

# ELECTROCHEMICAL INVESTIGATION OF QUANTUM DOTS BAND STRUCTURE

TYNKEVYCH O. O., OKREPKA G. M., KHALAVKA Y. B.  
*Department of Solid State Inorganic Chemistry and Nanomaterials,  
Yuriy Fedkovych Chernivtsi National University,  
Kotsiubynsky Str. 2, 58012, Chernivtsi, Ukraine  
o.tynkevych@chnu.edu.ua*

A cyclic voltammetry method was applied to determine band structure of the water-soluble CdTe quantum dots (QDs). The influence of synthesis conditions, temperature changes and impurities incorporation on the CdTe QDs band structure changes were evaluated. Influence of the concentration of a stabilizer demonstrates a significant impact on the electrochemical response of the CdTe QDs.

Quantum dots of  $A_{II}B_{VI}$  group (CdS, CdSe, CdTe) due to their unique shape-, structure-, size-, and composition-dependent optical and electrical properties are promising material for a number of applications such as chemical sensors, solar elements, LED devices, biomedical fields etc.

The modifications of the optical and electrical properties of such materials can be achieved using different techniques. For instance, Chu et al. and Van Hung et al. demonstrated that optical and electrical properties of QDs can be adjusted by changing synthesis conditions [1, 2]. The incorporation of transition metals impurities into QDs structure is a useful technique used for tuning their optical properties [3, 4] due to the band structure changes and appearance of additional energy levels. Also, as shown by Vyhnan et al., heating the CdTe colloidal solutions from 280 to 340 K leads to significant shift of PL maximum into the red spectral region. This shift was linearly dependent on temperature [5].

For a wide range of applications based on QDs it is important to understand the effects of impurities incorporation, temperature change and synthesis conditions on the QDs band structure changes. Cyclic voltammetry (CV) is the most widely used electrochemical method for the determination of band structure parameters of the quantum confined systems [6, 7]. Collection of CV data of oxidation and reduction reactions involving QDs enables calculation of the position of valence band, conduction band and levels various impurities and defect levels position [8]. In the present work we summarize application of cyclic voltammetry in the monitoring of band structure changes of CdTe QDs during a number of modification techniques.

## **Research methodology**

### Material characterization

The absorption and photoluminescence spectra were recorded at room temperature on OceanOptics USB-2000 and Specord 200 spectrophotometers. The CV measurements were performed using a Reference 3000 Potentiostat/Galvanostat or computer-controlled Potentiostat/Galvanostat PI-50-1. A three-electrode system with a glass carbon counter electrode, an Ag/AgCl reference electrode and the platinum electrode as the working electrode was used for the cyclic voltammetry measurements. The cyclic voltammograms were obtained by scanning the potential from  $-2$  to  $2$  V at a scan rate of  $100 \text{ mV}\cdot\text{s}^{-1}$ .

### Synthesis of CdTe QDs

CdTe QDs stabilized by thioglycolic acid (TGA) were synthesized at room temperature in alkali aqueous solution by the reaction of  $\text{CdSO}_4$  and  $\text{H}_2\text{Te}$ . The  $\text{H}_2\text{Te}$  was produced electrochemically via the reduction of tellurium cathode. The oxygen was removed from the reaction system by bubbling argon through it for 15 min. After the reaction, the temperature was raised to  $100^\circ\text{C}$  to form CdTe QDs of the required size. The first series of samples was prepared by varying the time of  $\text{H}_2\text{Te}$  passing through the solution. The second series of samples was synthesized with different heat treatment times, which allowed us to obtain a wide range of QDs sizes in both cases. Synthesis of CdHgTe QDs was carried out by addition of  $\text{Hg}(\text{NO}_3)_2$  different amounts to the freshly prepared CdTe nanocluster colloidal solutions with subsequent heat treatment.

## **Results and Discussion**

### Temperature Dependence of the band gap of CdTe QDs.

The series of samples was synthesized varying heat treatment times (1-4 hours). Prolongation of refluxing time leads to the growth of the CdTe QDs that can be clearly seen by the “red” shift of absorption and PL spectra. The characteristic absorption and PL peaks for a series of samples were observed in the range of 510–570 nm (Fig. 1A). The average sizes and optical band gap ( $E_{g_{\text{opt}}}$ ) of CdTe QDs were obtained from the absorption peak maxima.

Obtained series of QDs with an average size of 2.4-2.7 nm was chosen for the investigation of the temperature dependence of the electrochemical band gap variations. CV measurements have been carried out during the heating of the colloids to reveal the temperature dependent band gap variations of CdTe QDs.

Fig. 1 B shows the CV curves of the CdTe QDs measured at 293 K. The oxidation peak at 0.84 V (**A**) and redaction peak at -1.50 V (**C**) are observed. The difference between  $E_{\text{ox}}$  and  $E_{\text{red}}$  allows calculating the value of electrochemical band gap energy ( $E_{g_{\text{CV}}}$ ). The potential

difference of 2.34 V between  $E_{ox}$  and  $E_{red}$  agree well with the optical band gap of 2.4 eV ( $E_{g_{opt}}$ ).

The absolute energy positions of valence (VB) and conduction band (CB) edges were calculated by the equations:

$$E_{CB} = E_a = - (E_{red} + E_{ref}), \text{ eV} \quad (1)$$

$$E_{VB} = I_p = - (E_{ox} + E_{ref}), \text{ eV} \quad (2)$$

where  $E_{red}$  and  $E_{ox}$  are the potentials of the reduction and oxidation peaks relative to an Ag/AgCl reference electrode. The  $E_{ref}$  is the difference between the vacuum level potential of the normal hydrogen electrode ( $E_{NHE} = 4.44$  eV) and the potential of the Ag/AgCl electrode.

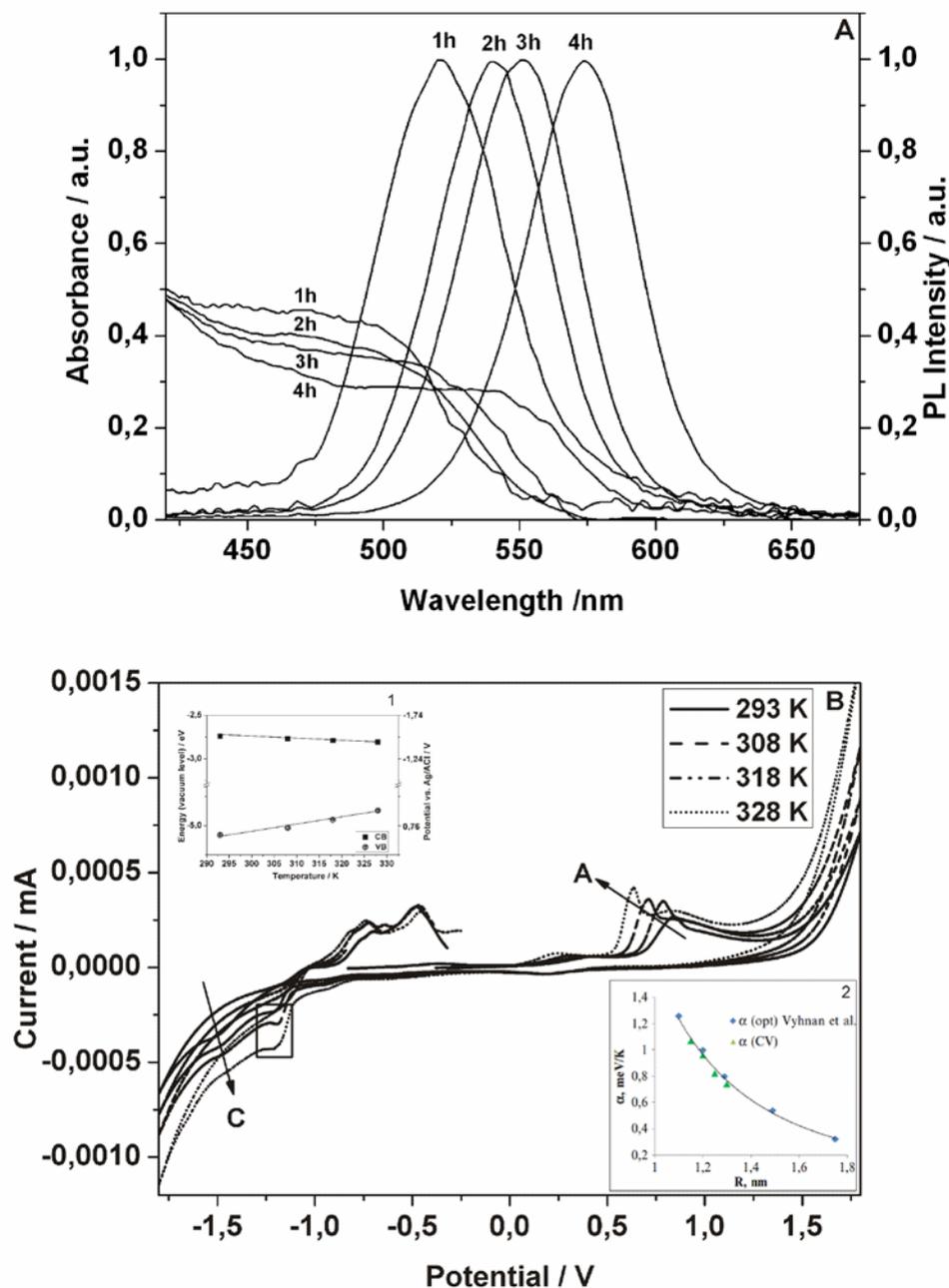
Upon heating and incubating CdTe QDs colloidal solutions at temperatures from 293 to 328 K, a symmetrical shift of the oxidation and reduction peaks was observed. This shift was linearly dependent on temperature. The estimated energy bandgap tends to decrease with increasing temperature (Fig. 1 B. *Inset 1*). A reason for such behavior may be caused by the increasing interatomic spacing when the amplitude of the atomic vibrations increases due to the increased thermal energy and as a result of enhanced quantum confinement effect [9]. It should be noted that on the CV curves recorded for CdTe QDs at 308-328 K there appears an additional cathodic peak in the range of -1.20 V. This may be caused by electrochemical activity of stabilizing ligand thermal degradation products.

To describe the temperature dependence of the energy gap of CdTe QDs the Varshni equation [10] was used. It should be noted that optical ( $E_{g_{opt}}$ ) and electrochemical ( $E_{g_{cv}}$ ) bandgaps of CdTe QDs demonstrates the same trend. Based on this fact the temperature sensitivity of CdTe QDs of a particular size can be determined from the slope of the linear regression approximation plotted in the coordinates  $E_g$  vs.  $\alpha T^2/(T+\theta)$ . In this case, the temperature coefficient  $\alpha$  will describe the change in the electrochemical bandgap energy ( $E_{g_{cv}}$ ) when the temperature is changed by 1 K, and  $E_0$  is the bandgap energy at 0 K. During such calculation we noticed that the temperature coefficient decreases with the increasing radius of the QDs (Fig. 1B. *Inset 2*) which is in accordance with the data obtained from optical studies reported by Vyhnan et al [5].

#### Monitoring band structure changes during the incorporation of $Hg^{2+}$ into CdTe QDs structure.

The TGA-stabilized CdHgTe QDs were obtained by incorporation of  $Hg^{2+}$  ions into freshly prepared CdTe nanoclusters and subsequent thermal treatment for 5 hour at 100°C. The amount of added  $Hg^{2+}$  ions was 2% and 4% of  $Cd^{2+}$  content in the solution. Such doping leads to significant changes in the optical properties. The bathochromic shift of PL peaks from 588 nm to the near-infrared regions of the spectrum 730

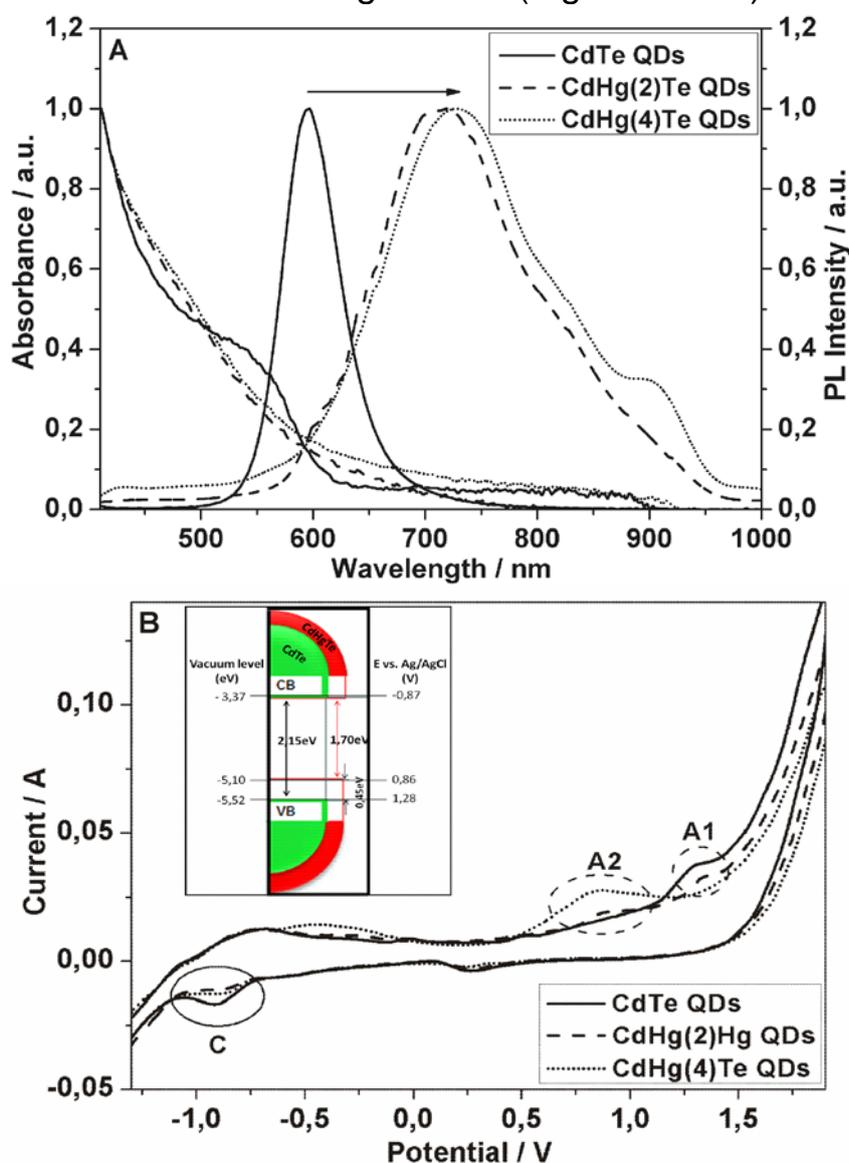
nm as result of Hg-doping on the valence band of the CdTe QDs (Fig. 2 A). The absorption maximum is shifted towards longer wavelengths and becoming less pronounced. Fig. 2 B shows the cyclic voltammograms for the CdTe QDs (linear line). The anodic (marked as **A**) and cathodic (marked as **C**) peaks at 1.28 and  $-0.87$  V are observed. The potential difference of 2.15 V between these two peaks is in good agreement with the optical band gap obtained from the absorption spectra (2.2 eV).



**Figure 1. A** Absorption and PL spectra of TGA-stabilized CdTe QDs of different sizes (time of ripening at 100 °C is shown in the legend); **B** CV recorded for the CdTe QDs ( $d = 2.5$  nm) colloidal solution at different temperatures. The scan rate was 100 mV/s; **Inset 1:** Plot of the valence (VB) and conduction (CB) band edge positions for CdTe, obtained from the respective oxidation and reduction peaks; **Inset 2:** Size dependence of the temperature sensitivity of CdTe QDs.

At the cyclic voltammograms for the CdHg(2)Te QDs (dash line) the same oxidation peak at 1.28V and reduction peak at -0.87V and appearance of additional oxidation peak at 0.86 V are observed. Such changes can be explained by formation of Hg energy levels in the band gap of Hg-doped CdTe QDs. It is important to note that in the case of CdHg(4)Te (dotted line), the oxidation peak at 1.28V has completely disappeared. Such an effect indicates that large amount of cadmium surface atoms is replaced by mercury, which leads to the formation of the core/shell structure CdTe/CdHgTe. A similar effect was reported in our previous work [11] for Hg-alloyed CdTe QDs.

Based on the obtained CV data and calculations we plotted energy levels diagram of CdTe and CdHgTe QDs (Fig. 2B. *Inset*).



**Figure 2 A.** Normalized Absorption and PL spectra of TGA-stabilized CdTe & CdHgTe QDs; **B.** Cyclic voltammograms recorder for TGA-stabilized CdTe, CdHg(2)Te and CdHg(4)Te QDs colloidal solutions. The scan rates were 100 mV/s; **Inset:** Scheme of the band structure parameters of CdTe & CdHgTe QDs, calculated from CV data.

### Influence of the stabilizing surface ligands on the electrochemical activity of CdTe and CdHgTe QDs.

To understand the effect of the stabilizing ligand concentration on the electrochemical activity of TGA-stabilized CdTe and CdHgTe QDs two samples have been synthesized according to previously described methods with 100% excess of TGA. The amount of added  $\text{Hg}^{2+}$  ions was 5% of  $\text{Cd}^{2+}$  content in the solution.

As shown in Fig. 3A, the absorption peaks at 550 nm can be seen only for the first sample (CdTe QDs). Upon addition of  $\text{Hg}^{2+}$  ions the absorption maximum disappeared, which is typical for CdHgTe QDs. We also observed the bathochromic shift of the PL peaks from 586 nm (for the CdTe QDs) to the infrared region of the spectrum and occurrence of double-peak structures of PL spectra with maxima at 838 and 907 nm (for the CdHgTe QDs). This effect can be explained by the formation of HgTe shell during cation exchange process [11].

However, as shown by the CV measurements, electrochemical signal from QDs was not detected. At the cyclic voltammograms for both samples only the oxidation peak at 1 V and reduction peak at -0.9V was observed (Fig. 3B). This corresponds to the signals obtained for 20 mg/L solution of thioglycolic acid. This result indicates that excess of stabilizing ligand on top of QDs hinders detection of the electrochemical response of QDs (Fig. 3B *Inset*).

### The impact of CdS shell growth on the CdTe band structure parameters.

It is well-known that the thermal decomposition of sulfur-containing stabilizing ligands favors the formation of CdS shell on the CdTe core [12]. Therefore, the thickness of the CdS shell can be controlled by variation of heat treatment process duration.

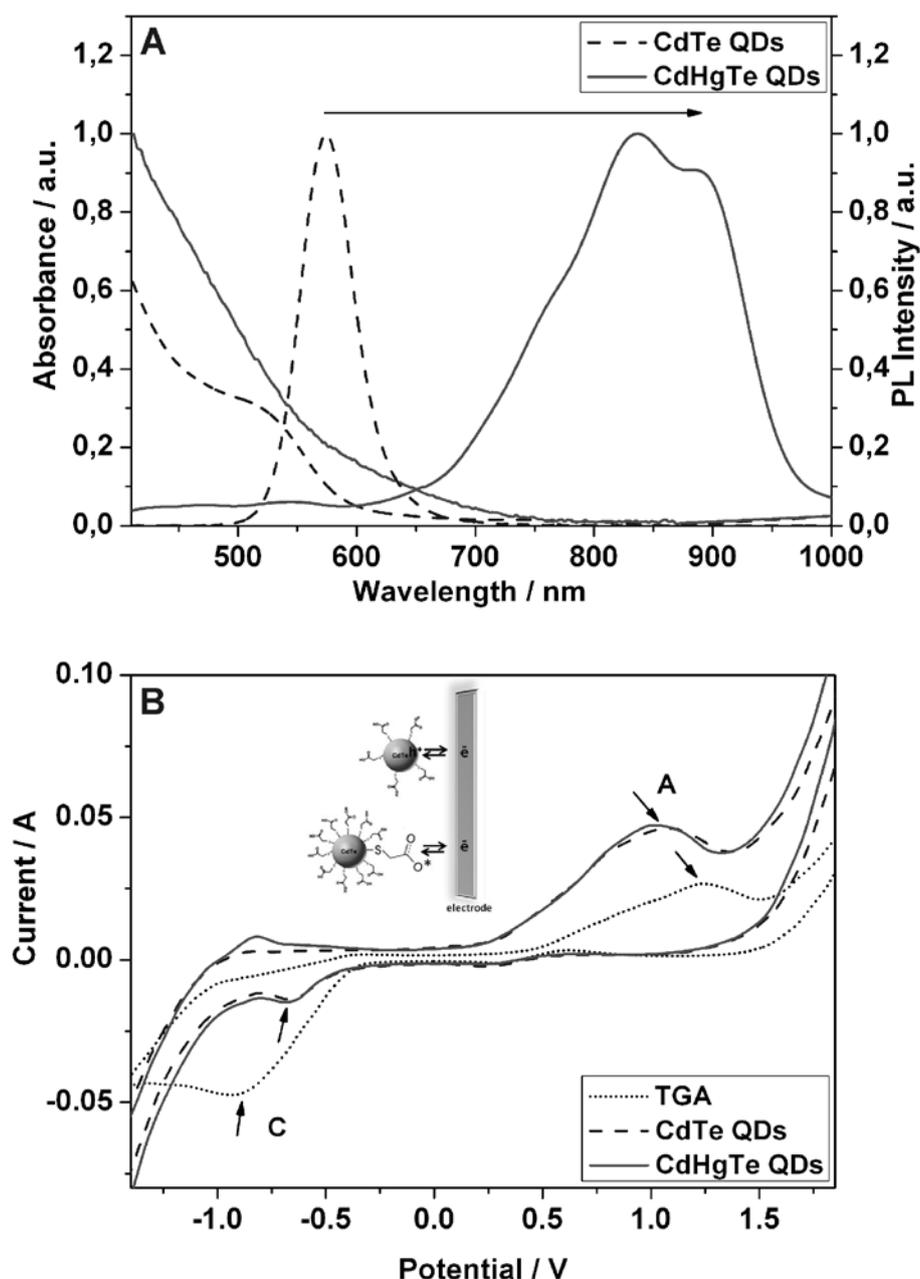
The CdTe/CdS core/shell structures were prepared by the refluxing of TGA-stabilized CdTe QDs solution at 100°C for 1 (sample 1) and 6 hours (sample 2).

Fig. 4A shows normalized absorption and PL spectra of TGA-stabilized CdTe QDs which were chosen for the electrochemical investigation of impact of the CdS shell growth on the CdTe band structure. The absorption maximum shifts to shorter wavelengths with decreasing the heat treatment time from 1 up to 6 hours as a consequence of CdTe core size increasing and CdS shell growth.

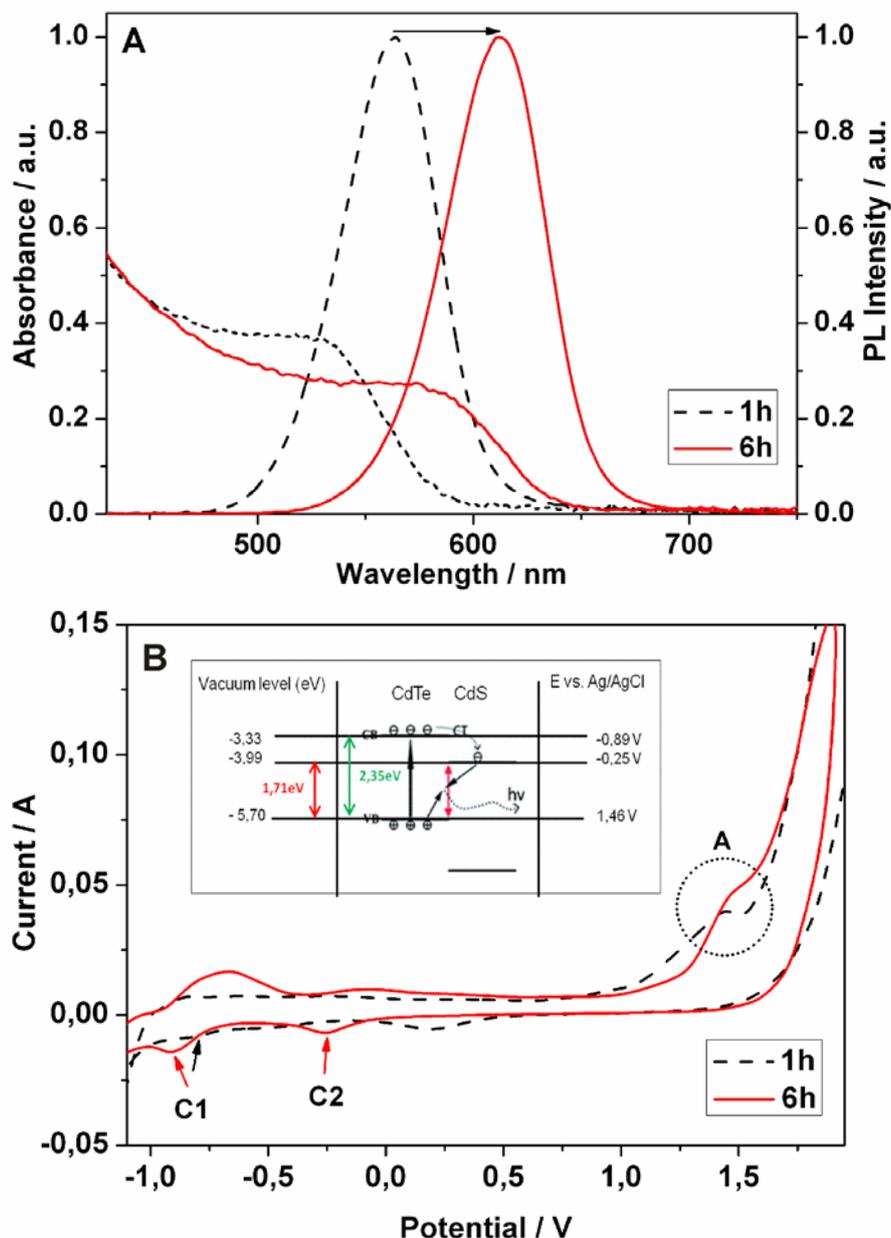
At CV curve recorded for sample 1 (dash line) an anodic peak at about 1.46 V (**A**) and less pronounced cathodic peak (**C1**) at -0.83 V were observed. They can be attributed to the degradation of QDs after the electron transfer (oxidation process) [13]. This effect is enhanced by *poor surface passivation as the result of short-time heat treatment*. At CV

curve recorded for the sample 2 (linear line) an anodic peak at about 1.46 V (**A**), cathodic peak (**C1**) at -0.89 and addition cathodic peak (**C2**) at -0.25 V were observed. The appearance of the cathodic peak **C2** may indicate the electrochemical activity of the CdS shell and corresponds to the conduction band edge energy of CdS. At the same time, the peak **C1** becomes more pronounced, which confirms the good surface passivation of CdTe QDs by CdS shell.

Energy levels of CdTe/CdS QDs that were determined from the CVs are plotted in the *inset* of Fig. 4B.



**Figure 3 A.** Normalized Absorption and PL spectra of CdTe and CdHgTe QDs stabilized with excess of TGA; **B.** Cyclic voltammograms recorder for thioglycolic acid-stabilized CdTe and CdHgTe QDs colloidal solutions & 20 mg/L TGA. The scan rates were 100 mV/s.



**Figure 4 A.** Normalized absorption and PL spectra of TGA-stabilized CdTe and CdTe/CdS QDs; **B** Cyclic voltammograms recorder for TGA-stabilized CdTe QDs after 1h and 6 hours of heat treatment process. The scan rates were 100 mV/s. **Inset:** Scheme of the band structure parameters of CdTe/CdS QDs, calculated from CV data.

## Conclusions

Cyclic voltammetry has been used to achieve valuable information about changes in the CdTe QDs properties under different influences: doping with Hg-ions, temperature changes, and CdS shell formation. Also, importance of rational choice of surface coverage for the detection of CV signal from quantum dot samples was clearly demonstrated. These results demonstrate that CV can be successfully used for the characterization of the QD band structure.

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