

## QUANTUM DOT-BASED FLUOROSENSOR FOR DETERMINATION OF CU(II) AND PB(II) IONS

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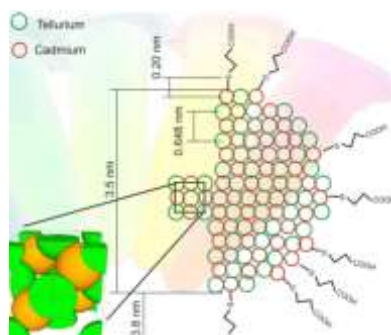
### Abstract

This paper deals with application of CdTe nanoparticles for analytical determination of Cu(II) and Pb(II) ions by means of laser-induced luminescence spectroscopy. The analytical procedure was optimized for experimental conditions (pH, concentration of nanoparticles and analyte) and then it was utilized for simultaneous determination of both metal ions in water samples. The proposed method is simple and fast and it can be employed for analysis out of lab.

**Keywords:** Nanoparticles, Quantum dots (QD's), Quenching effect, Cu(II), Pb(II), Thiol group, Mercaptopropionic acid (MPA)

### 1. INTRODUCTION

The recent nanotechnological methods enable the assembly and characterization of well-defined objects in nanometer scale. Nano-objects are intensively studied in chemistry as well in physics and biology. The quantum-dots colloid particles of diameter 1-10 nm are usually low-soluble cadmium compounds of CdX stoichiometry (X = S, Se, Te) [1-3]. Their solubility is increased by surface covering of thiol containing compounds (e.g. mercaptopropionic acid, glutathione, cysteine, etc.) and also by increase of solution pH which leads to dissociation of functional carboxylate groups (see **Fig. 1**, [1-3]). Their exceptional physico-chemical and optical properties as well as higher photostability compared with organic fluorophores can be used for development of new analytical methods for the detection and determination of ions and the molecules important in biology and medicine [1-3]. QD-based nanoparticles exhibit broad excitation and narrow emission band where their position depends on their kind, morphology and size and thus the maximum of emission band can be tuned by synthetic process. This paper deals with application of QD-CdTe nanoparticles for analytical determination of Cu(II) and Pb(II) ions by means of laser-induced luminescence spectroscopy.



**Fig. 1** The structure of QD-CdTe nanoparticles (adopted from ref. [4] with permission)

## 2. EXPERIMENTAL

The synthesis of QD-CdTe nanoparticles covered by MPA was carried out by one-step procedure [5]. The mixture of cadmium chloride, sodium tellurite, sodium citrate, MPA (surface modifier) and NaBH<sub>4</sub> (reducing agent) in aqueous solution was heated at temperature 95 °C for variable time 3, 4 and 5 hours. The samples of NP's were purified by precipitation with isopropanol (1:1 ratio) followed by centrifugation (12,000 rpm). The prepared NP's were characterized by measurement of their size distribution and zeta potential on Zetasizer Nano ZS equipment (Malvern). Solid nanoparticles were re-dissolved in water prior the analysis.

Luminiscence measurements were carried out on home-made equipment, where laser beam of 405 nm wavelength (Eclipsa X100H405) as excitation source of power 80 mW was introduced into cuvette space by optical guide and the emission spectrum was recorded on AvaSpec-2048 detector operating in region 350-1100 nm driven by AvaSoft software (both AVANTES) running on PC.

## 3. RESULTS AND DISCUSSION

The CdTe nanoparticles were synthesized according to procedure described in literature [5] and the heating time was varied within 3-5 hours. The purified samples were dissolved in water (pH ~ 6.5). The maximum of emission band is about 532 nm (see **Fig. 2 and 3**) and it is not dependent on procedure of preparation.

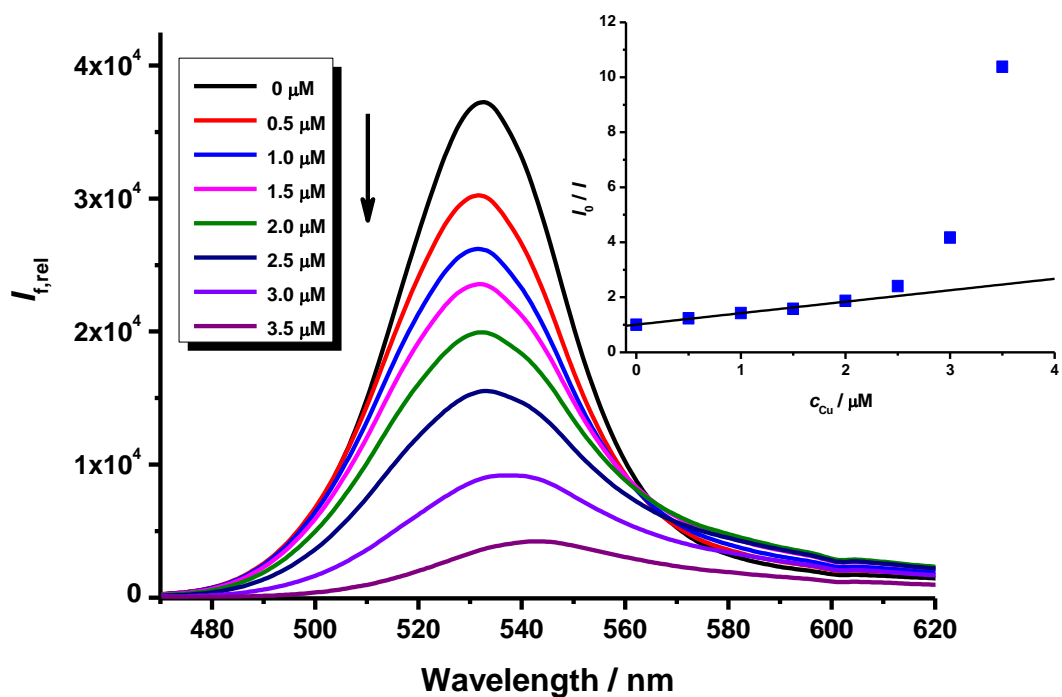
DLS experiments show that the diameter of NP's was estimated to be about 5 nm and zeta-potential was calculated about -40 mV. Decreasing the solution pH, the nanoparticles start to agglomerate due to neutralization of propionic acid arms covering surface of nanoparticles (see **Fig. 1**) while p*K*<sub>a</sub> value was estimated about 4. At pH < 3, the formation of uncharged agglomerate clusters of size 1500 nm was observed and the luminescence of solution was decreased to zero. It was also found out that the luminescence of solution containing NP's was decreased with higher pH and therefore pH ~ 6.5 was adjusted for next experiments. The quenching effect was also observed for NP's solution of concentration higher than 1.3 mg.ml<sup>-1</sup> and the solutions having this concentration were utilized for the next experiments.

Adding Cu(II) or Pb(II) metal ions to NP's solution, the quenching effect is observed (see **Fig. 2 and 3**). The phenomena does have both static and dynamic character as proved by curved dependence. The first linear part can be used for the calculation of Stern-Volmer constant

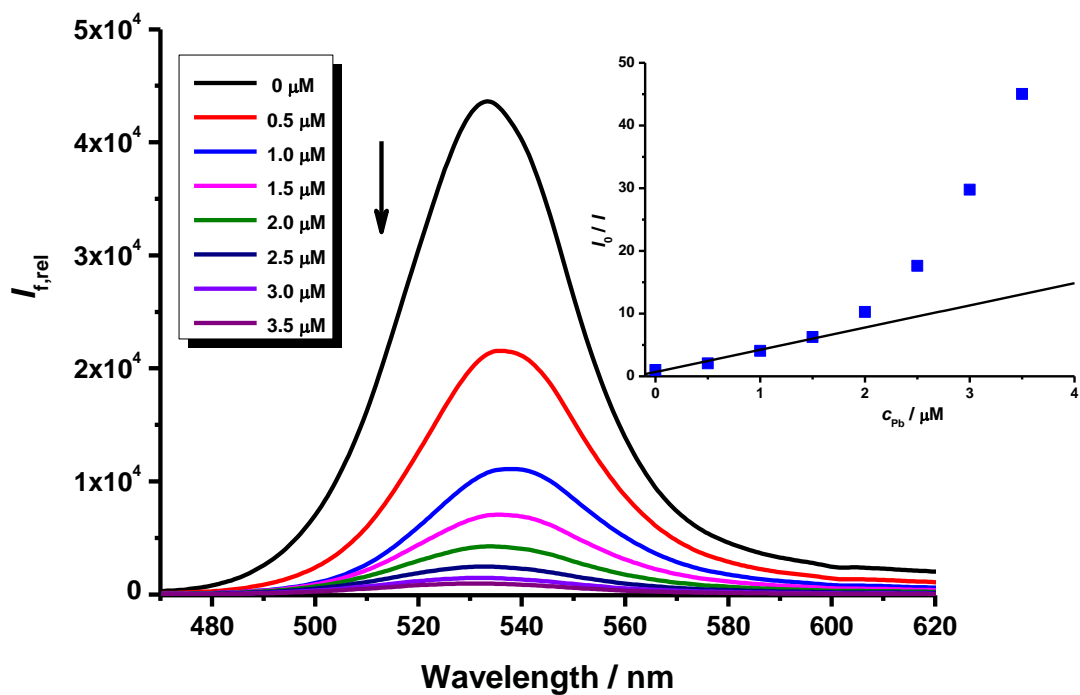
$$\frac{I_0}{I} = 1 + K_{sv} [M] \quad (1)$$

describing the dynamic character of quenching. The *K*<sub>sv</sub> values calculated for both metal ions are given in **Table 1**. This equation can be employed also for quantitative analysis of those ions in solution and therefore also the limits of detection were estimated (see Table 1). As one can observe, the *K*<sub>sv</sub> value is higher for Pb(II) than for Cu(II) ion while the LOD's are opposite. The explanation can be in the fact that Pb(II) ion is generally more efficient quencher due to larger diameter and higher polarizability.

The quenching effect of both metal ions was also tested for other concentration of NP's solution (*c* = 1.3-6.5 mg.ml<sup>-1</sup>). The highest sensitivity was observed for the lowest NP's solution concentration while the sensitivity decreased for higher concentration. This effect was opposite in some cases for Pb(II) ion probably as consequence of formation of less soluble PbTe compound by exchange reaction. It was also found out for quenching study that there is no interference of Pb(II) ions for determination of Cu(II) and *vice versa*.



**Fig. 2** The example of quenching effect of copper(II) ions on luminescence of CdTe nanoparticles ( $c = 1.3 \text{ mg.ml}^{-1}$ ,  $\text{pH} = 6.5$ ).

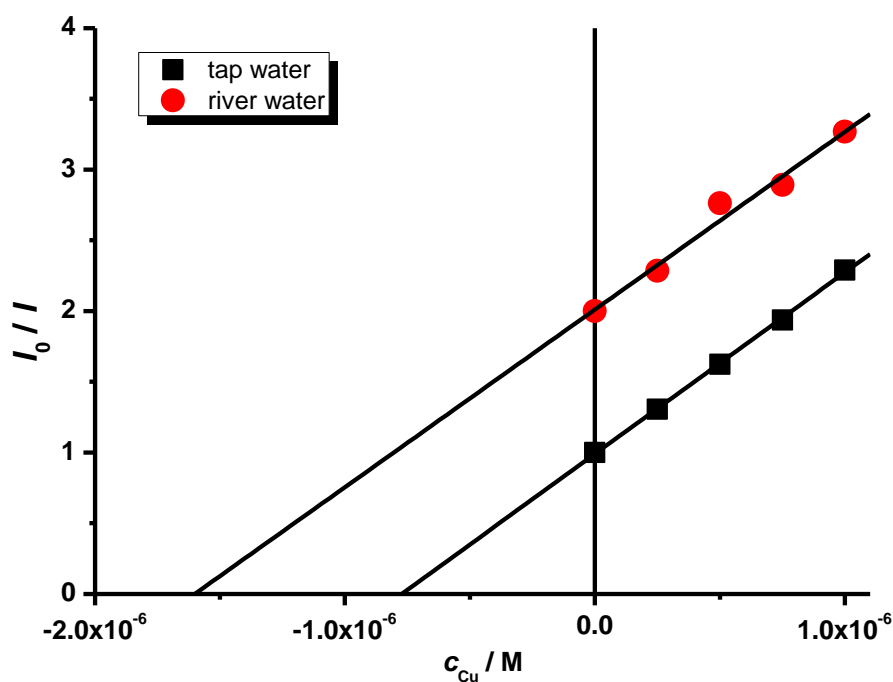


**Fig. 3** The example of quenching effect of lead(II) ions on luminescence of CdTe nanoparticles ( $c = 1.3 \text{ mg.ml}^{-1}$ ,  $\text{pH} = 6.5$ ).

**Table 1** The values of Stern-Volmer quenching constant and limit of detection (LOD) obtained for determination of Cu(II) and Pb(II) ions (see **Fig. 2 and 3**)

Metal Ion	$K_{SV}$ ( $M^{-1}/10^5$ )	LOD (nM)
Cu(II)	4.17	250
Pb(II)	35.4	45

The analytical procedure was verified by analysis of real samples (tap water, water taken from Svatka river). In order to eliminate the matrix effect of other ions present in samples, the standard addition method was used for the analysis. In case of Cu(II) ion analysis (see **Fig. 4**), the slopes of both calibration plots are almost the same which means that there is no matrix effect. On contrary, there is significant difference in slopes for Pb(II) ion analysis probably as consequence of exchange reaction. The results of analysis of real samples are presented in **Table 2**. The same samples were analyzed by ICP atomic emission spectroscopy. The results obtained by both experimental techniques are comparable in case of Pb(II) ion analysis while the Cu(II) concentrations slightly differ probably due to lower sensitivity and higher LOD.



**Fig. 4** The example of Cu(II) analysis of water samples using their quenching effect on luminescence of CdTe-QD nanoparticles ( $c = 1.3 \text{ mg.ml}^{-1}$ ,  $\text{pH} = 6.5$ ). The values for river water samples were increased by one in order to simplify the plot.

**Table 2** The results of analysis of water samples. Values for fluorosensor are average values from triplicates.

Metal Ion	Tap water		Svatka River water	
	Fluorosensor	ICP-OES	Fluorosensor	ICP-OES
Cu(II)	$4.7 \pm 0.6 \text{ ppm}$ ( $0.74 \pm 0.10 \mu\text{M}$ )	7.6 ppm ( $1.20 \mu\text{M}$ )	$5.1 \pm 0.4 \text{ ppm}$ ( $0.80 \pm 0.06 \mu\text{M}$ )	3.1 ppm ( $0.49 \mu\text{M}$ )
Pb(II)	$5.8 \pm 2.8 \text{ ppm}$ ( $0.28 \pm 0.14 \mu\text{M}$ )	4.9 ppm ( $0.24 \mu\text{M}$ )	$8.2 \pm 1.5 \text{ ppm}$ ( $0.39 \pm 0.07 \mu\text{M}$ )	6.9 ppm ( $0.33 \mu\text{M}$ )

#### 4. CONCLUSION

The synthesis of QD-CdTe NP's according to literature procedure (see ref. [5]) was successfully repeated and the prepared nanomaterials were characterized by DLS and electrophoretic measurements in broad pH region. The laser-induced luminescence spectroscopy was employed for the study of quenching effect of Cu(II) and Pb(II) ions on NP's in solution under different experimental conditions (pH, concentration of NP's). The highest quenching effect was optimized for the best experimental conditions which were utilized for analysis of both Cu(II) and Pb(II) ions in water samples (tap water, river water). The results are comparable with values found by ICP-OES. The proposed analytical procedure can be used for fast and simple analysis of these metal ion in environment by means of portable lab instrument.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

- [1] FREEMAN R., WILLNER I. Optical molecular sensing with semiconductor quantum dots (QDs). Chem. Soc. Rev., Vol. 41, No. 10, 2012, pp. 4067-4085.
- [2] MURPHY C.J. Optical Sensing with Quantum Dots. Anal. Chem., Vol. 74, No. 19, 2002, pp. 520A-526A.
- [3] HLAVÁČEK A., SKLÁDAL P. The Application of Quantum Dots in Bioanalytical Chemistry. Chemické Listy, Vol. 105, No. 8, 2011, pp.611-615.
- [4] HEZINOVÁ V., Development of Instrumentation and Methodology in Proteomic and Environmental Analysis, PhD. Thesis, Chemical Faculty, Brno University of Technology, Brno 2011.
- [5] 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<sup>2+</sup>-Sensitive Properties, Nano Research, Vol. 2, No. 1, 2009, pp. 61-68.