

Investigation of a Nanophotonic Sensor with Electrode Modified by Semiconductor Quantum Dots

O.A. Sushko, M.M. Rozhitskii*

Laboratory of Analytical Optochemotronics, Kharkiv National University of Radio Electronics, 14, Lenin Ave., 61166 Kharkiv, Ukraine

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This paper focuses on optical sensors, namely nanophotonic ones intended for liquid media contained polynuclear aromatics assay. Developed by us nanophotonic sensor includes optically transparent working electrode modified by quantum-dimensional structures such as spherical semiconductor quantum dots (QDs). Monomolecular layer of QDs is plotted onto the electrode by Langmuir-Blodgett technology. Particular attention is paid to the processes of assay in nanophotonic sensor. As an analyte we used polycyclic aromatic hydrocarbon (PAH) such as benzo[a]pyrene (BP), which is known for its carcinogenic properties. The developed nanophotonic sensor can be used in ecology for organic carcinogens detection in water objects of environment as well as for biomedical, physical chemical assays and some others.

Keywords: Analytical signal, Analyte, Band gap, Benzo[a]pyrene, Conduction band, Electrolysis, Electron transfer process, Langmuir-Blodgett technology, Luminescence, Molecular orbitals, Nanophotonic sensor, Semiconductor quantum dots, Valence band.

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1. INTRODUCTION

Sensors can collect, record, transmit, process and distribute information on the state of physical systems. Such information can be about physical and chemical properties of (in most cases) gas or liquid probes, their chemical composition and content, molecular dynamics etc. There are different types of sensors. Their principles of operation are based on known physical or chemical phenomena and properties [1].

Throughout the history of analytical chemistry one of its main objectives is to establish links between the composition of the sample and its measurement properties and to use these relationships to develop appropriate analytical methods and apparatus. The latter include physical and chemical sensors, which provide direct information about the medium composition, for example quantity definition of substances in an analyzed solution. Advances in related fields (solid state physics, nanophysics, microelectronics, microprocessor technology, nanotechnology and nanomaterials, near-field optics) led to the emergence of a new trend in sensors called nanophotonic sensors.

Nanophotonics is a quite new interdisciplinary science and technology field deals with the interaction of light and matter on a nanometer scale [2]. By adding new frontiers to nanoscale science and technology, nanophotonics provides opportunities for fundamental researches and creation of new technologies. Huge amount of research and development works in nanoscience can be considered as a realization of a famous lecture "There's Plenty of Room at the Bottom" presented by Richard Feynman in California Institute of Technology in December, 1959 [3].

Objects of nanophotonics are quantum-dimensional structures in particular QDs. Semiconductor QDs are promising candidates for the present and future of nanotechnology. The unique physical properties make QDs attractive tool for a wide range of applications in

nanophotonics, nanophotonic sensor including, materials science, biomedicine, ecology etc. [4, 5].

2. THE MAIN FEATURES OF A NANOPHOTONIC SENSOR

The main features of a nanophotonic sensor developed in this work are as follows:

- flow thin-layer cell with (at least) two optically transparent electrodes – working (WE) and auxiliary electrodes (AE);
- WE is modified by monolayer of semiconductor quantum-dimensional structures such as QDs;
- cell with electrodes is capable for accomplishment of solutions electrochemical (EC) analysis;
- non-optical excitation of QDs by electron-transfer processes (ETP) during electrolysis with subsequent light quanta emission;
- QDs are so called detector elements of the cell that represents a "nanophotonic sensor";
- monomolecular layer of QDs is attached to the WE by the Langmuir-Blodgett technology;
- inlet and outlet functions needed for test probes inserting and its deleting from the cell volume.

3. THE BASIC PHYSICAL PROCESSES IN A NANOPHOTONIC SENSOR DURING ELECTROCHEMICAL ASSAY

The process of electrolysis of solution immersed in above-mentioned cell (or nanophotonic sensor), generation and registration of analytical signals represents an assay procedure. Two types of analytical signals are been generated in pointed sensor – electrochemical current and light quanta flux emitted by quantum-confined structures – QDs. Light is emitted in a consequence of ETP between charged forms of QDs and analyte during appropriate electrode reactions.

So main physical processes occurred in a nanophotonic sensor during its operation can be divided onto

* rzh@kture.kharkov.ua

the following stages: electrochemical (with generation of electrochemical analytical signal), mass transport of analyte and optical (excitation and emission of luminescent analytical signal). Electrochemical reactions occurring in such sensor are characterized by **heterogeneous** electron transfer from (or to) WE or AE to (or from) particles (in this case – organic analyte like BP and detectors – quantum dots) having electron donor or acceptor properties. The products of such ETP are mentioned particles charged forms – ion-radicals. From the point of view of simple quantum-mechanical approach processes under consideration are electron transitions to or from corresponding energy levels in valence and conduction bands of QD or molecular orbitals (MO) of analyte, Fig. 1:

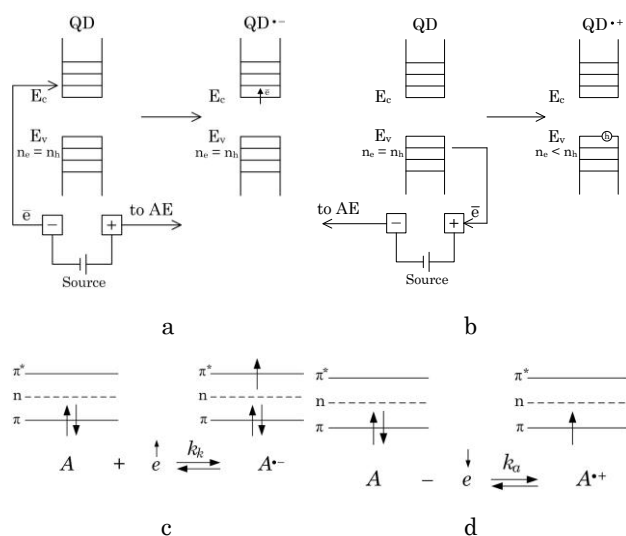


Fig. 1 – Schematic representation of electroreduction (a, c) and oxidation (b, d) processes of spherical semiconductor QDs and organic analyte *A* (PAH) in electrolyzed solution inside sensor during its operation: E_v , E_c – energy of valence band ceiling and conduction band bottom, correspondingly; π – highest occupied molecular orbital (HOMO) of *A*, π^* – its lowest unoccupied molecular orbital (LUMO); k_a , k_k – rate constants of analyte reduction and oxidation

Probability or rate constants k_{bi} of such ETP as first calculated by Marcus [6]:

$$k_{bi} = \chi_{tr} k_d \exp(-\Delta G^\# / RT), \quad (3.1)$$

where $\chi_{tr} \cong 1$, $k_d = 8RT/3000\eta$ – rate constant of diffusion meetings (η – solvent viscosity); $\Delta G^\#$ – activation energy of ETP, R – universal gas constant, T – absolute temperature.

The four possible and impossible ways of intermolecular ETP under consideration are schematically on Fig. 2. In our experiments luminescence of QDs was registered, so we can conclude that the case (b) can be realized with non-zero probability.

In nanophotonic sensor optical (luminescent) analytical signal $Nh\nu$, N – number of luminescence quanta $h\nu$ emitted during assay procedure, can be emitted by the detector elements QDs plotted as monomolecular layer on the WE when voltage needed to start appropriate electrode's Faraday processes is applied. This emission is a consequence of "heterogeneous" ETP, but

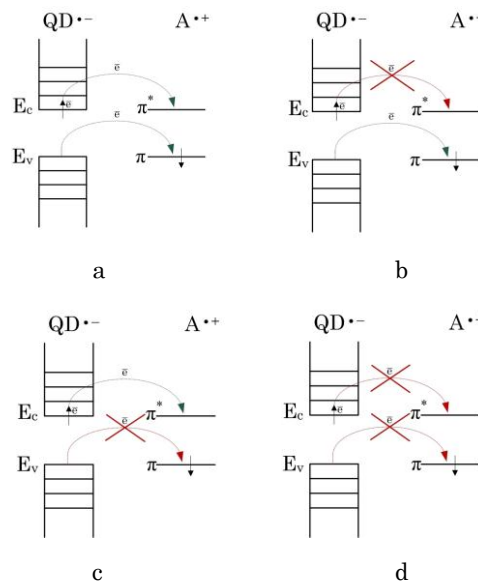


Fig. 2 – The possible and impossible ways of intermolecular ETP between ionic forms of QDs ($QD^{\bullet-}$) and analyte ($A^{\bullet+}$)

not between electrode and electroactive particles, but between charged particles immobilized in modified WE surface, namely, quantum dots, and oppositely charged analyte particles. As an example for negatively charged WE (cathode) and positively charged AE (anode) mentioned physical processes in nanophotonic sensor can be presented in scheme shown in Fig. 3:

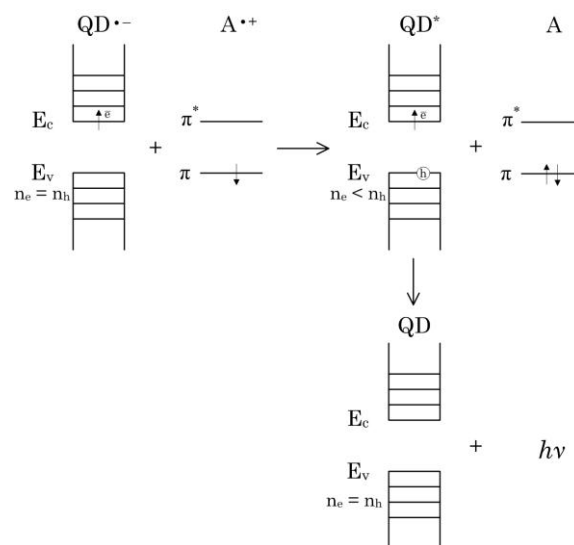


Fig. 3 – Scheme of ETP between organic analyte (PAH) and quantum dots immobilized on WE: (QD^* – excited state of QD)

As can be seen from this scheme, there ought to be fulfill several conditions for its realization with analytical optical signal emission.

1) Both analyte (PAH molecule) and QD (detector nanomaterial) must be electroactive in appropriate electrode processes (Faraday redox-reactions). This condition is valid for all PAHs substances benzo[a]pyrene including, but for semiconductor QDs it ought to be established for every nanomaterial under consideration depending upon its chemical composition and type of cover shells (see ref. [7, 8], where electro-

chemical behaviour of CdSe and CdTe QDs were studied under different conditions).

2) Electron transfer between the ionic forms of the quantum dot and the analyte will be possible if the QD band gap energy ΔE_{BG} will be equal to or less than the difference ΔE_A between energies of HOMO and LUMO of analyte molecule A:

$$\Delta E_{BG} \leq \Delta E_A. \quad (3.2)$$

From the point of view of energy that will be released in *exothermic* ETP processes under consideration it means also that free Gibbs energy ΔG of such ETP ought to be not less than the band gap of given QD (see below).

(Realization of this condition can increase the assay selectivity significantly).

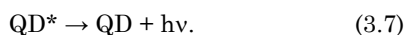
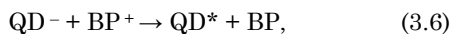
3) Time of mass transfer of analyte charged particles from AE to WE must not exceed their life-time. Only in this case one can expect analyte ions charge-transfer recombination with the oppositely charged QDs attached to the WE. For sensor under consideration it is fulfilled because of very small distance between WE and AE (thin-layer cell construction).

4) Non-zero probability of products of the mentioned recombination formation, namely, excited forms of QDs*. From physical point of view such non-optical excitation of semiconductor quantum dots means that electron moves from the charged analyte LUMO (where it was transferred from AE charged as a cathode) to QD conduction band. Emission of a photon $h\nu$ is possible during inter-band transition from conduction to valence bands. After recombination analyte charged particles are returning to ground state, moving to AE with subsequent participation in heterogeneous ETP starting new cycle of assay.

The total number of luminescence quanta N emitted during time of assay procedure $\Delta t = t_f - t_i$, t_f – final, t_i – initial time of assay, is a measure of analyte content c_a .

$$N = \int_{t_i}^{t_f} n(t) dt = f(c_a), \quad (3.3)$$

where $n(t)$ – current photon flux at time t . Function f can be linear but, more often, non-linear dependence that can be linearized by known standard procedures. With the help of calibration graph $N = f(c_a)$ obtained for test probes one can determine quantitatively the analyte content by measurement of optical (luminescent) signal. This characterizes the essence of nanophotonic detection method. The scheme of its realization using analyte (benzo[a]pyrene, BP) MO and quantum-confined structure energy levels approach shown on Fig. 2 can be presented as follows (the case of WE as cathode and AE as anode is presented, but the oppositely charged electrodes and respective particles can be used for assay also):



4. SEMICONDUCTOR QUANTUM DOTS AS DETECTOR ELEMENTS OF A NANOPHOTONIC SENSOR

Generally three types of semiconductor QDs structures are known, namely, core, core-shell and core-shell with polymer coating structures (Fig. 4).

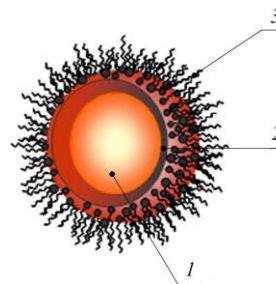


Fig. 4 – Schematic representation of colloid semiconductor QDs with CdSe core (1), ZnS shell (2) and hydrophobic polymer trioctylphosphine oxide (TOPO) coating (3)

Properties of semiconductor QDs essential for their use in assay technologies include high extinction coefficient at optical excitation and rather high yield of excited states at non-optical (by charge recombination) excitation; stability to photochemical and electrochemical processes; narrow and symmetric emission spectrum, its dependence upon QDs diameter. Those features represent also main advantages of semiconductor QDs in comparison with organic luminophores. As an example illustrating mentioned dependence Fig. 5 shows change in band gap energy and corresponding shift of emission to hypsochromic side of optical spectrum with decreasing of the QDs cores diameters [9].

QDs can be considered in some cases as large molecules. So QDs as for the most organic molecules can be characterized by oxidation and reduction processes [10]. These processes are illustrated schematically on Fig. 1.

When the working electrode potential is negative, electrons are injected into the conduction band (CB) and QD becomes an anion. Similarly if the WE potential is positive the electrons from QD CB move to appropriate energy states of WE (if its base is optically transparent ITO – to its CB also) with QDs transformation to the radical cation.

For the detector elements used in the proposed sensor device it is necessary to analyze energy peculiarities of quantum confinement nanoparticles. Because of a very small size of semiconductor QDs their physical properties differ significantly from those of bulk materials.

Bohr exciton radius in QD (Fig. 6) is determined by the following equation:

$$\alpha_B = \frac{\varepsilon h^2}{\mu e^2}, \quad \mu = \frac{m_e^* m_h^*}{m_e^* + m_h^*},$$

where ε is the dielectric constant of the QDs core; h is Planck's constant; μ is reduced effective mass of an electron-hole pair; e is the electron charge; m_e^* , m_h^* is the effective mass of charge carriers (electrons or holes).

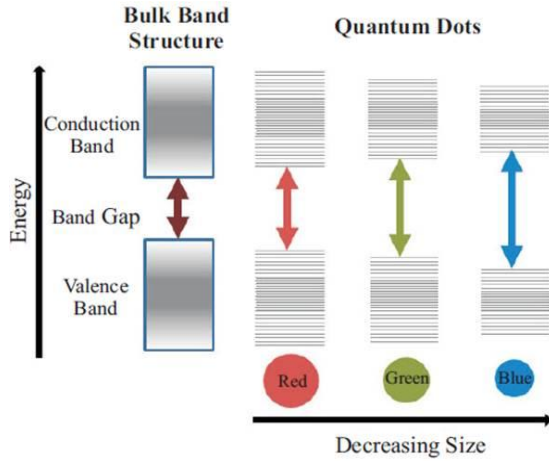


Fig. 5 – Dependence of quantum confined semiconductor band gaps and emission wavelength on QDs diameter

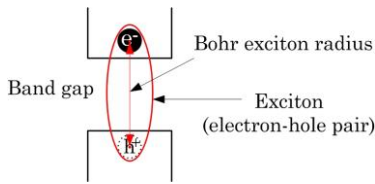


Fig. 6 – Bohr exciton radius in QD: h^+ – hole; e^- – electron

In a bulk semiconductor the distribution of energy levels in the conduction and valence bands are continuous, so electrons and holes can occupy any energy level depending on band gap and exciton energy. When the size of the semiconductor material decreases quantum confinement becomes noticeable. This leads to atomic-like energy levels distribution inside potential well representing a given quantum dot with distance between levels enlargement while QDs radius is diminished (effect of correlation of QDs radius and luminescence spectrum).

There are in general strong, average and weak quantum confinement regimes for QDs [11]:

- a) strong confinement mode ($r_{QD} \ll \alpha_B$). In this case the radius of the nanoparticles r_{QD} is less than $2\alpha_B$ ($r_{QD} \leq 2\alpha_B$). As a result, the exciton states can be considered as pure separate states of electrons and holes;

- b) average confinement mode ($\alpha_e > r_{QD} > \alpha_h$, where α_e

- Bohr radius of the electron; α_h – Bohr radius of the hole);
- c) weak confinement mode ($r_{QD} \gg \alpha_B$). When exciton can be considered as quasi-particle having effective mass $m_{ex}^* = m_e^* + m_h^*$.

In the last case a quantization of energy takes place. The result is the energy levels structures in the valence and the conduction bands. Consequently the luminescence spectrum in this case is converted into discrete bands.

The illustration of quantum confinement one can see on Fig. 7 showing the distribution of energy levels for a particle in a potential well (Fig. 7b) is having length a :

$$E_l = \frac{\hbar^2 \cdot n^2 \cdot \pi^2}{2m^* a^2},$$

where n is the principal quantum number; m^* is the effective particle mass. For spherical QD one outlet to use QD radius r_{QD} instead of a .

For a description of optical phenomena in semiconductor nanomaterials the effective mass approximation (EMA) model is used, which describes the transition of an electrons to the CB with the creation of holes in the valence band. The model is based on the effective mass of the electron (m_e^*) and hole (m_h^*).

EMA is based on the following assumptions:

- a) the QDs crystal structure is the same as in the bulk material;
- b) QD possesses spherical shape with a radius of r ;
- c) potential barrier is infinite at the QDs surface.

In the case of semiconductor nanoparticles energy band edge of delocalized electrons and holes can be described by quadratic equations

$$E_c = \frac{\hbar^2 \cdot k^2}{2m_e^*},$$

$$E_v = \frac{\hbar^2 \cdot k^2}{2m_h^*},$$

where k is wave vector modulus.

For an infinite potential outside and zero potential inside the nanoparticle it is proposed the following equation for determining the band gap (E_g) of spherical nanoparticle depending on its radius:

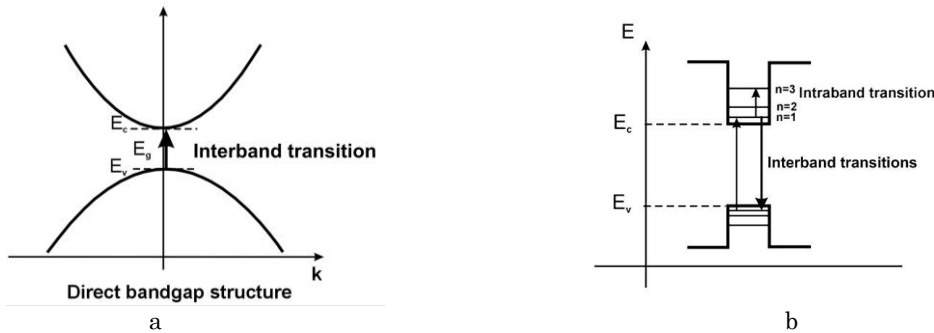


Fig. 7 – Quantum confined limitation of semiconductor nanomaterial like QD (b) compared with the bulk semiconductor (a)

$$E_g = E_g^{bulk} + \frac{\hbar^2 \pi^2}{2er^2} + \left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right) - \frac{1,8e^2}{4\pi\epsilon\epsilon_0 r} - \frac{0,124e^3}{\hbar^2 (4\pi\epsilon\epsilon_0)^2} \left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right)^{-1},$$

where E_g^{bulk} is the band gap of the bulk semiconductor of the same type as QDs; $m_0 = 9,1 \cdot 10^{-31}$ kg is mass of electron; r is QDs radius [12].

Based on this formula the calculated dependences of the band gap E_g on the radius r of the spherical QDs of CdSe and CdTe type using the software package Mathematica 9.0.1 are presented on Fig. 8.

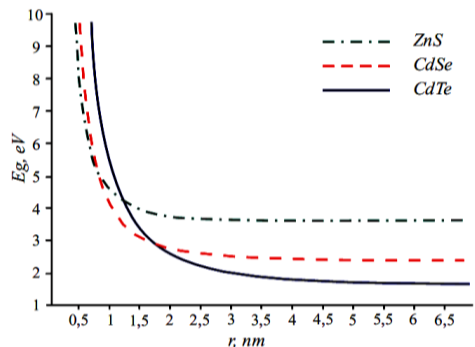


Fig. 8 – Calculated dependences of the QD band gap on its radius for ZnS, CdSe and CdTe QDs

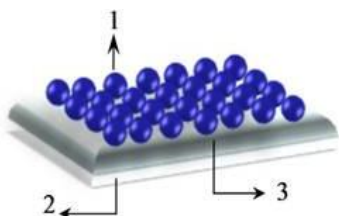


Fig. 9 – Scheme of the sensor working electrode: 1 – semiconductor QDs; 2, 3 – glass substrate with ITO coating

As the part of this work the most suitable for creating detector elements of the developed sensor device were selected CdSe QDs based on the nature of a sharp change of the band gap QD on its radius. This makes it possible

to improve the metrological characteristics of the sensor device for organic carcinogen in water solutions detection [13]. Physical-chemical parameters of CdSe QDs are shown in Table 1.

Developed nanophotonic sensor device presents flow cell with working and auxiliary electrodes [15]. The WE is performed from optically transparent glass substrate which is modified by transparent conductive coating such as indium oxide (In_2O_3) for electrical conductivity providing (Fig. 9). Ordered monomolecular layer of semiconductor QDs is applied on surface of the substrate by Langmuir-Blodgett technology [16].

Modification of the WE by QDs is not only significantly reduces the amount of consumables reagents, but also makes it possible to reuse sensor device.

5. EXPERIMENTAL METHODS AND RESULTS

Procedure of preparation and investigation of QDs detector layer on WE is shown on Fig. 10, 11

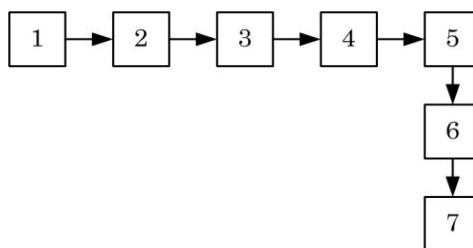


Fig. 10 – Preparation and investigation of modified WE: 1 – ITO substrate preparation (washing, drying), 2 – preparation of initial composition for LB through and its plotting onto the ITO substrate; 3 – preparation of QDs solution and their plotting on prepared ITO surface by LB technology; 4 – atomic force microscopy (AFM) testing of modified WE surface; 5 – spectroscopic testing; 6 – sensor’s EC studies; 7 – sensor’s luminescence studies

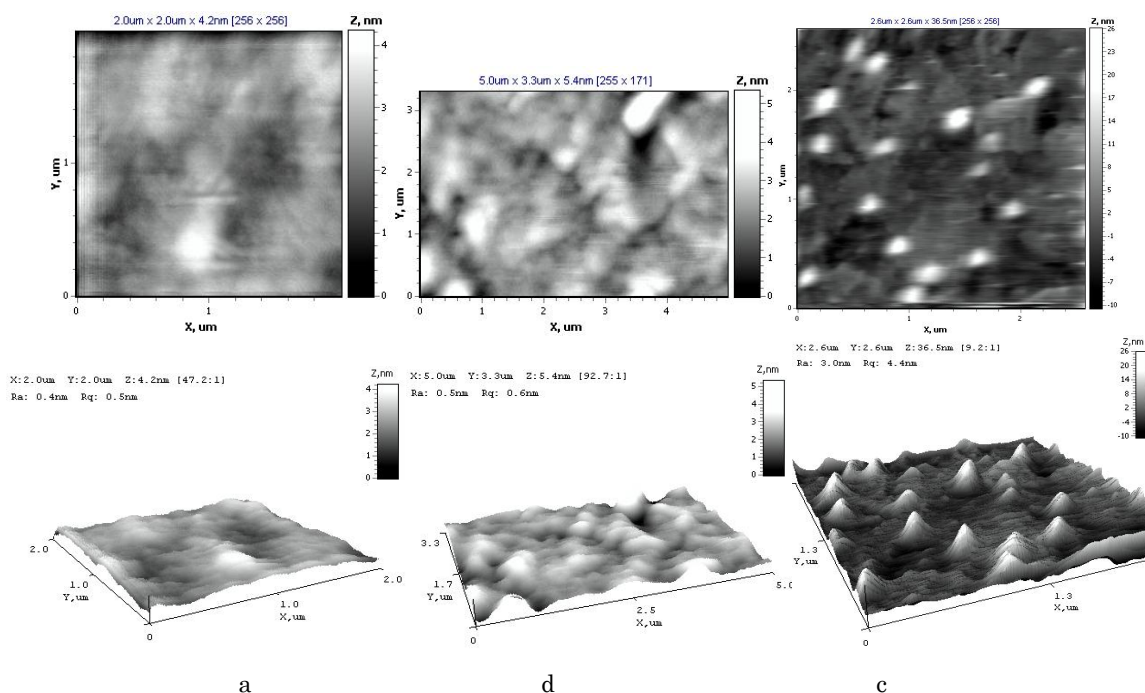


Fig. 11 – AFM investigation of WE: a – empty ITO substrate; b – ITO substrate + polyvinylcarbazole layer (by spin-coating method); c – ITO substrate + polyvinylcarbazole layer + CdSe / ZnS with TOPO coating QDs

Table 1 – Physical-chemical parameters of CdSe QDs [14]

QDs diameter, nm	Shell	Cover	λ_{exc} fluorescence, nm	ϕ_{ox} , V	ϕ_{red} , V	E_{BG} , eV
3.8	ZnS	TOPO	590	+ 1.77	- 1,25	2.0

The scheme of experimental set used for nanophotonic sensor testing is presented on Fig. 12.

The object of the analysis with use of sensor device was *Benzo[a]pyrene* $\geq 96\%$ by *Sigma-Aldrich Corporation*. In work we used such solvents as double distillation water and dimethylformamide (DMF) qualification "chemically pure" purified by the known method [17].

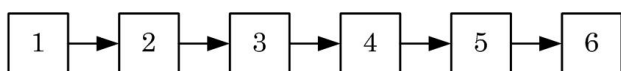


Fig. 12 – Composition of sensor device and its testing: 1 – auxiliary electrode preparation; 2 – sensor composition from WE and AE; 3 – sensor filing with test probe; 4 – sensor putting into test cell of ELAN-3d; 5 – measurement of EC and luminescent signal; 6 – data storage and acquisition

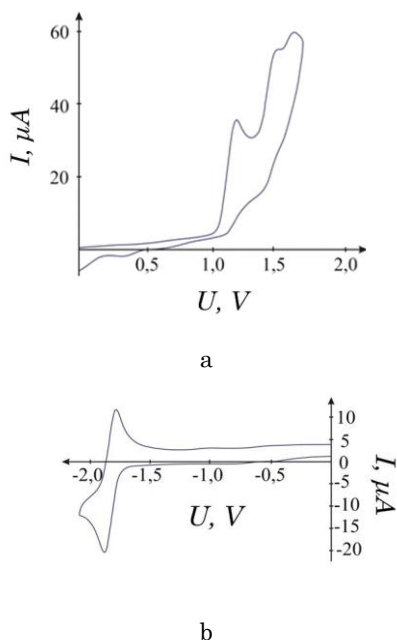


Fig. 13 – EC study of BP as analyte in water model solution (solvent – dimethylformamide:H₂O, 1:1; BP concentration – $4.1 \cdot 10^{-4}$ M): a – oxidation; b – reduction

On Fig. 13a, b sensor's EC testing are presented. First 3 ml of the BP solution in DMF – water with concentration $4.1 \cdot 10^{-4}$ M was prepared. Part of this solution was placed in an electrochemical cell of analyzer ELAN-3d which was developed by Laboratory of Analytical Optochemotronics scientists. This device allows registering the oxidation, reduction and electrochemiluminescent properties of tested solutions. Results of BP EC studies are shown on Fig. 11a, b.

Measured BP luminescence spectrum in the DMF – water mixture by Ocean Optics Spectrometer QE65000 is shown on Fig. 14. There is a luminescence maximum of BP at a wavelength of 430 nm.

It was further prepared 10 different model solutions of BP in DMF–water mixture with known concentrations.

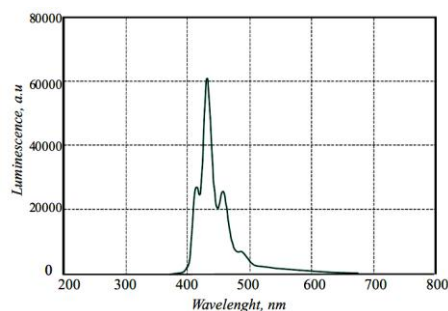


Fig. 14 – Luminescence spectrum of BP in DMF-water mixture (1 : 1)

Each of the model solution was placed in nanophotonic sensor and photon flux during certain time interval (usually 10 s) was measured as photomultiplier tube (PMT) current i_{PMT} in nA. After calibration graph was built (Fig. 15) which can be used for BP detection in water solutions.

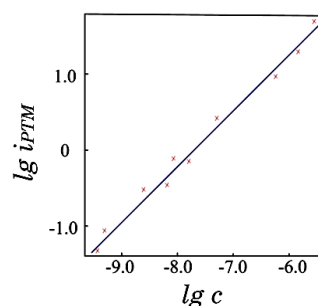


Fig. 15 – Calibration graph for BP detection in DMF-water mixture: c – in mole/l, PTM type *Hamamatsu H5784-20*

Consumption of detector (QDs) doesn't occur during the assay procedure because they are fixed on the WE surface.

For this reason, the analysis becomes more economical and environmentally safe (attached to WE detector elements are not washed during procedure of sensor cell washing) detector layer.

6. CONCLUSIONS

In this work the development and study of main physical (optical) processes in sensor based on semiconductor light-emitting nanostructures to measure the content of organic carcinogens in liquid media environment water including are described. The advantage of such type of so called nanophotonic sensor are low detection limit (nmole/l), high selectivity, simplicity and low cost of design and construction, small time of assay (about 10 min. with sample preparation). Changing the detector elements – semiconductor QDs – can result in the possibility of multiplex sensors creation important for obtaining devices with high selectivity important for assays of multicomponents probes.

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Дослідження нанофотонного сенсора з електродом модифікованим напівпровідниковими квантовими точками

О.А. Сушко, М.М. Рожицький

Лабораторія Аналітичної оптикоелектроніки, Харківський національний університет радіоелектроніки, пр. Леніна, 14, 61166 Харків, Україна

Подана стаття присвячена оптичним сенсорам, серед яких нанофотонні, призначені для аналізу рідких середовищ, в тому числі для визначення поліядерної ароматики. До складу розробленого нанофотонного сенсора входить робочий електрод, поверхня якого модифікована квантово-розмірними структурами, такими як сферичні напівпровідникові квантові точки (КТ). Мономолекулярний шар КТ наноситься на електрод методом Ленгмюра-Блоджетт. Особлива увага в роботі приділяється процесам, які відбуваються у нанофотонному сенсорі при визначенні аналіту. Аналітом виступають поліциклічні ароматичні вуглеводні (ПАВ), на прикладі бензо[а]пірену (БП), який відомий своїми канцерогенними властивостями. Розроблений нанофотонний сенсор може бути використаний в екології для виявлення органічних канцерогенів у водних об'єктах навколишнього середовища.

Ключові слова: Нанофотоніка, Нанофотонний сенсор, Напівпровідникові квантові точки, Бензо[а]пірен, Поліциклічні ароматичні вуглеводні.

Исследование нанофотонного сенсора с электродом модифицированным полупроводниковыми точками

О.А. Сушко, Н.Н. Рожицкий

Лаборатория Аналитической оптикоелектроніки, Харьковский национальный университет радиоэлектроніки, пр. Ленина, 14, 61166 Харьков, Украина

Представленная статья посвящена оптическим сенсорам, среди которых нанофотонные, предназначенные для анализа жидких сред, в том числе для определения полиядерных ароматики. В состав разработанных ного нанофотонных сенсора входит рабочий электрод, поверхность которого модифицирована квантово-размерными структурами, такими как сферические полупроводниковые квантовые точки (КТ). Мономолекулярный слой КТ наносится на электрод методом Ленгмюра-Блоджетт. Особое внимание в работе уделяется процессам, которые происходят в нанофотонном сенсоре при определении аналита. Аналитом выступают полициклические ароматические углеводороды (ПАУ), на примере бензо[а]пирена (БП), который известен своими канцерогенными свойствами. Разработанный нанофотонный сенсор может быть использован в экологии для определения органических канцерогенов в водных объектах окружающей среды.

Ключевые слова: Нанофотоника, Нанофотонный сенсор, Полупроводниковые квантовые точки, Бензо[а]пірен, Полициклические ароматические углеводороды.

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