

INFLUENCE OF SURFACE MODIFICATION ON CdTe QDs STABILITY

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Abstract

Quantum dots (QDs), which belong to the group of nanostructures, have great potential for use in many applications, technical, biological and medical. Despite of their great potential, there is an enormous disadvantage for quantum dots containing some metalloid elements and heavy metals especially. This disadvantage is caused by the gradual release of metal ions and instability of QDs under various conditionin. Covering QDs by various modifiers is usually used for QDs stabilization and decrease of heavy metals ions release. The accomplishment of desired effect and efficiency of QDs modifications is questionable [cit?]. In the present study, ODs stability via their fluorescent properties, size and release of cadmium ions were studied. To measure the release of Cd²⁺ from the core of QDs an electrochemical method, differential pulse voltammetry (DPV), was used. Study conducted in mildly alkaline pH, which was close to the actual pH of QDs was performed. Four types of CdTe based QDs were used: MPA - CdTe (mercaptopropionic acid), MSA - CdTe (mercaptosuccinic acid), GSH - CdTe (glutathione), CdTe / ZnSe (core/shell). During 14 days period measurement of fluorescence, zeta potential and release of Cd²⁺ ions from QDs in two alkaline buffers were performed. Fist was phosphate buffer pH 7.6 and and further used a special neutral buffer pH 7.6, which simulated the cellular environment. From these data the stability of given modified and core shell QDs were assessed. At the end of the study it was found that CdTe / ZnSe core shell QDs maintain high fluorescence values together with the lowest released cadmium ions concentration.

Keywords: Quantum dots, stability, fluorescence, zeta potential, electrochemistry

1. INTRODUCTION

Nowadays nanotechnology is often used in many fields because it shows great potential for many applications. To the group of nanomaterials belong QDs. Quantum dots may consists of metals or carbon materials [1]. Their unique chemical and physical properties suggest that in the future could replace organic fluorophores. The biggest advantage of QDs is their broad absorption and narrow emission spectra. A problem that reduces utilization of metal QDs is their toxicity [2, 3]. According to the literature various types of core / shell structures (CdSe / ZnS, CdTe / ZnS, CdTe / ZnSe) are solutions to reduce toxicity of metal QDs. However, release of heavy metals also depends on many other chemical and physical properties of QDs [1, 4, 5]. In the present study the stability of CdTe QDs covered different modifications (MPA-CdTe, MSA-CdTe, CdTe-GSH) compared to core / shell structure (ZnSe / CdTe) was investigated. Stability and toxicity of QDs are important indicators for their applications, such as using in *in vivo* imaging [6, 7]. The aim of this work is to determine how different types of QDs behave in time (measurements were performed in the short and long-term experiments - 2 h and 14 days) in a neutral pH (change in size, fluorescence, and the release of metal ions were monitored). Collected data were evaluated and served for individual type QDs stability assessment.

2. MATERIALS AND METHODS

2.1. Chemicals

All used chemicals were obtained from Sigma-Aldrich (St. Louis, MO, USA). High purity deionized water (Milli-Q Millipore 18.2 MΩ/cm, Bedford, MA, USA) was used throughout the study.

2.2. Preparation MPA - CdTe

CdTe MPA QDs were prepared according these steps: 5 mL of cadmium acetate (5.32 mg/mL) was dissolved in ACS water (43 mL) and 100 mg of trisodium citrate dihydrate was added with stirring. Mercaptopropionic acid (MPA) (1 mL; 60 mg/mL) was slowly added to stirred solution. Afterwards, 1.25 mL Na₂TeO₃ (4.432 g/L) was added. Solid sodium borohydride (50 mg) was added with vigorous stirring and hydrogen evolution was observed, followed by colour change of solution to slightly yellow. After 30 min of stirring 2 mL of solution was heated in glass vial in Multiwave 3000 Microwave Reaction System (Anton Paar, Graz, Austria) using rotor 64MG5. Reaction conditions were as follows - power 300 W, 80 °C, ramping time 10 min and hold 10 min [8].

2.3. Preparation GSH - CdTe[8]

Similarly, GSH-CdTe QDs were prepared according to procedure above, only instead of MPA, 246 mg GSH was added and reaction temperature 70 °C was used.

2.4. Preparation MSA - CdTe

10 mL of cadmium acetate (5.32 mg/mL) and 1 mL MSA (60 mg/mL) were added to 76 mL of deionized water and mixed on a magnetic stirrer. 1.8 mL 1M ammonia solution was added to adjust to neutral pH. In the end were added 1.5 mL of sodium tellurite (4.43 mg/mL) and 40 mg of sodium borohydride. The solution was stirred for 2 hours. The volume of the solution was made up to 100 mL with deionized water. Finally volume 2 mL of solution was in glass vial heated in Multiwave. Reaction conditions were as follows - power 300 W, 60 °C, ramping time 10 min and hold 10 min [9].

2.5. Preparation CdTe / ZnSe

The ZnSe solution was prepared from zinc acetate 10 mL (4.4 mg/mL) and 1 mL MSA (60 mg/mL) was added to 76 mL of milli-Q water with stirring. 1M ammonia solution (1.8 mL) was added followed by 1.5 mL of sodium selenite (5.26 mg/mL). In the end 40 mg of sodium borohydride was added to reaction mixture and thoroughly mixed for two hours. The volume of the solution was made up to 100 mL with milli-Q water. To prepare core/shell CdTe/ZnSe QDs 1 mL of ZnSe solution was added to 1 mL of CdTe QDs and heated at a temperature of 60 °C in Multiwave. Reaction conditions were as follows - power 300 W, ramping time 10 min and hold 10 min [9].

2.6. Preparation of neutral buffer pH 7.6

Neutral buffer was prepared according to the instructions [10].

2.7. Preparation of samples for measurement

QDs were four times diluted with milli-Q. Then was taken 3.18 mL of every type QDs and added to 44.86 mL phosphate buffer. Experiment was prepared in the same manner with neutral buffer. The prepared solutions were stored in the light in 25 °C.

2.8. Electrochemical determination of Cd²⁺ using DPV

Determination of cadmium by DPV were performed with 797 VA Computrace instrument (Metrohm, mesto, Switzerland), using a standard cell with three electrodes. A hanging mercury drop electrode with a drop area of 0.4 mm² was the working electrode. An Ag/AgCl/3M KCl electrode was the reference and platinum electrode

was auxiliary. The analysed samples were deoxygenated prior to measurements by purging with argon (99.999%). The parameters of the measurement were as follows: initial potential of -1.3 V, end potential $+0.12$ V, deoxygenating with argon 90 s, accumulation time 240 s, deposition potential -1.3 V, time interval 0.05 s, voltage step 5 mV, pulse amplitude 25 mV, volume of measurement cell 2 mL.

3. RESULTS AND DISCUSSION

First of all were QDs characterized using fluorescence and absorbance spectrophotometry (Tecan, Grödig, Austria) and measurement of particle sizes and zeta potentials thank to Dynamic Light Scattering (DLS) (NANO-ZS, Malvern Instruments Ltd., Worcestershire, U.K.). As an ideal excitation wavelength was chosen 400 nm. The greatest value of the fluorescence showed CdTe / ZnSe core shell QDs.

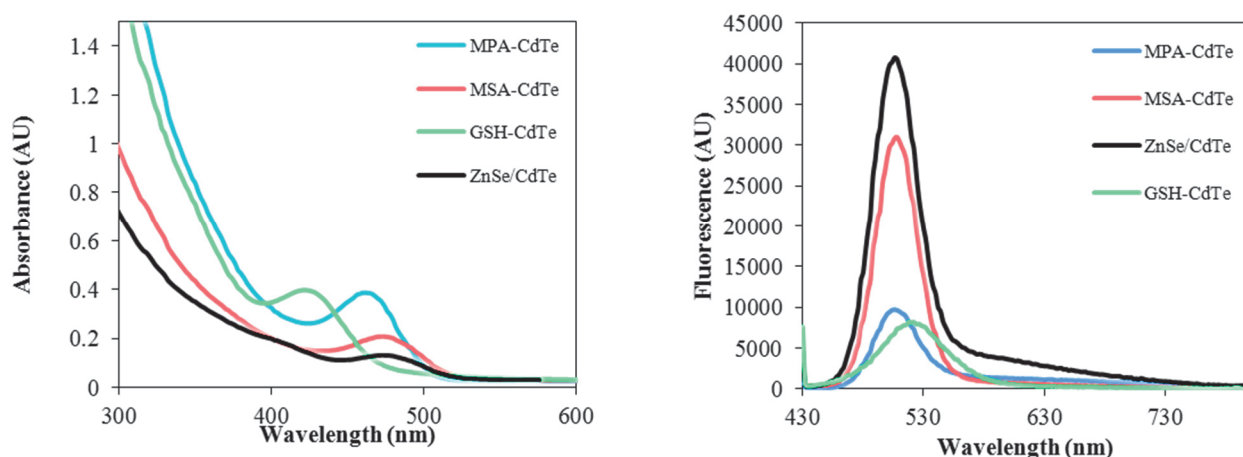


Figure 1 Absorbance and fluorescence of QDs. Utilized excitation wavelength was 400 nm within all cases

The particle size measurements were performed considering a refraction index of 2.682. The absorption coefficient in both cases was 10^{-3} respectively. The measuring temperature was set at a constant value of 25 °C. For measurement of size, disposable cuvettes type ZEN 0040, were used, containing 40 μ L of sample. For the measurements of zeta potential, a disposable cell DTS1070 was employed. In each case, the measurement duration depended on the number of runs, which varied between 20 and 40. The equilibration time was 120 s.

Table 1 pH and DLS characterization of QDs

Sample	pH	Zeta size (nm)	Zeta potential (mV)
MPA-CdTe	6.7	3.6 ± 0.5	-35.4 ± 0.2
MSA-CdTe	6.1	10.1 ± 0.9	-36.5 ± 0.1
GSH-CdTe	6.7	48.0 ± 3.5	-27.2 ± 0.4
CdTe / ZnSe	6.5	11.7 ± 2.7	-30.3 ± 0.2

During two hours, the largest increase of cadmium quantum dots modified MPA in both buffers. The smallest increase of cadmium after two hours showed MSA-CdTe. Conversely modification MSA showed the largest decrease in fluorescence, especially in a neutral buffer. Zeta potential decreased to half from initial values of all QDs. In neutral buffer were the zeta potentials significantly better than in phosphate buffer. Lowest zeta potential had MPA-CdTe.

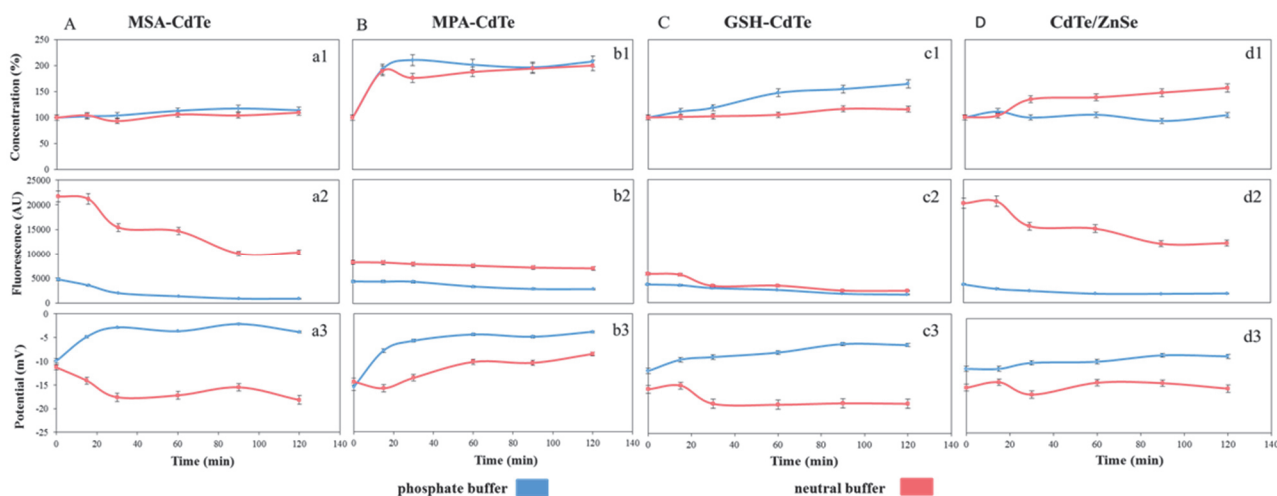


Figure 2 Study of stability QDs under neutral conditions depending on the time. Short-term interactions.

Even in the long run QDs modified MSA showed the lowest value in the release of cadmium ions. Simultaneously, this modification showed the worst photostability. The results from two-hour experiment correspond with the results of the two weeks experiment.

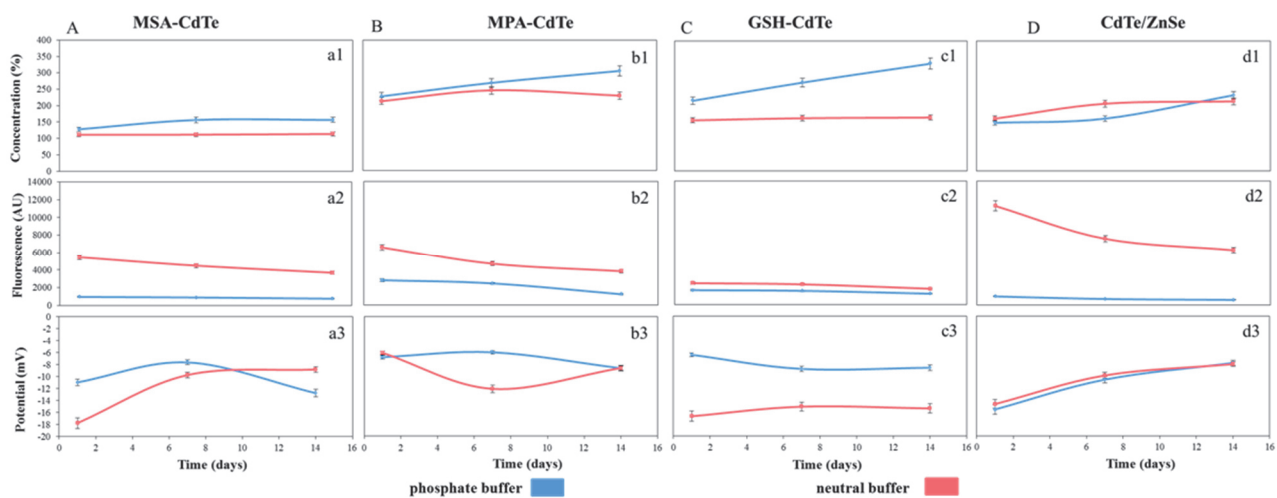


Figure 3 Study of stability QDs under neutral conditions depending on the time. Long-term interactions.

4. CONCLUSION

The objective of this experiment was to determine which preparation method of examined CdTe QDs provides the most stable quantum dots. Based on the literature has been raised the hypothesis that the most stable type of QDs should be core / shell [11]. The results show that the release of the cadmium ions are stable QDs modified MSA in a neutral environment. From the viewpoint of the photostability proved the most stable QDs modified with MSA. According to the results of fluorescence measurements were MSA-CdTe and CdTe / ZnSe least photostable. The results of the experiment show that it is not accurately detectable, that the examined QDs are the most stable. From the perspective of different criteria (applied to different applications), each QDs respond differently. For each experiment must be chosen QDs that will be appropriate for the selected application.

ACKNOWLEDGEMENTS

Research described in this paper was financed by the National Sustainability Program under grant LO1401. For the research, infrastructure of the SIX Center was used.

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