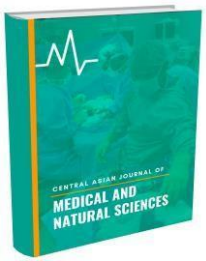

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Article

Photocatalytic Properties and Quantum Chemical Calculations of Cds Quantum Dots Modified with Hydrophilic Stabilizers

A.M. Zufarov[1], D.O. Sagdeev[2], Yu.G. Galyametdinov[2], N.K. Mukhamadiev[1]

[1]Samarkand State University named after Sh.Rashidov, Samarqand, Uzbekistan
[2]Kazan National Research Technological University, Kazan, Russia.
E-mail: zufarovasliddin@samdu.uz

Abstract: Currently, scientific research is being conducted on the synthesis of stable photocatalysts with high quantum efficiency and low cost for producing hydrogen from water as an alternative energy source to address the global energy problem. The main objective of this work is the synthesis of hybrid CdS and CdS/ZnS quantum dots, modified with stabilizers containing various anionic groups, to create a stable photocatalyst with a high quantum yield. The concentration of stabilizers plays an important role in controlling the size of the quantum dots. CdS and CdS/ZnS quantum dots of various sizes were synthesized by adjusting the stabilizer concentration. CdS quantum dots, stabilized with hydrophilic stabilizers, were synthesized at different temperatures, pH values, and molar ratios of reagents. Their absorption, photoluminescence, and optical properties were studied. The photocatalytic properties of the obtained catalysts were analyzed based on the decomposition reactions of the indicators: methylene blue, methyl orange, and rhodamine B. The absorption spectra of the synthesized samples were obtained using a Shimadzu UV-2600i spectrometer, and the luminescence spectra were measured using a Shimadzu RF-6000 spectrofluorimeter. Elemental characterization was conducted using Shimadzu EDX-800P and Shimadzu XRD 6000 devices.

Keywords: photocatalyst, quantum dot, spectrum, luminescence, stabilizer, indicator, synthesis, methylene blue, catalysis, nanoparticles.

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1. Introduction

One of the most pressing global issues today is the creation of alternative "green energy" sources, which has become a major global concern. The reserves of natural fuels are limited, and according to many experts, these reserves could be depleted in the near future. The reliability of this prediction depends on several factors, including the discovery of new reserves, advancements in extraction technologies, and the rate of energy consumption. For instance, according to the "Energy Outlook" report published by British Petroleum (BP) in 2023, if the current level of extraction and consumption continues, global oil reserves could last approximately 50-60 years. At the same time, natural gas reserves are expected to last around 50 years, while coal may remain sufficient for several more centuries[1]. Currently, in order to address global energy challenges, scientists are actively conducting research on various alternative energy sources, including solar, wind, biofuels, and hydrogen energy. For example, hydrogen technologies are considered one of the most promising directions in the energy sector today[2]. This process mainly emphasizes the creation of environmentally friendly, cost-effective, and renewable energy sources, which will help mitigate global warming and reduce harmful emissions into the atmosphere.

The aim of this work is to synthesize hybrid CdS and CdS/ZnS quantum dots modified with hydrophilic stabilizers, which have high quantum yield and stability, and to replace hydrophilic stabilizers with saponins extracted from local plants. Since the roots of the plant Acanthophyllum are rich in saponins, it is often used as a foaming agent in the industry. This substance is particularly used in soap production and other cosmetic products. Saponins extracted from the local plant Acanthophyllum were used as stabilizers in CdS quantum dots and compared with hydrophilic stabilizers. The physicochemical and photocatalytic properties of CdS and CdS/ZnS hybrid quantum dots stabilized with saponins were studied. The aim of this work is to synthesize a photocatalyst based on CdS quantum dots with high quantum yield and stability that can efficiently produce hydrogen gas from water. The problem addressed in this work is the coating of CdS quantum dots with stable stabilizers and increasing the quantum yield. The novelty of this work is that for the first time, saponins extracted from the local plant Acanthophyllum were used for stabilization, and their analysis results were studied.

2. Materials and Methods

As the size of the quantum dots decreases, the agglomeration process increases and makes the synthesis of stable quantum dots significantly more difficult. Previously, CdS quantum dots were usually prepared from surfactants and polymers as stabilizers [3-5]. Semiconductors are materials with an energy dimension, and the optical and electrical properties of quantum dots are between the valence band (Valence band VB) and the conduction band (Conduction band) in the forbidden zone Eg (band gap). determined by the width [6]. The value of the band gap energy Eg has a direct effect on the electrical conductivity and light absorption of quantum dots [7]. CdS quantum dots effectively absorb solar radiation and are used in photocatalysis to generate hydrogen (photochemical splitting of water) [8]. CdS is another semiconductor widely used for the photocatalytic degradation of organic pollutants and water splitting. CdS is an n-type semiconductor with a band gap of 2.42 eV and a visible light able to absorb light well in the region [9]. Smaller particle sizes lead to longer separation of electron-hole pairs, resulting in greater catalytic activity. When CdS quantum dots are coated with various stabilizers or metal oxides, their photoactivity and stability are improved [10]. ZnS-coated CdS quantum dots are resistant to erosion and easy recombination and provide high photocatalytic results. CdS quantum dots effectively absorb UV and visible radiation, making them multifunctional in photocatalytic processes. Depending on the size of CdS quantum dots, their lowest energy range (band statement) changes [11].

The source of cadmium is cadmium acetate dihydrate $Cd(CH_3COO)_2 \bullet 2H_2O$ (Khimreaktiv, Russia), sodium sulfide nanohydrate $Na_2S \bullet 9H_2O$ ("Zolotoe runo", Uzbekistan) as a source of sulfur, L-cysteine, mercaptoethanol, mercaptoacetic acid (Meyer, China), saponin obtained from the saponin plant, mercaptopropionic acid stabilizers, methyl blue, methyl red, rhodamine B, methyl violet blue indicators, sodium alkali, and distilled water were used in the synthesis [12]. The synthesis was carried out in a three-necked flask. Initially, 0.25 mmol or 66.7 mg of $Cd(CH_3COO)_2 \bullet 2H_2O$ cadmium acetate dihydrate was dissolved in 10 mL of distilled water. 0.25 mmol or 60 mg of sodium sulfide nanohydrate $Na_2S \bullet 9H_2O$ was dissolved in 10 ml of distilled water. Stabilizers were measured on an analytical balance from 1 mmol. When the synthesis was carried out in the presence of the stabilizer L-cysteine, cadmium acetate was added dropwise to the solution of the stabilizer L-cysteine until a precipitate formed. A 2 M solution of NaOH was added to the resulting white precipitate until pH=12, and the precipitate was dissolved. Then sodium sulfide solution prepared in advance was added dropwise to the solution. The synthesis was carried out under nitrogen atmosphere. The synthesis time was from 30 minutes to 1 hour. The resulting nanoparticle was dried in a vacuum drying oven[13]. Ethanol was added to the dried sample until turbidity was formed. The resulting colloidal solution was centrifuged at a speed of 6000 revolutions per minute for 10 minutes

(CENTIRIFUGE typeMPW-331). The absorption spectra of the synthesized samples were recorded on a SHIMADZU UV-2600i spectrophotometer [14].

Stabilization of CdS QDs with hydrophilic molecules significantly improves their photocatalytic properties and stabilizes their structure. Quantum-chemical calculations help to better understand the nature of interactions between the stabilizer and the CdS surface.

Luminescence spectra were obtained on a SHIMADZU RF-6000 spectrofluorimeter. Photocatalytic studies were carried out using a model decomposition reaction of rhodamine B, the concentration of which was monitored by spectrophotometric method by reducing the intensity of the absorption peak at 554 nm.

To carry out the reaction, a methyl blue dye solution with a concentration of 5·10-5 mol/l and quantum dots with a mass concentration of 0.25 g/l were loaded into the photoreactor.

3. Results and Discussion

Absorption, luminescence, EDS, XRD, IR spectra of KNs obtained as a result of synthesis were analyzed. Figure 1 shows the results of an energy dispersive X-ray spectrum (EDX or EDS). The analysis of the EDX spectrum shows the distribution of certain elements in the sample by X-ray energies. X-ray energy is shown in kiloelectronvolt keV. The intensity measured along the Y (Intensity cps/mA) axis determines the strength of the X-ray signal. At 1.5-3 keV, the CdS S element, at 3-4 keV, Zn, and at 20-25 keV, Cd peaks are shown. Multipliers (X 70, X 0.070, X 2.0): These multipliers likely indicate different scaling factors applied to the intensity for different regions of the spectrum. For instance, the intensity for the low-energy region (Low-Z) is multiplied by 70 to enhance the visibility of lower peaks, while the intensity in the mid-Z region is reduced (multiplied by 0.070), and the high-Z region is scaled by a factor of 2. The chemical elemental composition of the prepared samples is included in Table 1.

Table 1. Elemental composition of CdS quantum dots (XRF analysis)

№	Element Name	Element Mass Fraction (%)	Statistical Error	Lower Detection Limit	X-ray Radiation Intensity (cps/μA)
1	Na	ND	-	-	-
2	S	96.6	0.0362	0.0056	426.31065
3	Zn	0.0058	0.0003	0.0005	0.04291
4	Cd	3.43	0.0054	0.0005	43.26488

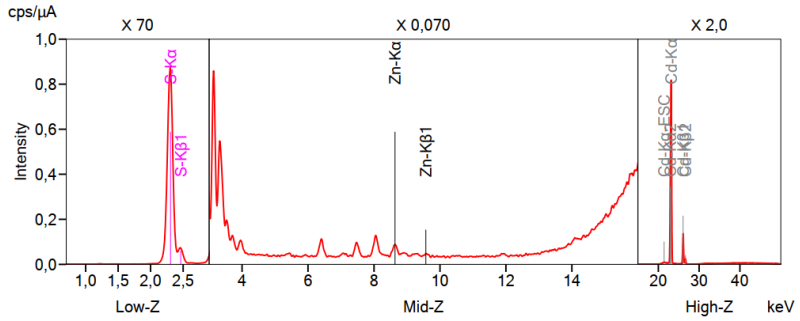

Figure 1. Elemental analysis of CdS quantum dots

Infrared spectra of the sample were taken and analyzed. Since the composition of the stabilizer in the sample is an organic substance, it can be seen in the IR spectrum of Figure 2. In the spectrum below, significant absorption signals were formed in the areas of 3261 cm^{-1}, 2922 cm^{-1}, 1637 cm^{-1}, 1544 cm^{-1}, 1070 cm^{-1}, 1012 cm^{-1}, 630-690 cm^{-1}. According to it, the 3261 cm^{-1} and 1637 cm^{-1} areas belong to the $–NH_2$ and –NH group, and the 3261 cm^{-1} area also belongs to the –OH group, and it is concluded that these groups are present in the composition of the compound. can be done.

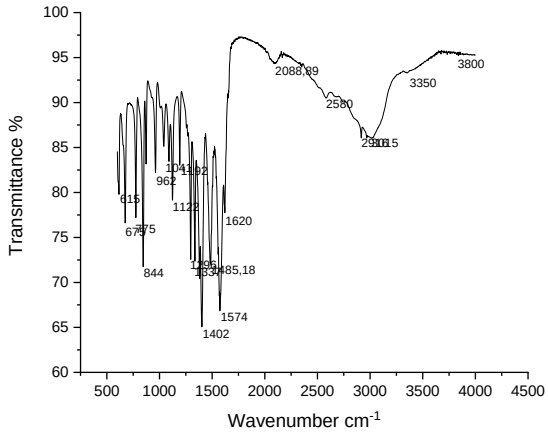

Figure 2. IR spectrum of CdS quantum dots

It was observed that the quantum size effect of quantum dots, that is, as their size decreases, the energy absorption range shifts towards short wavelengths. As a result of the analysis of the position of the absorption spectrum of the CdS nanoparticle covered with L-cysteine at 90^0C in Fig. 3, it can be seen that the spectrum is shifted towards the short wavelength. CdS quantum dots exhibit an absorption spectrum in the wavelength range of 300-500 nm. In Figure 3, it can be seen that the maximum absorption is around 380 nm. This absorption maximum corresponds to the band gap of CdS quantum dots. Around 380 nm indicates that the nanoparticle size is relatively small. The emission maximum at 640 nm shows how the quantum dots emit photons during the recombination process. This radiation also confirms the photoactivity of CdS quantum dots. CdS quantum dots show distinct absorption peaks in the UV-Vis spectrum. The position of the first excitonic absorption peak indicates the quantum dot size, typically 350 nm to 500 nm for CdS KN. CdS NPs should exhibit strong photoluminescence, with emission peaks typically observed between 400 nm and 600 nm depending on quantum dot size.

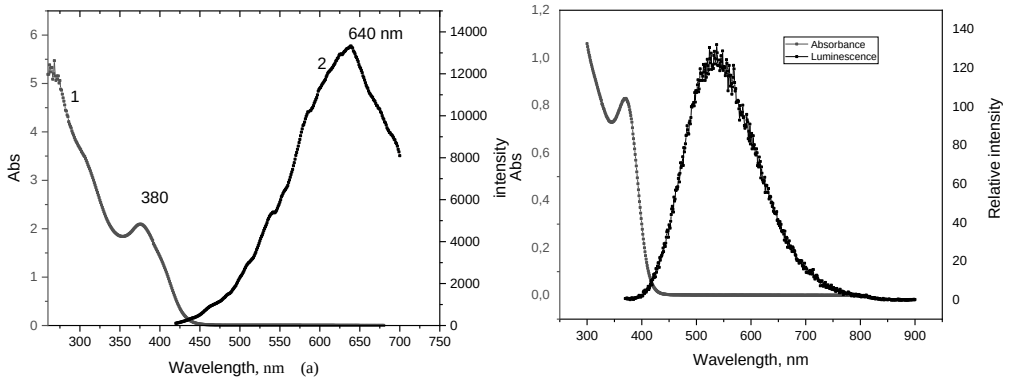

Figure 3. Absorption and luminescence spectra of L-cysteine (a) and mercaptoethanol (b) coated CdS quantum dots

In the CdS/TiO_2 hybrid quantum dot, it was observed that the photocatalytic property of CdS is more actively increased with TiO_2. This hybrid quantum dot was modified with the presence of saponin stabilizers obtained from the local plant Acanthophyllum. The CdS/TiO_2 hybrid system exhibited high photoluminescence intensity when absorbing light. TiO_2 nanoparticles increase the photostability of CdS quantum dots, protect them from decay and ensure efficient separation of electrons. Figure 4 shows that the absorption spectrum of the CdS/TiO_2 hybrid quantum dot has a maximum around 380 nm.

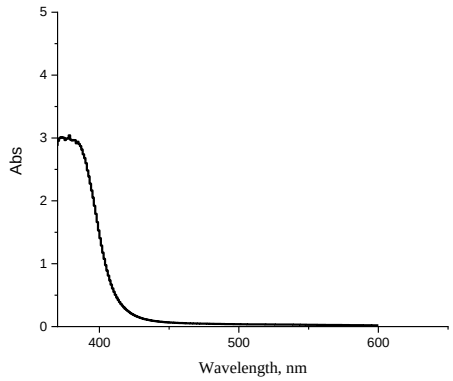

Figure 4. Absorption spectrum of CdS/TiO_2 hybrid quantum dot

This graph shows the wavelength (nm) and optical absorption (Abs) spectra of samples under different test conditions and CdS nanoparticles in different solvents and stabilizers. Based on the graph, the wavelengths range from about 350 nm to 500 nm.

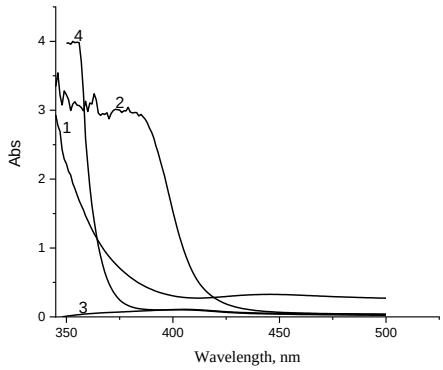

Figure 5. Absorption spectra of CdS, CdS/TiO_2 and CdS/ZnS quantum dots coated with different stabilizers

Rows 1, 2, 3, 4 represent different samples or test cases, each with its own absorption spectrum. CdS quantum dots were coated with ZnS and TiO2 hybrid shells and modified with mercaptoethanol, saponins. The obtained results can be analyzed in Figure 5. In the spectrum of black line 1, CdS quantum dots are stabilized by DMSO and saponin, and the absorption is strong and broad. This means that organic solvents have a strong effect on the quantum dot. 2 - red line CdS quantum dots stabilized by TiO_2 and saponin. This shows that it has the ability to absorb in a wide spectrum. In blue line 3, CdS/ZnS quantum dots are stabilized with saponin. In green line 4, CdS/ZnS quantum dots are stabilized with mercaptoethanol.

Figure 6 shows the absorption spectra of samples taken every 5 min during the decomposition of methyl violet dye in the presence of CdS quantum dot photocatalyst stabilized with L-cysteine. Due to the small size of the synthesized quantum dot samples, it can be seen that the absorption spectra are shifted towards short wavelengths. The photocatalytic process was carried out in sunlight. Samples were taken every 5 minutes. It can be analyzed from Figure 6 that the photocatalyst is working well. A decrease in

absorption over time indicates the participation of quantum dots in photochemical processes or their degradation.

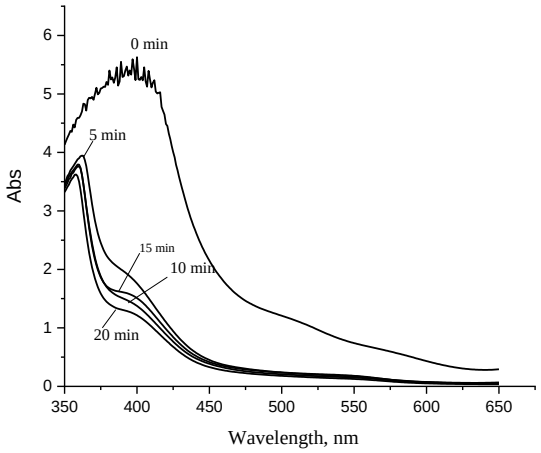

Figure 6. Absorption spectra obtained from methyl violet blue decomposition in the presence of L-cysteine-stabilized CdS quantum dot photocatalyst

X-ray diffraction (XRD) spectrum analysis of L-cysteine-stabilized CdS/ZnS hybrid quantum dots shows several large peaks between 20°-30°, which indicates the crystal structure of CdS quantum dot materials. Diffraction peaks are observed in the 2θ range from 10° to 60°. These diffraction peaks correspond to the crystallographic data of the synthesized material. The resulting values were checked to match the value given in the reference. The examined sample indicates high-quality crystallization.

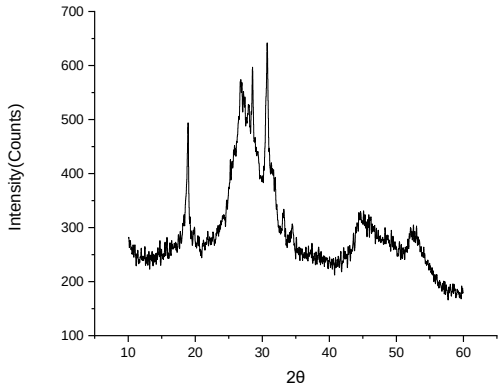

Figure 7. X-ray diffraction (XRD) of L-cysteine-stabilized CdS/ZnS hybrid quantum dots

The parameters of CdS quantum dots stabilized by L-cysteine were theoretically studied based on the data obtained by quantum chemical calculation. CdS quantum dot structure surface topology analyzes were performed using Crystal Explorer 17.5 software to generate 2D fingerprint plots and Hirshfeld surfaces. Also, calculation of the charge density distribution in the molecule based on the optimized structure of CdS and the stabilizer L-cysteine using semiempiric (PM3), electrostatic potential, reactivity descriptors, values of stable ergies, density functional theory (DFT), Monti-Carlo algorithm and B3LYP/6-31G* * implemented using the basis set. The values of the HUMO and LUMO levels were obtained for easy access to calculations of molecular orbital energies. All quantum chemical calculations were performed in Gaussian 09 and HyperChem software.

Also, the nature of intermolecular interactions and complex non-covalent interactions in the nanomolecular structural complex formed between L-cysteine and CdS was studied using the CrystalExplorer 17.5 software based on Hirschfeld surface analysis. (Figure 8).

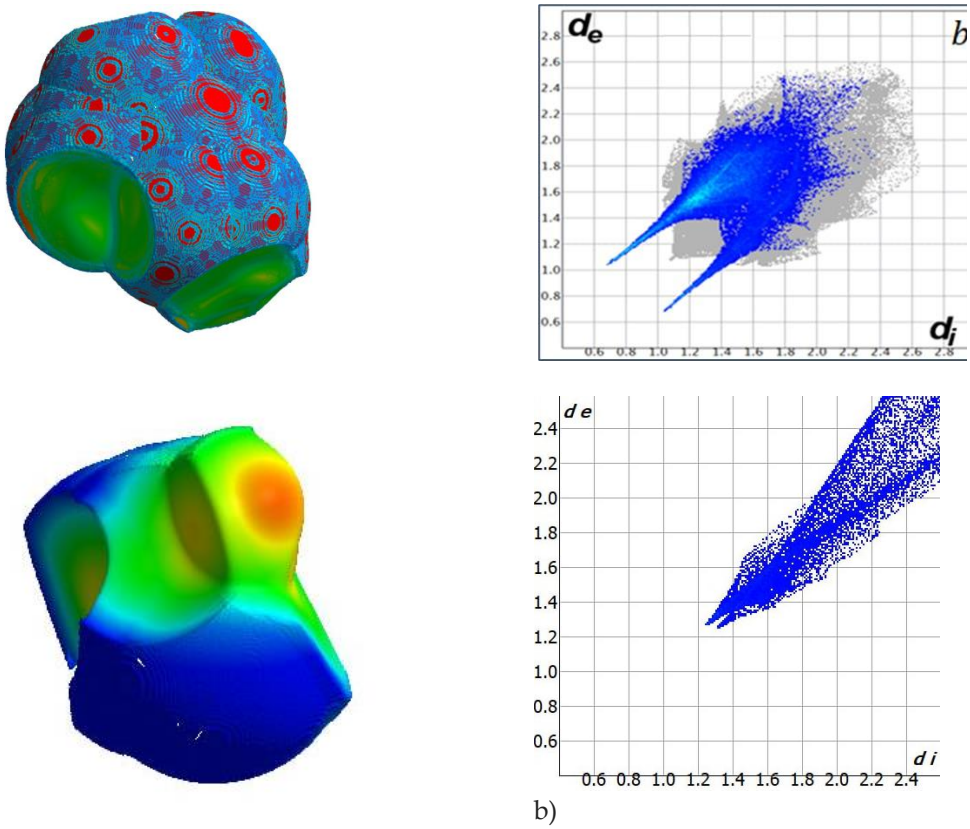

Figure 8. Hirschfeld surface (a) and Hirschfeld fingerprint (b) of CdS and L-cysteine complex

It can be seen from the figure that there are some red spots (a) in the d(norm) map. These red spots are associated with regions involved in short non-covalent interactions with neighboring molecules. The most important non-covalent interactions are Cd....S; It was found that it was formed between Cd....N and O....H atoms. From the two-dimensional Hirschfeld fingerprints, (b) Cd….O non-covalent interactions account for 59.8% (pictured; blue regions), while non-covalent interactions between O….H atoms interactions were found to account for 9.8% (in the figure; red colored regions).

The energies of HUMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) orbitals of the complex formed from L-cysteine and Cd^{2+} cation were calculated (Fig. 9). The HUMO energy of the complex is -1.905 eV, the LUMO energy is equal to 4.75 eV, and the energy difference between them is DE = 2.802 eV. These calculations are important in evaluating the electronic structure and reactivity of a molecule, providing basic information for intermolecular interactions and potential chemical reactions.

HOMO and LUMO energies are very important in photocatalytic processes. When photons excite electrons from HOMO to LUMO, this process initiates photocatalysis. When L-Cysteine binds to CdS nanoparticles, it stabilizes them and participates in the delivery or acceptance of electrons for photocatalytic reactions. This combination increases the efficiency of the CdS-L-Cys system. HOMO and LUMO energies can be determined using DFT (Density Functional Theory) and this information helps to predict photocatalytic processes and other optical properties. CdS quantum dots are

semiconductor materials whose photocatalytic properties depend on their HOMO-LUMO energy gap. The HOMO orbitals of CdS are more likely to be related to the electrons in the sulfide, while the LUMO can be located in the empty d-orbitals of cadmium. The energy gap of CdS quantum dots is usually large, which determines their UV and visible light absorption properties(Figure 9).

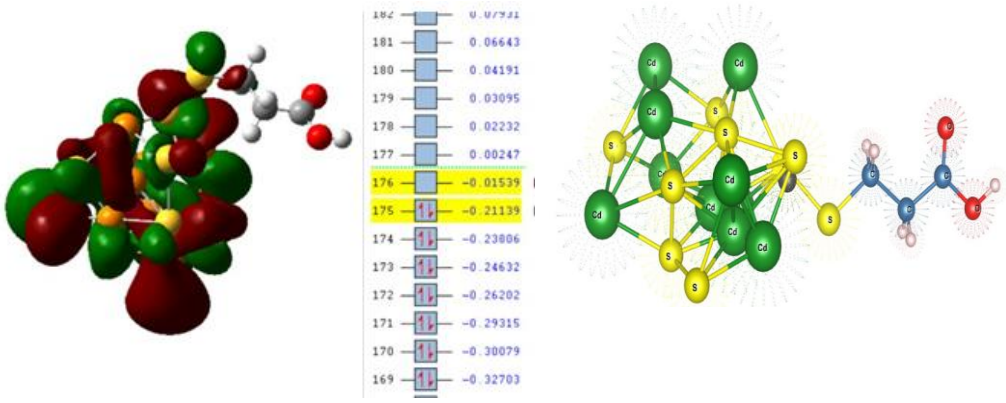

Figure 9. Difference between HUMO and LUMO molecular orbitals and their energies of L-cysteine and CdS nanoparticles

4. Conclusion

1. The optical properties of CdS quantum dots were determined from the analysis of the spectra of synthesized quantum dots using different stabilizers.
2. Photocatalytic properties of CdS, CdS/ZnS and CdS/TiO2 hybrid quantum dots stabilized with saponins obtained from Acanthophyllum plant were studied using the kinetics of decomposition reaction rate of methyl violet blue indicator.
3. The structure of the crystal structure is consistent with the X-ray diffraction (XRD) crystallographic data of the synthesized material with the theoretically calculated results using quantum chemical calculations.
4. It was found that the difference between HUMO and LUMO energies in the complex is equal to DE = 2.802 eV by DFT method. Hirschfeld fingerprint analysis revealed that Cd....S interactions make up 30-40% of non-covalent bonds in the analysis and Cd....N interactions make up 20-25% of the complexes.

REFERENCES

1. Raimi, D., Zhu, Y., Newell, R. G., Prest, B. C., & Bergman, A. (2023). Global energy outlook 2023: Sowing the seeds of an energy transition. Resources for the Future.
2. Guan, D., Wang, B., Zhang, J., Shi, R., Jiao, K., Li, L., ... & Ni, M. (2023). Hydrogen society: From present to future. Energy & Environmental Science, 16(11), 4926-4943.
3. Entezari, M. H., & Ghosh, N. (2011). Micro-emulsion under ultrasound facilitates the fast synthesis of quantum dots of CdS at low temperature. Ultrasonics Sonochemistry, 18(1), 127-134.
4. Ma, N., Yang, J., Stewart, K. M., & Kelley, S. O. (2007). DNA-passivated CdS nanocrystals: Luminescence, bioimaging, and toxicity profiles. Langmuir, 23(26), 12783-12787.
5. Baig, M. S., Suryawanshi, R. M., Zehravi, M., Mahajan, H. S., Rana, R., Banu, A., ... & Emran, T. B. (2023). Surface decorated quantum dots: Synthesis, properties and role in herbal therapy. Frontiers in Cell and Developmental Biology, 11, 1139671.
6. Lundström, M. S., & Schuelke, R. J. (1982). Modeling semiconductor heterojunctions in equilibrium. Solid-State Electronics, 25(8), 683-691.

7. Sun, P., Xing, Z., Li, Z., & Zhou, W. (2023). Recent advances in quantum dots photocatalysts. Chemical Engineering Journal, 458,
8. Preethi, V., & Kanmani, S. J. M. S. I. S. P. (2013). Photocatalytic hydrogen production. Materials Science in Semiconductor Processing, 16(3), 561-575.
9. Heiba, Z. K., Mohamed, M. B., El-Naggar, A., & Albassam, A. (2020). Effect of Mg and Cu doping on structural, optical, electronic, and thermal properties of ZnS quantum dots. Journal of Materials Science: Materials in Electronics, 31, 21342-21354.
10. Bajorowicz, B., Kobylański, M. P., Gołąbiewska, A., Nadolna, J., Zaleska-Medynska, A., & Małankowska, A. (2018). Quantum dot-decorated semiconductor micro- and nanoparticles: A review of their synthesis, characterization, and application in photocatalysis. Advances in Colloid and Interface Science, 256, 352-372.
11. Mintcheva, N., Gicheva, G., Panayotova, M., Wunderlich, W., Kuchmizhak, A. A., & Kulinich, S. A. (2019). Preparation and photocatalytic properties of CdS and ZnS nanomaterials derived from metal xanthate. Materials, 12(20), 3313.
12. Zufarov, A. M. (2023). Synthesis and photocatalytic properties of CdS quantum dot nanoparticles stabilized with mercaptoethanol and mercaptoacetic acid. Universum: Chemistry and Biology, (12-2)(114), 50-54. https://doi.org/10.32745/chem.biolog.2023.114
13. Sagdeev, D. O., Zufarov, A. M., Ishankulov, A. F., Mukhamadiev, N. K., & Galyametdinov, Y. G. (2023). Influence of stabilizer on photocatalytic properties of CdS nanoparticles. Bulletin of the Technological University, 26(7).
14. Zufarov, A. M., Sagdeev, D. O., Galyametdinov, Y. G., & Muxamadiyev, N. K. (2023). Turli xil anion stabilizatorlar bilan stabilizatsiyalangan CdS sintezi va uning fotokatalitik xossalari. Issue 5 of 2023 (141/1), 5(137), 5-12.
15. Ishankulov, A. F., Khalilov, K. F., Shamilov, R. R., Galyametdinov, Y. G., & Mukhamadiev, N. K. (2023). Size-optical characteristics of CdSe/ZnS quantum dots modified by thiol stabilizers. Journal of Sol-Gel Science and Technology, 108(2), 292-297.
16. Samadi, N., & Narimani, S. (2016). Citrate-capped CdS quantum dots as fluorescence sensor for simple and selective determination of metronidazole. Sensor Letters, 14(5), 530-535.
17. Widness, J. K., Enny, D. G., McFarlane-Connelly, K. S., Miedenbauer, M. T., Krauss, T. D., & Weix, D. J. (2022). CdS quantum dots as potent photoreductants for organic chemistry enabled by Auger processes. Journal of the American Chemical Society, 144(27).
18. Kargozar, S., Hoseini, S. J., Milan, P. B., Hooshmand, S., Kim, H. W., & Mozafari, M. (2020). Quantum dots: A review from concept to clinic. Biotechnology Journal, 15(12), 2000117.
19. Nikazar, S., Sivasankarapillai, V. S., Rahdar, A., Gasmi, S., Anumol, P. S., & Shanavas, M. S. (2020). Revisiting the cytotoxicity of quantum dots: An in-depth overview. Biophysical Reviews, 12, 703-718.
20. Yang, H.-Y., Zhao, Y.-W., Zhang, Z.-Y., Xiong, H.-M., & Yu, S.-N. (2013). One-pot synthesis of water-dispersible Ag2S quantum dots with bright fluorescent emission in the second near-infrared window. Nanotechnology, 24(5), 055706.