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Short Communication

Optical Properties of ZnSe Quantum Dots in Carbon Matrices

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The ZnSe quantum dots in a matrix of nanoporous carbon are synthesized in the work. For this purpose, nanoporous carbon was synthesized with the required pore size distribution. From the received photoluminescence spectra, it was found that the peak near the band edge in the excitation spectrum can be assigned to the highest transfer efficiency of photogenerated carriers at the correlated sub-band states (about 34 meV below the conduction band of ZnSe) to the deep center states.

Keywords: Quantum dots, ZnSe, Nanoporous carbon, Photoluminescence spectra.

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1. INTRODUCTION

In recent years, optical investigations on single semiconductor quantum dots (QDs), often designated as «artificial atoms», opened a new and exciting field of basic physics studies. In contrast to «real» atoms or molecules, a unique feature of solid state QDs is the formation of Wannier excitons giving experimental access to both the Coulomb and the electron-hole (e-h) exchange interaction in three-dimensional confined solid state systems. Therefore, semiconductor QDs with geometries smaller than or comparable to the bulk exciton Bohr radius can be regarded as a model system in order to study the impact of Coulomb and exchange interaction on the optical properties of zero-dimensional excitons and excitonic complexes [1].

Quantum confinement of both the electron and hole in all three dimensions leads to an increase in the effective band gap of the material with decreasing crystallite size. Consequently, both the optical absorption and emission of QDs shift to the blue (higher energies) as the size of the dots gets smaller.

ZnSe QDs are key research interest of many groups from past few decades because of their novel optoelectronic properties. It is a direct wide band gap semiconductor having a band gap of 2.70 eV. ZnSe based QDs have many applications in various fields such as solar cells, scintillators, Schottky diodes etc.

2. MATERIALS AND METHODS

For the implementation of semiconductor QDs with high quantum efficiency, several methods have been developed that allow them to be obtained in corresponding matrices. The promising material of the matrix is nanoporous carbon, which can be controlled to obtain the required pore size.

Nanoporous carbon material (NCM) was obtained from the plant biomass using thermochemical activation by potassium hydroxide. The biomass precursor has been dried under 80 °C until the mass is stabilized and then fractioned onto 0.25-1 mm particles. The carbonization of the grinded apricot kernels has been conducted in the closed oven under 380-400 °C temperature with heating speed of 10 °C/min. Resulting carbonized material has been mechanically grinded to obtain the fraction size 200-250 μm and mixed with equal quantities of potassium hydroxide and water. This mixture was thoroughly stirred during 1-2 hours and then dried in the thermostat under the constant temperature of 90 °C until the mixture mass stabilization. This dry substance was placed into the oven and heated in the argon atmosphere up to the 850-920 °C with heating speed of 10 °C/min, keeping the given temperature for 20 min. After the cooling, the resulting substance has been washed in the 5 % HCl solution with distilled water to reach the neutral pH and dried under 90 °C until the mass is stabilized. The resulting NCM is marked as NCM-1.

Another NCM for the comparison (NCM-2) was obtained using the method of the carbonization of phenol-formaldehyde resin.

Two obtained types of the nanoporous carbon (depending on the technological conditions) were incorporated later into the QD pores.

The porous structure properties (total surface area and total pore volume) of the NCM have been determined based on the nitrogen adsorption/desorption isotherms analysis under its boiling temperature (77 K) obtained using the Quantachrome Autosorb Nova 2200e appliance. The carbon samples have been decontaminated under 180 °C during 18 hours before the analysis. The resulting properties of the carbon materials porous structure by the analysis of adsorption/desorption isotherms are the following: 1) total surface area (S_{BET}) by Multipoint BET method in the isotherm area limited to the relative pressure range of $P/P_0 = 0.050…0.035$; 2) total pore volume (V_{total}, cm^3/g,) calculated by nitrogen sorption amount under $P/P_0 \sim 1$; 3) micropore volume (V_{micro}, cm^3/g) and micropore/mesopore (S_{micro}, S_{mezo}, m^2/g) specific surface areas, found using t-method and DFT theory.

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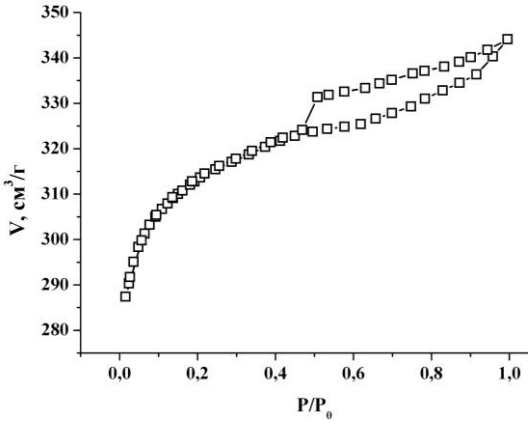
To obtain ZnSe:C QDs, 0.8 g of gelatin, 0.8 g of carbon and 50 ml of distilled water were used, the resulting mixture was heated to 200 °C and kept for 3 hours, followed by natural cooling to room temperature. Subsequently, 1.48 g of ZnSe were added, carefully stirred, heated to 200 °C and held for 2.5 hours. Centrifugation at 1600 rpm for 30 min, the resulting material was dried for 14 hours at 74 °C.

Spectral-luminescent properties were studied on the FLS920 Photoluminescence Spectrometer manufactured by Edinburg Instruments.

3. DISCUSSION OF RESULTS

The nitrogen adsorption/desorption isotherms for carbon materials NCM-1 and NCM-2 are shown in the Fig. 1.



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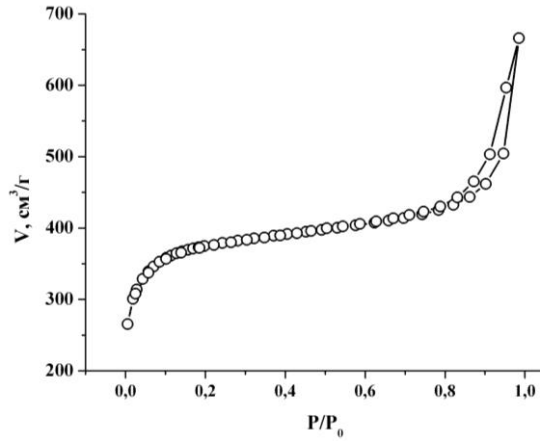

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Fig. 1 – Nitrogen sorption isotherms (77 K) for carbon materials: NCM-1 (a), NCM-2 (b)

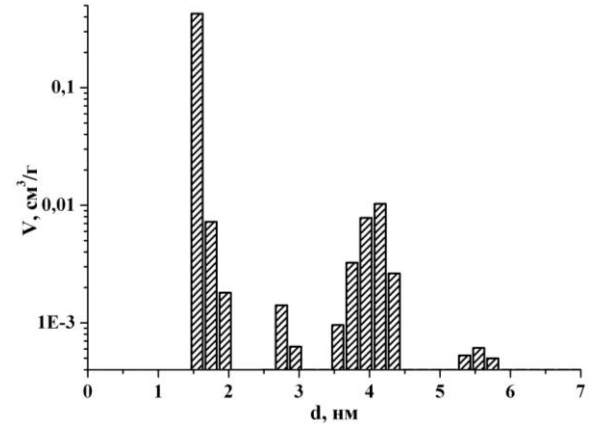
Isotherms (Fig. 1) are typical for the polymolecular adsorption in the micro- and mesopores in the materials of organic origin [2]. All the samples demonstrate hysteresis loop of H4 type by the IUPAC classification [3] that is known as related to the capillary condensation in the mesopores. The isotherm adsorption graph line growth near the $P/P_0 = 1$ is caused by multiple nitrogen condensations and evaporations in the micro- and mesopores.

The main parameters of the NCM nanostructure are shown in the Table 1.

NCM pore size distribution was evaluated using the density functional theory (DFT) (Fig. 2). The inspected NCMs have a large quantity of micropores that significantly increases the specific surface area, as it is shown in Table 1 and Fig. 2. Mesopores amounted to 8-12 % of the total quantity of pores in the mentioned carbon materials.

Table 1 – Structural and adsorption properties of the NCM

Parameter	NCM-1	NCM-2
Surface area Multipoint BET, m^2/g	1438	1187
Total pore volume, cm^3/g	1.03	0.521
Micropore volume, cm^3/g	0.57	0.452
Micropore surface area, m^2/g	1275	1110
Pore average diameter, nm	2.86	1.76



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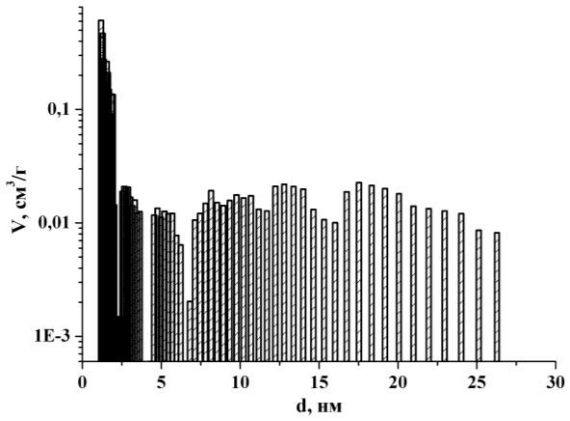

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Fig. 2 – Pore size distribution (DFT method) for NCM: NCM-1 (a), NCM-2 (b)

The examined NCMs (NCM-2 samples in particular) have pores of all sizes in range 1-20 nm with maximum quantity at 1.5-1.7 nm; pores near 5-15 nm are amounted to 15 % of total pore count. There are 1.4-5.8 nm pores in the NCM-1 samples, with size distribu-

tion maximum in range r = 0.8-1 nm; pores near 2-5 nm are amounted to 10 % of total.

Fig. 3 shows the photoluminescent (PL) spectra of ZnSe:C measured at different excitation wavelengths at room temperature (T = 300 K) and low excitation density. At the excitation with λ = 466 nm a single intense PL band is observed centered at λ = 643 nm (1.928 eV) that has near-Gaussian line shape. Taking into account that the energy band gap of bulk ZnSe at room temperature is 2.7 eV (459 nm), the PL emission is spectrally shifted to red side by 0.772 eV. This strong red shift gives ground to attribute this emission to a deep center one. Earlier, such PL bands were observed in ZnSe nanowires [4, 5], ZnSe nanoribbons [6].

It has been shown that such deep center emission is strongly dependent on the excitation intensity and temperature. The line shape evolves into multiband

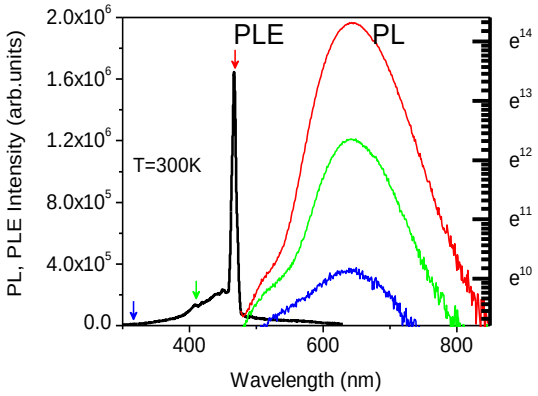

Fig. 3 – PL and PLE spectra of ZnSe:C measured at room temperature

structure which results from the saturation of the DD state from deeper to shallower energy level in ZnSe nanoribbons. Such a mechanism can be actual also for the ZnSe:C structure. In order to get more information about the origin of 643 nm emission, the PL excitation spectrum has been recorded at the λ = 643 nm, at room temperature. As can be seen from Fig. 3a, a strong resonance at λ = 466 nm takes place. The latter implies that the 466 nm transition mainly contributes the emission at 643 nm. While this resonance is observed very close to the ZnSe band edge, one can attribute it to the exciton transition. However, the exciton binding energy in ZnSe is ~ 14 meV and at room temperature the excitons will be dissociated. On the other hand, we do not see any near-band emission in Fig. 1. Therefore, the peak near the band edge in the excitation spectrum can be assigned to the highest transfer efficiency of photogenerated carriers at the correlated subband states (about 34 meV below the conduction band of ZnSe) to the deep center states. It is seen also from Fig. 1 that the change of the excitation wavelength, practically, does not shift the position of the PL maximum, and only short wavelength tail of the PL band weakly reacts on this change.

4. CONCLUSIONS

1. The ZnSe QDs in a solid-state matrix of nanoporous carbon are obtained.

2. It was found that the peak near the band edge in the excitation spectrum can be assigned to the highest transfer efficiency of photogenerated carriers at the correlated subband states (about 34 meV below the conduction band of ZnSe) to the deep center states.

REFERENCES

1. S.D. Bardashevska, I.M. Budzulyak, S.I. Budzulyak, B.I. Rachii, *J. Nano- Electron. Phys.* **10**, 06024 (2018).
2. H. Marsh, F. Rodriguez-Reinoso, *Activated carbon* (Amsterdam: Eslevier: 2006).
3. E. Fitzer, K.-H. Kochling, H.P. Boehm and H. Marsh, *Int. Union Pure Appl. Chem.* **67**, 473 (1995).
4. X.T. Zhang, Z. Liu, K.M. Ip, Y.P. Leung, Q. Li, S.K. Hark, *J. Appl. Phys.* **95**, 5752 (2004).
5. U. Philipose, S. Yang S, T. Xu, Harry E. Ruda, *Appl. Phys. Lett.* **90**, 063103 (2007).
6. C. Fan, Q. Zhang, X. Zhu, X. Zhuang, A. Pan, *Sci. Bull.* **60**, 1674 (2015).

Оптичні властивості квантових точок ZnSe в вуглецевих матрицях

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У роботі синтезуються квантові точки ZnSe в матриці нанопористого вуглецю. Для цього синтезували нанопористий вуглець з необхідним розподілом розміру пор. З отриманих спектрів фотолюмінесценції було встановлено, що пік біля краю смуги в спектрі збудження може бути віднесений до найвищої ефективності передачі фотогенерованих носіїв у корельованих станах підзіапазону (приблизно на 34 меВ нижче зони провідності ZnSe) до стану глибокого центру.

Ключові слова: Квантові точки, ZnSe, Нанопористий вуглець, Спектри фотолюмінесценції.