MICROWAVE IRRADIATION AS A TOOL FOR QUANTUM DOTS SYNTHESIS

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INTRODUCTION

A microwave irradiation reduction way in an aqueous solution has been used for the synthesis of CdTe quantum dots using Na_2TeO_3 as the Te source and sodium borohydride as reduction agent. Quantum dots have been stabilized by mercaptosuccinic acid (MSA), where different amounts of added stabilizer have been studied. The synthesis parameters as power, reaction time, temperature and pH of the reaction solution have been optimized. According to reaction conditions size of prepared quantum dots can be tuned. Very short reaction time (10 – 15 min) and temperature from 50 to 130 ºC suffice to prepare highly luminescence dots. Absorption spectra and photoluminescence spectra were measured to characterize prepared dots in water solution. The peak positions in the absorption spectra ranged from 470 nm to 652 nm and the photoluminescence emission peaks ranged from 500 nm to near infrared region (NIR) 720 nm.

MATERIALS AND METHODS

Preparation of CdTe QDs

General method for preparation of CdTe QDs was as follows. 5 ml of $Cd(OAc)_2 \cdot 2H_2O$ (0.266 g/50 ml) was diluted with water (20 ml) and MSA (30 mg in 1 ml of water) was added with stirring. pH of solution was adjusted to 8.13 by addition of 1 M NH_3, (0.9 ml). Afterwards, Na_2TeO_3 (0.0066 g) in water (23 ml) was added, stirred for 30 min and solid $NaBH_4$ (20 mg) was added. Evolution of hydrogen was observed and color slowly turned to light yellow. After 1 h of stirring, 2 ml of solution was pipetted into reaction vessel and heated in Multiwave 3000 Microwave Reaction System (Anton Paar, Graz, Austria) using rotor 64MG5. The reaction conditions were as follows: temperature 50-130°C, power 300 W and time of heating 10-18 minutes. Prepared CdTe QDs were stored in dark at 4ºC.

Fluorescence measurement

Fluorescence spectra were acquired by multifunctional microplate reader Tecan Infinite 200PRO (Tecan Group Ltd. Männedorf, Switzerland). The absorbance scan was measured within range from 230 to 800 nm per 5 nm. For emission wavelength was chosen excitation wavelength 400 nm. The detector gain was set to 80. The sample (100 µl) was placed in transparent 96 well microplate with flat bottom by Nunc.

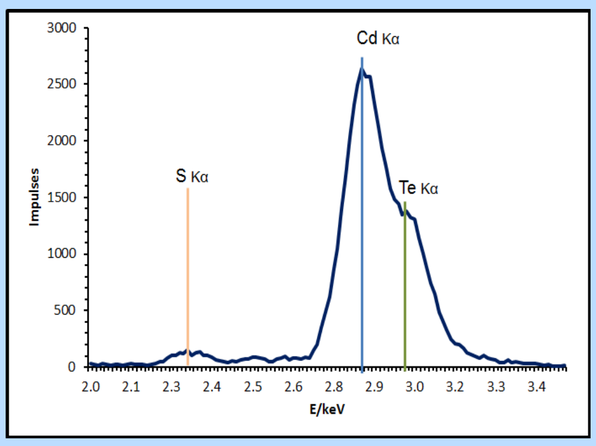
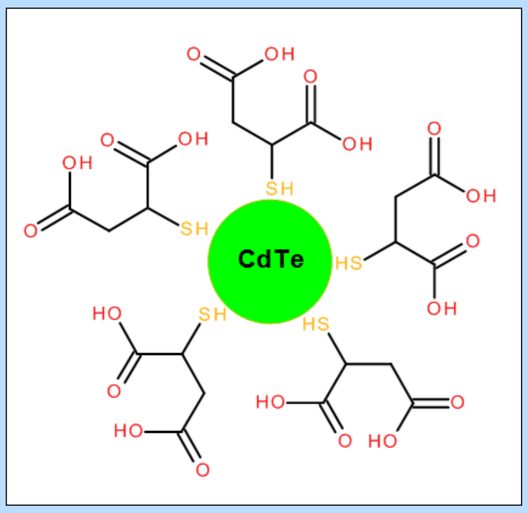


Fig. 1: Typical XRF spectrum of CdTe QDs with fluorescence lines measured on Spectro Xepos (Spectro Analytical Instruments, Kleve, Germany



Scheme of CdTe QDs covered with MSA

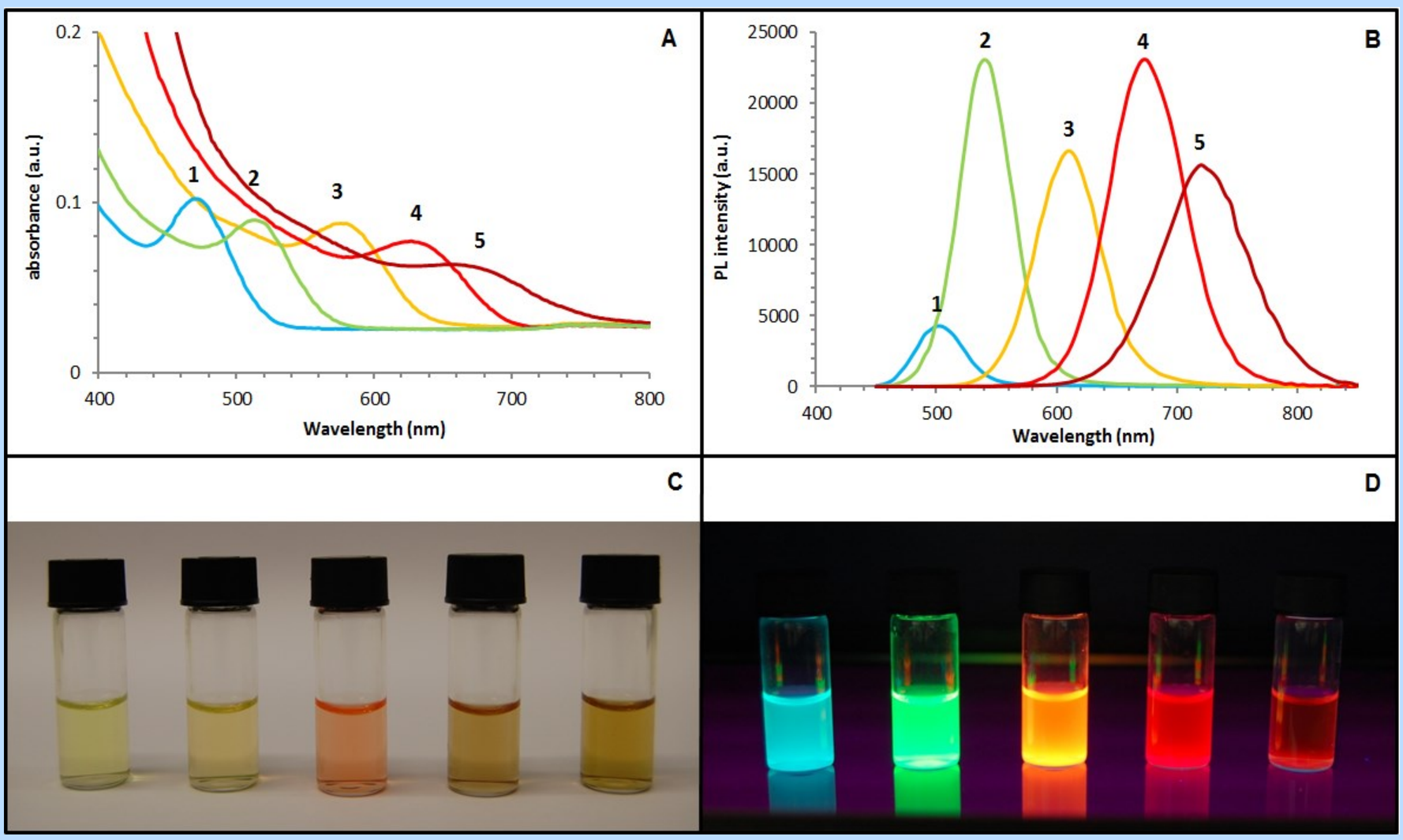


Fig. 2: Optical properties of CdTe QDs: **A**) Absorbance spectra of synthesized quantum dots (400 – 800 nm). Temperature of preparation is given in parenthesis: **1** (80 ºC), **2** (100 ºC), **3** (110 ºC), **4** (120 ºC), **5** (130 ºC). **B**) Fluorescence spectra of synthesised quantum dots (400 – 900 nm); number of flashes: 5; emission wavelength step size: 5 nm; gain: 80. **C**) Image of QDs irradiated with ambient light. **D**) Image of QDs taken at 312 nm in the same order (total concentrations of components in the mixture: Na_2TeO_3 – 1.4 mg/ml, $Cd(OAc)_2$ – 2.66 mg/ml and MSA – 0.6 mg/ml).

RESULTS AND DISCUSSION

Five samples presented here (**1** – **5**) were prepared under different temperature. The CdTe QDs solutions have different particle sizes as can be seen on snaps (**Fig. 2C and 2D**). The growth of CdTe QDs is obvious as the reaction proceeded from low to higher temperature. Both absorption and emission spectra shifted to longer wavelengths with increasing the reaction temperature or prolonging the reaction time, as expected on the basis of quantum-confined size effects. The excitonic peak positions in the absorption spectra ranged from 470 nm (**1**) to 652 nm (**5**) and the PL emission peaks of CdTe QDs with excitation wavelength at 400 nm from 500 nm (**1**) to 720 nm (**5**). The most intense peaks show green (**2**) and red (**4**) QDs with nearly the same intensity (23000 a.u.). The lowest intensity was observed for blue (**1**) emitting QDs (4260 a.u.), whereas middle intensity show yellow (**3**) and dark red (**5**) QDs (16000 a.u.). It is also well seen that band of dark red (**5**) QDs, with maximum at 720 nm, extends to 825 nm and intensities are 11000 a.u. at 750 nm and 2270 a.u. at 800 nm. The observed fluorescence of (**5**) in NIR region seems to be promising for imaging in biological samples [1-2].

CONCLUSION

In the study was shown that quantum dots with required fluorescence properties can be prepared under relatively mild conditions. Conditions of preparation were optimized which results in reproducible synthesis of stable and water soluble CdTe QDs. Nearly neutral pH is also very important for biological applications of these QDs and fluorescence in NIR region is necessary for better and deeper imaging of tissue. A study on application of these QDs for imaging purposes is presented in the conference proceeding paper by Blazkova et al.

REFERENCES

[1] T. Pons, E. Pic, N. Lequeux, E. Cassette, L. Bezdetnaya, F. Guillemin, F. Marchal, B. Dubertret, Cadmium-Free CuInS2/ZnS Quantum Dots for Sentinel Lymph Node Imaging with Reduced Toxicity, ACS Nano, 4 (2010) 2531-2538.
[2] P. Jiang, C.N. Zhu, Z.L. Zhang, Z.Q. Tian, D.W. Pang, Water-soluble Ag2S quantum dots for near-infrared fluorescence imaging in vivo, Biomaterials, 33 (2012) 5130-5135.

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