The analytical application of quenching phenomena of CdTe-QD nanoparticles

Petra HUMAJOVÁ, Patrik BALIAK, Ivan Landry Yumdjo YOUMBISSI,

Alžběta JEBAVÁ, Lenka ŘEZÁČOVÁ and Přemysl LUBAL

Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, CZ-625 00, Brno

Electronic supporting informations (ESI)

Experimental Section:

Instrumentation

- Spectrofluorimeter QuantaMaster 300 Plus (PTI, Canada)
- Modular spectrofluorimeter: excitation source laser (λ = 445 nm, power 50 mW, Viasho), CCD detector AvaSpec 2048 (200–1100 nm), optical fibers (diameter 800 μm, length 1 m), cuvette holder 1×1 × 3 cm (all Avantes Netherland)
- Absorption spectrophotometer Hewlett-Packard 8453 (Agilent, USA)
- Spectrofluorimeter SPC-130 EM (Becker & Hickl, Germany) for measurement of luminescence decay by time correlated single photon counting (TCSPC): excitation source pulse ps diode laser (λ = 408 nm, f = 20 MHz) TCSPC-SPC-130 EM module with picosecond resolution. The instrumental response function was measured with non fluorescent dispersive medium Ludol. The experimental data were exported and analyzed by DecayFit software.
- Zetasizer nano ZS (Malvern, UK): light source: He – Ne Laser (wavelength 633 nm, output power 4 mW, measurement range: 0.3nm - 10μm
- AFM microscope JPK NanoWizard 3 (Bruker, Germany)
- BioSAXS 1000 (Rigaku, Japan): λ = 14 nm, *t* = 5 min; samples in 1.5 mm borosilicate glass capillaries (WJM-Glas). Data Analysis by Primus and GNOM software.
- electrophoretic equipment Mini-PROTEAN 3 Cell (Bio-Rad, Sweden). The polyacrylamide 15% gel for analysis of CdTe-QD nanoparticles was prepared by UV-initiated radical polymerization of the following solution for 60 min (redestillled water 1.04 ml, 30% acrylalamide/bisacrylamide…4 ml, 1.5 M TRIS buffer (pH 8.8)…2.08 ml, 10% APS….0.08 ml, TEMED…0.008 ml, 20 mM GSH….0.8 ml). The electrophoretic buffer containing 192 mM glycine, 2 mM GSH a 25 mM Tris (pH 8.8) was mixed with solution containing CdTe-QD (1 mg/ml) and 1% bromphenol Blue , 2.5% glycerol, 1 mM GSH a 62.5 mM Tris/HCl, pH 6,8. The PAGE analysis was run under 150 V for 75 min.
- ICP-OES spectrometer iCAP 6500 Duo (Thermo, UK).
- pH meter Orion 3 Star (Thermo Scientific) Electrode type: HC 133 glass electrode

Table S1: The list of applied chemical compounds.

Name	Chemical Formula	M_r	Purity	Supplier
Cadmium chloride	$CdCl_2$	183.32	p.a.	Lachema
Sodium citrate	$Na_3C_6H_5O_7 \cdot 2H_2O$	294.12	p.a.	Lachema
Sodium Telurate	Na_2TeO_3	221.58	99%	Sigma-Aldrich
Tellurium	Te	127.6		Fluka
Sodium tetrahydroborate	$NaBH_4$	37.83	≥ 99%	Sigma-Aldrich
Sodium hydroxide	NaOH	40.00	p.a.	Sigma-Aldrich
Hydrochloric acid	HCl	36.46	p.a.	Lach-Ner
Isopropanol	C_3H_8O	60.10	99,9%	Sigma-Aldrich
HEPS	$C_8H_{18}N_2O_4S$	238.30	≥ 99,5%	Sigma-Aldrich
Copper chloride	$CuCl_2.2H_2O$	170.48	p.a.	Merck
L – glutathione (GSH)	$C_{10}H_{17}N_3O_6S$	307.32	≥ 98%	Sigma-Aldrich
3-mercaptopropionic / thioglycolic acid (MPA)	$C_3H_6O_2S$	106.14	≥ 99%	Acros Organics
Dimercaptosuccinic acid (DMSA)	$C_4H_6O_4S_2$	182.21	99%	Acros Organics
2-mercapto-ethanesulfonic acid (MESNA)	$C_2H_5O_3S_2Na$	164.18	≥98 %	Sigma Aldrich

Synthesis and characterization of the CdTe-QD nanoparticles

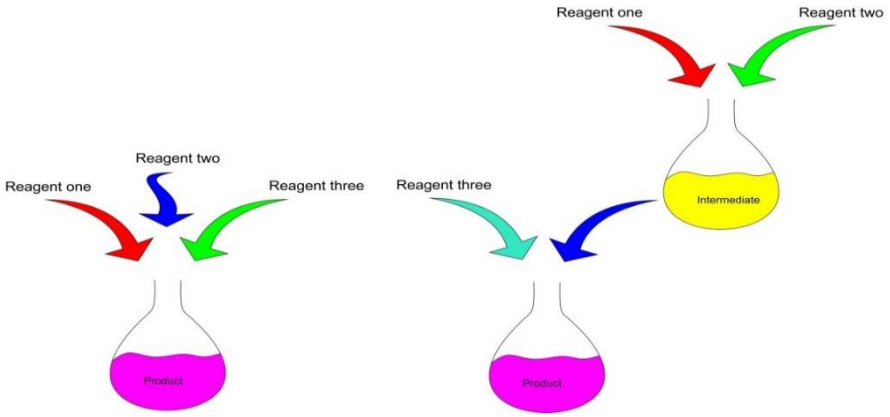


Figure S1: The description of one-step vs. two-step synthetic procedures of CdTe-QD's nanoparticles.

Synthesis of CdTe-QD nanoparticles

Procedure for one-step preparation of CdTe-QD nanoparticles covered by ligand concerning thiol group

The synthetic procedure was adopted and modified from literature [1, 2]:

1. Preparation of aqueous solution consisting of 188 mg cadmium chloride, 547 mg of sodium citrate and 1.2 mmol of modifying molecule (MPA/GSH). pH adjustment of solution to 8-9 with 0.1 M sodium hydroxide solution.
2. Addition of 44 mg of sodium tellurate and 100 mg of sodium tetrahydroborate.
3. Heating under reflux for fixed time period (30-360 min).
4. Cooling.
5. Precipitation with nonpolar solvent (aqueous isopropanolic solution, 1:1 (*v*/v)
6. Separation of CdTe-QD's precipitate by centrifugation (3400 rpm) for 10-20 mins.
7. Drying for 24 hours at 40-60 ºC.

Procedure for two-step preparation of CdTe-QD nanoparticles covered by ligand concerning thiol group

Figure S2: The first step of synthesis of NaHTe used for preparation of CdTe.

The first step of synthesis is preparation of NaHTe compound according to equation:

$$4\ NaBH_4 + 2\ Te + 7\ H_2O \rightarrow 2\ NaHTe + Na_2B_4O_7 + 14\ H_2 \qquad (A1)$$

The second step is precipitation of the CdTe-QD nanoparticles:

$$Cd^{2+} + HTe^- \rightarrow CdTe + H^+ \qquad (A2)$$

The stabilization of CdTe nanoparticles is achieved by presence of covering ligand with thiol-group in solution. The pH > 9 is necessary for the formation of CdTe compound as well as presence of thiol group in deprotonated form to cover the surface of nanoparticles by binding thiolate into CdTe crystal structure (see Fig. 2).

The procedure was adopted and modified from literature [3, 4] where more experimental details could be found there.

1. Preparation of aqueous solution (S1) concerning 188 mg cadmium chloride, 623 mg of sodium citrate and 1.2 mmol of thiol containing organic ligand. pH adjustment of aqueous solution to 9.5 with 0.1 M sodium hydroxide solution.

   2. Preparation of mixture of solid-state compounds (84.9 mg $NaBH_4$, 127.0 mg Te (powder) in glass vessel to which 2 ml of distilled water are added through septum (see Figure S2) which is kept there to remove gaseous hydrogen formed during the chemical reaction (see A1). In addition, cooling (~ 0°C) and vigorous stirring of solution for two hours is crucial point of this synthesis. The time for the NaHTe preparation could not exceed 5 hours and it should be used for synthesis of CdTe-QD nanoparticles as soon as possible.
3. The violet NaHTe compound is then carefully transferred into a three-necked flask containing solution, this solution is heated under reflux for several (optimum 1-4) hours at temperature of 90 °C.
4. Precipitation with nonpolar solvent (aqueous isopropanolic solution, 1:1 (*v*/v)
5. Separation of CdTe-QD's precipitate by centrifugation (3400 rpm) for 10-20 mins.
6. Drying for 24 hours at 40-60 ºC.

DLS/ ζ potential measurements of CdTe-QD nanoparticles

Table S2. The characterization of prepared CdTe-QD nanoparticles.

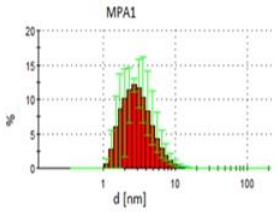
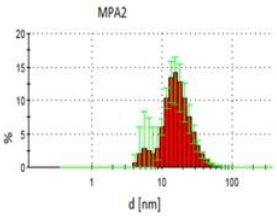
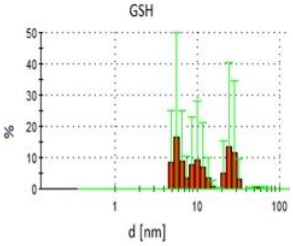
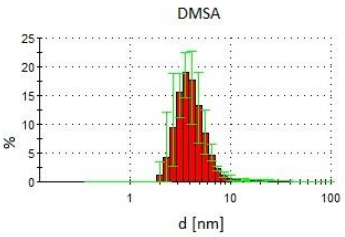
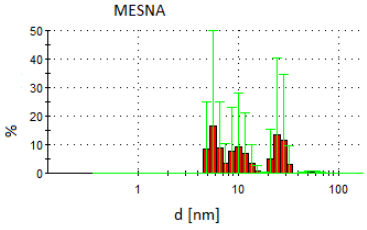
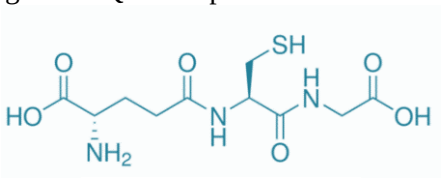
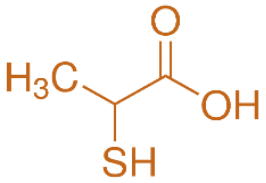
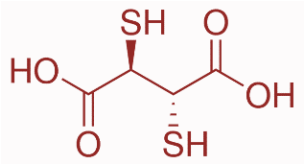
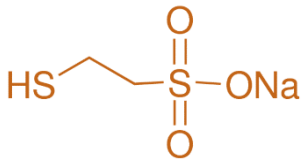
CdTe-QD nanoparticles with covering ligand	pH	ζ potential / mV	Size distribution
MPA (1-step synthesis)	**10.1**	**-50 ± 9**	
MPA (2-step synthesis)	**10.1**	**-45 ± 10**	
GSH (1-step synthesis)	**9.5**	**-45 ± 14**	
DMSA (1-step synthesis)	**9.5**	**-52 ± 7**	
MESNA (1-step synthesis)	**9.9**	**-58 ± 8**	

Table S3: The chemical structural formulas of organic ligands covering CdTe-QD nanoparticles.

Glutathione (GSH)	
Mercaptopropionic acid (MPA)	
Dimeracptosuccinic acid (DMSA)	
2-mercapto-ethanesulfonic acid (MESNA)	

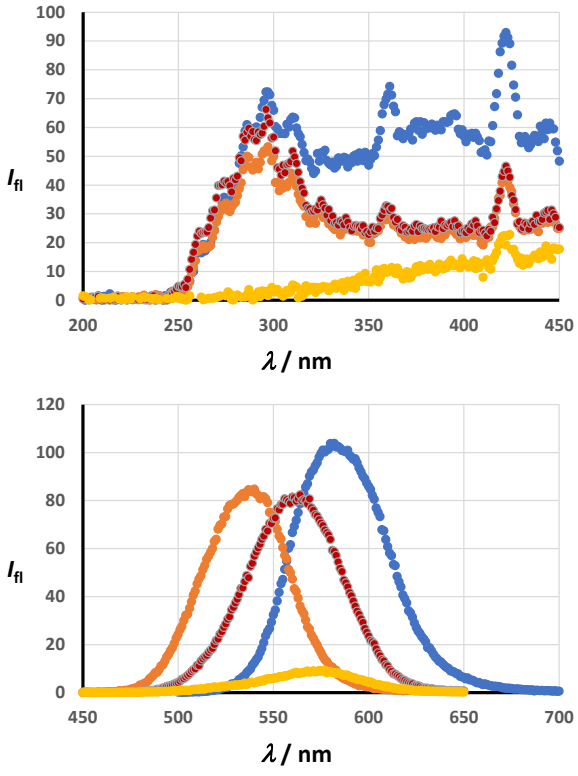


Figure S3: The example of excitation and emission (λ_{exc} = 297 nm) spectra of CdTe-QD nanoparticles covered by GSH (blue), MPA (orange), DMSA (gray) and MESNA (yellow) organic ligands. The heating time was 180 min.

SAXS experiments

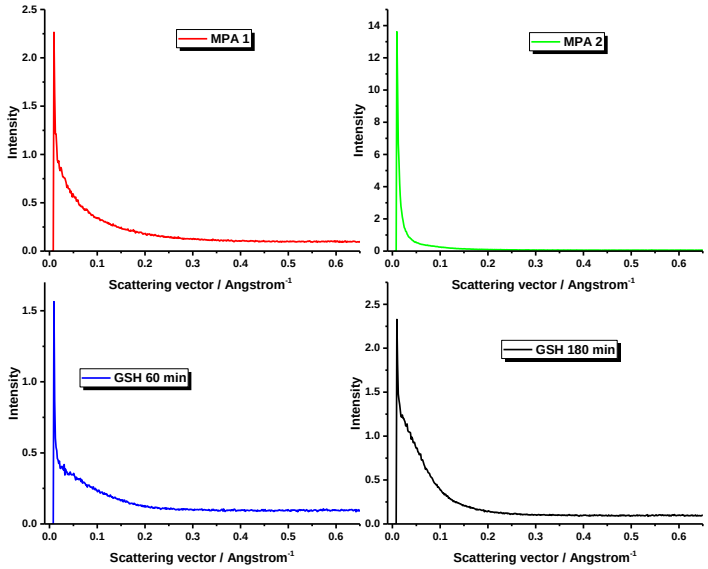
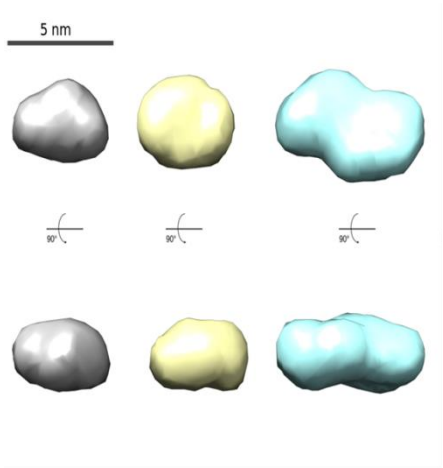


Figure S4 Experimental data for SAXS analysis of CdTe-QD nanoparticles prepared by one-step approach.



CdTe Nanoparticle	*Length /nm*	*Width /nm*
MPA (3 hours)	*4.5*	*2.9*
GSH (1 hour)	*4.5*	*3.2*
GSH (3 hours)	*6.9*	*4.3*

Figure S5 *Models of average CdTe nanoparticles with different covering ligands prepared by one-step synthesis (MPA (180 Min, left), GSH (60 min, middle), GSH (180 min, right)) obtained from the SAXS data analysis (see Fig. S4)*

AFM experiments

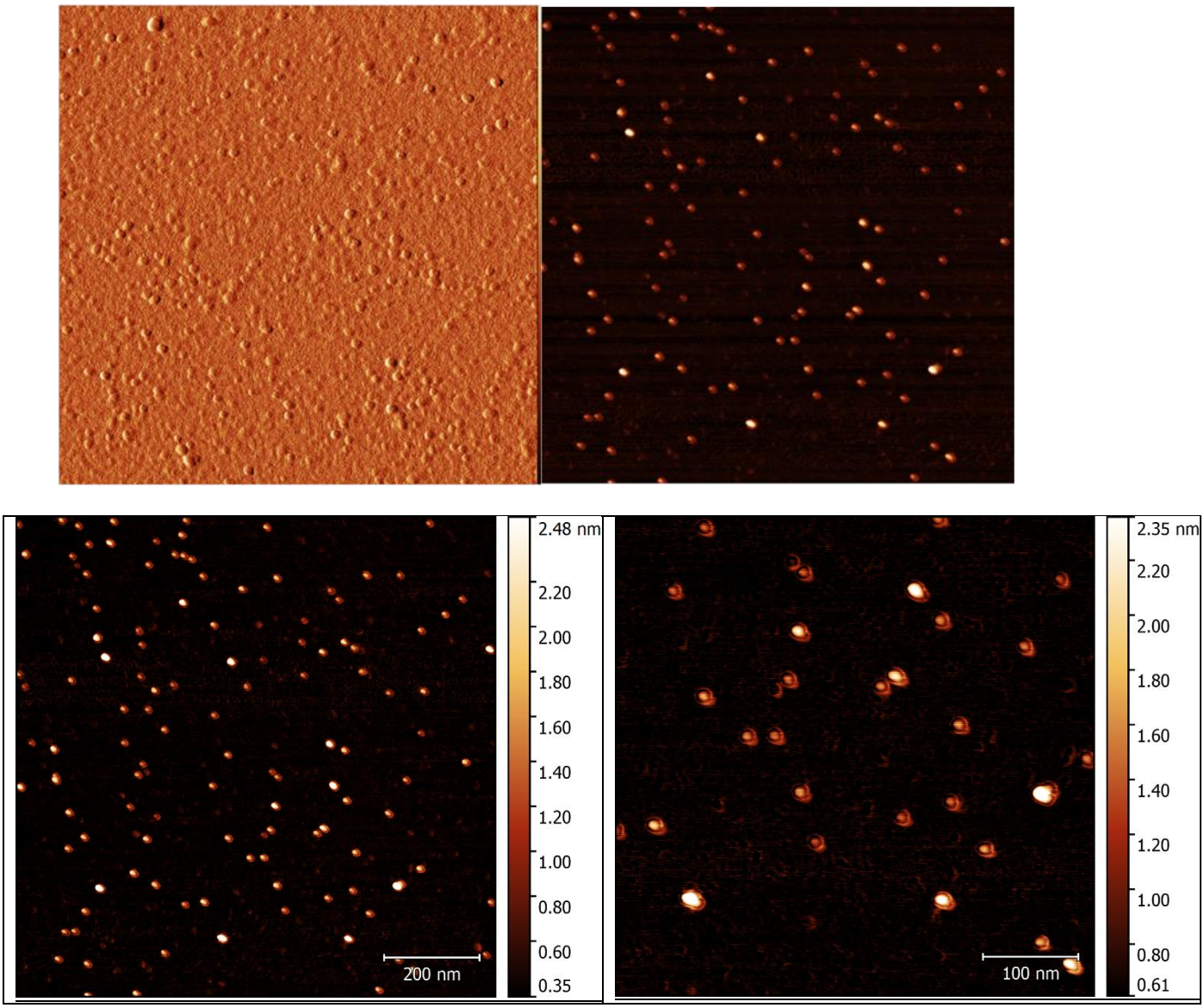


Figure S6. The pictures for CdTe-QD nanoparticles covered by MPA taken by AFM and analyzed by Gwideon software. The diameter 1.6 ± 0.5 nm was estimated from histogram of 100 randomly chosen nanoparticles.

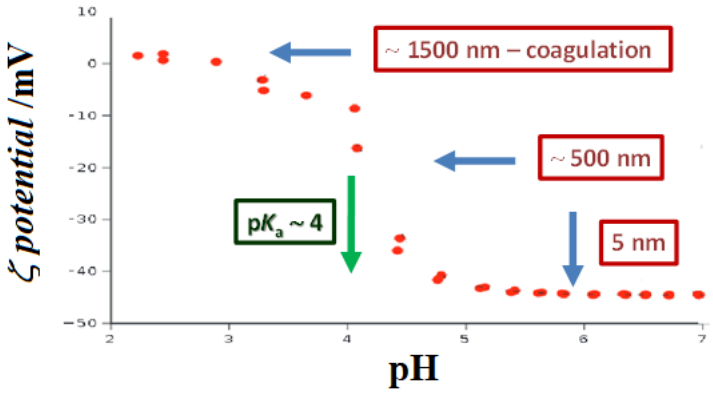


Figure S7. The pH dependence of size and charge of the CdTe-QD nanoparticles covered by MPA.

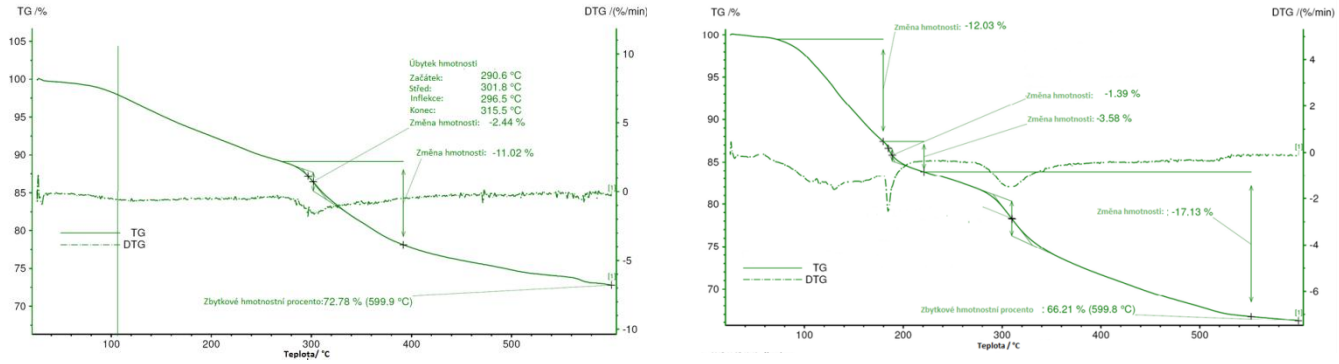


Figure S8: TG curve of CdTe nanoparticles covered by GSH synthesized 1 hour (left) and 3 hours (right)

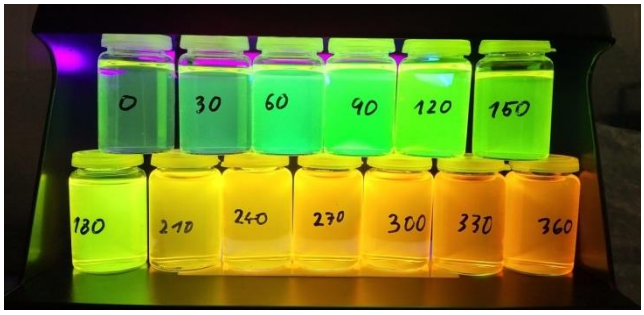


Figure S9: The picture of samples of CdTe-QD nanoparticles covered by MPA. The samples were taken in the course of heating of mixture under reflux.

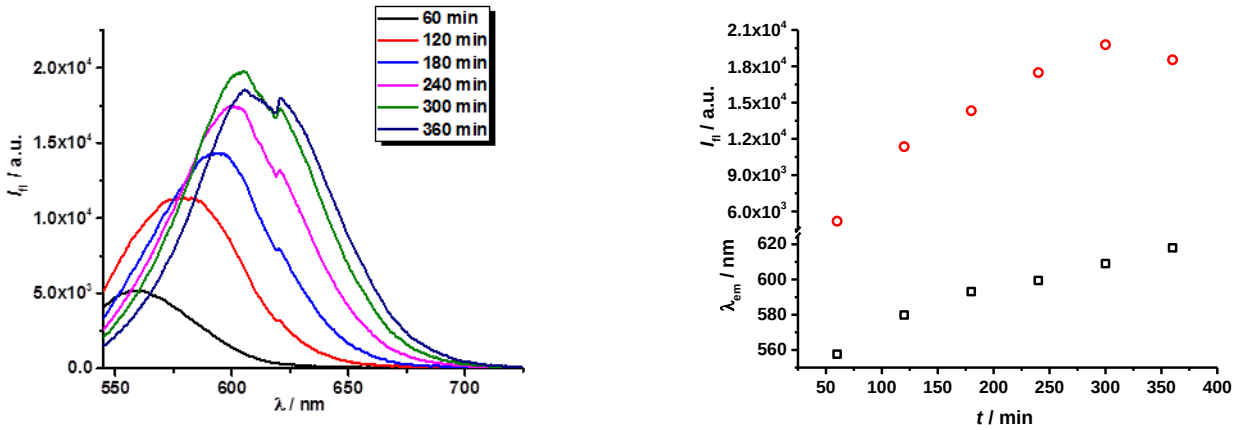


Figure S10 The emission spectra (λ_{exc} = 445 nm) of CdTe-QD nanoparticles covered by MPA prepared by heating (left) characterized by maximum of band of emission spectra (right).

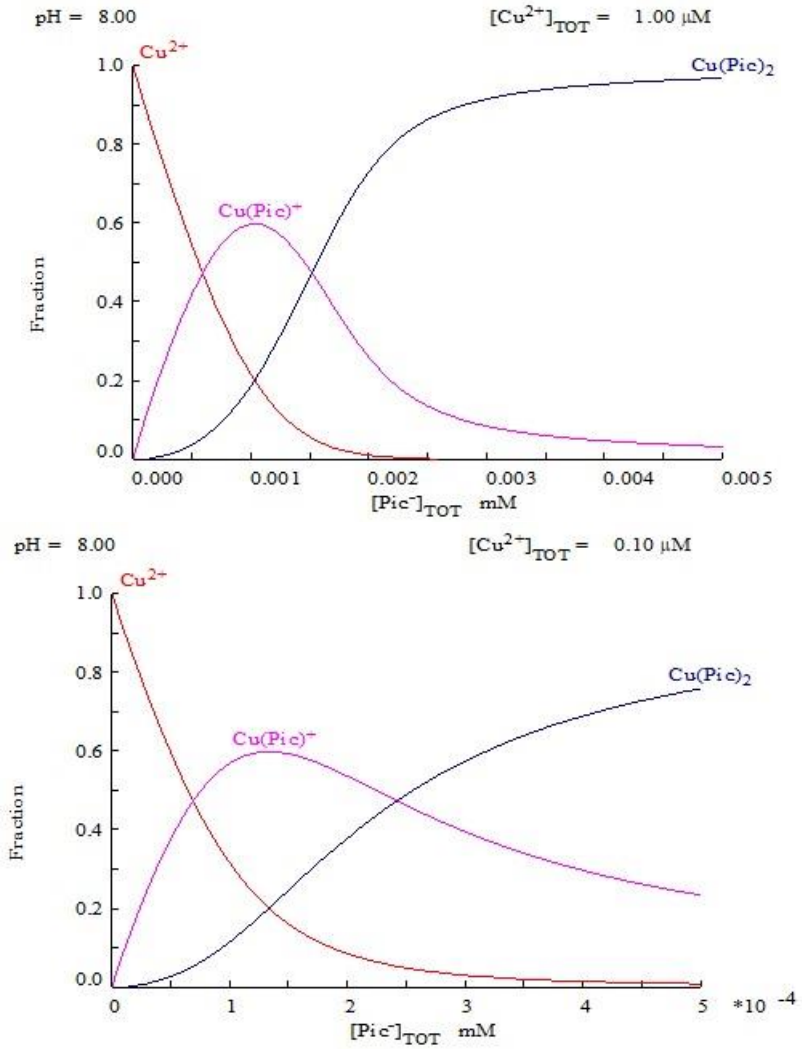


Figure S11. The distribution diagram of Cu(II) ion in presence of picolinic acid (HPic)

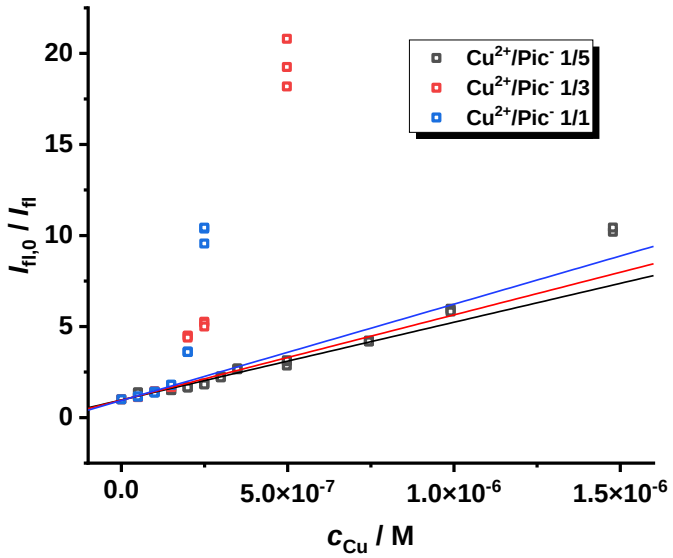


Figure S12 The quenching effect (λ_{exc} = 445 nm, λ_{em} = 580 nm) of CdTe-QD nanoparticles covered by MPA in presence of Cu(II) complex $[Cu(Pic)_n]^{2-n}$ species (see Fig. **S11** - distribution diagram).

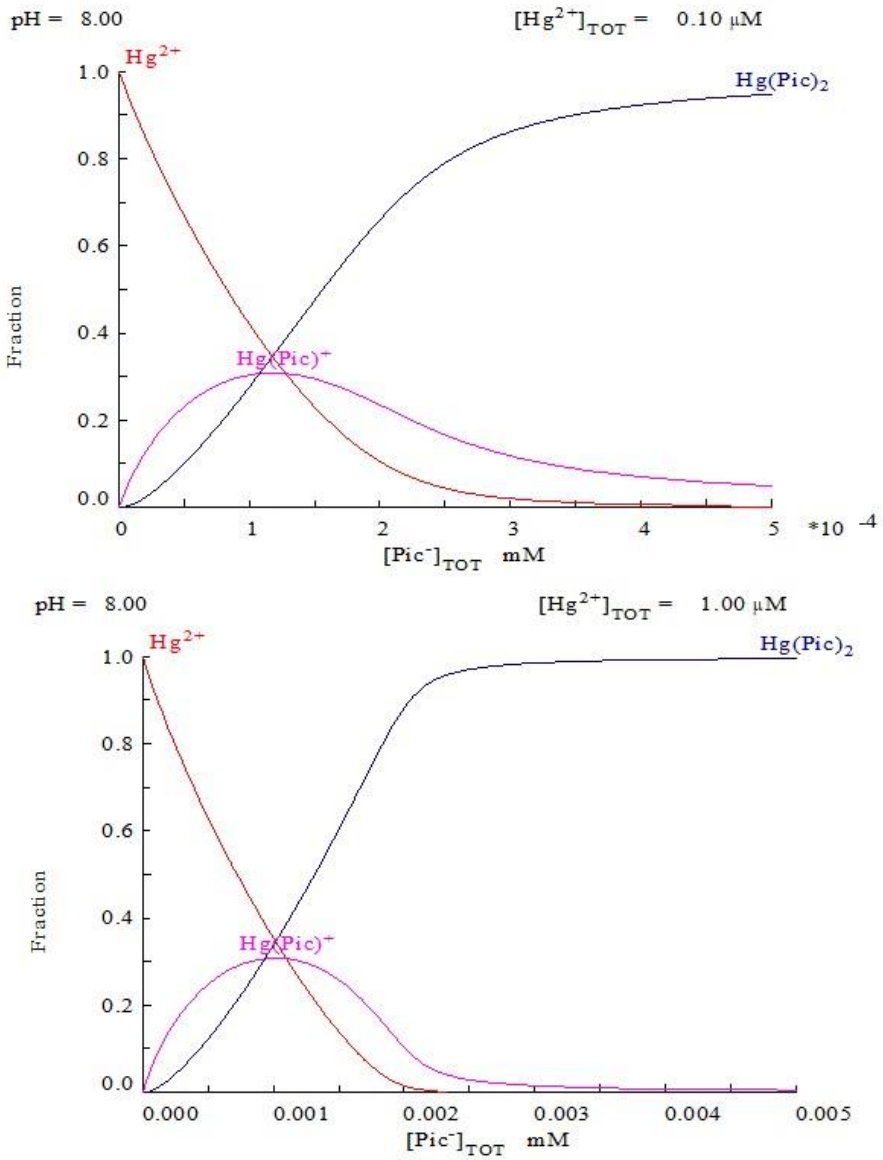


Figure S13. The distribution diagram of Hg(II) ion in presence of picolinic acid (HPic)

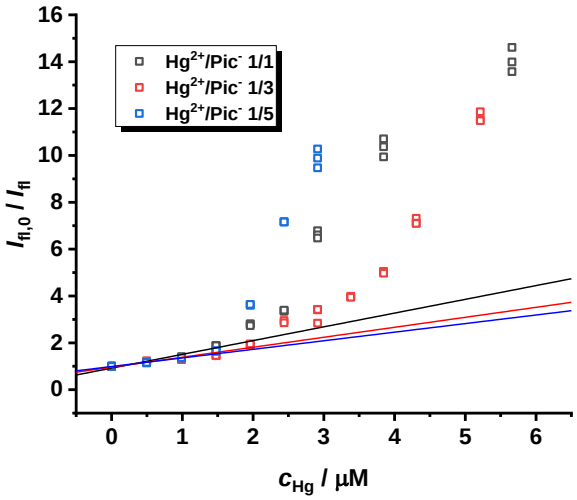


Figure S14. The quenching effect (λ_{exc} = 445 nm, λ_{em} = 580 nm) of CdTe-QD nanoparticles covered by MPA in presence of Hg(II) complex $[Hg(Pic)_n]^{2-n}$ species (see Fig. **S13** - distribution diagram).

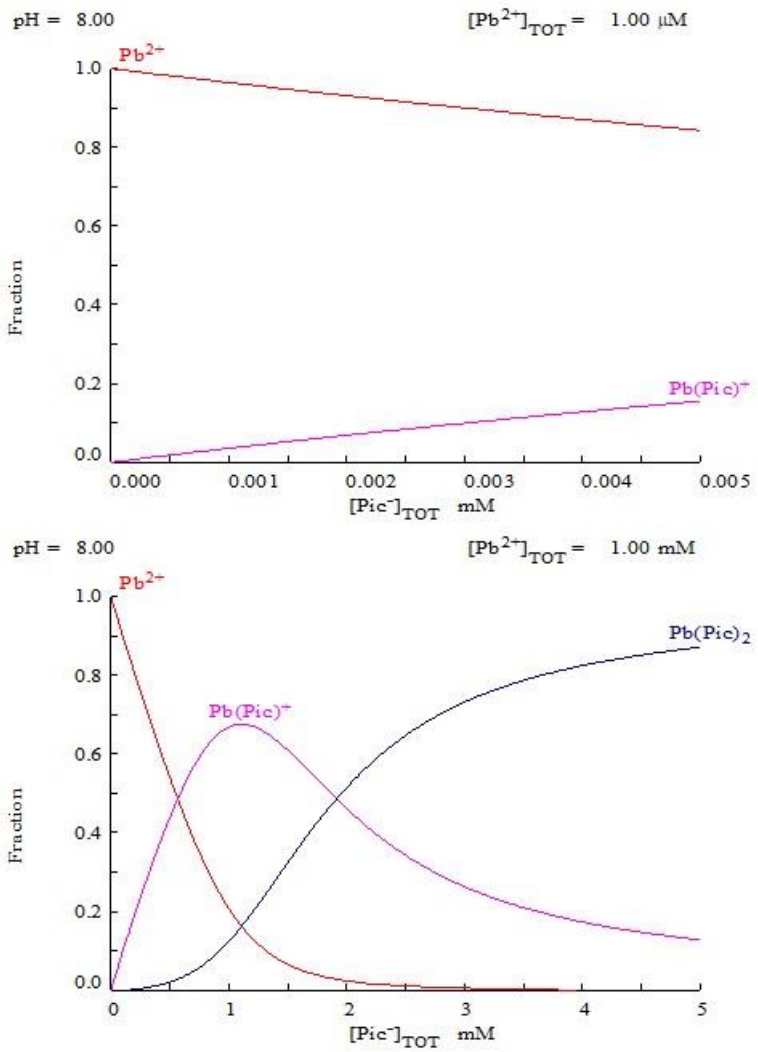


Figure S15. The distribution diagram of Pb(II) ion in presence of picolinic acid (HPic)

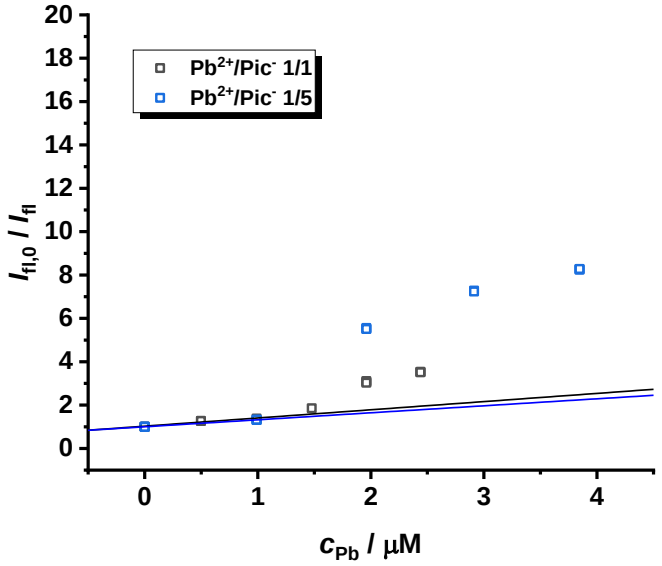


Figure S16 The quenching effect (λ_{exc} = 445 nm, λ_{em} = 580 nm) of CdTe-QD nanoparticles covered by MPA in presence of Pb(II) complex species (see Fig. **S15** - distribution diagram).

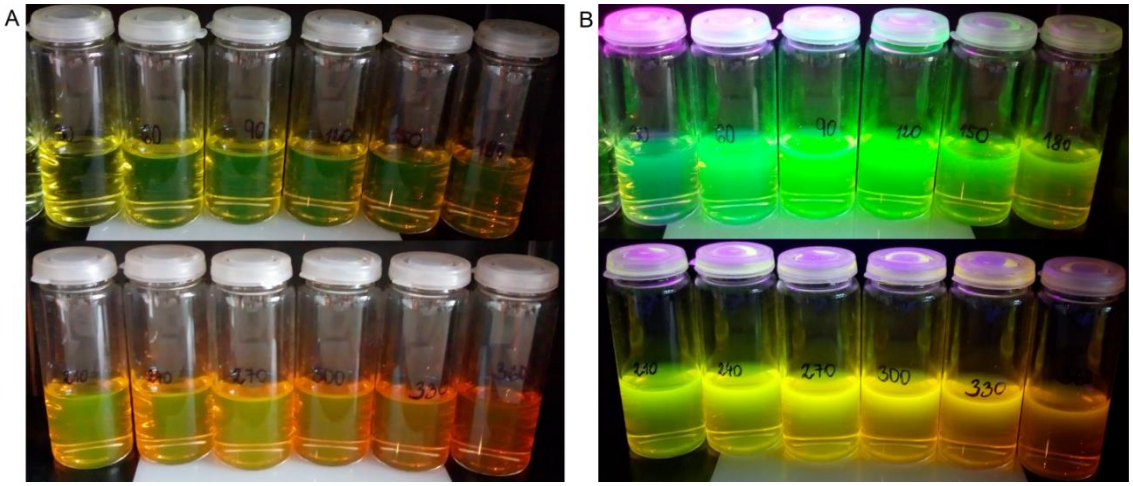


Figure S17: The picture of samples of CdTe nanoparticles covered by GSH. The samples were taken in the course of heating of mixture under reflux.

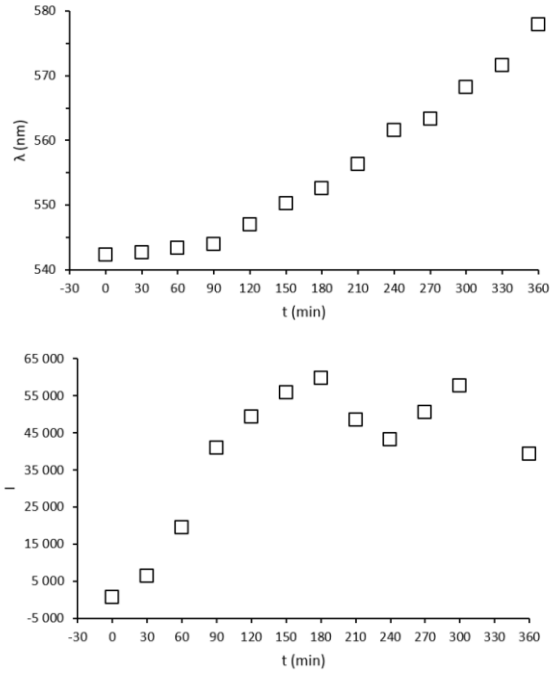


Figure S18: The photophysical properties of GSH CdTe-QD nanoparticles differing by heating time 0-360 min.

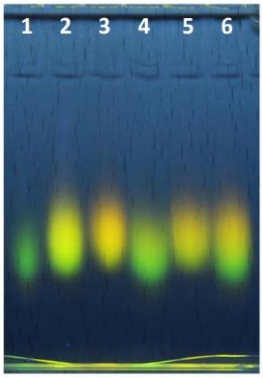


Figure S19: The PAGE picture under UV light for CdTe-QD nanoparticles prepared 120 min (1), 180 min (2), 240 min (3), mixture NP's 180 + 240 min (4) 180+240 min (5), 120 + 240 min (6)

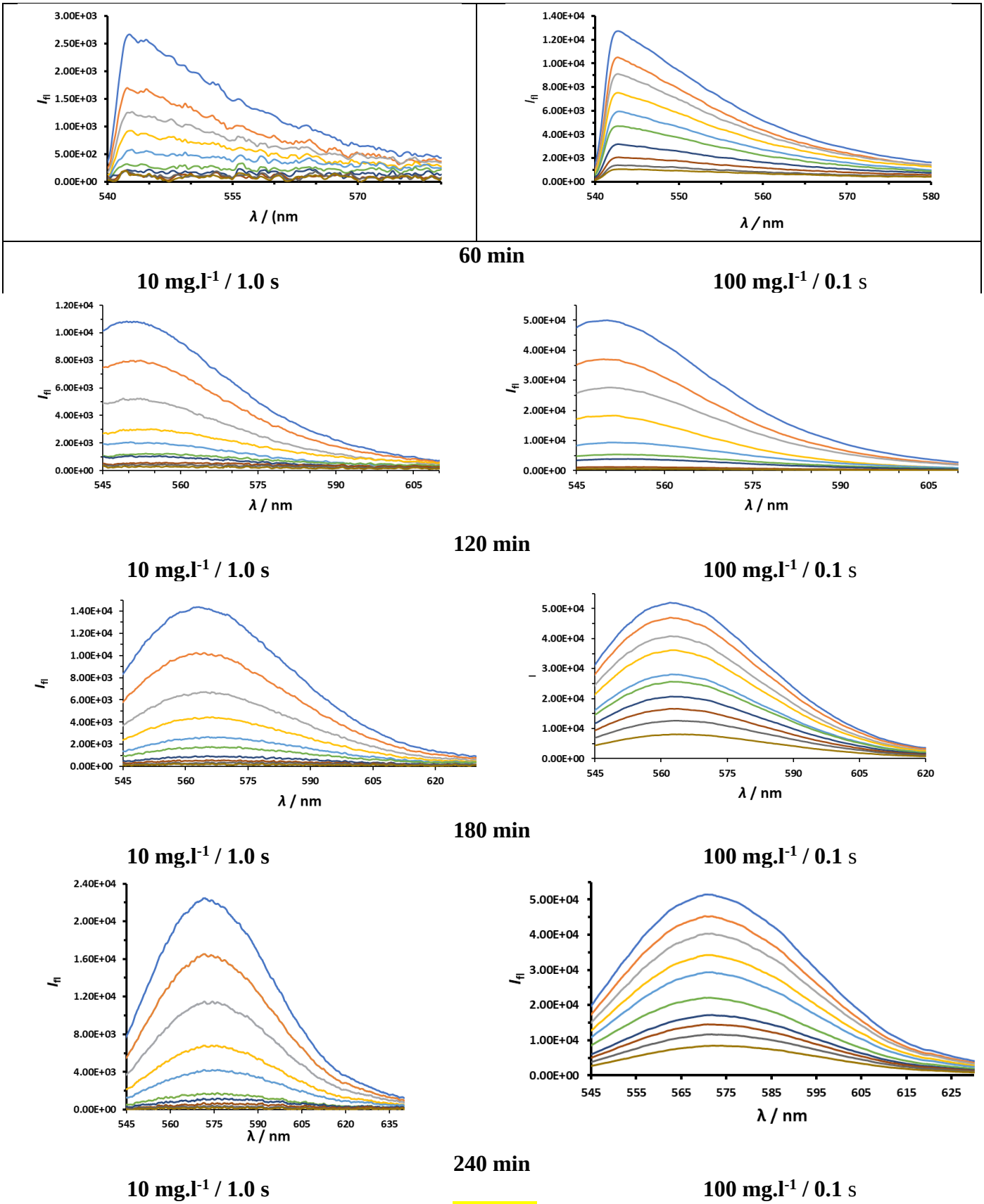


Figure S20: The quenching effect of Cu(II) ions (0-5 μM) on photophysical properties of GSH CdTe-QD nanoparticles of different size achieved by heating time 0-240 min. The normalized experimental data are in Fig. 7.

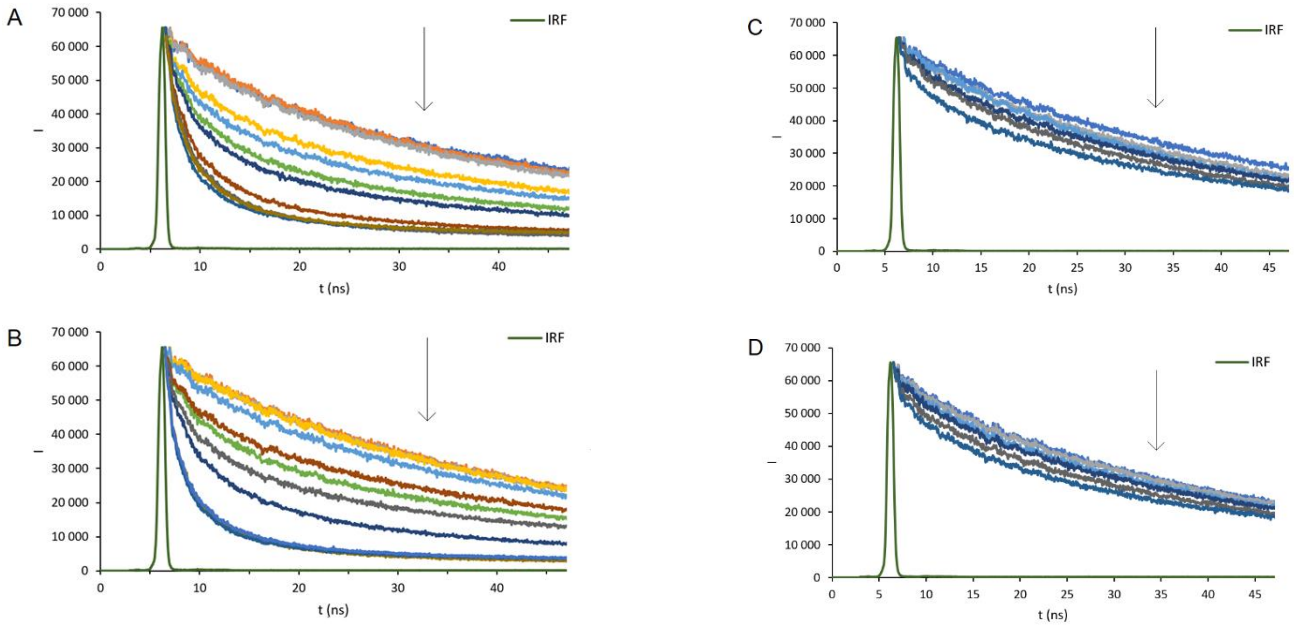


Figure S21: The quenching effect of Cu(II) ions (0-5 μM) on photophysical properties of GSH-CdTe-QD nanoparticles of different size (λ_{exc} = 445 nm) achieved by heating time 60 min (A), 120 min (B), 180 min (C) and 240 min (D).

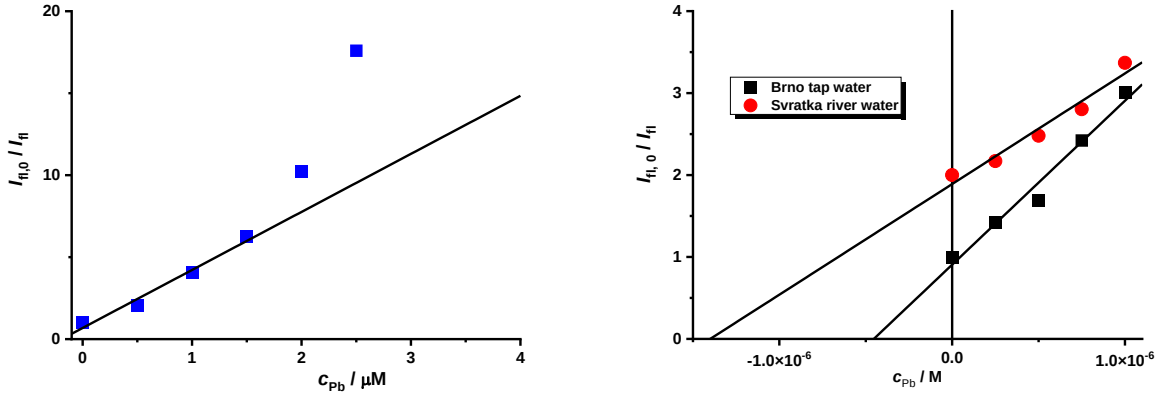


Figure S22 The example of analysis of real water samples by MPA-CdTe-QD nanoparticles (c = 1.3 mg.ml^{-1}, pH = 6.5, λ_{exc} /λ_{em} = 405/540 nm). Samples: distilled water(left), Brno tap water, Svratka river water (right). The values for Svratka river samples (Brno damm) were subtracted by value 1 for the sake of clarity.

References:

1. Duan J. L., Song L. X., Zhan J. H., One-Pot Synthesis of Highly Luminescent CdTe Quantum Dots by Microwave Irradiation Reduction and Their Hg^{2+}-Sensitive Properties, *Nano Res.* 2 (**2009**) 61-68. https://doi.org/10.1007/s12274-009-9004-0
2. Bao, H.F.; Wang, E.K.; Dong, S.J. One-pot synthesis of CdTe nanocrystals and shape control of luminescent CdTe-cystine nanocomposites. *Small* **2006**, 2, 476 – 480. https://doi.org/10.1002/smll.200500346
3. Klepárník K., Voráčová I., Lišková M., Přikryl J., Hezinová V., Foret F., Capillary electrophoresis immunoassays with conjugated quantum dots, *Electrophoresis* 32 (**2011**) 1217-1223. https://doi.org/10.1002/elps.201000652
4. Voráčová I., Klepárník K., Lišková M., Foret F., Determination of zeta-potential, charge, and number of organic ligands on the surface of water soluble quantum dots by capillary electrophoresis, *Electrophoresis* 36 (**2015**) 867-874. https://doi.org/10.1002/elps.201400459