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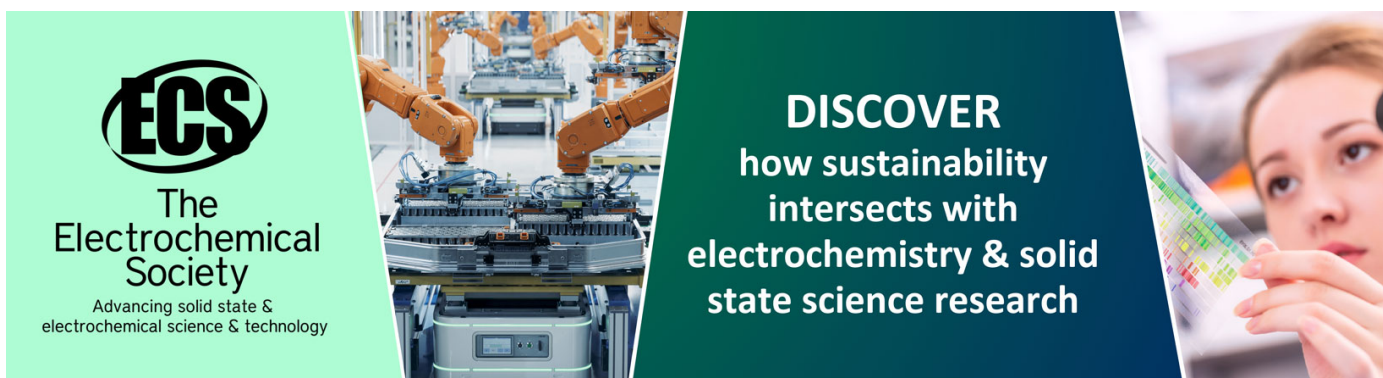
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Quenching of quantum dots luminescence under light irradiation and its influence on the biological application

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Abstract. Applications of quantum dots (QDs) can be limited by their stability under intensive irradiation. We have studied the stability of core/shell QD photoluminescence under the irradiation typical for the laboratory or industrial environment. Our results show that QD photoluminescence stability is determined by the structure and thickness of their shell; the latter factor has the strongest effect on the QD resistance to irradiation. It has been shown that the observed photodegradation of QDs is basically caused by the transfer of excited charge carriers outside the QD. An increase in the carrier tunneling length has been shown to be an efficient way to prevent quenching of QD photoluminescence. Storage of chloroform QDs solution under the light should be avoided due to the decrease of the biological applicability.

1. Introduction

Size-tunability of the absorption and fluorescence properties of colloidal quantum dots (QDs) makes them an attractive material for modern science and technology. Size-controllable optical properties of QDs allow their applications in multiplexed biolabeling, solar cells, light emitting diodes, catalysis, etc. QDs may gradually replace organic dyes from these fields because of their higher linear absorption cross-sections, photoluminescence (PL) quantum yields (QY), and photostabilities. However, in contrast to organic dyes, QDs are known to be susceptible to environmental factors such as oxygen; in addition, intense laser irradiation is known to alter their PL QY. Therefore, understanding of the mechanisms and factors causing instability of QD optical properties is one of the most important issues for the development of new generations of QDs and QD-based devices.

In this study, we have investigated the influence of long-term visible-light irradiation on the PL QY of QDs in order to model their storage and/or operation under common laboratory or industrial conditions. Two types of light sources with the same light power output (15 mW/cm^2) were used for QD irradiation: a 40 W incandescent lamp and an array of light-emitting diodes with a radiation wavelength of 405 nm. Three types of core/shell QDs with different shell compositions and thicknesses, CdSe/ZnS(3ML), CdSe/ZnS(1ML)/CdS(1ML)/ZnS(1ML), and CdSe/CdS(7ML)/ZnS(1ML), all with initial PL QYs exceeding 70%, were used to estimate the effects of the shell thickness and confinement potential on the stability of their PL.



2. Materials and methods

2.1. Materials

Cadmium oxide (powder, 99.5%), zinc oxide (powder, 99.99% trace metals basis), 1-octadecene (ODE, technical grade, 90%), oleylamine (OLA, technical grade, 70%), selenium (powder, 100 mesh, 99.5%), thiourea (ACS reagent, $\geq 99.0\%$) tri-n-octylphosphine (TOP, technical grade, 97%), tri-n-octylphosphine oxide (TOPO, reagent grade, 99%), 2-ethylhexanoic acid (2-EHA, 99%), tri-n-octylamine (TOA, 98%), triethylene glycol dimethyl ether (TEGDME, ReagentPlus, 99%), cysteine hydrochloride hydrate (98%), sodium hydroxide and anhydrous solvents (chloroform, hexane, acetone, methyl acetate and 2-propanol) were purchased from Sigma-Aldrich; n-hexadecylphosphonic acid (97%) was purchased from PlasmaChem GmbH. All chemicals were used as received without any purification.

2.2. Synthesis of the QDs

CdSe cores were synthesized via the standard procedure reported in [1]. 1 mmol of cadmium oxide, 2 mmol of 2-ethylhexanoic acid, and 8 ml of ODE were placed in three-neck round bottom flask. The flask was heated to 220°C under argon atmosphere to complete dissolution of CdO. Then the flask was cooled to room temperature and 0.5 mmol of n-hexadecylphosphonic acid, 2 ml of tri-n-octylamine was added to flask. Then the reaction mixture was heated to 120 °C and evacuated in order to remove residual water. Selenium precursor was prepared by the dissolution of 2 mmol of Se in 2 ml of TOP and 0.5 ml of ODE under the argon flow. The selenium precursor was quickly injected in to the cadmium precursor solution at 240 °C. Reaction solution was kept under the argon atmosphere and continuous stirring. The growth of the CdSe cores was controlled via the UV-vis spectroscopy and the reaction was stopped by the cooling on reaching predetermined size. CdSe cores were separated from other reaction media by the precipitation with 2-propanol and then were purified by the cycles of precipitation/dissolution with using of acetone and hexane.

QDs cored were covered by CdS and ZnS in different proportions. Solutions of cadmium 2-ethylhexanoate, zinc 2-ethylhexanoate and thiourea in triethylene glycol dimethyl ether were used as cadmium, zinc and sulphur precursor respectively. Amount of precursors which are necessary for cores covering were calculated using a spherical nanoparticle model according to the SILAR technique [2]. Solution of cores was evacuated and heated up to 180°C under argon atmosphere and continuous stirring, then the precursors were added dropwise, after the end of precursor addition the reaction media was maintained under the same conditions for 20 minutes in order to reach the end of shell formation reaction. Then QDs were purified by the same method as cores with using of 2-propanol, hexane and acetone.

2.3. QDs solution irradiation

Obtained QDs were dissolved in chloroform as a most common solvent, optical density at 400 nm for all solutions were equal to 0.1. Each solution was divided into two parts and each part was irradiated by UV or visible light under the continuous stirring. Incandescent lamp (40W) was used as the source of the visible light, massive of the UV LEDs were used as the source of the UV light. The light flow was the same for the both light source and equal to 15 mW/cm². Solutions were irradiated for 3 hours and in order to evaluate the dynamic of optical properties of the obtained solution the photoluminescence quantum yield was measured (PLQY). PL QY was measured relative fluorescein (QY = 95 %) for CdSe/ZnS(3ML), relative rhodamine 6G (QY = 95%) for CdSe/ZnS/CdS/ZnS and relative rhodamine 102 (QY = 96 %) for CdSe/CdS(7ML)/ZnS. Choice of the comparison dye is due to the region of the QD's luminescence. PLQY was measured every 10 minutes during the first hour, every 20 minutes during the second hour and every 30 minutes during the third hour, also PLQY was measured after 2.5, 5 minutes of the light irradiation.

2.4. Solubilization of the irradiated QDs

In order to investigate the influence of the different type of the light irradiation on the size of the agglomerates of the solubilized QDs, CdSe/CdS/ZnS QDs irradiated for 0.5, 1, 2 and 3 hours were solubilized with using of cysteine by the following procedure. QDs were purified by the precipitation with using of methyl acetate and collect by the centrifugation. Ethanol solution of DL-cysteine was added dropwise to the chloroform solution of purified QDs and stirred for 5 minutes. In order to remove cysteine not bounded with QD's surface, solution was twice purified by the centrifugation, supernatant decantation and addition of pure methanol. Then QDs were dissolved in 0.1 M water solution of NaOH and sonicated for 15 minutes. Then the size of the solubilized QDs was measured by the dynamic light scattering.

3. Results and discussion

Irradiations of QDs with an incandescent lamp and a LED array have revealed two parallel counteracting processes: an increase in and quenching of the PL. The kinetic curves of these processes are shown in figure 1, the values of the relative PLQY are presented in table 1.

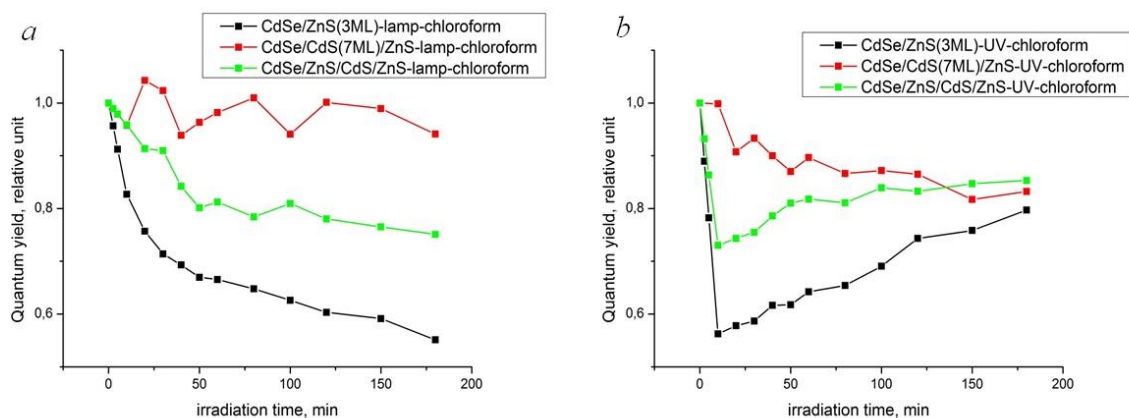


Figure 1. Dynamic of the PLQY for CdSe/ZnS/CdS/ZnS irradiated with visible (a) and UV (b) light.

Table 1. Relative photoluminescence quantum yield of QDs irradiated with UV or visible light for 3 hours

QDs type	UV irradiation	Visible irradiation
	Relative photoluminescence quantum yield, %	
CdSe/ZnS(3ML)	0.79(0.56)*	0.55
CdSe/ZnS/CdS/ZnS	0.85(0.73)*	0.75
CdSe/CdS(7ML)/ZnS	0.83	0.94

*- the minimum QD's PL QY value after the end of the photodarkening

In the case of CdSe/ZnS(3ML) QDs, irradiation with an incandescent lamp caused a slow PL decline to 55% of the initial PLQY value, while irradiation with LEDs caused a rapid PL quenching to 56% followed by slow restoration of luminescence to 79% of the initial level.

Multishell CdSe/ZnS/CdS/ZnS QDs exhibited a similar kinetic of PL QY decrease, but the degree of PL quenching was much lower. Thus, irradiation with an incandescent lamp caused a 25% drop of

PL, while irradiation with a LED array resulted in a 27% loss of PL QY followed by restoration to 85% of the initial PL QY during the remaining period of irradiation.

Thick-shell CdSe/CdS(7ML)/ZnS QDs exhibited a totally different response to irradiation with both light sources, without considerable PL quenching under visible light irradiation and without PL restoration under UV light irradiation. These QDs were found to be almost completely stable under long-term irradiation; under irradiation from either source. The reference samples representing the same solutions of QDs incubated in the dark did not exhibit detectable variation of PL QY, thus proving that the observed effects originated from light irradiation rather than from other possible environmental factors.

Transfer of the excited charge carriers from the core of QDs to the surface ligands or the surrounding molecules is known to be an efficient pathway of QD PL quenching [3]. We suppose that the difference in charge transfer rates is the reason of the observed differences in the PL quenching kinetics of the QDs studied. This difference can be related to the variation in (i) the shell thickness or (ii) the confinement potentials determined by the structure and composition of the shells. Specifically, a 3ML-thick ZnS shell ensures a high potential barrier of moderate length for electrons and holes to tunnel through and to escape the QD core. The multishell structure provides a slightly higher potential barrier than a 3ML-thick ZnS shell does, due to the strong quantum confinement effect in monolayer-thick shell layers [4], while having the same barrier length. Finally, thick-shell CdSe/CdS(7ML)/ZnS QDs have the lowest energy of potential barrier created by CdS, but the barrier length is 2.5 times larger than that in other QDs. From the obtained results, one can conclude that the barrier length has a much stronger effect on the stability of QD colloidal solutions to irradiation, and a sufficiently thick shell could completely protect QDs from photoinduced degradation.

The difference in PL quenching kinetics under irradiation from different light sources can be attributed to different spectral overlaps of the light source emissions and QD absorption spectra. The entire incident photon flux from the blue LED array falls within the absorption range of all types of QDs, while a major part of the incandescent lamp irradiation cannot be absorbed by QDs. However, we can conclude that, even in the latter case, significant quenching of QD PL can occur under long-term irradiation.

Formation of the wide gap material shell on surface of the cores is one of the most effective methods for increase the QDs properties [5] due to the passivation of the surface trap states and preventing of charge transfer in QD or out. In the paper [6] authors collective report about the PbSe QDs treatment by the chlorine, which cause the increase of the QD's PLQY due to the formation of the PbCl_x layer on QD's surface. In our case the restoration of PLQY of CdSe/ZnS(3ML) and CdSe/ZnS/CdS/ZnS irradiated by UV light. It is well known that QDs is very promising photocatalyst and cause the decomposition of chloroform to the formation of hydrogen chloride and carbon dioxide [7]. Interaction of hydrogen chloride with QDs cause the formation of ZnCl_x layer on its surface, which is dielectric and form giant confinement potential, that cause the restoration of the PLQY. The absence of PLQY in case of CdSe/CdS(7ML)/ZnS QDs is caused by shell width, ZnCl_x formation don't cause the changes in charge recombination kinetic.

The influence of the longterm storage of chloroform QDs solution under different type light irradiation on their biological application was investigated on the example of CdSe/ZnS/CdS/ZnS QDs. The first step on way to the QDs biological application is QDs transfer from hydrophobic phase to water. The transfer was carried out by the exchange of hydrophobic ligands to cysteine on multishell QDs irradiated by UV or visible light for 0.5, 1,2 and 3 hours. Then the size of the solubilized QDs was measured with using of dynamic light scattering, the mean size of the solubilized QDs are presented in the table 2.

Obtained results show, that irradiation causes the agglomeration of the QDs during the solubilization and UV light irradiation cause the significantly greater increase compare to visible light. The mean size of the particles in not irradiated solution is 4.1 nm, which correspond to the QD size, mean sizes of the particles irradiated by UV light for 2 hours and visible light for 3 hours are 11.7 and 7.5 respectively, that close to the sizes of the trimmer and dimmer agglomerates. Significant greater

effect of UV irradiation on the described process compare to visible irradiation allows to propose that the observed effect is connected with the chlorination of the QDs surface during the irradiation of the chloroform solution. Cysteine binds with the QDs surface by the formation of S-S and Zn-S bond between QD surface and –SH group. Substitution of sulfur atoms by chlorine atoms cause the decrease of the amount of the surface site for bond formation and hence decrease the concentration of the ligand molecules on the QD's surface, that cause the decrease of the steric stabilization level that cause the agglomerate formation. Difference between levels of agglomeration for QDs irradiated by UV and visible light is due to the fact that UV light irradiation causes more intensive QD's surface chlorination that cause low level of stabilization and bigger agglomerate formation. The size of the particles is the one of the most parameter for biological application as it determine the ability to penetrate throw the different kinds of membranes in biological system, hence it necessary to avoid the long term storage of QDs in chloroform solution under the different type of light irradiation or propose the another type of the solvent in which photodegradation process of QDs are absence, it will be the subject of the further studies.

Table 2. Mean size of the solubilized QDs.

Irradiation time, h.	Size of UV irradiated QDs, nm	Size of vis. irradiated QD, nm
0	4.18	4.18
0.5	7.5	4.9
1	10.7	-
2	11.7	-
3	-	7.5

4. Conclusions

The results obtained in this work could be important for application-driven design of novel QDs. The high stability of PL QY is an advantage in engineering of photostable fluorescent biolabels or QD-LEDs; on the other hand, QDs that are prone to fast photoinduced PL quenching could be efficient tags in high-resolution stimulated emission depletion (STED) optical microscopy. The main conclusions for this study is (i) Shell structure and solvent have an unambiguous effect on the stability of colloidal QDs under intense irradiation, (ii) transfer of the photoexcited charge carriers is the reason of QDs luminescence quenching, (iii) formation ZnCl_x passivation monolayer on the QD's surface can be the reason of observed photobrightening in chloroform, (iv) Shells width, rather than confinement potential created by it, is a key factor that determines photostability of QDs, (v) Storage of QDs in the form of chloroform colloidal solution should be avoided if any surface ligand exchange is necessary in the future – eg. solubilization using bifunctional thiols for biology applications.

5. Acknowledgments

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