



INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

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Influence of the pH on the stability of CdTe QDs investigated by fluorescence and particle size analyses

Brno, 12.12.2014

Reg.č.projektu: CZ.1.07/2.3.00/20.0148

Název projektu: Mezinárodní spolupráce v oblasti "in vivo"

zobrazovacích technik



QDs are used mainly as biological markers (labels)

Compared to fluorescent proteins also used as labels
QDs display:

- size and composition tunable emissions
- narrow emission spectra
- wide excitation profiles
- long luminescence lifetimes

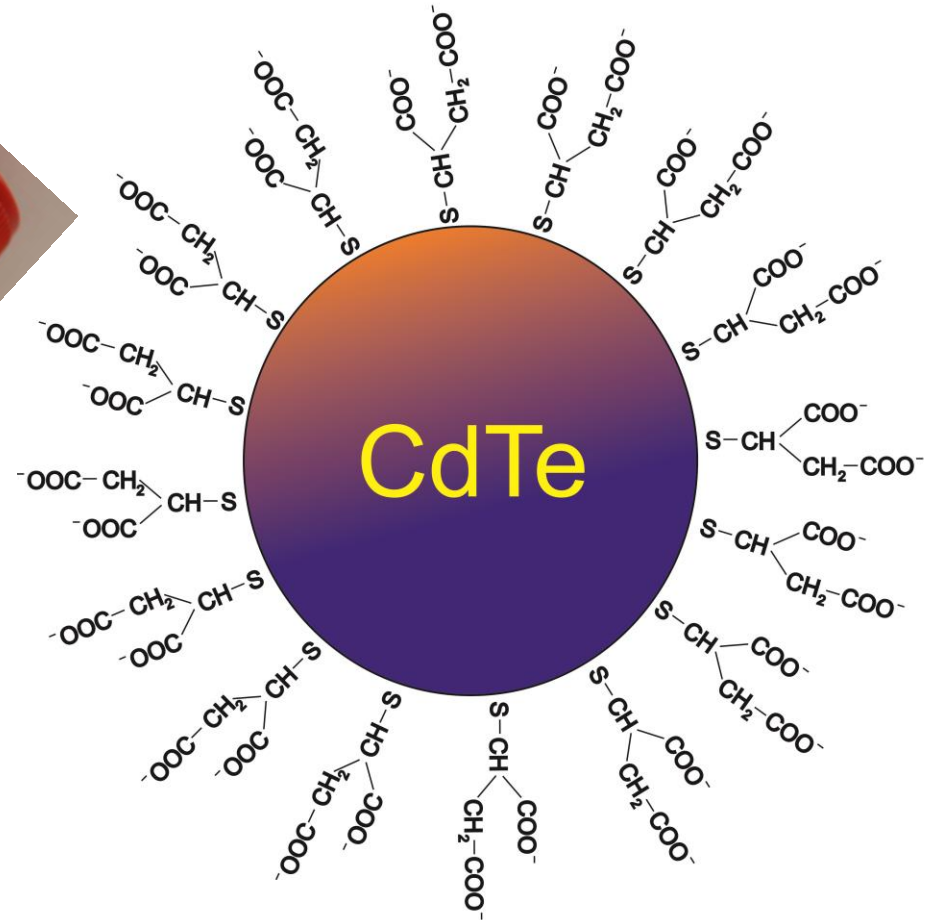
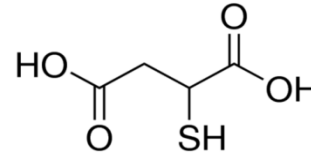
The aim of this study!

The environment around tumor cells shows often decreased pH values compared to healthy cells!

The pH values of certain organs in the human body vary considerably!
(stomach 1-2 till 4-5)

Preparation of CdTe QDs

Preparation of CdTe QDs:



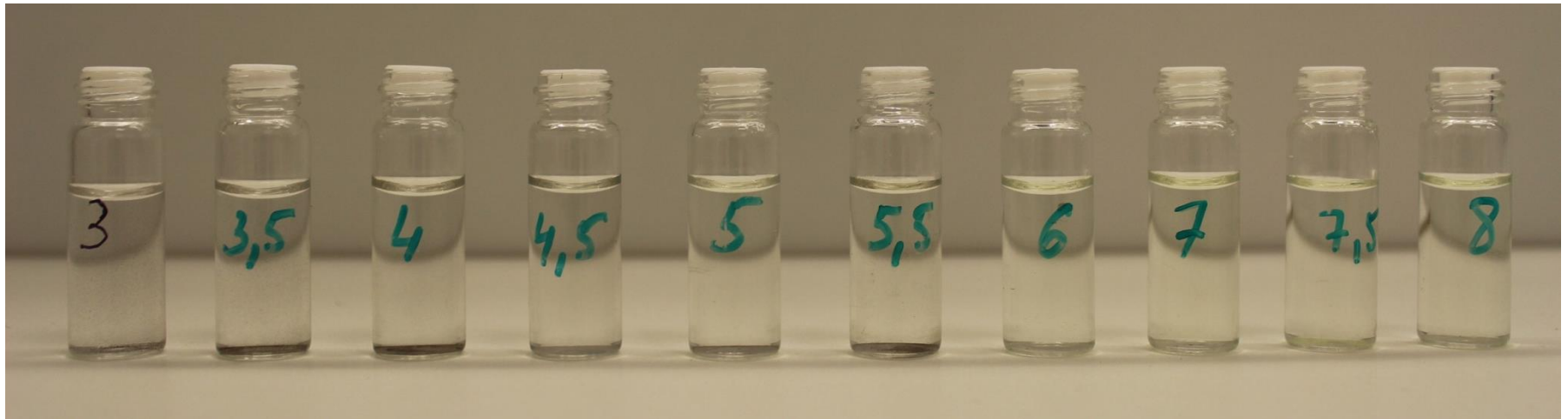
Cadmium telluride particles stabilised by mercaptosuccinate ions

Preparation of buffer solutions:

Citric acid (0.1N) and K_2HPO_4 (0.1N)

3 ml for each pH value were prepared ranging from 3 to 8 according to the following order:

3, 3.5, 4, 4.5, 5, 5.5, 6, 7, 7.5, 8



0.3 ml of each solution is removed and substituted original CdTe QDs solution
respecting the dilution ratio 1:10

Fluorescence spectra for at different times for individual pH



Increase of alkalinity



**Particle determination using zetasizer apparatus
(Malvern)**

Excitation wavelength: 350 nm*

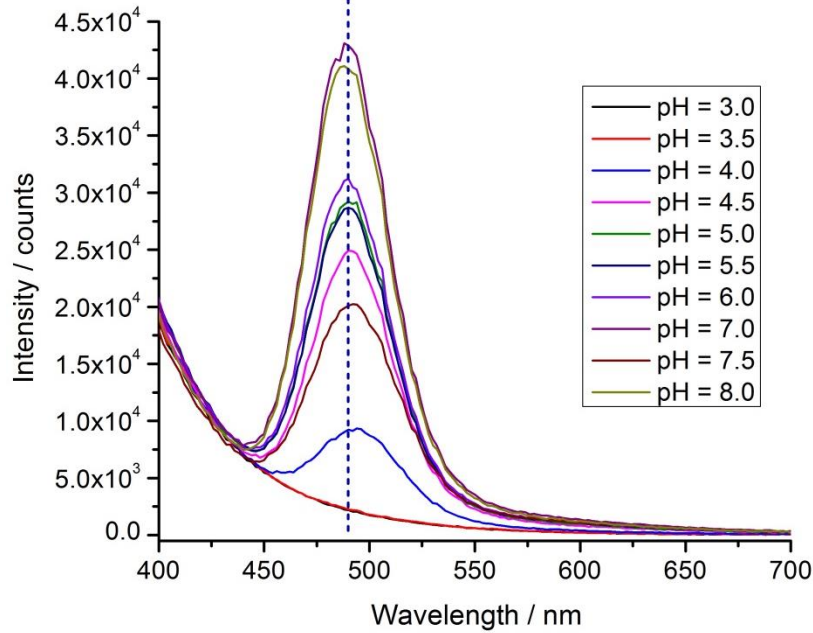
Emission wavelength recorded: 380 – 700 nm

*Fluorescent behaviour of QDs solution is not dependent on the excitation wavelength (emission spectra recorded for different wavelengths show no maxima shifts!)

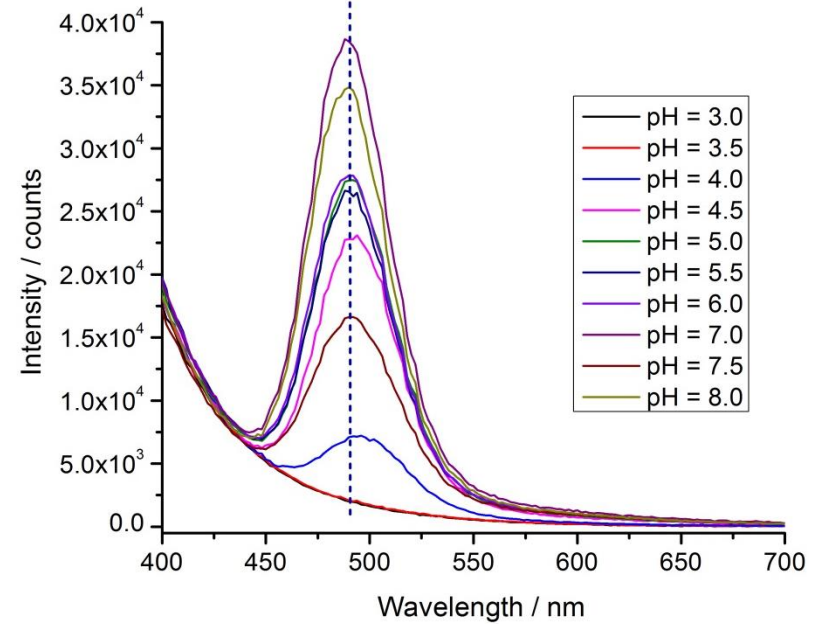
*Beato-López, J.J., Fernández-Ponce, C., Blanco, E., Barrera-Solano, C., Ramírez-del-Solar, M., Domínguez, M., García-Cozar, F., Litrán, R. Preparation and Characterization of Fluorescent CdS Quantum Dots used for the Direct Detection of GST Fusion Proteins. *Nanomater. Nanotechnol.*, 2012, 2, 1-9.

Fluorescence spectra of each pH for t = 0, 20, 40 and 120 min

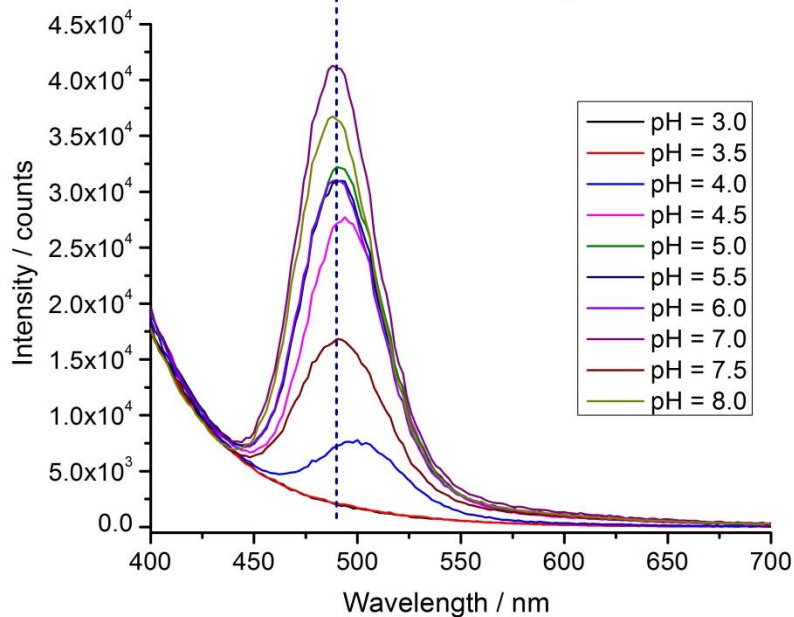
CdTe QDs fluorescence emission spectra for t = 0



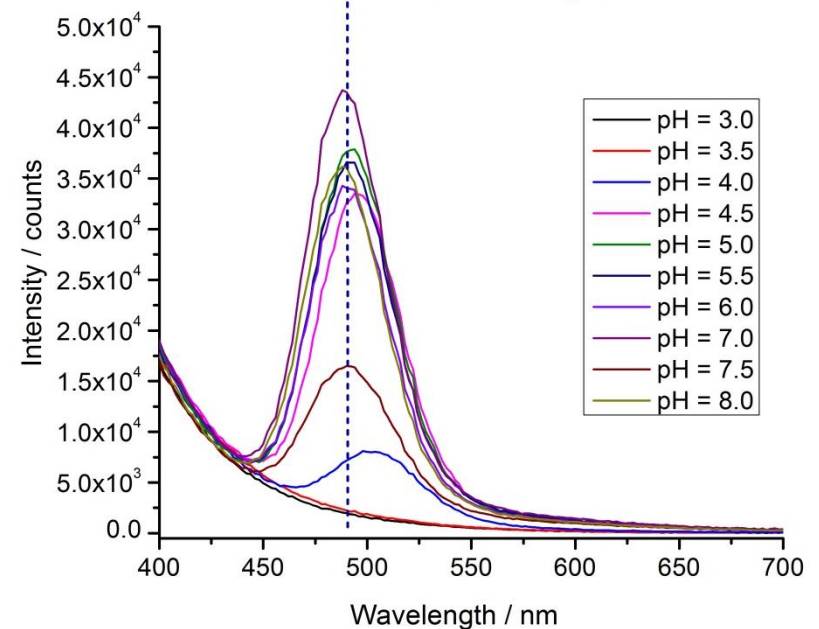
CdTe QDs fluorescence emission spectra for t = 20 min



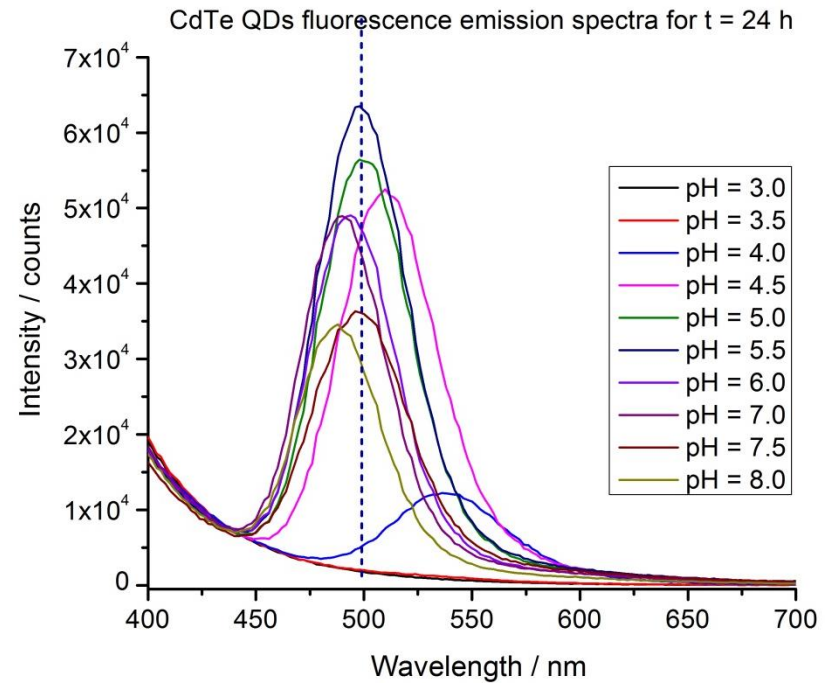
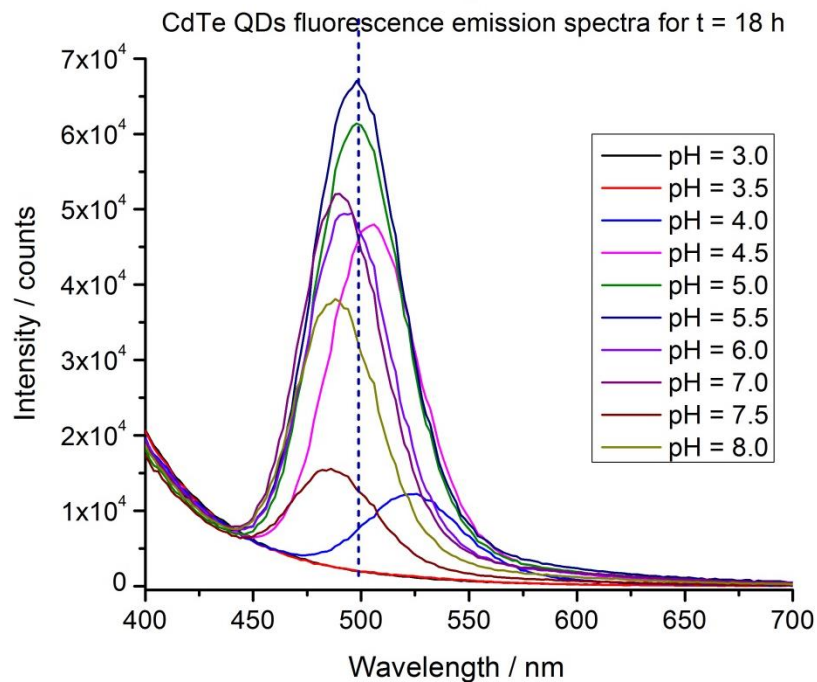
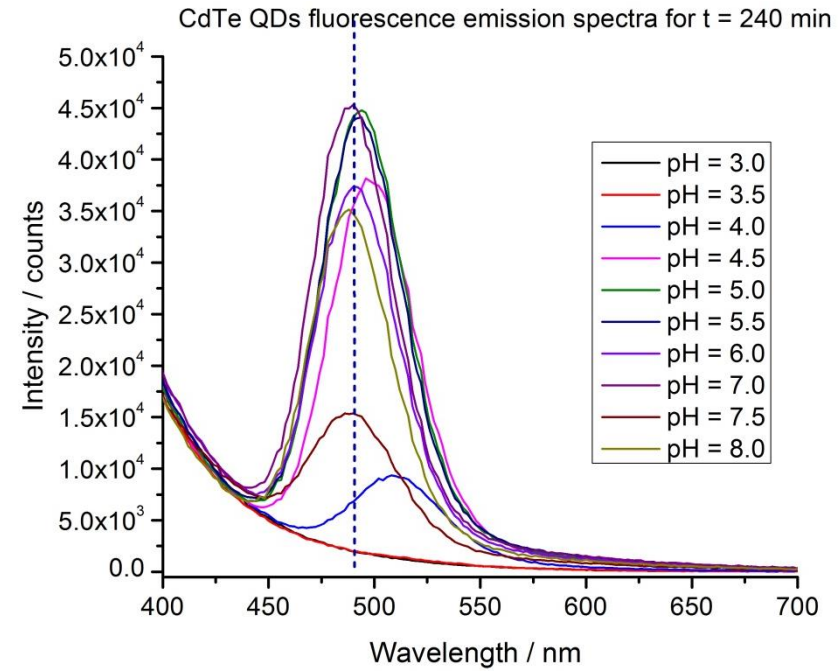
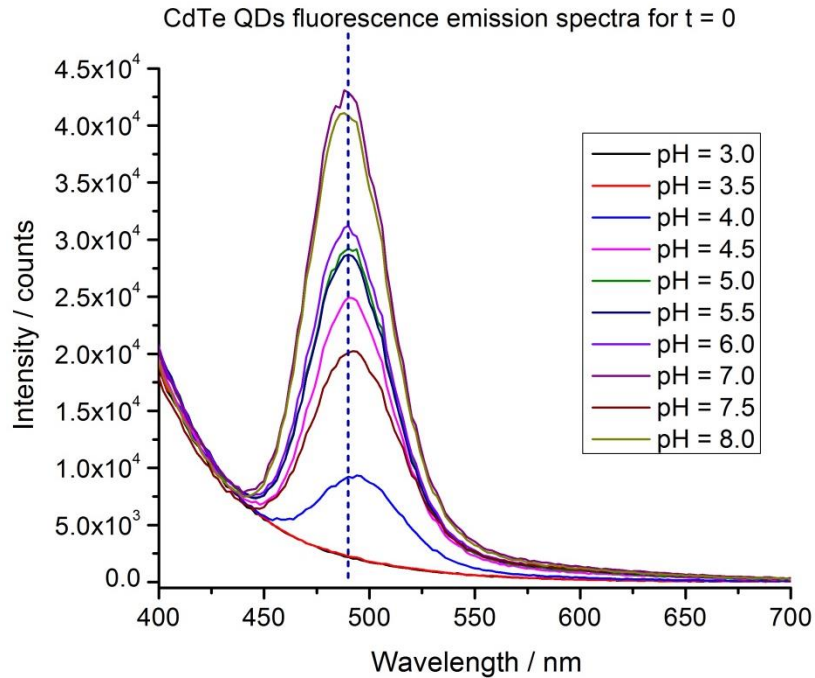
CdTe QDs fluorescence emission spectra for t = 40 min



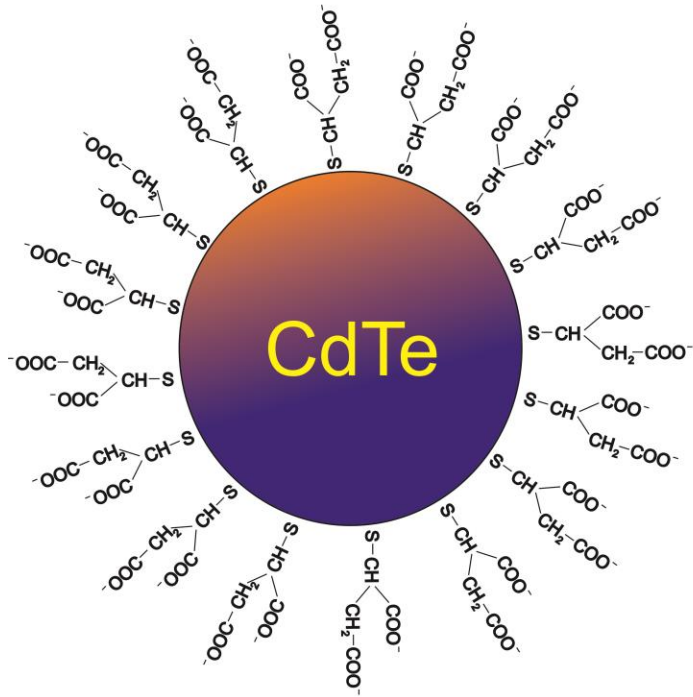
CdTe QDs fluorescence emission spectra for t = 120 min



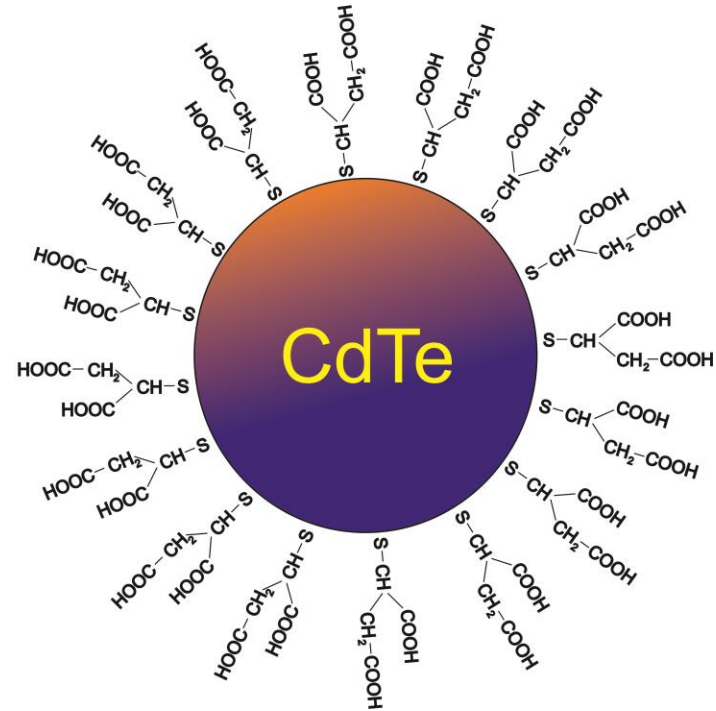
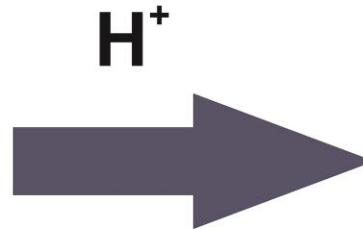
Fluorescence spectra of each pH for t = 0, 4, 18 and 24 h



Particle charge at low pH values

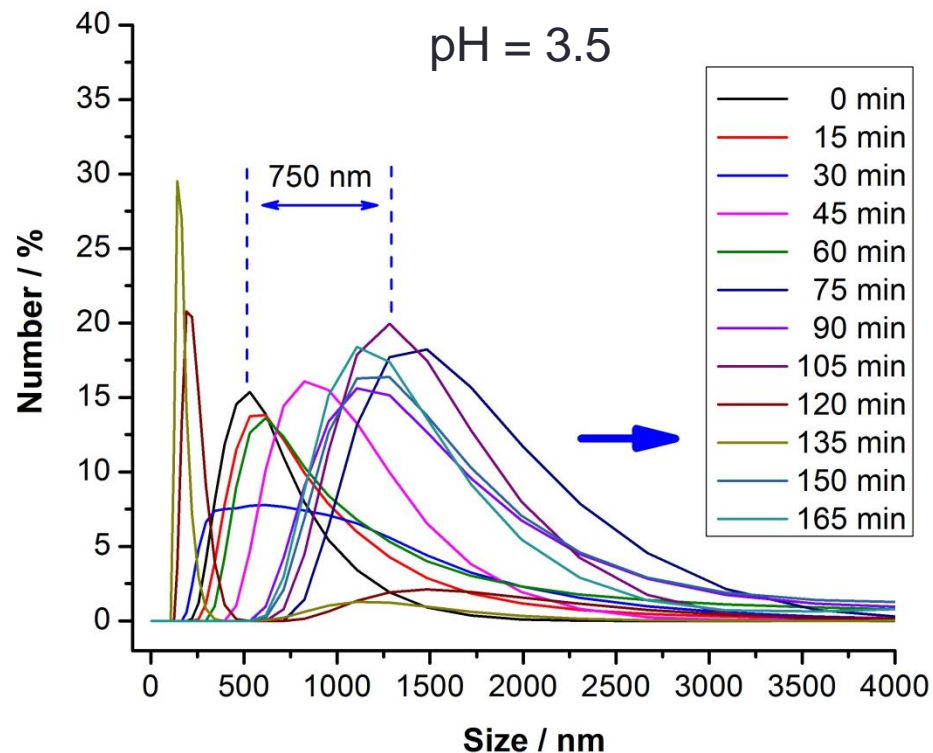
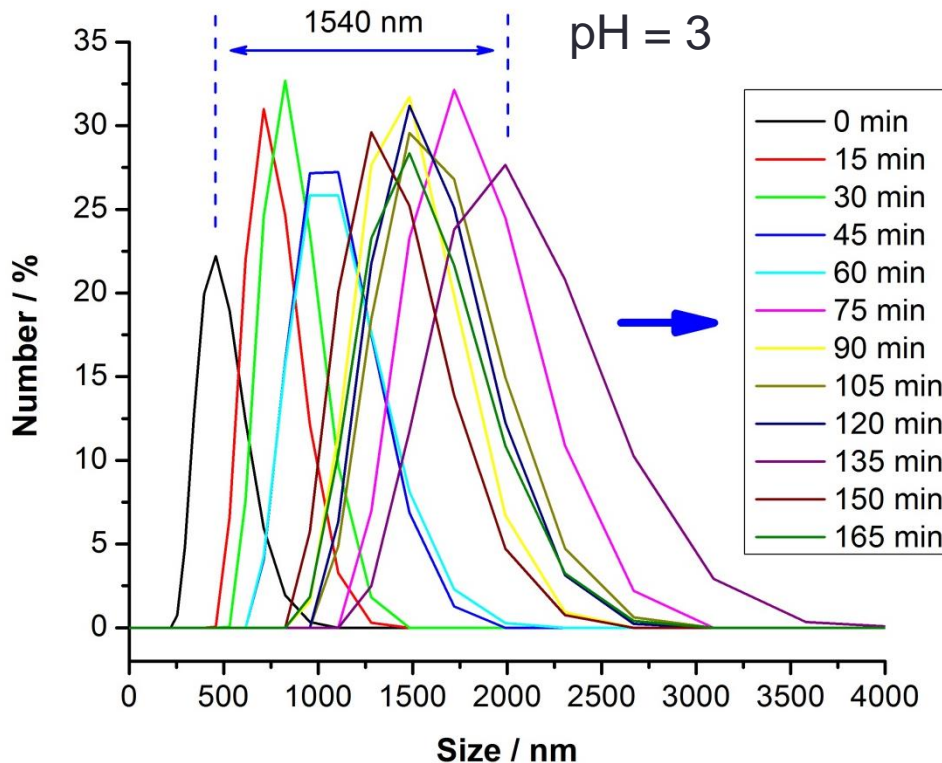
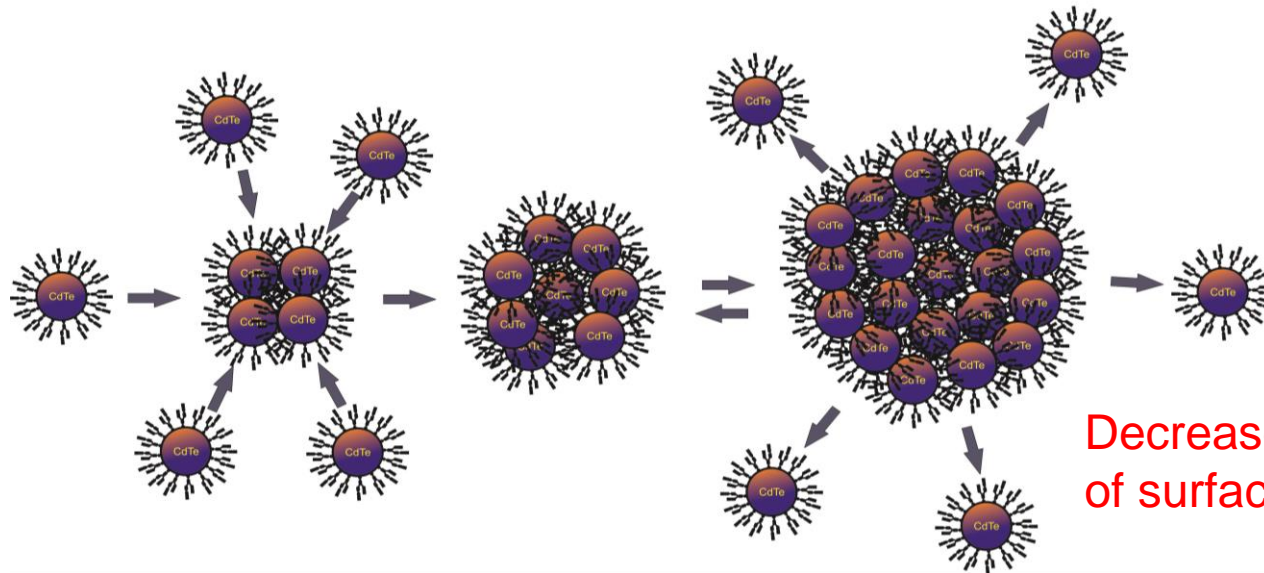


Dissociated carboxyl groups
(negatively charged particle)



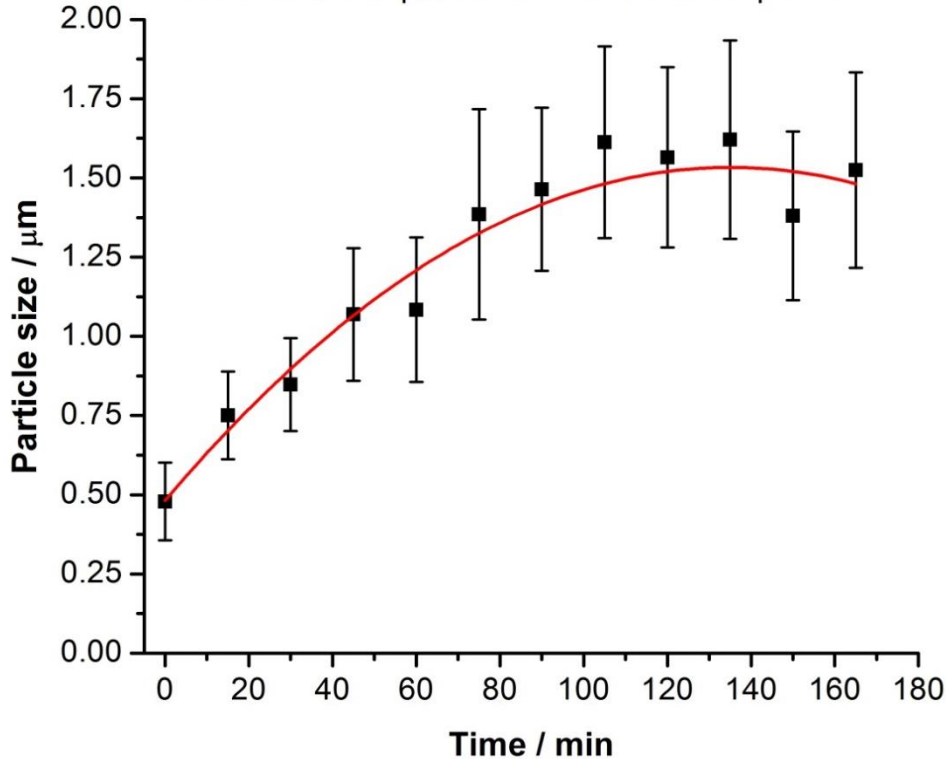
Undissociated carboxyl groups
(neutral particle)

Dynamics of particle size increase at low pH values

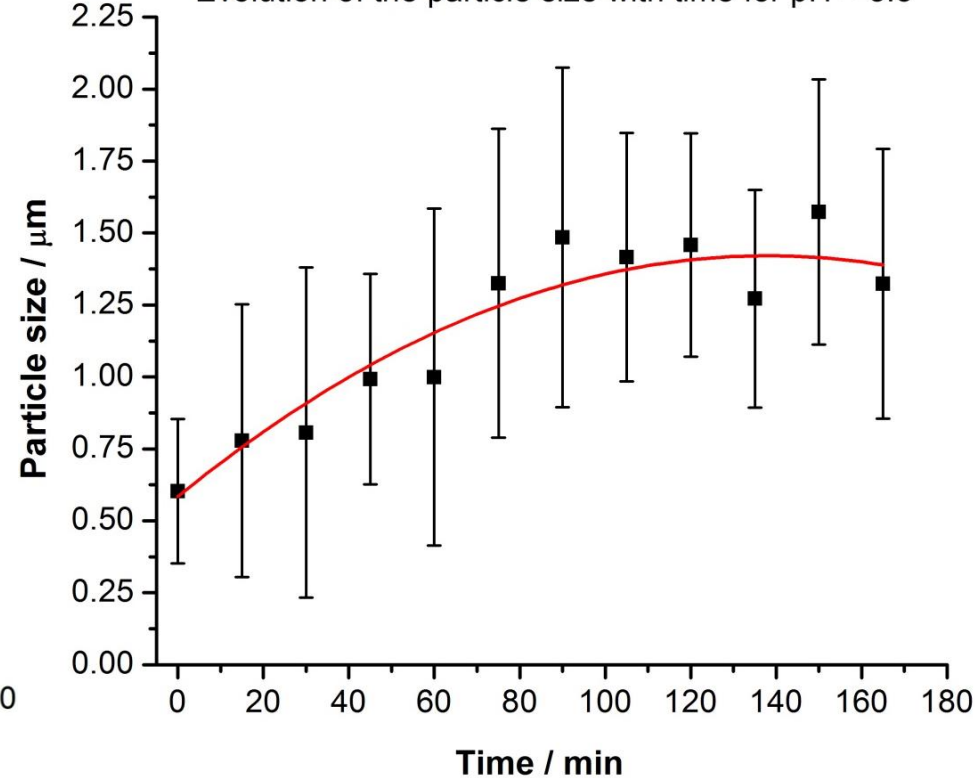




Evolution of the particle size with time for pH = 3



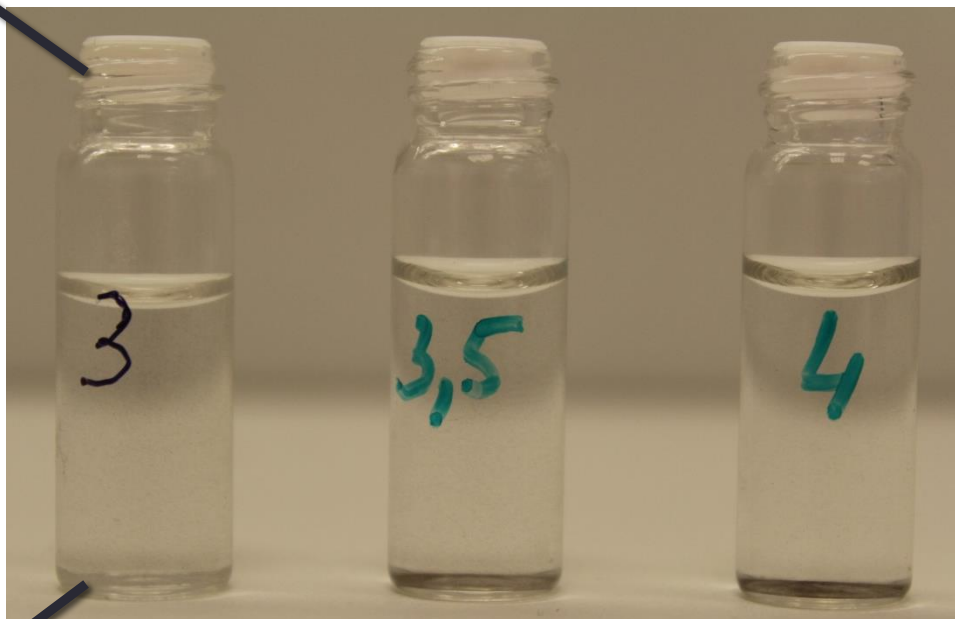
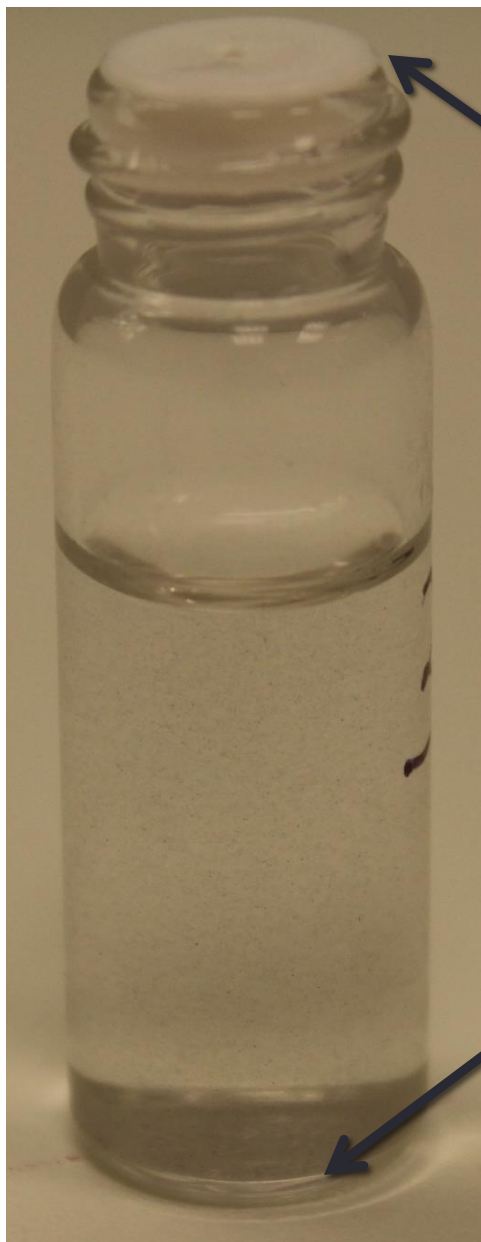
Evolution of the particle size with time for pH = 3.5



Parabolic – like particle size increase
(the particle reaches quite fast the max)

Particle size reaches sizes up to 1.5 μm !!!

CdTe QDs instability at $\text{pH} \leq 4$

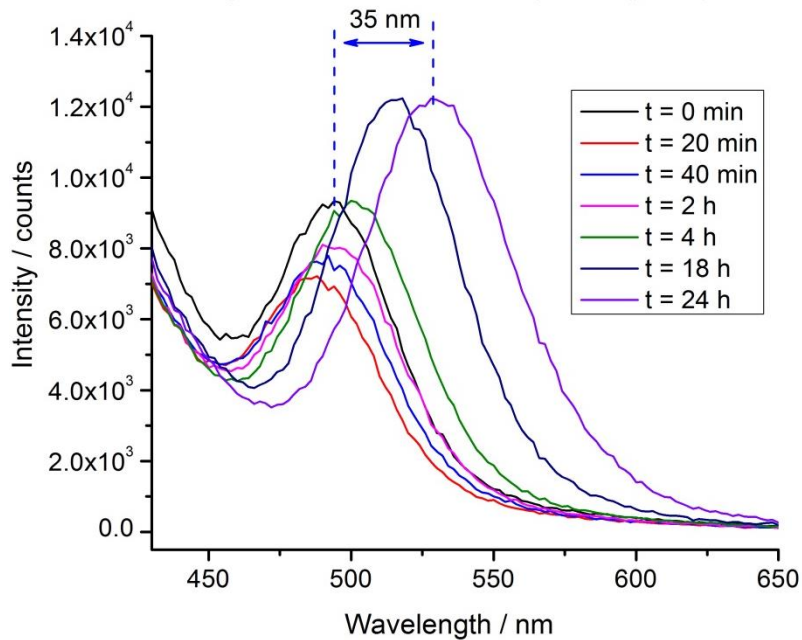


Visible particles
(coagulation & sedimentation)

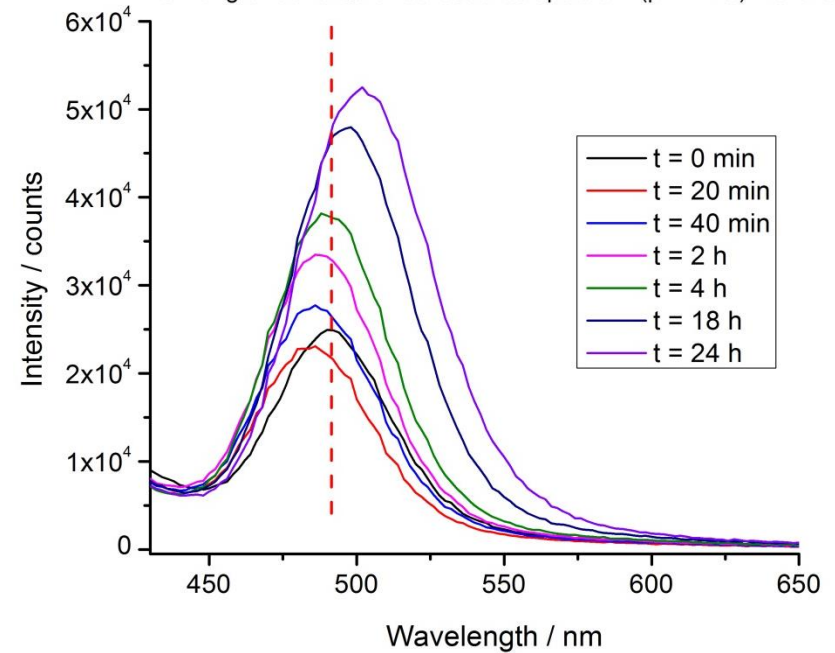
Why does that happen?

Maxima shifting for different pH (4 – 5.5) with the time

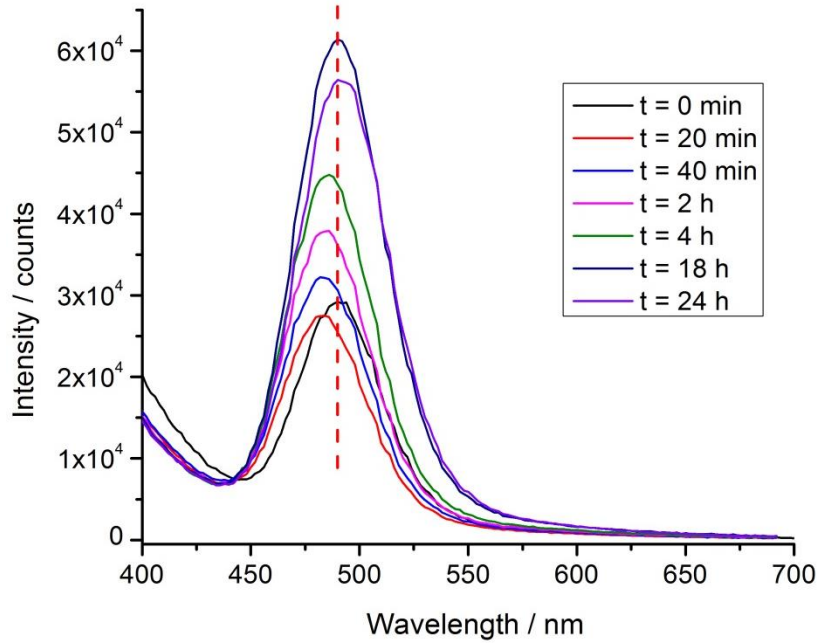
Shifting of CdTe QDs fluorescence spectrum (pH = 4) with the time



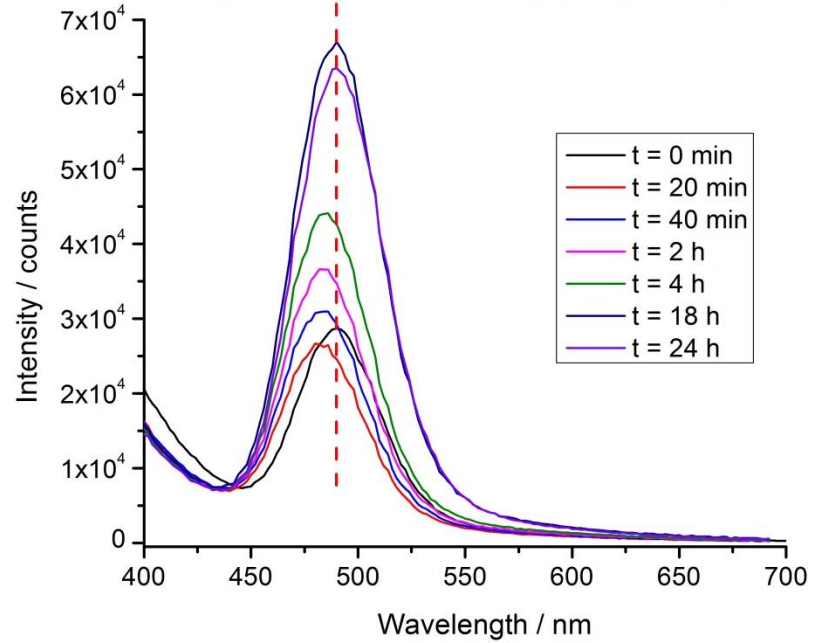
Shifting of CdTe QDs fluorescence spectrum (pH = 4.5) with the time



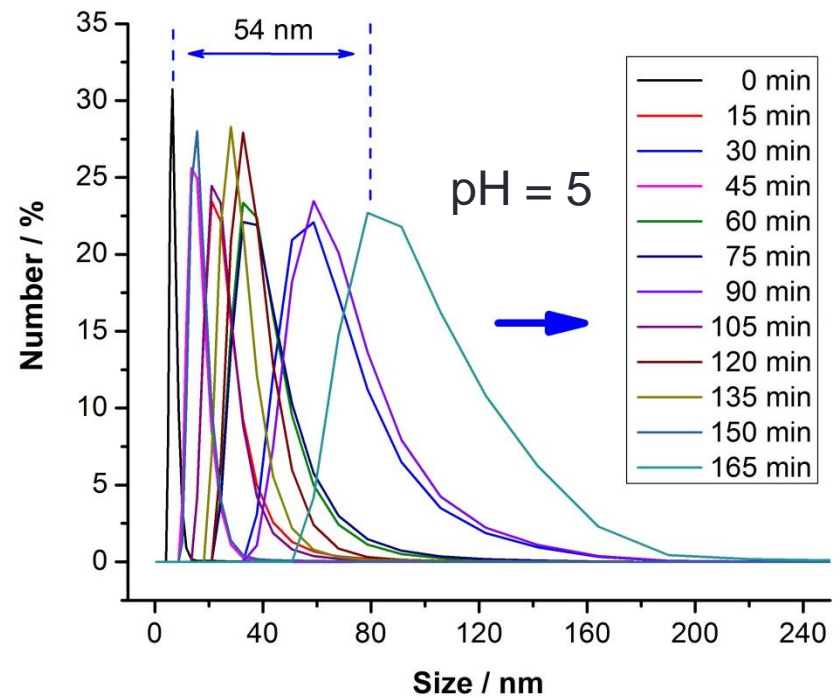
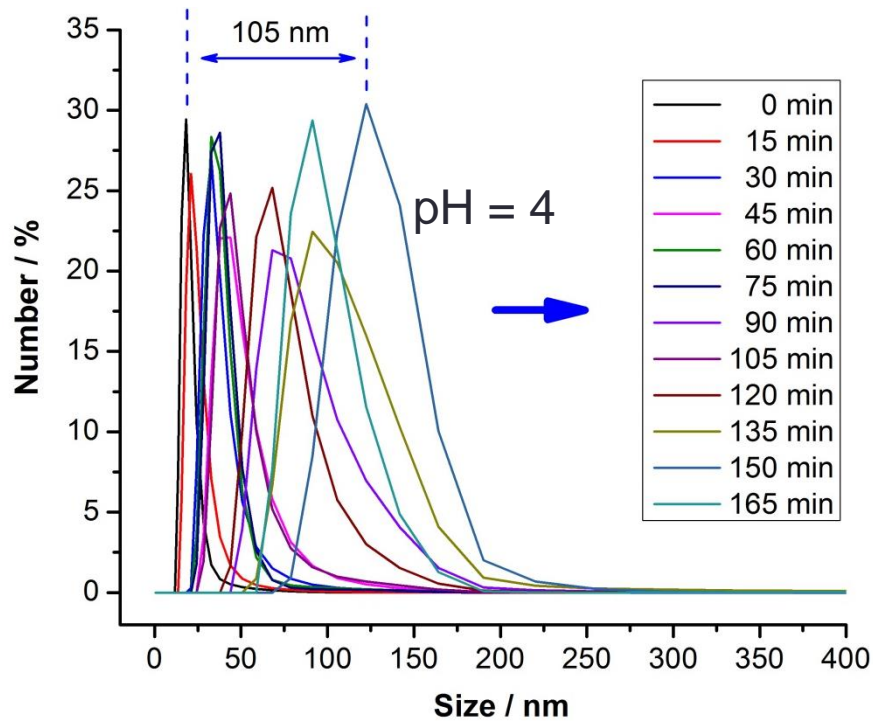
Shifting of CdTe QDs fluorescence spectrum (pH = 5) with the time



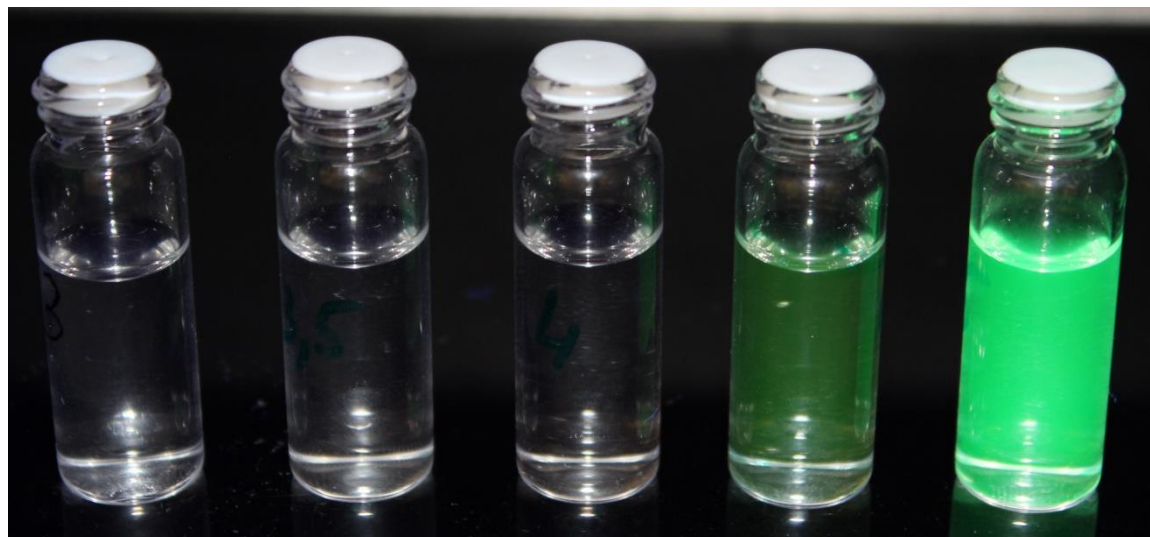
Shifting of CdTe QDs fluorescence spectrum (pH = 5.5) with the time

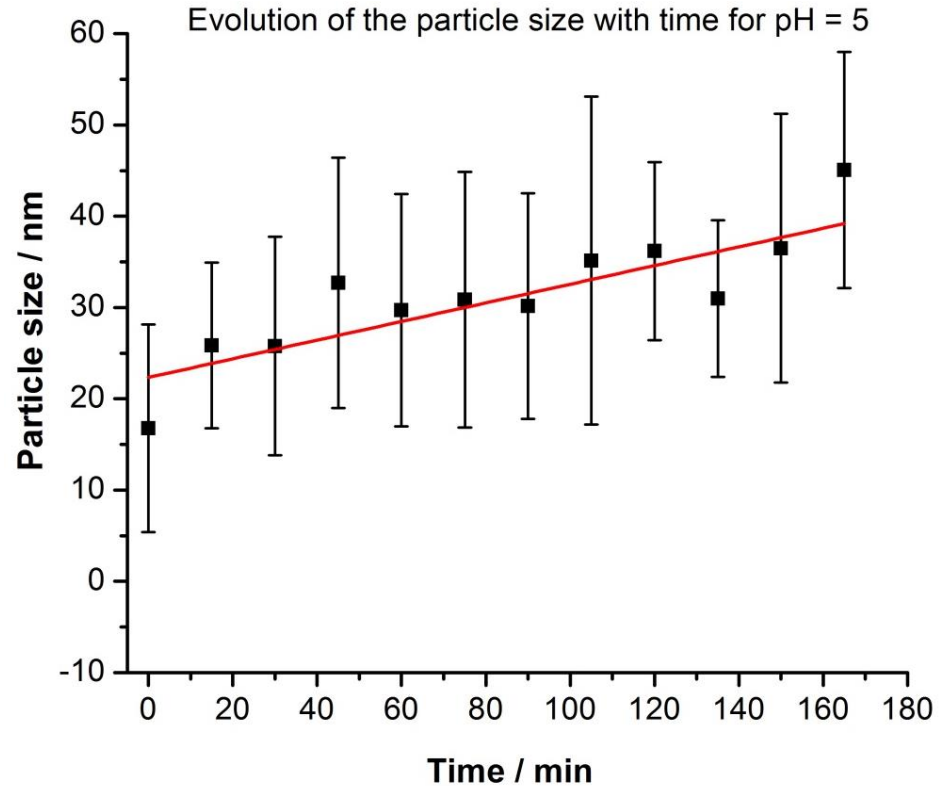
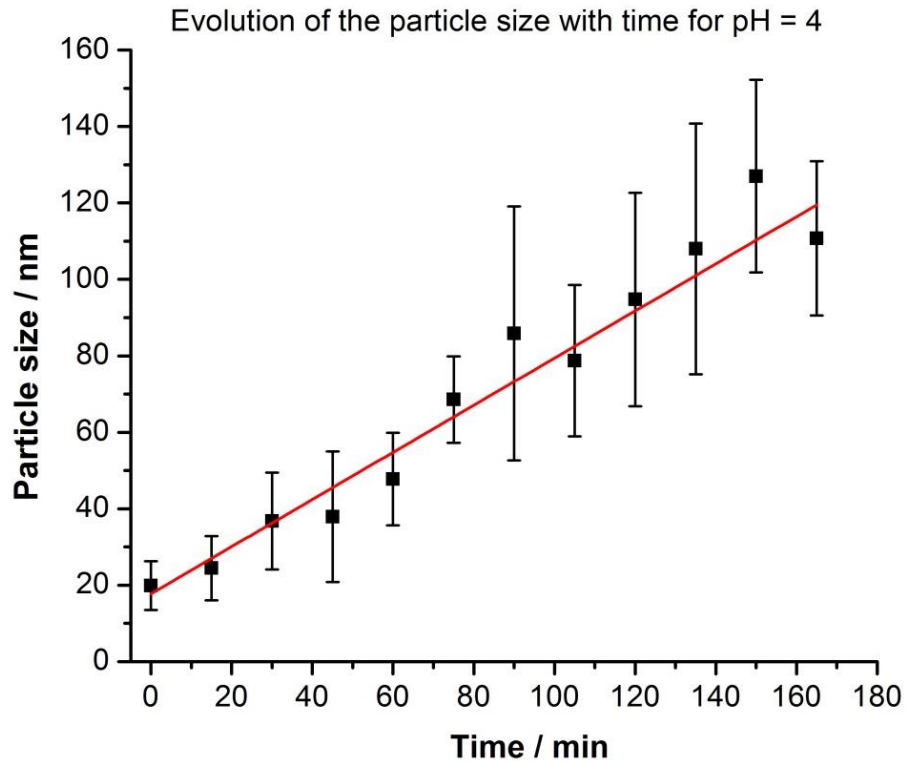


Dynamics of particle size increase at low pH values



The increase of pH slows down the process of coagulation!



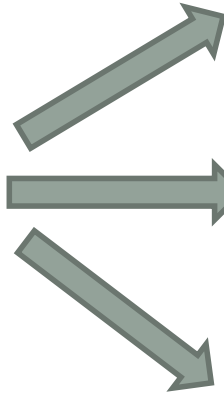


Linear particle size increase

(the particle have not reached the maximum size, in this case it is time conditioned)

Increase of particle size

(decrease of the particle concentration in solution)



a) initial enhancement of fluorescence intensity

b) peak broadening as a consequence of polydispersity

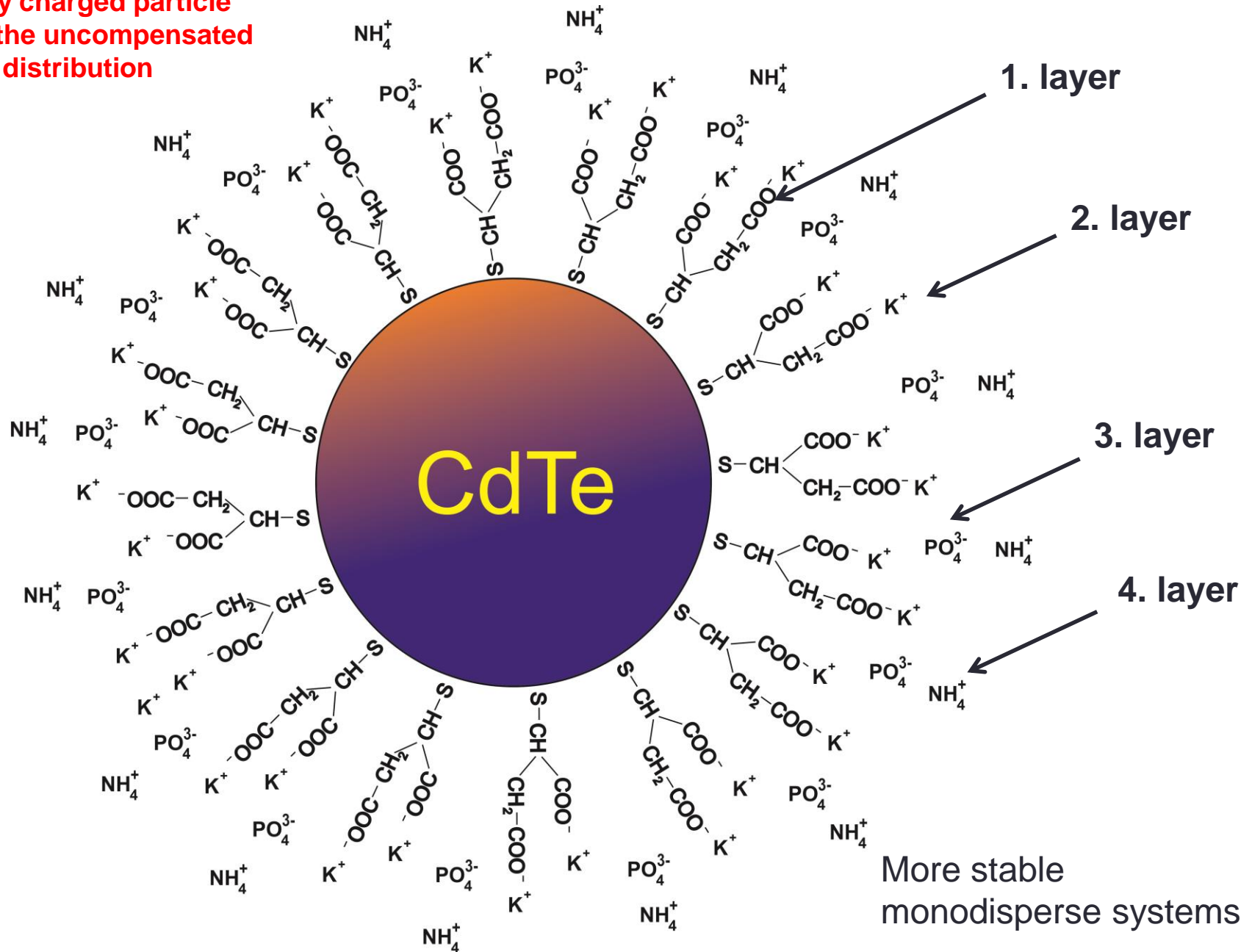
c) shifting of intensity maxima toward greater wavelengths

The phenomena (a) and (c) cease when the particle size reaches beyond the critical size!!!

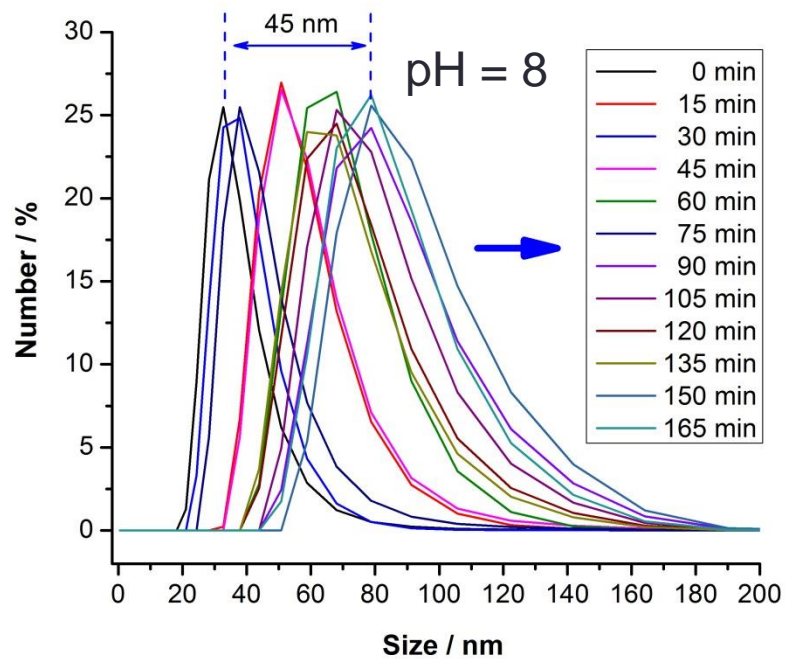
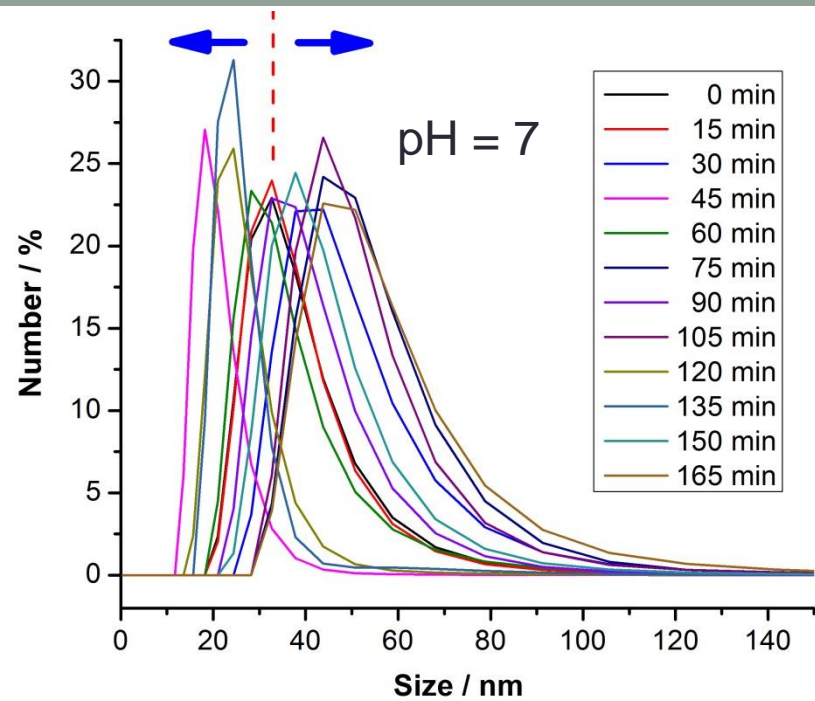
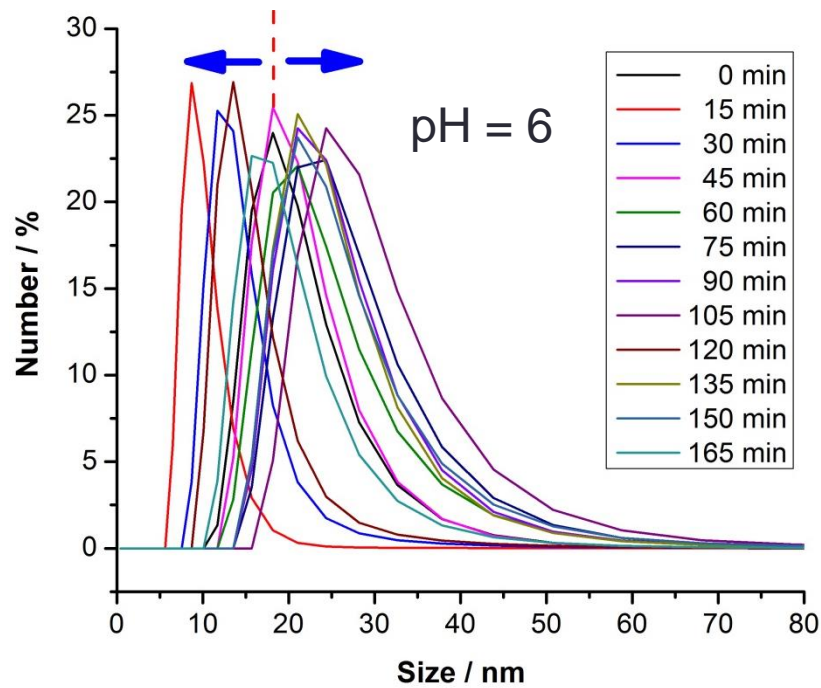
Why???

Particle coverage in alkaline medium

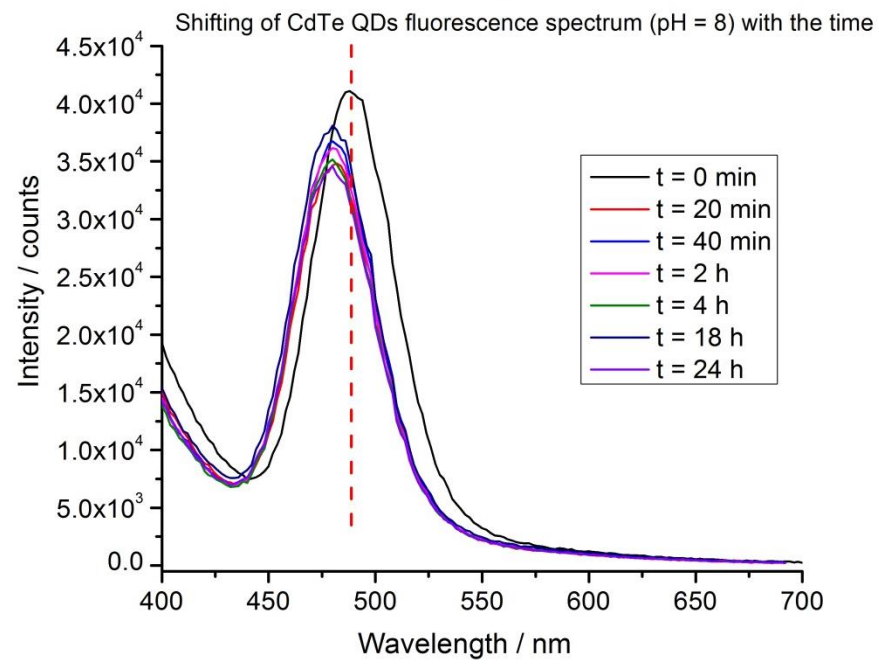
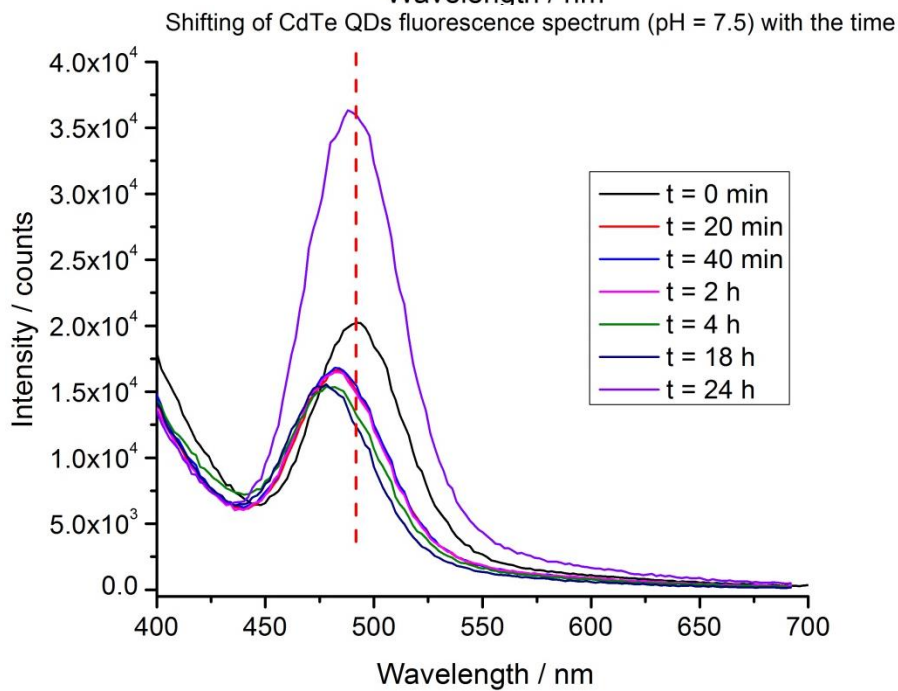
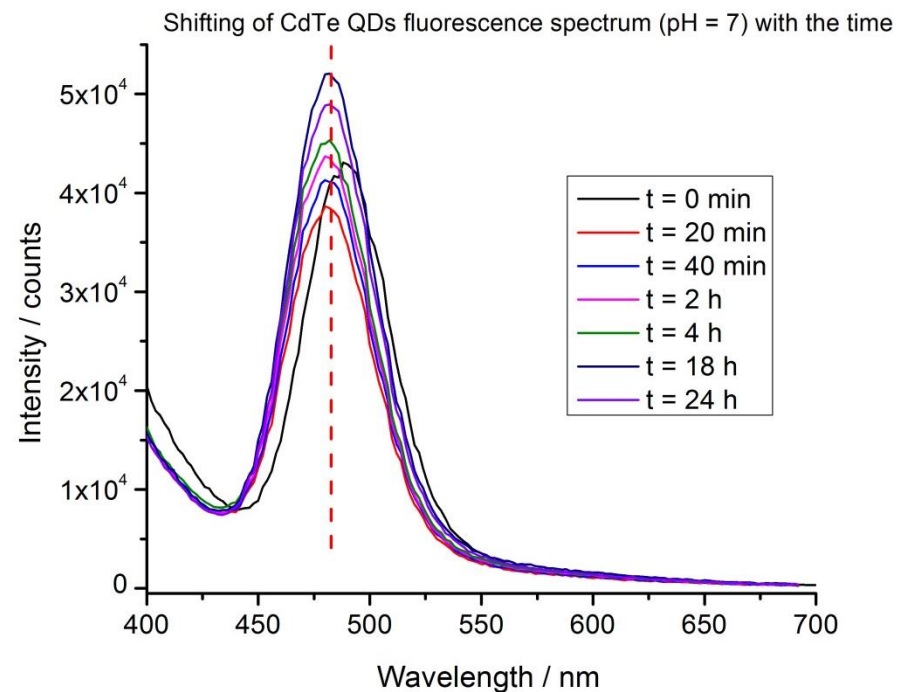
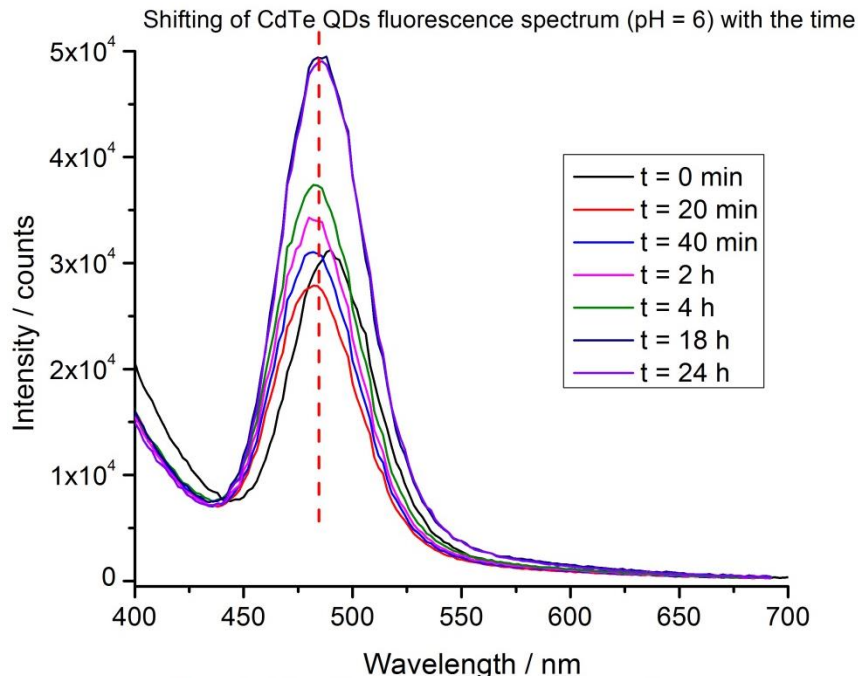
Partially charged particle
due to the uncompensated
charge distribution

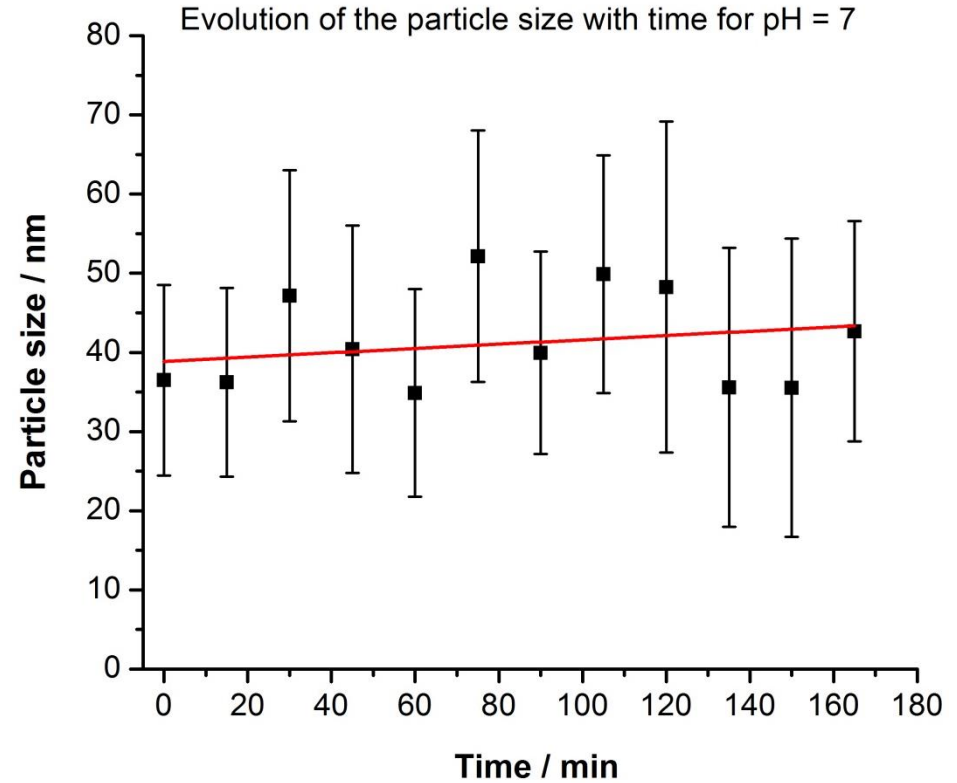
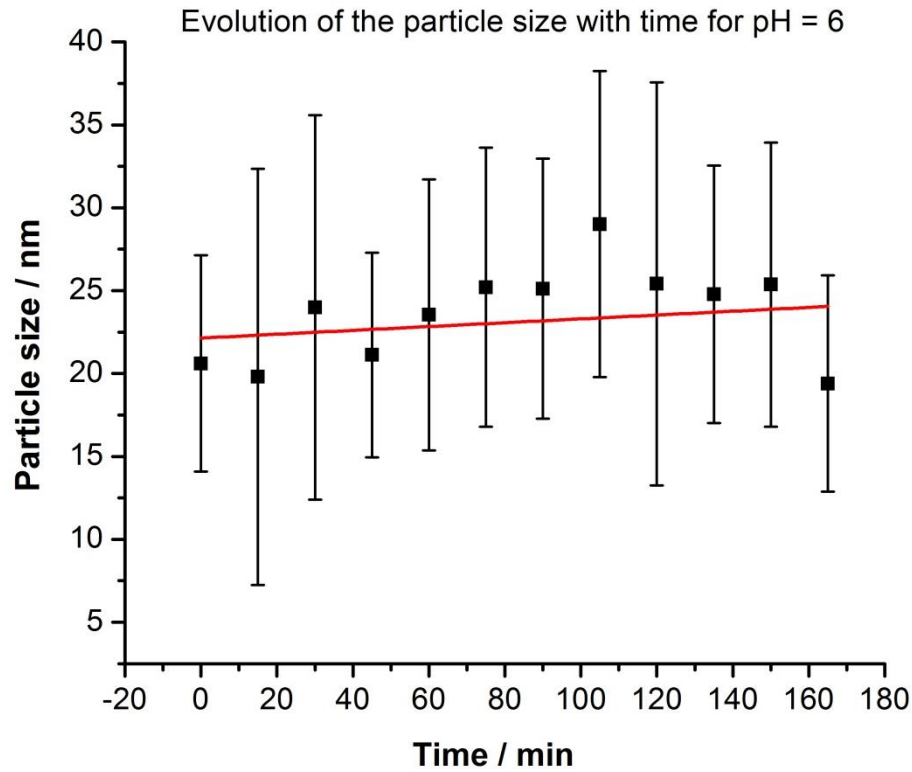


Behavior of particle size increase at pH ≥ 6

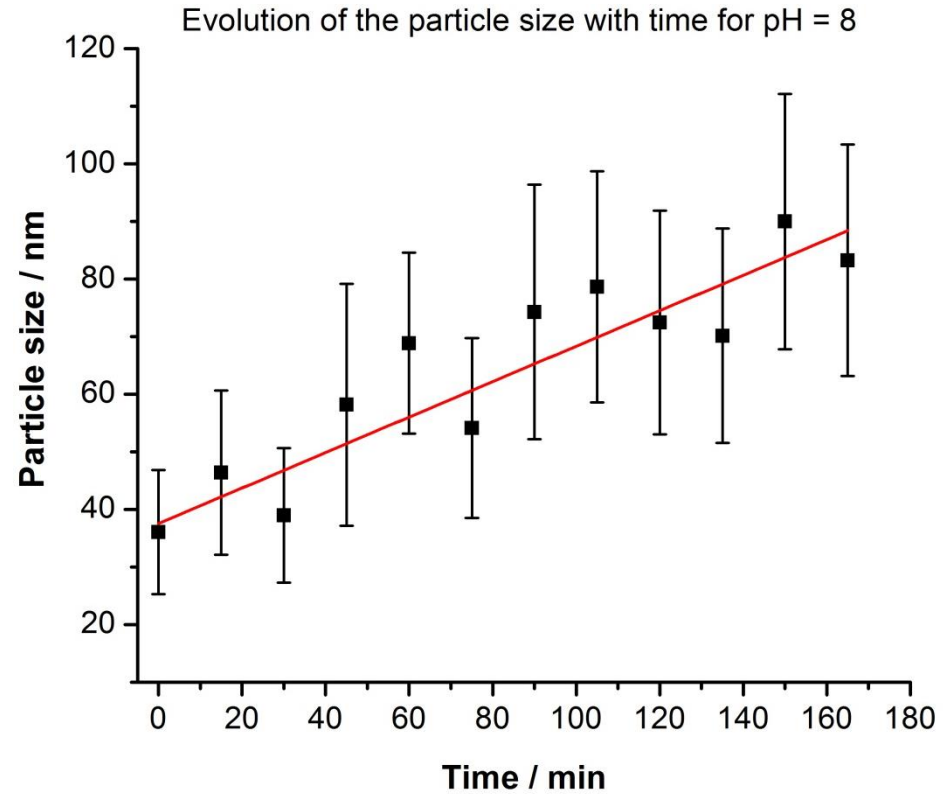
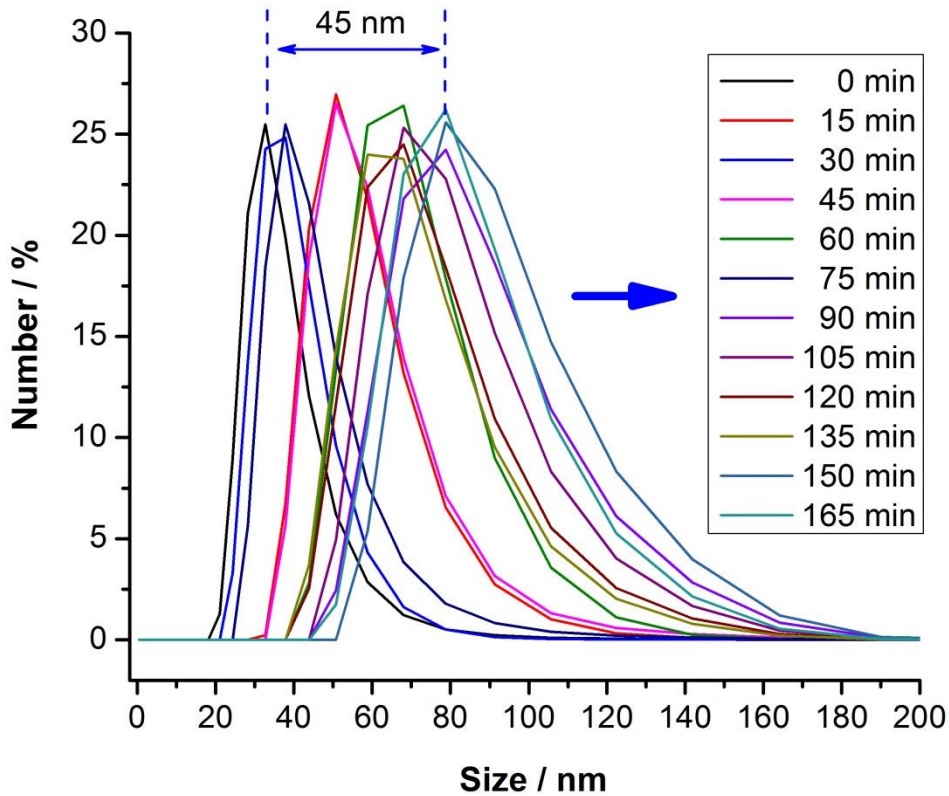


Maxima shifting for different pH (6 – 8) with the time





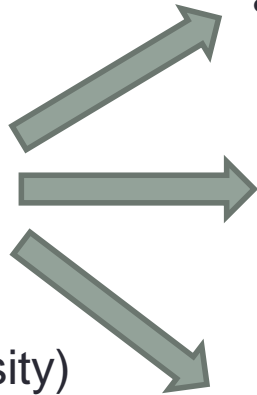
Almost steady particle size!!!



Slightly increased particle size due to the particle coverage

**Slightly increased
particle size as a
consequence of
surface modification**

(conservation of monodispersity)



a) Enhanced system stability

*b) Surface modifications leading to **lattice contraction** and the **recombination of surface delocalized charge carriers**

c) slight shifting of intensity maxima toward smaller wavelengths

*For tiny particles, the number of the electronic states of the surface is comparable to that of the internal part!!!

$$\zeta = f(t)$$

Measurement of time dependence of zeta-potential for each pH value not only simplifies the explanation of coagulation but also makes the overall explanation more reliable

At low pH values there is a fast coagulation of CdTe QD particles leading to:

- a) Drastic decrease of colloid system stability
- a) Increase of polydispersity
- b) Fast sedimentation

The increase of pH slows down the process of coagulation and sedimentation

Particles size stability is observed at neutral pHs (6-7)

In alkaline pHs there is a slight increase of the particle size due to the particle coverage by multiple layers

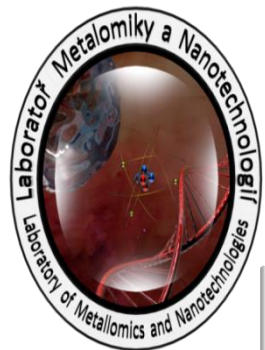
Acknowledgements

Dr. Ludmila Krejčová

Mgr. Vedran Milosavljevic

All the other members of the Laboratory of Metallomics and Nanotechnology





Děkuji vám za vaši
pozornost!

Thank you for your
attention!



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EVROPSKÁ UNIE



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MLÁDEŽE A TĚLOVÝCHOVY



OP Vzdělávání
pro konkurenceschopnost

INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ