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Electrochemical Characterization of Various Synthesized Quantum Dots and the Effect of Aging and Storage Way

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New type of quantum dots (QDs) are synthesized using various types of passivators, thus the question of their stability and way of storage is still opened not only due to characterization but also due to their wide application (chemistry, chemical biology and biomedicine, gene technology, tumour biology investigation, and fluorescent labelling). In our study, we are interested in the electrochemical changes as a result of aging and storage. We employed a series of aqueous solutions of QDs from various materials with different capping agents (PbS and CuS capped with 3-mercaptopropionic acid, CdS and CdTe capped with mercaptosuccinic acid) and the changes in typical peaks for metals and passivators (acids) were detected by difference pulse voltammetry, after 28 days storage in daylight (25^{o}C) and dark (4^{o}C). Anodic stripping difference pulse voltammetry offers simple and inexpensive approach for monitoring of nanoscaled products behaviour in time, based on evaluation of both - metal and passivator peak.

Keywords: quantum dots, toxicity, stability, differential pulse voltammetry

1. INTRODUCTION

Quantum dots (QDs) belong to a group called engineered nanoparticles (ENPs) and can have size range 2−100 nm [1]. QDs can be used for applications for example as solar energy conversion, drug biosensing application, diagnostics in medical fields and light-emitting diodes [2]. Semiconductor QDs have a big potential for applications in the fluorescence imaging and sensing applications due to their good absorption properties, bright luminescence, high photostability and size tunable spectra [3]. Main composition of QD is a metalloid crystalline nucleus (e.g., CdTe, CdSe) and often a protective

shell (e.g., ZnS, CdS). By process called the encapsulation in hydrophilic polymers with carboxylic groups the nanoparticles can be become water-soluble [4,5].

Aging is the dependence of the kinetics of a physical process on the time since its original time of preparation. Aging is spotted in systems ranging from the motion of carriers of charge in amorphous semiconductors over the quantum dots blinking dynamics in living biological cells to the tracer dispersion [6]. The aging process of some of these particles (e.g., PbSe) leads to a change in morphology from QDs to nanotubes, which is associated with a decrease in absorption coefficient in the visible range along with an increase in absorption in the NIR region. Quantum dots become less emissive and exhibit a shorter emission lifetime [7].

The process of aging in ambient air has the very strong impact on photoluminescence (PL) spectra of non-conjugated core and shell (e.g., CdSe/ZnS) QDs covered with polymer. The aging process relates to the modification of polymer in ambient air is attended by the three effects: A) polymer transparency increasing for the emission of core, B) the intensity stimulation of high energy PL bands related to the interface states at the polymer interface, C) the elastic strain modification in QD systems [8].

CdSe (CdSe–ZnS core–shell) QDs are at normal conditions characterized by high PL quantum yield (70% and more) and high resistance to metabolic and photo-degradation. The luminescence intensity of QD depends on concentration of additional bio-molecules, allowing QD application as protein sensors. The aging of the PL in bio-conjugated and non-conjugated quantum dots (e.g., CdSeTe) can be studied by the micro-PL, micro-Raman and X-ray diffraction in the samples of buffered QD solution dried on a crystalline Si wafer and stored in the atmospheric ambience for approximately 2 years [9]. The automatic recovery of the PL in some QDs (e.g., PbS) stored for example in the water and in the dark for 3 months was observed only for the subset of smaller QDs and is largely due to the removal of surface defects with aging, as evidenced by the decreased percentage of un-passivated surface atoms [10].

Effects of aging and cell culture medium on the properties of the CdSe QDs were also studied by luminescence and dynamic light scattering (DSL) techniques. DLS data showed QDs to be stable, and there was no effect on the integrity of the QDs after various modifications [11]. By electrochemical impedance spectroscopy could be evaluated the main function of quantum dots layer to enhance the aging behaviour by improving the electron lifetime and charge recombination [12]. The composition of nanoparticles and their fragments degradation processes during aging could be studied by high-performance liquid chromatography coupled to electrospray ionization mass spectrometry [13]. The impact of aging of QDs on their fluorescence intensity is possible to investigate by modified quantum dots fluorescence spectrum [14]. And also sulphide coatings on silver nanoparticles can be detected as a potential instrument to determine environmental aging of nanoparticles [15]. The aim of our study was electrochemical evaluation of aging parameter of four types of QDs - PbS, CdS, CdTe and CuS, passivated by 3-mercaptopropionic acid (MPA) and mercaptosuccinic (MSA) acid. The QDs were stored for 30 days in dark at 4^{o}C and analyses were carried out by using differential pulse voltammetry, where both – metal and passivator peaks were evaluated.

2. EXPERIMENTAL PART

2.1 Chemicals and material

All chemicals for preparation QDs were purchased from Sigma-Aldrich (USA) in ACS purity. Other chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) in ACS purity unless noted otherwise. The deionised water was prepared using reverse osmosis equipment Aqual 25 (Czech Republic). The deionised water was further purified by using apparatus MilliQ Direct QUV equipped with the UV lamp. The resistance was 18 MΩ. The pH was measured using pH meter WTW inoLab (Weilheim, Germany).

2.2 Synthesis of QDs

All chemicals were used without further purification. PbS QDs were prepared according to follow steps: lead acetate trihydrate (0.038 g, 0.1 mM) was dissolved in ACS water (25 mL). MSA (0.08 g, 0.53 mM) was slowly added to stirred solution. White precipitate was formed, which disappeared after addition of 1.8 mL of 1M ammonium hydroxide. Sodium sulphide nonahydrate (0.012 g, 0.05 mM) in 23.2 mL of ACS water was added with vigorous stirring. Colour of solution was brown.

CuS QDs were prepared by reaction of copper acetate monohydrate (0.02 g, 0.1 mM) dissolved in ACS water (25 mL) with mercaptosuccinic acid (0.08 g, 0.53 mM). 0.5 ml of 1M ammonium hydroxide was added with stirring to yellow solution, followed by sodium sulphide nonahydrate (0.012 g, 0.05 mM) in 24.5 mL of ACS water. Colour of solution turned to light brown.

CdS MPA QDs were prepared according these steps: cadmium nitrate tetrahydrate (0.031 g, 0.1 mM) was dissolved in ACS water (25 mL). MPA (35 μL, 0.4 mM) was slowly added to stirred solution and pH was adjusted to 6.8 with 1M ammonium. Sodium sulphide nonahydrate (0.024 g, 0.1 mM) in 24 ml of ACS water was poured into the first solution with vigorous stirring. Obtained yellow solution was stirred for 1 h.

CdTe QDs were synthesized from cadmium acetate dihydrate (0.027 g, 0.1 mM) which was dissolved in ACS water (44 mL) and 100 mg of trisodium citrate dihydrate was added with stirring. Solution of 0.0055 g (0.025 mM) sodium telluride in 1.25 mL of water was poured into the first solution followed by MPA (100 μL, 1.14 mM). 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, 120ºC and time 18 min. All of the obtained QDs were stored in dark at 4ºC or in daylight at 25^{o}C, respectively for 28 days.

2.3 Particle size distribution determination

The average particle size and the size distribution of the nanoparticles in ACS water were determined using a Zetasizer (Malvern-zetasizer Nano ZS, Malvern, UK) at 25°C.

The measurement was performed after diluting the nanosphere suspension with deionized water.

2.4 Electrochemical determination

Measurements were performed with 747 VA Stand instrument connected to 746 VA Processor and 695 Autosampler (Metrohm, Switzerland) using a standard cell with three electrodes. A hanging mercury drop electrode (HMDE) with a drop area of 0.4 mm^2 was the working electrode. An Ag/AgCl/3M KCl electrode was the reference and platinum electrode was auxiliary. For data processing VA Database 2.2 by Metrohm CH was employed. The analysed samples were deoxygenated prior to measurements by purging with argon (99.999%) saturated with water for 90 s. Acetate buffer (0.2 M CH_3COONa and CH_3COOH, pH 5.0) was used as supporting electrolyte. The supporting electrolyte was exchanged after each analysis. The parameters of the measurement were as follows: initial potential of -1.0 V, end potential of 0.2 V, pulse step 4 mV, amplitude 25 mV, sweep rate 13.3 mV/s, volume of sample 10 μL, volume of electrolyte 1990 μL, accumulation time on HMDE 120 s.

2.5 Statistical Analysis

Data were processed by using MICROSOFT EXCEL® (USA) and STATISTICA.CZ Version 8.0 (Czech Republic). Results are expressed as mean ± standard deviation (S.D.) unless noted otherwise (EXCEL®).

3. RESULTS AND DISCUSSION

QDs have great attention because of their optical properties and wide utilization in biological and biomedical studies. The utilization of functional nanomaterials in biology and biomedicine has been extensively explored and become one of the fast moving and exciting research directions [16-18]. QDs are prepared primarily *via* two approaches, organometallic synthesis and aqueous synthesis. The organometallic route has been well established for synthesis of QDs with excellent optical properties. However, such organic synthesized QDs are of hydrophobic nature and cannot be directly used in bioapplications. Post-treatment with hydrophilic ligands and polymers or silica coating is thus required to render these QDs with aqueous dispersibility [19]. Such post-treatment may have adverse effects on optical/ physical/chemical properties of QDs.

Toxicity of QDs is mainly influenced by distribution of QDs in intracellular compartment of cells. According to available information, the distribution of QDs inside the cells is not uniform and mainly QDs are distributed in the cytoplasm. High-intensity dots were concentrated in the perinuclear area and marginal area of the cell. Just uneven distribution of nanoparticles might cause abnormally high local concentrations of metal (forming the QDs core) due to their release from QDs in biological

environment [20]. This local concentration effect around the nuclei or certain cellular organelles such as mitochondria or lysosomes enhanced damage to these organelles [20].

Global systematic evaluation of toxicity of QDs used for bioapplications was not proposed yet. It was found that the cytotoxicity of QDs was not only caused by the nanocrystalline particle itself, but also by the surface-covering molecules of QDs, i.e., surface-covered functional groups [21-23]. It can be suggested that the chemical composition and structure of QDs determine the amount of metals released inside the cell which can cause a series of stress responses [24,25]. Possible evaluation of the effect of metal released from QDs core through the electrochemical determination of individual parts of QDs is discussed in this paper.

3.1 Characterization of QDs

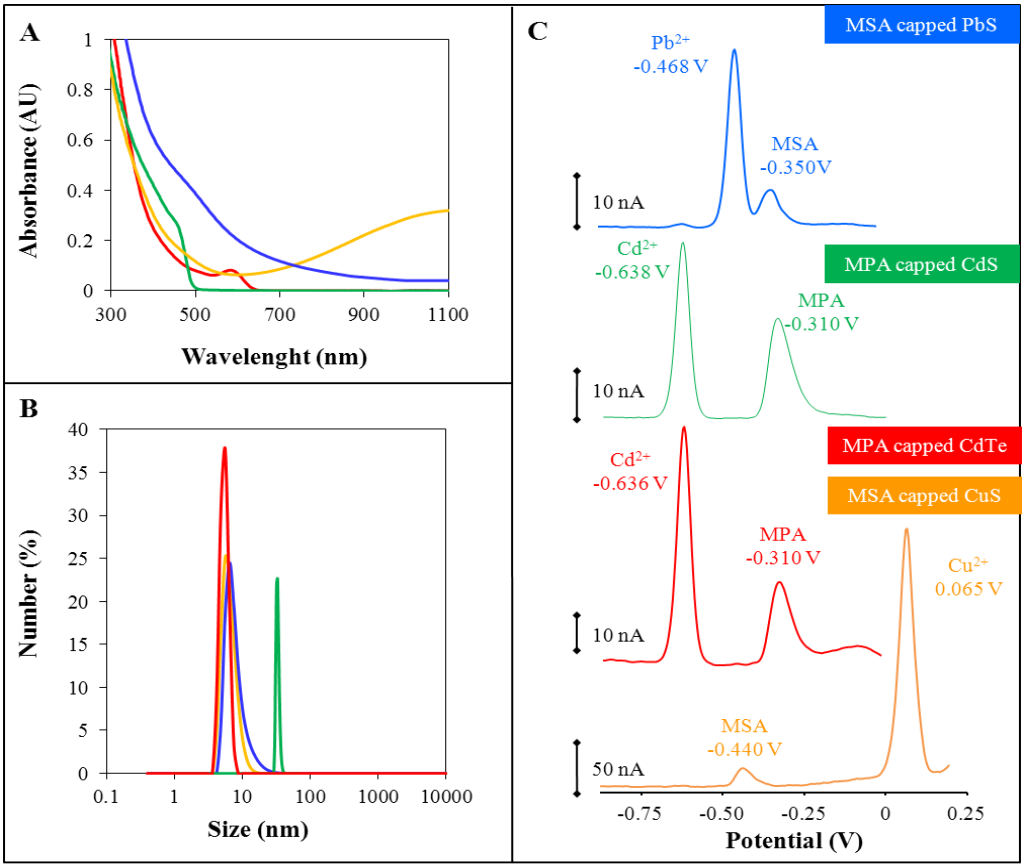

Figure 1. Basic characterisation of four types of QDs labelled as follows: blue lines MSA-PbS, orange lines MSA-CuS, green lines MPA-CdS and red lines MPA-CdTe. (**A**) Absorption spectra of prepared QDs. (**B**) Size distribution of prepared QDs based on number distribution. (**C**) Anodic stripping differential pulse voltammetry records related to the individual QDs in the presence of acetate buffer pH 5.

In our study four types of QDs were used. Two of them were capped by MSA (CuS and PbS) and two by MPA (CdS and CdTe). Prepared QDs were characterized by the absorbance determination (Fig 1A). Only MPA capped CdS and CdTe exhibited absorption maxima in obtained spectra. MPA

capped CdS had absorption maximum at 462 nm and MPA capped CdTe at 582 nm. Sizes of all prepared quantum dots were determined by dynamic light scattering measurements (Fig. 1B). The smallest QD was MPA capped CdTe with diameter 5.6 nm and the next were diameters as follows: MSA-CuS 5.8 nm, MSA-PbS 6.5 nm and MPA-CdS 43.2 nm.

The electrochemical records obtained by anodic stripping differential pulse voltammetry of individual QDs determined at hanging mercury drop electrode (HMDE) (vs. Ag/AgCl/3M KCl reference system) contain two peaks for each QDs (Fig. 1C). The first one is the peak related to the oxidation of individual metals which created core of QDs. Detected potentials of oxidation were as follows: Pb/Pb^{2+} (-0.468 V), Cu/Cu^{2+} (0.065 V), Cd/Cd^{2+} in CdS QDs (-0.638 V) and Cd/Cd^{2+} in CdTe QDs (-0.636 V). The second peak visible in individual voltammograms is connected with the MSA/MPA oxidation. The oxidation of these acids would be similar to the behaviour of cysteines (on the surface of mercury electrode) [26,27]. Oxidation peaks of MSA/MPA were located at the potential range from -0.31 V for MPA to -0.44 V for MSA in CuS QDs.

3.2 Monitoring based on metal oxidation peak

Aging of QDs is connected with negative effects such as decomposition and/or photobleaching [28-31]. By applying two storage conditions (dark + 4°C and daylight + 25°C) the stability of QDs was affected and the influence on obtained electrochemical records was studied. Electrochemical detection of the basic electrochemical behaviour of mercaptosuccinic (MSA)/mercaptopropionic (MPA) acid and metal ions was investigated. The changes of electrochemical records were monitored within 28 days. During this time the first part of QDs samples were stored in the dark at 4°C and the second part was stored in the daylight at 25°C. Anodic stripping differential pulse voltammetry records of individual QDs contained two characteristic oxidation peaks related to metal and MSA/MPA. The monitoring of changes in metal peak height and potential is summarized in Figure 2. The first part of the picture (Fig. 2A) shows the change of relative metal peak height (related to the start of experiment) during 28 days of influenced by the storage in the dark at 4°C. All data were interpolated by linear trend for the comparison of monitored time changes.

It is clear that all used QDs, except MSA capped CuS, are stable during the whole time period because no important increase of signal during time period was observed. This conclusion is visible by the comparison of individual slopes. The most stable were MPA capped CdTe and MSA capped PbS. Very slight increase of signal was detected for MPA capped CdS. Similar dependences were detected by the storage in the daylight at 25°C (Fig. 2B). Here the slopes of individual dependences had the same order as in the previous case: MSA-CuS > MPA-CdS > MSA-PbS > MPA-CdTe. Except of peak height the peak potentials were evaluated (Fig. 2C). It was interesting that the peak potentials were slightly shifted with time to more negative values, in case of dark stored QDs. Contrary to this, peak potentials related to daylight stored QDs were shifted with time to more positive values. From this, it can be concluded that photooxidation during storage period affected (disturb) the surface structure of QDs and thus facilitate the oxidation of metal ions.

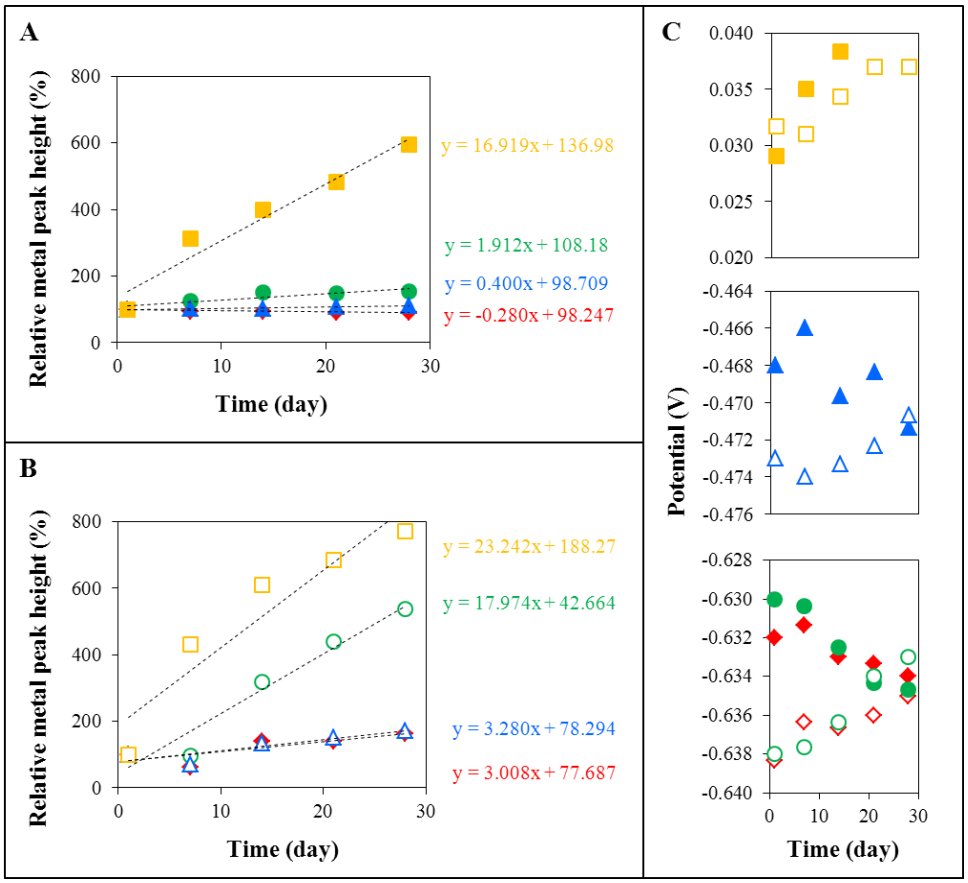

Figure 2. Monitoring of QDs stability in the time range from 1 to 28 days using anodic stripping differential pulse voltammetry (HMDE *vs*. Ag/AgCl/3M KCl reference system). Monitoring was based on metal peak detection in the presence of acetate buffer with pH 5. Four types of QDs labelled as follows were used: blue points MSA-PbS, orange points MSA-CuS, green points MPA-CdS and red points MPA-CdTe. Fill marks were related to the storage of QDs in the dark at 4°C, empty marks were related to the storage of QDs in the daylight at 25°C. (**A**) Dependence of relative metal peak height (related to the start of experiment) on time of storage of QDs in the dark at 4°C. (**B**) Dependence of relative metal peak height (related to the start of experiment) on time of storage of QDs in the light at 25°C. (**C**) Dependence of detected potential (metal peak) on time of storage of QDs in the dark at 4°C or in the light at 25°C.

3.3 Monitoring based on MSA/MPA oxidation peak

Another point of view on the changes of QDs was based on the evaluation of MSA/MPA peaks (Fig. 3). The presented dependences of relative MSA/MPA peak heights for QDs stored in the dark (Fig. 3A) had increasing character, similar as dependences presented for metal peak evaluation (Fig. 2A). This comparison had just one other result, the same order of slopes of individual dependences (MSA-CuS > MPA-CdS > MSA-PbS > MPA-CdTe). Different situation was obvious for obtained dependences related to the storage of QDs in the daylight at 25°C (Fig. 3B). Here the obtained dependences had various slopes according to individual QDs. The increasing relative peak height of MSA (capped CuS) was the only one among others. MSA (capping PbS) had the constant trend (slope of dependence was close to zero) and MPA (capping CdS and CdTe) had decreasing trend

with increasing time of storage. These results show that difference in behaviour of capping agent of QDs could be electrochemically monitored. If we compared results for metal peak evaluation (Fig. 2B) and these related to MSA/MPA evaluation, the conclusion is not uniform because the order of slopes is different as follows: MSA-CuS > MSA-PbS > MPA-CdTe > MPA-CdS. Evaluation of peak potentials was done for MSA/MPA peaks too (Fig. 3C). It was observed that peak potentials were shifted with time to more negative values, irrespective of the way of QDs storage. It seems that photooxidation during storage period did not affect the electrochemical behaviour of capping agents themselves but influenced the metal oxidation (Fig. 2C).

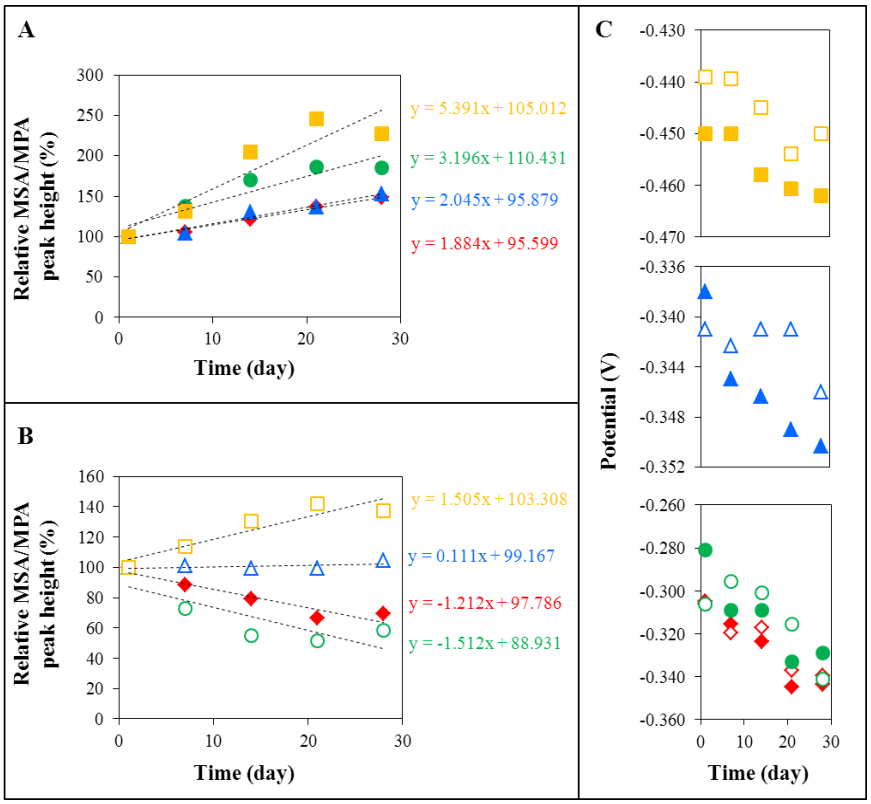

Figure 3. Monitoring of QDs stability based on MSA/MPA peak detection in the presence of acetate buffer pH 5. Four various QDs labeled as follows were used: blue points MSA-PbS, orange points MSA-CuS, green points MPA-CdS and red points MPA-CdTe. Fill marks were related to the storage of QDs in the dark at 4 °C, empty marks were related to the storage of QDs in the daylight at 25 °C. (**A**) Dependence of relative MSA/MPA peak height (related to the start of experiment) on time of storage of QDs in the dark at 4 °C. (**B**) Dependence of relative MSA/MPA peak height (related to the start of experiment) on time of storage of QDs in the light at 25 °C. (**C**) Dependence of detected potential (MSA/MPA peak) on time of storage of QDs in the dark at 4°C or in the light at 25 °C.

3.4 Influence of storage conditions

Above the discussed results were related to the individual ways of QDs storage. But the aim of the experiment was to describe the influence of the change of storage conditions on the electrochemical records. Therefore the differential dependences for metal and MSA/MPA relative

peaks heights were evaluated (Figs. 4A and 4B). These relations were set as time dependences of difference, which was calculate as the value of relative peak height (for daylight at 25°C) minus relative peak height (for dark at 4°C). This difference expressed the change of relative peak height due to change of storage condition from dark at 4°C to daylight at 25°C. Figure 4A shows increasing dependences with time related to the changes of metal peaks. It is interesting that the highest changes were observed for MPA capped CdS while the highest change of metal peak according to increasing time was observed for MSA capped CuS for both storage conditions (Figs. 2A and 2B). The slopes of dependences had various order than all other mentioned in previous text and were as follows: MPA-CdS > MSA-CuS > MPA-CdTe > MSA-PbS. Similar evaluation of measured data based on MSA/MPA peak detection was done (Fig. 4B). Here all dependences had decreasing character with time and it means that the recorded signal of capping agent decrease by the exposure of QDs to daylight and higher temperature (25°C). The slopes of dependences (Fig. 4B) had the right opposite sequence than in previous case based on metal peak detection (Fig. 4A) and were as follows: MSA-PbS > MPA-CdTe > MSA-CuS > MPA-CdS. This was the confirmation of sensitivity of individual prepared QDs to the changes of storage conditions. In thus way the most sensitive were MPA capped CdS and less MSA capped PbS.

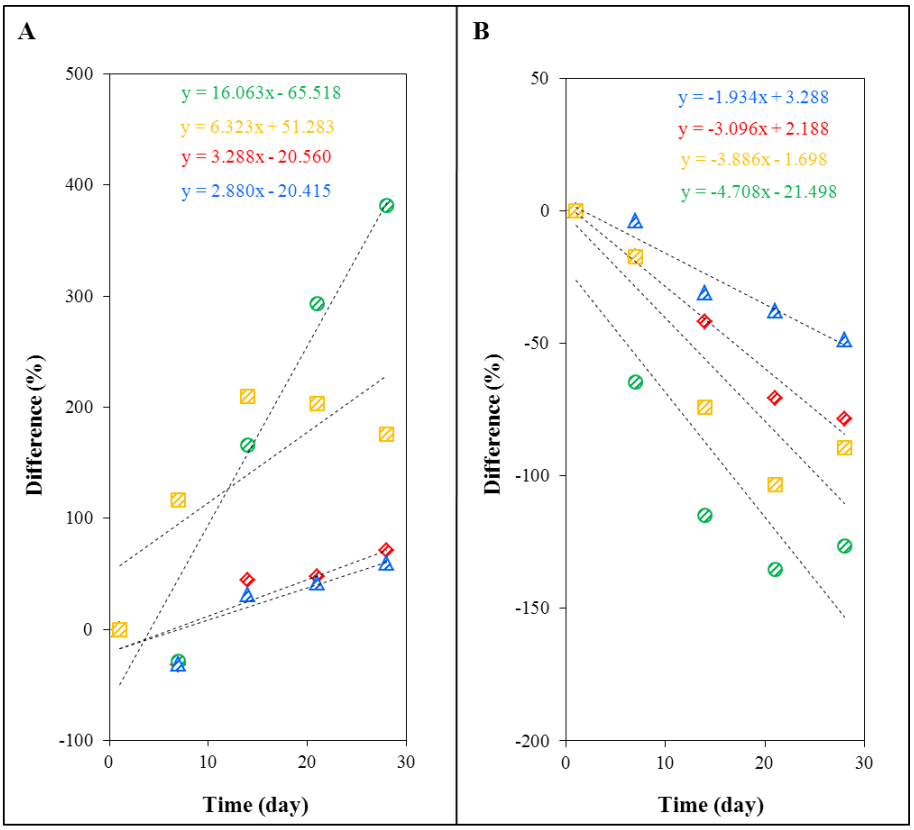

Figure 4. Influence of the storage way expressed as change of detected peak heights for (**A**) metal peaks and (**B**) MSA/MPA. The presented changes were calculated as difference between the values related to the storage in the daylight at 25°C and in the dark at 4°C (all in percent). Four various QDs labelled as follows were used: blue points MSA-PbS, orange points MSA-CuS, green points MPA-CdS and red points MPA-CdTe.

4. CONCLUSIONS

Systematic evolution of QDs toxicity is still the great task for researchers. Systematic evaluation studies of QDs toxicity could be useful for understanding the *in vitro* toxicity of QDs and for systematic assessment of cytotoxicity of QDs. This paper suggested simple method using anodic stripping differential pulse voltammetry for monitoring of QDs changes caused by the various storage conditions. Impact of such and similar parameters evaluated through the electrochemical records could be useful for the prediction of nanoparticles toxicity *in vitro*.

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Conflict of interest
The authors have declared no conflict of interest.

References

1. Y. W. Jun, J. E. Koo and J. Cheon, *Chem. Commun.* 2000 (2000) 1243.
2. Z. Zhelev, R. Bakalova, H. Ohba, R. Jose, Y. Imai and Y. Baba, *Anal. Chem.*, 78 (2006) 321.
3. M. K. Singh, P. A. Hassan and A. Kadam, *Mater. Chem. Phys.*, 146 (2014) 136.
4. M. Bruchez, M. Moronne, P. Gin, S. Weiss and A. P. Alivisatos, *Science*, 281 (1998) 2013.
5. S. Torkzaban, S. A. Bradford, J. M. Wan, T. Tokunaga and A. Masoudih, *Environ. Sci. Technol.*, 47 (2013) 11528.
6. H. Krusemann, A. Godec and R. Metzler, *Phys. Rev. E*, 89 (2014) 5.
7. A. Kumar and B. Singh, *Dalton Trans.*, 42 (2013) 11455.
8. L. G. V. Macotela, T. V. Torchynska, J. Douda, R. P. Sierra and L. Shcherbyna, *Mater. Sci. Eng. B-Adv. Funct. Solid-State Mater.*, 176 (2011) 1349.
9. T. G. Kryshtab, L. V. Borkovska, O. F. Kolomys, N. O. Korsunska, V. V. Strelchuk, L. P. Germash, K. Y. Pechers'ka, G. Chornokur, S. S. Ostapenko, C. M. Phelan and O. L. Stroyuk, *Superlattices Microstruct.*, 51 (2012) 353.
10. H. G. Zhao, M. Chaker and D. L. Ma, *Phys. Chem. Chem. Phys.*, 12 (2010) 14754.
11. D. Painuly, A. Bhatt and V. K. Krishnan, *J. Biomater. Appl.*, 28 (2014) 1125.
12. K. Kim, J. E. Park, E. S. Park, Y. C. Park, J. Kim, C. Im and M. J. Lee, *Electrochim. Acta*, 121 (2014) 223.
13. C. Truillet, F. Lux, O. Tillement, P. Dugourd and R. Antoine, *Anal. Chem.*, 85 (2013) 10440.
14. G. R. Bardajee and Z. Hooshyar, *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.*, 114 (2013) 622.
15. A. J. Bednar, A. R. Poda, D. M. Mitrano, A. J. Kennedy, E. P. Gray, J. F. Ranville, C. A. Hayes, F. H. Crocker and J. A. Steevens, *Talanta*, 104 (2013) 140.
16. D. N. T. Kumar and Q. F. Wei, *Res. J. Biotechnol.*, 8 (2013) 78.
17. J. B. Li, D. D. Wu, Z. R. Miao and Y. Zhang, *Curr. Pharm. Biotechnol.*, 11 (2010) 662.
18. J. J. Lia and J. J. Zhu, *Analyst*, 138 (2013) 2506.
19. T. Pellegrino, L. Manna, S. Kudera, T. Liedl, D. Koktysh, A. L. Rogach, S. Keller, J. Radler, G. Natile and W. J. Parak, *Nano Lett.*, 4 (2004) 703.
20. Y. Y. Su, M. Hu, C. H. Fan, Y. He, Q. N. Li, W. X. Li, L. H. Wang, P. P. Shen and Q. Huang, *Biomaterials*, 31 (2010) 4829.

21. N. Lewinski, V. Colvin and R. Drezek, *Small*, 4 (2008) 26.
22. P. Rivera-Gil, D. J. De Aberasturi, V. Wulf, B. Pelaz, P. Del Pino, Y. Y. Zhao, J. M. De La Fuente, I. R. De Larramendi, T. Rojo, X. J. Liang and W. J. Parak, *Accounts Chem. Res.*, 46 (2013) 743.
23. W. H. Song, J. Y. Zhang, J. Guo, J. H. Zhang, F. Ding, L. Y. Li and Z. T. Sun, *Toxicol. Lett.*, 199 (2010) 389.
24. Y. H. Lee, F. Y. Cheng, H. W. Chiu, J. C. Tsai, C. Y. Fang, C. W. Chen and Y. J. Wang, *Biomaterials*, 35 (2014) 4706.
25. G. L. Cheng, W. Guo, L. Han, E. L. Chen, L. F. Kong, L. L. Wang, W. C. Ai, N. N. Song, H. S. Li and H. M. Chen, *Toxicol. Vitro*, 27 (2013) 1082.
26. I. M. Kolthoff and S. Kihara, *Anal. Chem.*, 49 (1977) 2108.
27. I. M. Kolthoff, W. Stricks and N. Tanaka, *J. Am. Chem. Soc.*, 77 (1955) 5211.
28. A. P. Litvin, P. S. Parfenov, E. V. Ushakova, A. V. Fedorov, M. V. Artemyev, A. V. Prudnikau, I. D. Rukhlenko and A. V. Baranov, *Nanophot Mater X*, 8807 (2013) 1.
29. D. Gonzalez, J. G. Lozano, M. Herrera, N. D. Browning, S. Ruffenach, O. Briot and R. Garcia, *J. Appl. Phys.*, 105 (2009) 1.
30. R. Sarma, A. Chetry and D. Mohanta, *Nanosci. Nanotechnol. Lett.*, 4 (2012) 775.
31. P. Sobrova, M. Ryvolova, J. Hubalek, V. Adam and R. Kizek, *Int. J. Mol. Sci.*, 14 (2013) 13497.