ON A POSSIBLE SELF-ORGANIZATION IN A SYSTEM OF ZnO COLLOIDAL QUANTUM DOTS

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Abstract

Colloidal ZnO quantum dots have been synthesized, in the UV-Vis spectra of which a multiplet structure of the 1S exciton absorption line is revealed. This structure is interpreted qualitatively as a possible self-organization in the system of ZnO quantum dots with the formation of clusters consisting of a small number of nanoparticles.

1.Introduction

Semiconductor quantum dots (QDs) are of great scientific and practical interest primarily in connection with the general property of QD systems (artificial atoms), consisting in the possibility of changing the position of the exciton luminescence line within the entire visible (and partly ultraviolet) spectrum in a simple way, namely by changing the dimensions of nanoparticles. The atomic-like behavior of quantum dots leads to a relatively easy generating of single excitons, single spins per dot, and to long lifetimes and coherence times of these excitations [1-5]. In addition, quantum dots are widely used in the processes of photocatalytic decomposition of water. In particular, colloidal CdSe quantum dots with dimensions of the order of 2 nm and less increase the hydrogen yield in such processes [6,7]. Equally important is the use of quantum dots for solar cells [8-10], as well as their use in biology and medicine as cellular imaging [11-16] and in molecular detection and bioimaging of cancer [17-18].

As for ZnO colloidal quantum dots, their doping with Co^{2+} ions leads to the acquisition of ferromagnetic properties at room temperature by ZnO:Co^{2+} nanoparticles [19]. Due to this, such nanomaterials are promising for their use in storage and information processing systems.

In the present paper it is shown that ZnO colloidal quantum dots obtained by a newly developed synthesis technology are characterized by a multiplet structure of the 1S exciton absorption band. There are discussed possible reasons for appearance of such a structure.

2. Experimental procedure

For synthesis of ZnO quantum dots, we used zinc acetate dihydrate, $Zn(Ac)_2$•2H2O (99,9%, Sigma Aldrich Co.) and methanol (99,9%, Sigma Aldrich Co.) without further purification. In a typical experiment, 2.195 g of Zn (Ac) $_{2.2H2O}$ were dissolved in 50 mL of methanol under rigorous stirring at room temperature followed by ultra-sonicating for 10 min. It was obtained a transparent solution, which was heated during 12 hours at 65^{o}C by the method described in [21].

However, in contrast to Ref. [21], the chemical reaction with the formation of ZnO quantum dots occurred in the presence of molecules of the inert gas Ar. It has been chosen such a rate of flow of argon molecules through the solution of zinc acetate dihydrate in methanol, at which the 1S exciton absorption band in the UV-vis spectrum of ZnO quantum dots has a multiplet structure. The precipitate was carefully collected, washed three times in absolute ethanol, centrifuged at 5000 rot/min and dried at 60^{o}C for two hours. As a result, a white material containing ZnO quantum dots was obtained.

Identification of the crystal structure and determination of the crystal size were performed with a DRON-UM1 X-ray diffractometer using a FeKα radiation source with a Mn filter.

The UV-vis absorption spectra of the reference nanoparticle solutions were recorded using the Perkin Elmer Lambda 25 spectrometer.

3. Results and discussion

The XRD patterns of ZnO samples are given in Fig 1, where the sign x indicates the lines of Zinc acetate dihidrate not decomposed at heating. The XRD shows that ZnO quantum dots are present in the single crystal of hexagonal wurtzite structure in accordance with JCPDS database of card number 36-1451. The size *D* of nanoparticles in the samples was determined using the Scherrer formula [21]

$$D = \frac{k\lambda}{B\cos\theta}, \qquad (1)$$

where D is the nanoparticle size, k = 0,9, λ is the X-ray wavelength, θ is the Bragg's angle in grads, and B is the full half-maximum width of the main peak in radians.

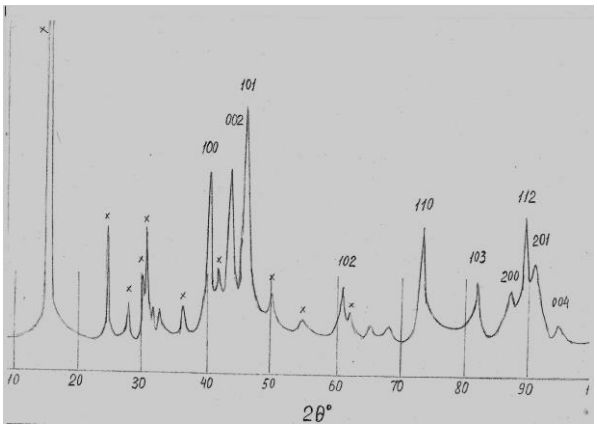

Fig. 1. XRD patterns of ZnO nanoparticles.

Since in our experiment the X-radiation FeKα with λ = 0,193728 nm was used, for the (101) $\theta = 23{,}05^{o}$ at B = 0,0153 rad), we obtained that the average ZnO quantum dot size is D_{ZnO} = 12,4 nm.

The optical properties of synthesized ZnO quantum dots were studied by UV-vis absorption spectroscopy. Fig.2 shows the typical absorption spectrum of pure ZnO quantum dots. A similar multiplet structure of 1S exciton absorption line is also characteristic for ZnO quantum dots doped with Co^{2+} ions (1%, 3%, 5%, and 8%).

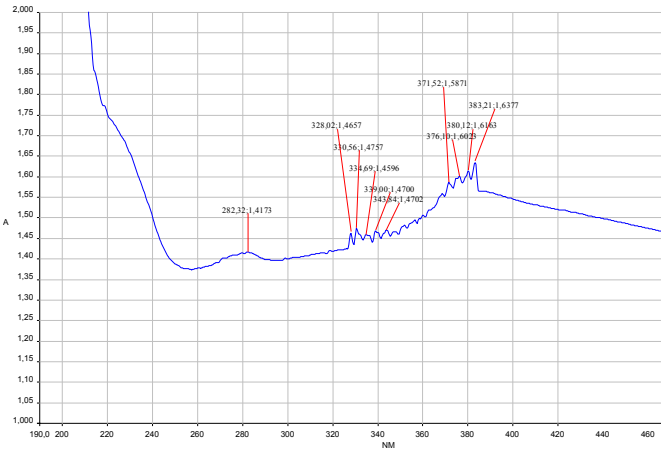

Fig. 2. UV-vis spectrum of ZnO nanoparticles at room temperature.

The multiplet structure of the 1S exciton absorption band can be explained qualitatively by analogy with the multiplet structure of EPR line caused by the superhyperfine interaction of the paramagnetic center magnetic moment with magnetic moments of neighboring nuclei. In this case, the multiplicity M is determined by the formula

$$M = (2I_1N_1 + 1)(2I_2N_2 + 1) \dots (2I_nN_n + 1), \quad (2)$$

where N_i is the number of nuclei with corresponding spins I_i. If the optical quantum transition from the ground state of a quantum dot to the 1S state is described as a transition between two states of some effective spin S′ =1/2, then the super-hyperfine interaction problem can be reformulated into the problem of interaction between neutral quantum dots. In this case the multiplicity of the 1S-exciton absorption band (Fig.2) can be explained by assuming that there are two types of clusters formed by three and, respectively, four interacting ZnO quantum dots. It is to mention that such an estimation is approximate.

The X-Ray spots in Fig.1 not belonging to ZnO quantum dots do not affect the mentioned multiplet structure. This is proved by the absence of absorption lines in the UV-Vis spectrum of pure $Zn(Ac)_2$•2H2O above 250 nm (Fig.3).

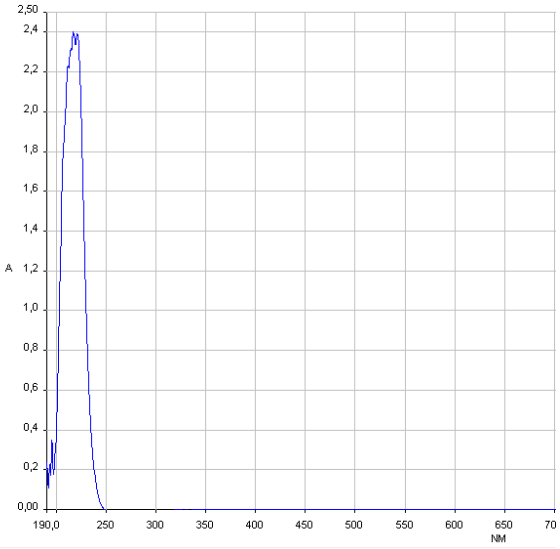

Fig. 3. UV-vis spectrum of zinc acetate dihydrate at room temperature.

A quantitative explanation of both the presence of the multiplet structure of the 1S exciton absorption line and the number of components of this structure can be obtained only based on molecular dynamics calculations.

4. Conclusions

- The synthesis of ZnO quantum dots with a multiplet structure of the 1S exciton absorption band has been carried out.
- The X-ray diffraction data confirm that ZnO colloidal quantum dots have a hexagonal structure with space group $C^4{}_{6v}$.
- The multiplet structure of the 1S exciton absorption band of studied ZnO samples can be caused by self-organizing processes in a system of ZnO quantum dots leading to formation of clusters consisting of a small number of quantum dots.

- For a quantitative theoretical interpretation of the discovered multiplet structure of the 1S exciton absorption band, molecular dynamics calculations are necessary.

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