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Influence of surfactants on the formation and growth of cadmium telluride nanoplatelets

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The article presents a comprehensive review of the current research on the use of surfactants in CdTe nanoplatelet synthesis, including a discussion of the various types of surfactants that have been used and their effects on nanoplatelet size, shape, and optical properties. Additionally, the article examines the mechanisms by which surfactants influence the growth and morphology of CdTe nanoplatelets, with a focus on the role of surfactant, size, and structure. Overall, this article provides a detailed analysis of the use of surfactants in the synthesis of CdTe nanoplatelets and highlights the potential for this approach to improve the performance of CdTe-based technologies. The dependences of the NPL absorption and photoluminescence spectra on acids used as surfactants are shown. The dependence of the shape and size of the NPL on the length of the surfactant ligand was found.

Keywords: CdTe; nanoplatelets; colloidal synthesis; ligand; surfactants; TEM

Introduction

The advent of the first colloidal quantum dot light emitting diodes opened a new direction in LED technology [1–4]. Colloidal nanocrystals have such advantages as: low cost, manufacturability, and adjustable wavelength of emission, which makes them promise luminescent materials. Semiconductor nanoparticles are particles 1–100 nm in size stabilized by a surfactant ligand and can be placed in a row between molecular compounds and single crystals. They have received vital attention due to their controllable optical and electronic properties by

customizing size, shape, core/shell formation and surface [5–7]. Most LEDs with colloidal nanocrystals are currently based on spherical quantum dots. Compared to quantum dots, nanoplatelets (NPLs) have a narrower emission peak, higher exciton binding energy, and higher emission recombination rate, which makes them more suitable as luminescent materials for LEDs [8]. The narrow emission line of NPL is of great importance for improving the color purity of LEDs, which is difficult to achieve with other materials. Various structures have been reported, including type II core/shell and core/crown heterostructures [9]. Two-dimensional semiconductor nanostructures are mainly concentrated on the CdSe system [10, 11]. However, in recent years, studies have also begun for CdTe, which is considered an important component of these structures.

CdTe is characterized by a low band gap of 1.44 eV compared to its selenium-or sulfur-based counterparts (CdSe \sim 1.74 eV; CdS \sim 2.24 eV), which makes it an intriguing and tunable resource for application in photovoltaics [12] and photodetection [13].

The synthesis of cadmium telluride (CdTe) nanoplatelets (NPLs) is highly dependent on the use of surfactants, which can affect the morphology, size, and properties of the nanoparticles. Among the various types of surfactants used in the synthesis of CdTe NPLs, acids have gained attention due to their ability to promote the growth of highly crystalline and uniform NPLs. However, the influence of different acids on the optical properties of CdTe NPLs, including their absorption and photoluminescence spectra, has not been extensively studied.

Recent studies have shown that the use of nanoparticles is becoming increasingly popular in various fields, including medicine, energy, and electronics. Cadmium telluride (CdTe) is one such nanoparticle material that has been gaining attention due to its unique optical and electronic properties. CdTe nanoparticles have been synthesized in various shapes and sizes, including spheres, rods, and plates, but the synthesis of CdTe nanoplatelets has recently gained attention due to their unique properties. However, the synthesis of CdTe nanoplatelets is highly dependent on various factors, including the use of surfactants. Surfactants are molecules that can be used to control the shape and size of nanoparticles, as well as their stability and dispersion.

The surface ligands or surfactants are crucial for the controlled generation of nanomaterials with a well-tuned size, shape and surface and volume composition. Ligands are beneficial to provide a certain morphology to the particles during their growth, while also ensuring their dispersibility in selected solvents and their ability for post-synthetic functionalization.

Several studies have explored the influence of surfactants on the formation and growth of CdS nanoparticles, including plates. Similarly, the authors of [14] reported that the use of oleylamine (OA) and trioctylphosphine oxide (TOPO) as surfactants resulted in the formation of CdTe nanoplatelets with a high degree of uniformity and crystallinity.

Recent studies have explored the dependences of the absorption and photoluminescence spectra of CdTe NPLs on the use of different acids as surfactants. For example, the authors of [15] investigated the influence of three different acids, including acetic acid, hydrochloric acid, and sulfuric acid, on the absorption and

photoluminescence spectra of CdTe NPLs. The authors found that the absorption spectra of CdTe NPLs synthesized using acetic acid and hydrochloric acid exhibited redshifts compared to those synthesized using sulfuric acid. Furthermore, the photoluminescence spectra of CdTe NPLs synthesized using hydrochloric acid showed a blueshift compared to those synthesized using acetic acid and sulfuric acid.

Similarly, the authors of [16] investigated the influence of oleic acid and stearic acid on the absorption and photoluminescence spectra of CdTe NPLs. The authors found that the absorption spectra of CdTe NPLs synthesized using oleic acid exhibited a blueshift compared to those synthesized using stearic acid. Furthermore, the photoluminescence spectra of CdTe NPLs synthesized using oleic acid showed a higher intensity and narrower linewidth compared to those synthesized using stearic acid.

Recent studies have investigated the dependence of the shape and size of CdTe NPLs on the length of the surfactant ligand. For example, the authors of [14] investigated the influence of the length of the surfactant ligand on the morphology and size of CdTe NPLs synthesized using oleylamine (OA) and trioctylphosphine oxide (TOPO) as surfactants. The authors found that the length of the OA ligand had a significant effect on the shape and size of the NPLs. NPLs synthesized using shorter OA ligands exhibited a more irregular shape and larger size compared to those synthesized using longer OA ligands. Similarly, the length of the TOPO ligand also affected the shape and size of the NPLs, with longer TOPO ligands resulting in smaller and more uniform NPLs.

Similarly, the authors of [17] investigated the influence of the length of the surfactant ligand on the morphology and size of CdTe NPLs synthesized using thiol ligands. The authors found that the length of the thiol ligand had a significant effect on the shape and size of the NPLs. NPLs synthesized using shorter thiol ligands exhibited a more irregular shape and larger size compared to those synthesized using longer thiol ligands.

The authors of [18] investigated the influence of oleic acid and myristic acid on the concentration of Cd and Te elements in CdTe NPLs. The authors found that the concentration of Cd and Te elements in CdTe NPLs synthesized using oleic acid was higher compared to those synthesized using myristic acid.

The authors of [10] showed that significant control over the synthesis and properties of nanocrystals can be achieved by choosing the appropriate ligands in the synthesis processes. Organic capping ligands used in colloidal synthesis have a strong effect on the shape, size, composition, and morphology of nanocrystals [19, 20]. An important step in NPL development is the selection of suitable surface ligands.

Vasiliev et al. report spontaneous NPL folding under the influence of surfactant ligands [21]. Anand et al., report the synthesis of colloidal CdTe NPLs with high PLQY, emphasizing the effects of giant oscillator strength transitions at intermediate temperatures (100 K) and the effects of exciton fine structure at T < 50 K [22].

Although there are many works on the colloidal synthesis of CdTe quantum dots, the synthesis of CdTe NPLs of a controlled shape [23] and the effect of the

ligand capping length on the formation and growth of CdTe NPLs have not yet been studied.

The objects of study are samples of CdTe NPLs synthesized by high-temperature pulsed nucleation in a high-boiling solvent. CdTe NPLs grown by colloidal methods with a fatty acid capping ligand end up with cadmium atoms bound to the acid ligands. Fatty acids commonly used in the synthesis of nanocrystals should be chosen based on the condition that cadmium chalcogenide ligands and salts can be used as a Cd precursor [24]. Based on this, we synthesized samples of CdTe NPLs according to a previously mastered technique [21, 25, 26].

Despite the growing interest in the synthesis of CdTe nanoplatelets, there is still a need to further explore the influence of different surfactants on the morphology, size, and properties of the nanoparticles.

In this article, we will explore the influence of surfactants on the formation and growth of CdTe nanoplatelets. We will discuss the different types of surfactants used in the synthesis of CdTe nanoplatelets and how they affect the morphology and size of the particles. We will also delve into the mechanism behind the surfactant-assisted synthesis of CdTe nanoplatelets and its potential applications in various fields.

In this work, optical characteristics were obtained by spectrophotometric analysis on a Jasco V-770 spectrophotometer and luminescent properties on a Solar CM 2203 spectrofluorimeter. Because the system must have a relatively high ratio of Cd to Te precursors, this ratio was verified by ICP MS on a Perkin-Elmer ELAN DRC-II. Transmission electron microscopy (TEM) images are acquired using a JEM 1400 Plus (Japan) Jeol.

Results and discussion

According to a modified procedure at a synthesis temperature of 230 $^{\circ}$ C, NPL samples were synthesized in an inert atmosphere, using cadmium acetate dehydrate as a cadmium precursor, and tellurium dissolved in trioctylphosphine 100 μ l of 1M TOP-Te was used as a metal precursor. We used stearic acid (sample 1), myristic acid (sample 2), and oleic acid (sample 3) as surfactants.

In Figures 1–3, in each absorption spectrum, one can recognize a broader peak corresponding to the electron/light hole transition (447–451 nm), followed by a longer sharp peak corresponding to the first exciton transition: electron/heavy hole (498–502 nm). Such transitions are characteristic of two-dimensional nanoparticles and can be attributed to NPL populations containing 5 monolayers, respectively [6]. The repetition of the same series of bands with absorption and photoluminescence peaks around 550 and 600 nm is associated with the presence of 6 and 7 monolayer NPLs. The presence of peaks at about 629–650 nm indicates the presence of tetrapod-like nanoparticles in the sample (Figure 1, 3). It is important to note that NPL nucleation does not occur immediately after injection but appears after 15–20 s and persists throughout the entire reaction time [26].

The use of long-chain surfactant ligands significantly changes the growth conditions. Simultaneous growth of 5–7-monolayer NPLs with emission bands

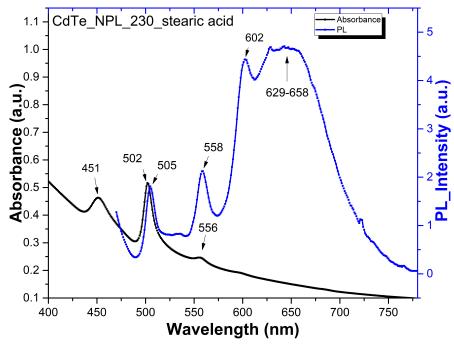


Figure 1. Absorption and photoluminescence spectra of NPL CdTe on stearic acid $\,C_{18}H_{36}O_2$.

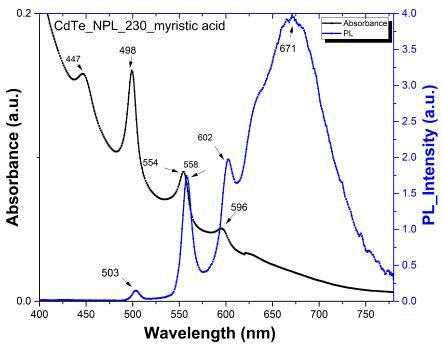


Figure 2. Absorption and photoluminescence spectra of NPL CdTe on myristic acid $\,C_{14}H_{28}O_{2}$.

at 503 nm, 558 nm, and 602 nm occur, accompanied by the formation of CdTe quantum dots with a wide luminescence band at \sim 671 nm (Figure 2). Separation of CdTe nanoparticles compared to CdSe is slower and work on purification and separation of nanoparticles is still ongoing.

According to the results of ICP MS (Tables 1–3) the concentration of the content of Cd to Te is about in the samples: 1) 2 to 0.8; 2) 3 to 1; 3) 2 to 1.

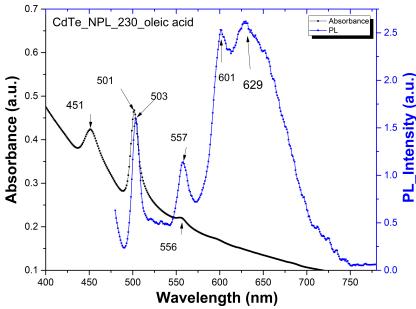


Figure 3. Absorption and photoluminescence spectra of NPL CdTe on oleic acid $\,C_{18}H_{34}O_2$.

Table 1.

Concentration Results CdTe NPL 230 C stearic acid

Analyte	Mass	Net Intens.	Conc. Mean	Conc. SD	Conc.	Sample
		Mean			RSD	Unit
Cd	111	2594284.903	19.645212	0.11	0.560	mg/L
Cd	112	5076639.180	24.008207	0.12	0.515	mg/L
Cd	113	2691198.119	19.539794	0.11	0.539	mg/L
Te	128	7938563.472	13.649317	0.15	1.071	mg/L
Te	130	9031814.193	13.615078	0.11	0.833	mg/L

Table 2. Concentration Results CdTe NPL 230 C myristic acid

Analyte	Mass	Net Intens.	Conc. Mean	Conc. SD	Conc.	Sample
		Mean			RSD	Unit
Cd	111	9911510.717	75.054874	0.19	0.248	mg/L
Cd	112	19489291.047	92.167851	0.60	0.653	mg/L
Cd	113	10358159.996	75.206767	0.58	0.777	mg/L
Te	128	16595163.378	28.533203	0.22	0.767	mg/L
Te	130	19047609.614	28.713466	0.19	0.678	mg/L

Table 3.

Concentration Results CdTe NPL 230 C oleic acid

Concentration results care in L 250 C office acid							
Analyte	Mass	Net Inten	s. Conc. Mean	Conc. SD	Conc.	Sample	
		Mean			RSD	Unit	
Cd	111	7118374.565	53.903862	0.19	0.77	mg/L	
Cd	112	13910840.912	2 65.786504	0.60	0.95	mg/L	
Cd	113	7397075.521	53.707428	0.58	0.65	mg/L	
Te	128	19397573.824	33.351580	0.22	0.09	mg/L	
Te	130	22143623.424	4 33.380576	0.19	0.26	mg/L	

The luminescence properties of semiconductor nanoparticles, including cadmium telluride (CdTe) nanoplatelets (NPLs), are strongly influenced by the presence of defect states. Defects in the crystal lattice can result in the creation of trap states that can act as recombination centers for electrons and holes, leading to the emission of light. The excitation of luminescence from these defect states is highly dependent on the coordinating ligand used in the synthesis of the NPLs.

This difference in photoluminescence to the variation in the binding strength of the ligands to the Cd and Te atoms, which can affect the passivation of the defect states.

These findings highlight the importance of careful selection of coordinating ligands in the synthesis of CdTe NPLs to achieve desired luminescence properties. Further studies are needed to explore the mechanism behind the influence of different coordinating ligands on the excitation of luminescence from defect states and to investigate their potential applications in various fields, including optoelectronics, bioimaging, and sensing.

To elucidate further structural features of NPLs and understand the mechanism of their growth, we proceeded to a detailed analysis of purified NPLs by transmission electron microscopy.

As shown in Figures 4–6, the length of the surfactant ligand directly affects the shape and size of the NPLs. The figure shows that with an increase in the length of the ligand, the shape changes from round (Figure 4, 5) to square (Figure 6). When using myristic acid, small but thick NPLs are formed, and the presence of both CdTe NPLs and small CdTe nuclei and various forms of nanoparticles was also found in the samples (Figure 5), which is also evidenced by the photoluminescence spectra.

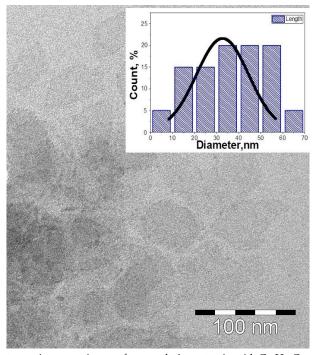


Figure 4. Transmission electron microscopy images for sample 1 on stearic acid $C_{18}H_{36}O_2$. Insert – histogram of NPL size analysis.

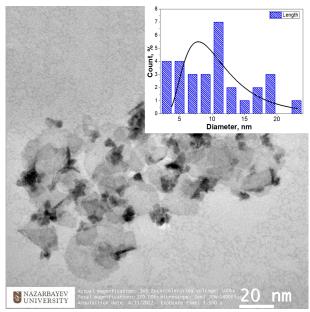


Figure 5. Transmission electron microscopy images for sample 2 on myristic acid $C_{14}H_{28}O_2$. Insert – histogram of NPL size analysis.

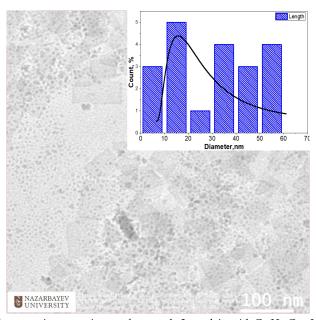


Figure 6. Transmission electron microscopy images for sample 3 on oleic acid $C_{18}H_{34}O_2$. Insert – histogram of NPL size analysis.

Conclusion

The dependences of the concentration of elements in CdTe NPLs on acids used as surfactants can be attributed to the effect of the acid on the nucleation and growth of the nanoparticles, which can affect the incorporation of Cd, Te, and other elements.

The dependences of the absorption and photoluminescence spectra of CdTe NPLs on acids used as surfactants can be attributed to the effect of the acid on the crystal structure, size, and shape of the nanoparticles.

The dependence of the shape and size of CdTe NPLs on the length of the surfactant ligand can be attributed to the effect of the ligand on the surface energy

and growth rate of the NPLs.

The use of short-chain surfactants (sample 1) leads to the growth of small nanoparticles with a Cd to Te concentration of 3 to 1. The small size of the particles formed, together with the appearance of various microstructures in the product solution, indicates a strong surface stabilization active substances and strong supersaturation, which persists for a long time of synthesis. For the growth of highly anisotropic nanostructures and requires additional research. The use of longer surfactants (samples 2 and 3) leads to the formation of laterally enlarged NPLs. With an increase in the length of the ligand, the shape of the NPL changes from round to square, and the concentration of Cd to Te is approximately 2 to 1, which is ideal for the formation of the NPL of the correct shape [5, 11, 12].

These findings highlight the importance of careful selection of surfactants with appropriate ligand lengths in the synthesis of CdTe NPLs to achieve desired morphologies and sizes. Further studies are needed to explore the mechanism behind the influence of surfactant ligand length on the shape and size of CdTe NPLs and to investigate their potential applications in various fields, including optoelectronics and biomedicine.

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