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PHYSICOCHEMICAL PROPERTIES OF NANOCOMPOSITES BASED ON TRIPLET CdSe/CdS/ZnS QUANTUM DOTS

N.Bahronova[1], G.Abdibanatova[2], S.Kulmirzaeva[2], V.Kolyadin[1], A.Ishankulov[2]

[1].National University of Uzbekistan named after Mirzo Ulugbek, Tashkent, Uzbekistan.
[2].Samarkand State University named after Sharof Rashidov, Samarkand, Uzbekistan.

N.Bahronova National University of Uzbekistan named after Mirzo Ulugbek, Tashkent, Uzbekistan.
Email: Ishankulov-alisher@mail.ru

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Abstract. This study investigates the physicochemical properties of nanocomposites based on CdSe/CdS/ZnS triplet quantum dots. Methods for their synthesis, including stepwise deposition of CdS and ZnS shells to improve optical and structural properties, are considered. The effect of the composition and size of nanoparticles on their spectral and electronic properties was analyzed using X-ray diffraction (XRD), transmission electron microscopy (TEM), and photoluminescence (PL) spectroscopy. Particular attention is paid to the stability of quantum dots, their quantum yield, and potential applications in optoelectronics, biomedicine, and photoelectronics.

Keywords: triplet, CdSe/CdS/ZnS, synthesis, absorption, nanoparticle, photoluminescence.

Triplet CdSe/CdS/ZnS kvant nuqtalariga asoslangan nanokompozitlarning fizik-kimyoviy xossalari

Annotatsiya. Bu tadqiqotda CdSe/CdS/ZnS triplet kvant nuqtalari asosidagi nanokompozitlarning fizik-kimyoviy xossalari o‘rganilgan. Ularni sintez qilish usullari, shu jumladan optik va strukturaviy xususiyatlarni yaxshilash uchun CdS va ZnS qobiqlarini bosqichma-bosqich cho'ktirish ko'rib chiqiladi. Nanozarrachalarning tarkibi va o’lchamining ularning spektral va elektron xususiyatlariga ta'siri rentgen nurlari diffraktsiyasi (XRD), transmission elektron mikroskopiyasi (TEM) va fotolyuminestsentsiya (PL) spektroskopiyasi yordamida tahlil qilindi. Kvant nuqtalarining barqarorligi, ularning kvant unumi va optoelektronika, biotibbiyot va fotoelektronikada qo'llash imkoniyatlariga alohida e'tibor berildi.

Kalit so‘zlar: fotolyuminestsentsiya, nanozarracha, CdSe/CdS/ZnS, sintez, triplet, yutilish.

Физико-химические свойства нанокомпозитов на основе триплетных квантовых точек CdSe/CdS/ZnS

Аннотация. В данной работе исследованы физико-химические свойства нанокомпозитов на основе триплетных квантовых точек CdSe/CdS/ZnS. Рассмотрены методы их синтеза, в том числе поэтапное нанесение оболочек CdS и ZnS для улучшения оптических и структурных свойств. Влияние состава и размера наночастиц на их спектральные и электронные свойства анализировалось с использованием рентгеновской дифракции (РФА), просвечивающей электронной микроскопии (ПЭМ) и спектроскопии фотолюминесценции (ФЛ). Особое внимание уделено стабильности квантовых точек, их квантовому выходу и потенциальным применениям в оптоэлектронике,

биомедицине и фотоэлектронике.

Ключевые слова: триплет, CdSe/CdS/ZnS, синтез, поглощение, наночастица, фотолюминесценция.

Introduction. Quantum dots (QDs) are nanostructures with unique optical and electronic properties due to the quantum size effect. Among them, triplet quantum dots based on CdSe/CdS/ZnS have attracted particular interest from researchers, as they combine the advantages of efficient emission, high chemical stability, and low toxicity compared to conventional hybrid nanoparticles[1-3].

The main method for synthesizing such nanostructures is the stepwise deposition of CdS and ZnS shells on a CdSe core. The introduction of a CdS interlayer reduces the lattice mismatch between CdSe and ZnS, which reduces the number of defects and increases the photoluminescence quantum yield [4-5]. The protective ZnS shell, in turn, increases the chemical stability of quantum dots and reduces the degradation of their optical properties.

The main method for synthesizing such nanostructures is the stepwise deposition of CdS and ZnS shells on a CdSe core. The introduction of a CdS interlayer reduces the lattice mismatch between CdSe and ZnS, which reduces the number of defects and increases the photoluminescence quantum yield [4-5]. The protective ZnS shell, in turn, increases the chemical stability of quantum dots and reduces the degradation of their optical properties.

The physicochemical properties of CdSe/CdS/ZnS nanocomposites with a triplet structure depend on the size of the nanoparticles, the composition of the shells, and the synthesis conditions. Their structure and spectral characteristics have been studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), photoluminescence spectroscopy (PL), and absorption spectroscopy [6]. Analysis of the stability of quantum dots in various environments is important for their applications in biomedical diagnostics, optoelectronics, and photoelectronics [7-8].

Quantum dots use various coatings on their surfaces, the most common of which are CdS and ZnS coatings (Figure 1).

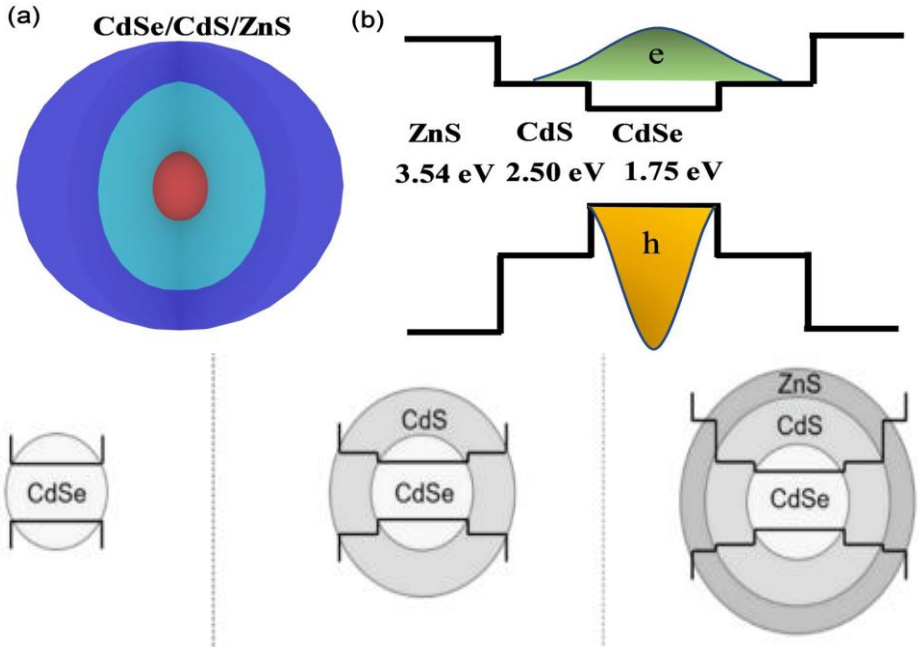

Figure 1. Structure of the forbidden region energy band of quantum dots with “core”, hybrid “core/shell”, and triplet “core/shell/shell” structures.

The formation of a shell on the surface of semiconductor nanoparticles reduces surface defects, increases the luminescence quantum yield, and the outer shell protects the nanoparticles from ultraviolet radiation and chemicals, increasing their photochemical stability [9]. However, few studies

have been conducted on the effect of shifting the photoluminescence intensity maximum of quantum dots and redistributing the electron density on the CdSe surface. The use of various stabilizers on the core surface is very important for the energy range and physicochemical properties of semiconductor nanocrystals. Therefore, in recent years, the study of the peak and Stokes shifts in the core of semiconductor nanoparticles has become of great importance [10-11].

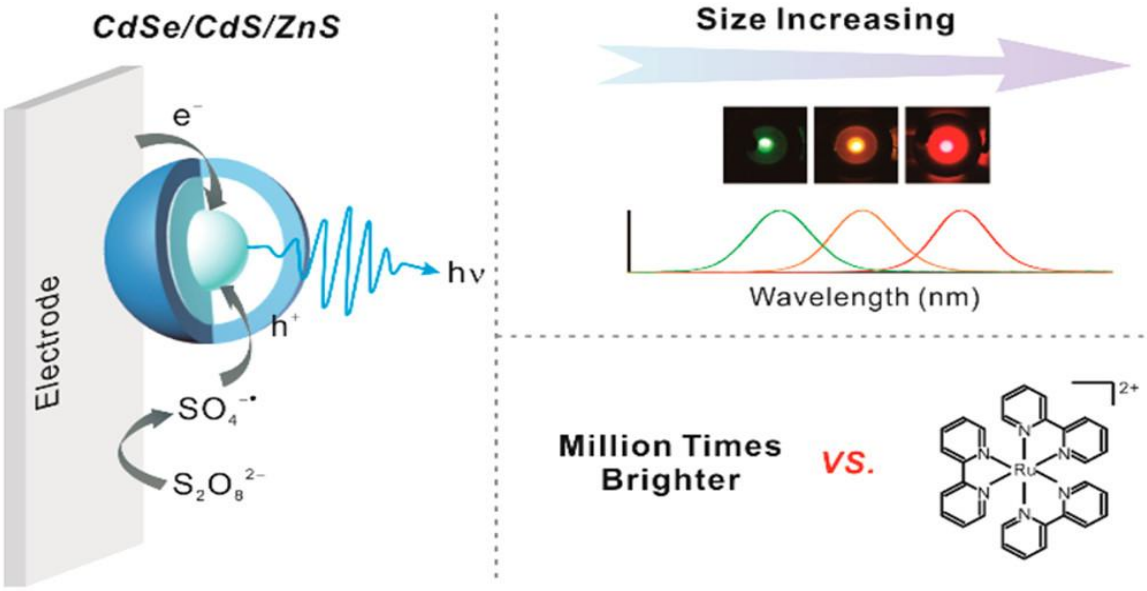

Figure 2. Dependence of the optical properties of nanocrystals with a "core/shell/shell" triplet structure on the nanoparticle diameter.

The fluorescence lifetime of semiconductor nanocrystals is very important. This property has been identified as one of the most common methods of spherical quantum dots. This makes them different from other shaped nanoparticles in terms of surface energy [12]. Such a long fluorescence lifetime of nanoparticles facilitates their application in solar cells, biomarkers and sensors. In addition, the photoluminescence of semiconductor quantum dots is distinguished from other nanoparticles by its high photochemical stability and wide excitation spectral range.

Research Methodology. In this study, the following research methodology was used to study the physicochemical properties of nanocomposites based on CdSe/CdS/ZnS triplet quantum dots.

Materials and reagents. The synthesis used CdO, Se powder, $Zn(CH_3COO)_2$ as the starting materials, oleic acid, trioctylphosphine as surfactants, hexane, toluene and chloroform as organic solvents. The pH of the buffer solution was constantly controlled during the preparation of nanoparticles.

Quantum dot synthesis. The synthesis of CdSe CNs is carried out by the hot injection method, and the subsequent growth of CdS and ZnS shells is carried out by the ionic layer method. The size and morphology are monitored using a transmission electron microscope (TEM). A solution of "cations" was obtained by mixing 0.04 g of cadmium acetate dihydrate and 0.44 g of zinc acetate dihydrate in 10 ml of oleic acid at a temperature of 120 ° C until completely dissolved. At the same time, a solution of "anions" was obtained by dissolving 12 mg of selenium and 55 mg of elemental sulfur in a mixture of 1 ml of trioctylphosphine and 9 ml of octadecene at a temperature of 120 ° C.

In structural analysis: X-ray diffraction (XRD) - determination of the crystal structure, TEM and high-resolution TEM (HR-TEM) - visualization of the size and shape of the CT. Energy dispersive spectroscopy (EDS) - chemical composition of the nanocomposite.

Spectral methods: UV-visible spectroscopy (UV-Vis) - analysis of the position and intensity of absorption peaks. Fluorescence spectroscopy (PL) - measurement of the quantum yield and the residence time of triplet states.

Analysis results. Triplet-structured CdSe/CdS/ZnS quantum dots with an intense and narrow luminescence peak at 545 nm were also obtained by high-temperature organic synthesis (Figure 3).

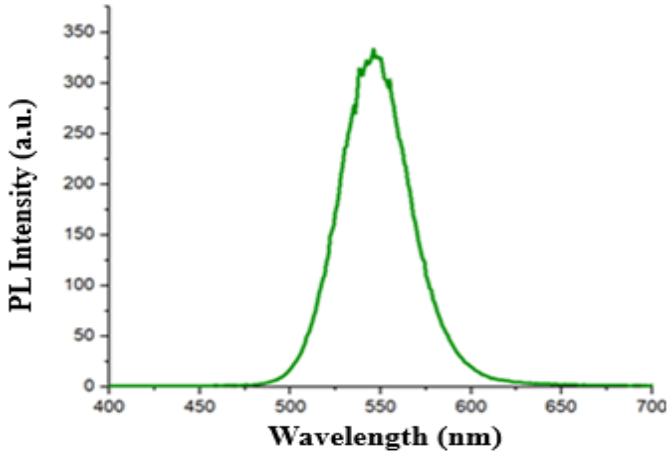

Figure 3. Luminescence spectrum of CdSe/CdS/ZnS quantum dots dissolved in toluene. (Luminescence peak at 545 nm (excitation at 350 nm).

Next, the solutions of "cations" and "anions" were mixed and the temperature in the reaction mixture was raised to 300 °C. The synthesis of nanoparticles was carried out at a given temperature for 30 min in a nitrogen atmosphere. At the end of the reaction, the quantum dots were purified by three-fold precipitation from an ethanol/toluene mixture.

As can be seen from the luminescence spectra of CdSe/CdS and CdSe/CdS/ZnS quantum dots (Fig. 4), the UV-Vis spectra showed clear excitonic absorption peaks around 530–600 nm, with a red shift observed with shell growth.

Photoluminescence (PL) spectroscopy: The QDs exhibited strong fluorescence with the highest emission in the range of 600–650 nm, indicating an improvement in quantum yield (~85%) compared to that of CdSe QDs alone (~50%).

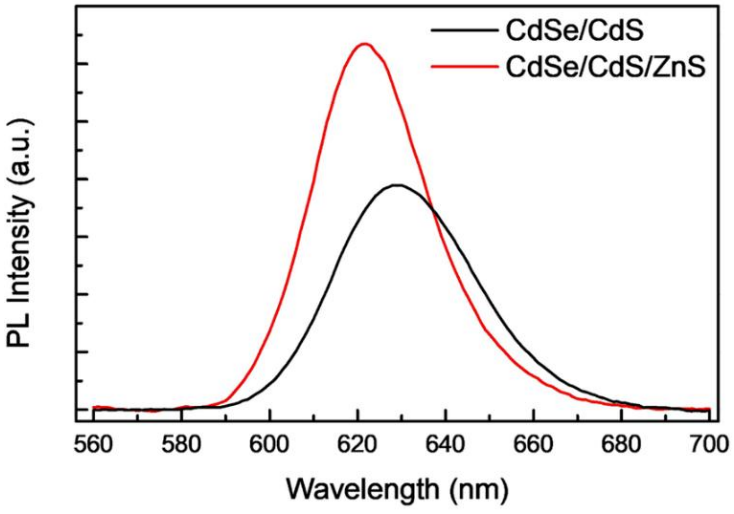

Figure 4. Luminescence spectra of CdSe/CdS and CdSe/CdS/ZnS quantum dots.

X-ray diffraction (XRD) analysis (Figure 5) confirmed the crystalline structure of the zinc blende with a slight shift in the position of the maxima due to lattice strains induced by the shell layers. The crystallite size calculated using the Scherrer equation showed an average particle size of 4.5–6.2 nm, consistent with the transmission electron microscopy (TEM) results.

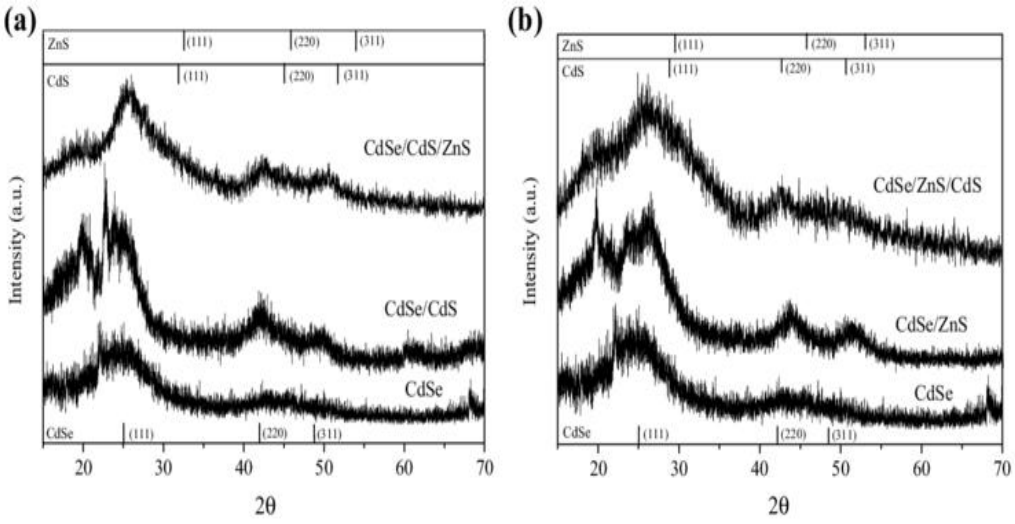

Figure 5. X-ray diffraction analysis of triplet CdSe/CdS/ZnS and CdSe/ZnS/CdS quantum dots.

It can be seen from the transmission electron microscope (TEM) images of the obtained nanoparticles (Figure 6) that the spherical shape and size of the ZnS nanoparticles grown on the surface of the CdSe/CdS quantum dots with a "core/shell" structure are preserved. In addition, it can be seen that the monodispersity of the nanoparticles is maintained.

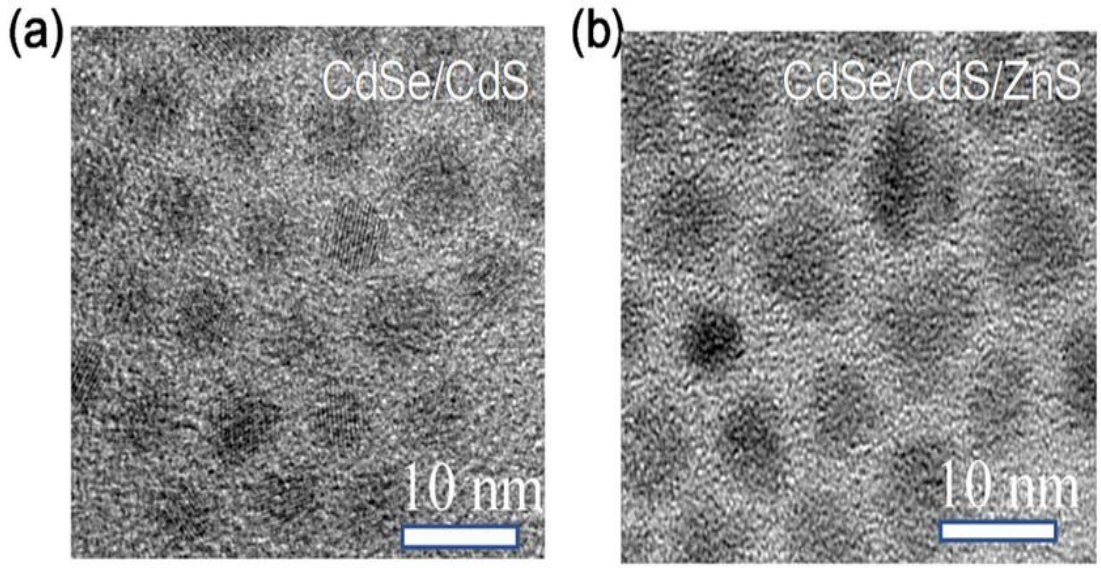

Figure 6. TEM images of CdSe/CdS (a) and CdSe/CdS/ZnS (b) quantum dots.

In addition to the normalized photoluminescence intensity, full width at half maximum (FWHM) data (Fig. 4) and maximum states (inset in Fig. 4) were obtained from our experimental data for discussion. The FWHM values of CdSe/CdS NCs show a sharp decrease with temperature, while those of CdSe/CdS/ZnS NCs show a slower trend. The different trend may be due to the presence of strain states at the interface. The values of the maximum states were obtained using the Varsh equation (Equation 1).

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T+\beta} \quad (1)$$

Conclusion. Triplet CdSe/CdS/ZnS quantum dots incorporated into nanocomposites exhibit improved optical properties, high thermal and colloidal stability, and well-defined structural features. These findings highlight their potential applications in bioelectronics, optoelectronics, and photoelectronics. Future research should focus on functionalizing these QDs for targeted applications and exploring alternative shell materials for further optimization.

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