of CdS colloidal particles in aqueous solutions. Note that an average particle diameter changed from 2 nm to 5 nm depending on the initial concentration of reagents [10]. For the deposition of Pt nanoparticles on the surface of the GaAs, there was used a method of Pt electro-deposition for chlor-platinic acid solutions under strong light on the semiconductor in the area of fundamental absorption light. Average diameters of Pt particles  $\sim 10 \text{ nm}$  on the surface coverage were 30-70%.

Nb<sub>2</sub>O<sub>5</sub> particles were deposited on the surface of CdSe by means of photo-electrochemical method from the solution of aqueous electrolyte based on poly peroxy niobium acids. Electrolyte content constituted Nb<sub>2</sub>O<sub>5</sub>·xH<sub>2</sub>O - 0.01 mol / L (in terms of pure Nb<sub>2</sub>O<sub>5</sub>); 20 ml / L the solution of 35 mass % of H<sub>2</sub>O<sub>2</sub>. The solution was adjusted to pH = 3 by sulfuric acid. The electrochemical dissolution powder of Nb<sub>2</sub>O<sub>5</sub> carried out in a pocket\_ like a titanium cathode in the solution of 40 mass % of H<sub>2</sub>SO<sub>4</sub> and 5 mass % of H<sub>2</sub>O<sub>2</sub> at a current density of  $0.5 \div 1 \text{ A} / \text{cm}^2$  [11].

Graphene oxide (GO) and reduced graphene oxide (RGO) were obtained by chemical synthesis from multiwalled carbon nanotubes (MCNT) [12-14]. An outer diameter of carbon nanotubes was about 10-30 nm; a specific surface area -  $130 \text{ m}^2 / \text{g}$ ; a bulk density -  $25\text{-}30 \text{ g} / \text{dm}^3$ ; an amount of wall from 8 to 15. Fig. 1 shows graphene oxide prepared out of multiwalled carbon nanotubes.



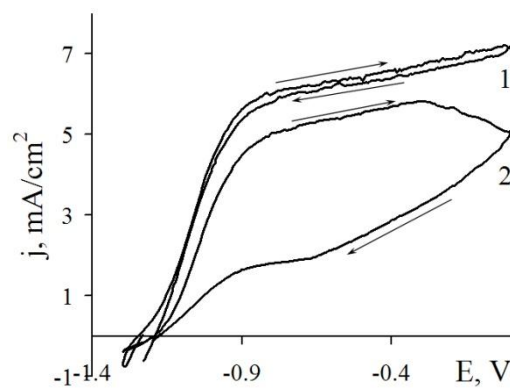
**Figure 1.** Micrograph of graphene oxide.

When using semiconductor electrodes for solar energy conversion, in particular, for

production of hydrogen, it is necessary to estimate the value of photo-voltage  $E \leq -1$  V (with respect to silver chloride reference electrode) at which hydrogen can be efficiently reduced on cathodes [2, 15]. The main difficulty in the use of relatively narrow-gap semiconductors to produce hydrogen lies in small negative value of photo-voltage ( $E_{ph}$ ) and recombination processes occurring on the surface, and as a result, low voltage of photo-electrochemical cell. Nano-structuring Ti substrate by  $TiO_2$  nanotubes contributes to the gathering of major carriers in this hetero-structure and leads to an increase of  $E_{ph}$  [6] thus improving the adhesion of photoactive coating with a substrate.

Studies into the effect of modifying the surface of a semiconductor on its surface charge, which is determined from the photo-voltage values under illumination [16] and measurements of voltage-capacitance characteristics of the Schottky layer [15] made it possible to establish that the modified  $TiO_2$  nanotubes / CdSe / GO - electrode result in raising potentials of flat bands  $E_{fb}$  in the cathode area by  $60 \div 100$  mV, which, in turn, leads to rise in photopotential  $\Delta E_{pf}$ . A similar increase in the negative area of  $E_{pf}$  after modifying the surface by Zn was observed by us in the matter of GaAs electrodes. We found that the modification of the semiconductor electrode by  $Nb_2O_5$  raises load parameters of  $TiO_2$  nanotubes / CdSe- electrode by  $10 \div 20\%$  and reduces relaxation processes arising from adsorption processes and slowing recombination processes, as well as traps carriers charge on the electrode surface (Fig. 2).

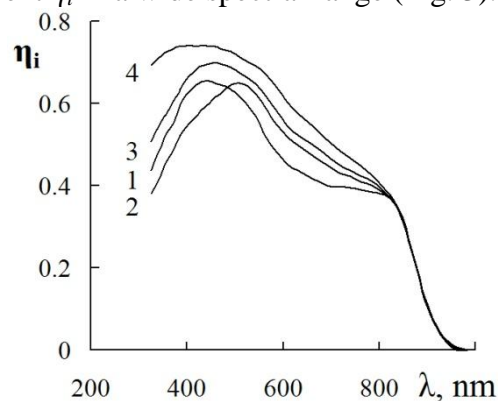
A reason for improved performance of the  $TiO_2$  nanotubes / CdSe / GO - electrode composite structure is to improve the separation of electron-hole pairs in the space charge area (SCR) modified CdSe, which contacts with the electrolyte, since graphene structures are electron acceptors [17, 18] and contribute to an increase in negative charge of the surface of semiconductor in contact with CdSe / GO and, as a consequence, leads to an increase of electric field in the SCR.



**Figure 2.** Photocurrent density  $j$  dependence on potential  $E$  for modified  $Nb_2O_5$  (1), and for initial  $TiO_2$  nanotubes / CdSe- electrode (2). 1M  $Na_2S$  + 1M  $NaOH$  solution. The light output  $P=16$   $mW/cm^2$ .

Changes in the value of flat-band potential can also be related to an increase in negative surface charge as a result of the restructuring of the "slow" surface electron states, interaction of quantum dots of metals and semiconductors with semiconductor surfaces, in particular, GaAs, and cause changes in the content of the surface oxide layer.

It was found that modification of the surface semiconductors led to an increase in quantum yield of photo-electrochemical current  $\eta_i$  in a wide spectral range (Fig. 3).



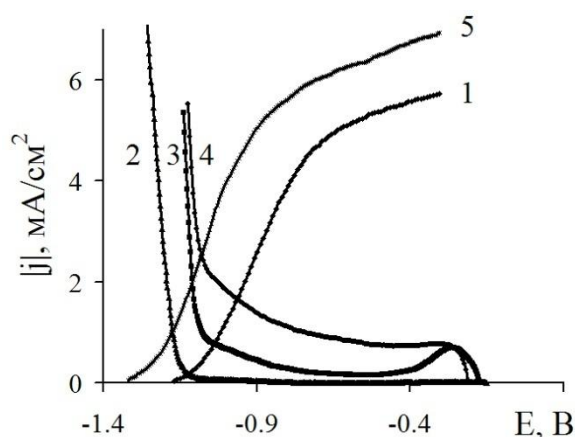
**Figure 3.** Spectral dependence of the quantum yield of photo-electrochemical current,  $\eta_i$ , in the solution of 1 mol/L KCl for a GaAs electrode at the potential  $E = 0.4$  V. 1-initial electrode, and modified with Pt (2); (3); CdS (4).

Maximum value of  $\eta_i$  for the modified GO-CdSe electrode was  $\eta_i = 0.65$  at a potential of 0.4 V. A decrease in  $\eta_i$  in the short-wavelength area of the spectrum is characterized by the start of GaAs electrode, on whose surface there were no nanoparticles (Fig. 3, curve 1) [16]. The largest increase in  $\eta_i$  was observed in the case of CdS (Fig. 3, curve 4) and the least in Pt (Fig. 3, curve 2). The deposition of Pt nanoparticles was accompanied by the increase in  $\eta_i$  in the visible area and the decrease in the ultraviolet one (Fig. 3, curve 2).

To analyze the obtained results, we applied to the theory of photo-generated charge carrier transfer across the semiconductor/electrolyte interface [15, 16] bearing in mind that the total photocurrent across the interface consists of minority-carrier current (hole photocurrent) and majority-carrier current (electronic photocurrent), while in the course of interfacial charge transfer through the interface there were involved surface electronic states. Note that the rise in the quantum yield of photocurrent,  $\eta_i$ , in the visible area after the modification of Pt, Zn, CdS and GO (Fig. 3)

surfaces may be accounted for by intensification of photo-catalytic activity of nanostructured surface and, hence, the increase in anodic photocurrent together with the decrease in the surface recombination velocity of the holes and, consequently, rise in the hole photocurrent [16]. At the same time, to explain the decrease in  $\eta_i$  after deposition of Pt in the ultraviolet area it is essential to assume that the cathodic photocurrent contributes to the rise in the cathodic reaction rate in total photocurrent. Analysis of experimental data shows that the modification of the GaAs surface by Pt gives rise to the cathodic reaction rate (in this case, the reaction of hydrogen photo evolution). This is proven by a significant decrease in the overvoltage of hydrogen evolution on GaAs after the deposition of Pt nanoparticles on its surface [19].

It should be noted that the loss of photo-generated carrier on the recombination after modification of semiconductors also manifested itself in the rise of characteristic relaxation time and the increase in photo-voltage amplitude, which leads to the rise in photosensitivity electrode.



**Figure 4.** Comparative summarized current-voltage characteristics of different photo-anodes in the solution of 1M KOH + 1M Na<sub>2</sub>S and cathodes in the solution of 30 % of KOH: CdSe –photo-anode (1); Pt – cathode (2); cathode from MCNTs with deposited Pt (3); cathode from RGO with deposited Pt (4); composite photo-anode from CdSe with 1 % of GO.  $P=16 \text{ mW} / \text{cm}^2$ . Potential sweep rate of 20 mV/s.

Fig. 4 shows the current-voltage characteristics of photo-anodes and different cathode materials for the production of hydrogen. As is seen from Fig. 4, photo-

anodes obtained provide a hydrogen evolution on platinum and carbon nano-composites. Composite photo-anodes from TiO<sub>2</sub> nanotubes / CdSe with GO have better load

characteristics than non-modified films of CdSe. As a cathode material, we applied nano-composites based on carbon nanotubes and RGO with deposited Pt. Note that modified Pt

carbon materials can effectively generate the hydrogen gas in the system, as well as on the cathodes based on RGO with essentially improved electro-catalytic parameters.

### Conclusions

It revealed that modification of the surface of CdSe and GaAs electrodes with nanoparticles of CdS, Zn, Pt, graphene oxide and Nb<sub>2</sub>O<sub>5</sub> leads to an increase in the negative surface charge, reduces the surface recombination and as a consequence raises the photo-conversion efficiency. The formation of TiO<sub>2</sub> nanotubes on titanium substrate increases the adhesion of CdSe polycrystalline, and reduces the amount of the cathode dark current. It found that base materials for the cathode in

photo-electrochemical cell for hydrogen production might be identified as materials with low hydrogen evolution over-potential and new nano-composites based on multi-walled carbon nanotubes and reduced graphene oxide, which are apparent in the reaction of hydrogen evolution close to the platinum metal. Results obtained testify that the analyzed photo-electrochemical system is highly promising for solar hydrogen production.

### References

1. Solonin Yu.M., Kolbasov G.Ya., Rusetski I.A. et al. Hydrogen storage in metal hydride under action of sunlight. *Fuel Cell Technologies: State and Perspectives, NATO Science Series. II Mathematics, Physics and Chemistry. Ed. N. Sammes, A. Smirnova, O. Vasylyev.* 2005, 202, 193–198.
2. Shcherbakova L.G., Dan`ko D.B., Muratov V.B. et al. Metal hydride use for solar energy accumulation. *NATO Security through Science Series – A: Chemistry and Biology. Hydrogen Materials Science and Chemistry of Carbon Nanomaterials. Ed. T.N. Veziroglu, S.Yu. Zaginaichenko, D.V. Schur et al.* 2007, Springer, 699–706.
3. Ng Yu.H., Iwase A., Bell N.J., et al. Semiconductor / reduced graphene oxide nano-composites derived from photocatalytic reactions. *Catal. Today.* 2011, 164 (1), 353–357.
4. Lim P.S., Pandikumar A., Huang N.M. et al. Reduced graphene oxide–titania nano-composite-modified photo-anode for efficient dye-sensitized solar cells. *International J. of Energy Research.* 2015, 39 (6), 812–824.
5. Xiang Z., Zhou X., Wan G. et al. Improving energy conversion efficiency of dye-sensitized solar cells by modifying TiO<sub>2</sub> photo-anodes with nitrogen-reduced graphene oxide. *ACS Sustainable Chem. Eng.* 2014, 2 (5), 1234–1240.
6. Rusetskii I.A., Slobodyanyuk I.A., Danilov M.O., et al. Photosensitive nano-composites based on nanotubes TiO<sub>2</sub>, CdSe and graphene oxide. *Him. Fiz. Tehnol. Poverhni.* 2016, 7(2), 195–201. (in Russian).
7. Macak J.M., Hildebrand H., Marten-Jahns U., et al. Mechanistic aspects and growth of large diameter self-organized TiO<sub>2</sub> nanotubes. *J. Electroanal. Chem.* 2008, 621 (2), 254–266.
8. Tripathy A.K., Tien H.T. Dual electrolyte-semiconductor contact CdSe electrochemical photocell. *J. of Applied Electrochemistry.* 1987, 17, 1100–1103.
9. Ikuma Y., Bessho H. Effect of Pt concentration on the production of hydrogen by a TiO<sub>2</sub> photocatalyst. *International J. of Hydrogen Energy.* 2007, 32 (14), 2689–2692.
10. Danilov M.O., Kolbasov G.Ya. Modification of carbon nanotubes with cadmium sulfide quantum dots to obtain electrode materials for current sources. *American J. of Energy Research.* 2013, 1 (2), 33–35.

11. Fomanyuk S.S., Krasnov Yu.S., Kolbasov G.Ya. et al. Electrochemical deposition of electrochromic niobium oxide films from an acidic solution of niobium peroxy complexes. *Russian J. of Applied Chemistry*. 2013, 86 (5), 644–647.
12. Danilov M.O., Slobodyanyuk I.A., Rusetskii I.A. et al. Influence of the synthesis conditions of reduced graphene oxide on the electrochemical characteristics of the oxygen electrode. *Nanoscience and Nanotechnology Research*. 2014, 2, 12–17.
13. Danilov M.O., Slobodyanyuk I.A., Rusetskii I.A. et al. Synthesis of reduced graphene oxide obtained from multiwalled carbon nanotubes and its electrocatalytic properties. *Graphene Science Handbook: Fabrication Methods*. Ed. M. Aliofkhazraei, N. Ali, W.I. Milne et al. CRC Press Taylor & Francis Group, 2016, Chapter 13, 205–226.
14. Danilov M.O., Rusetskii I.A., Slobodyanyuk I.A. et al. Synthesis and electrocatalytic properties of materials based on graphene structures. *Nanomaterial chemistry and technology*. 2016, 1 (1), 1–5. (NMCT 104:1-5).
15. Pleskov Yu.V., Gurevich Yu.Ya. *Semiconductor Photoelectrochemistry*. New York and London, Consultants Bureau, 1986.
16. Kuzminskii Ye.V., Kolbasov G.Ya. Electrochemical systems for converting solar energy. *Solar Energy Materials & Solar Cells*. 1999, 56, 93–115.
17. Williams G., Seger B., Kamat P.V. TiO<sub>2</sub>-graphene nano-composites. UV-assisted photocatalytic reduction of graphene oxide. *ACS Nano*. 2008, 2 (7), 1487–1491.
18. Lightcap I.V., Kosel T.H., Kamat P.V. Anchoring semiconductor and metal nanoparticles on a two-dimensional catalyst materials. Storing and shuttling electrons with reduced graphene oxide. *Nano Letters*. 2010, 10 (2), 577–583.
19. Rusetskii I.A., Kolbasov G.Ya., Dan`ko D.B. et al. Photo-electrochemical system for hydrogen storage based on a modified GaAs-platinum electrode. *Ukraine. Chem. Zh.* 2004, 70 (9), 44–46.

**ФОТОЭЛЕКТРОХИМИЧЕСКАЯ СИСТЕМА, ОСНОВАННАЯ НА  
ПОЛУПРОВОДНИКОВЫХ НАНОМАТЕРИАЛАХ И ГРАФЕНОВЫЕ СТРУКТУРЫ  
ДЛЯ ПРОИЗВОДСТВА “СОЛНЕЧНОГО” ВОДОРОДА**

**Г.Я.Колбасов, Л.А.Русецкий, И.А.Слободьянюк, М.О.Данилов**

*Институт общей и неорганической химии им. В.И.Вернадского  
Национальной Академии Наук Украины,  
пр. Палладина 32-34, 03680 Киев 142, Украина; e-mail: g\_kolbasov@inbox.ru*

*Изучены фотоэлектрохимические процессы на эпитаксиальных пленках n-GaAs и поликристаллических пленках CdSe после модифицирования их поверхности наноразмерными частицами CdS, Zn, Pt, оксидом графена и Nb<sub>2</sub>O<sub>5</sub>. Показано, что модифицирование электродов приводит к увеличению их фоточувствительности, что связано с уменьшением скорости поверхностной рекомбинации и фотокатодной реакции с участием поверхностных электронных состояний. Показано, что базовыми материалами катода в фотоэлектрохимической ячейке для получения водорода могут быть как известные материалы с низким перенапряжением выделения водорода, так и нанокмозиты на основе углеродных нанотрубок и восстановленного оксида графена, характеристики которых в реакции выделения водорода близки к значениям на платиновых металлах. Исследованные материалы перспективны для применения в качестве электродов электрохимических преобразователей солнечной энергии для получения водорода.*

**Ключевые слова:** GaAs, CdSe, наноструктуры, оксид графена, восстановленный оксид графена, производство “солнечного” водорода.

*Поступила в редакцию 30.10.2016.*