

TUNABILITY OF OPTICAL PROPERTIES OF WATER-SOLUBLE SEMICONDUCTOR NANOCRYSTALS VIA ZETA-POTENTIAL

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Tunable optical properties combined with size control are the key characteristics of semiconductor nanocrystals (NCs), or quantum dots (QDs), due to a wide spectrum of possible applications of these phenomena in light-harvesting systems, photovoltaics, biosensing, and bioimaging [1]. Encapsulation with an amphiphilic polymer of hydrophobic QDs is proven an effective solubilization technique since NCs preserves small hydrodynamic size and relatively high quantum yield (QY). To improve colloidal stability, biocompatibility, and increase a non-specific interaction with cellular membranes the surface of QDs is modified with various molecules leading to change of zeta-potential (ξ) [2].

This work aimed to investigate the dependence of the optical characteristics of water-soluble QDs with the sign and magnitude of their surface charge and propose the physical model for describing obtained dependencies.

The idea of the experiment was to modify poly(maleic anhydride-*alt*-1-tetradecene) (PMAT) with derivatives with different functional groups of encapsulated QDs. The nature of functional groups determines the sign of surface charge, while the ratio of them influences the magnitude of ξ -potential. Further, the optical characteristics such as quantum yield, emission wavelength, and luminescence lifetime were measured as a function of ξ -potential.

Chemical modification of PMAT was performed according to the standard carbodiimide procedure. ξ -potential and hydrodynamic size of water-soluble QDs were measured with the dynamic light scattering analyzer Malvern Zetasizer NanoZS90. QY was measured relative to rhodamine 6G (95% in ethanol). Photoluminescence (PL) decay times were measured with PicoQuant Microtime200 fluorescence lifetime imaging confocal microscopy system.

According to the obtained results, QY of water-soluble QDs has the highest value when ξ -potential approaches zero. QY is not influenced by the nature of the functional group on the surface only by ξ -potential.

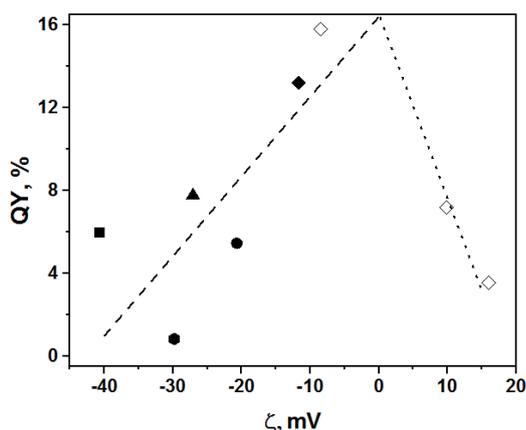


Fig. 1. QY dependency on zeta-potential of QDs with different functional groups on the surface: square – COOH, triangle – PO₃H₂, round – OPO₃H₂, hexagon – SO₃H, colored diamond – SO₄H, bare diamonds – quaternary ammonia.

Table 1. Summary of measured fluorescence lifetime and QY.

ξ -potential, mV	QY, %	τ_1 , ns	A ₁	τ_2 , ns	A ₂	$\langle\tau\rangle$, ns
-39.8	6.0	7.6	0.507	29.8	0.493	18.5
-4.3	18.2	10.8	0.462	32.5	0.538	22.5
+16.0	3.5	4.3	0.553	17.5	0.447	10.2

Highly positive or negative ξ -potentials result in similar radiative rates, while nonradiative rates increase by a factor of two. The increase of the QY near-zero ξ -potential is due to an increase of the radiative rate and less via decrease of nonradiative rates via e.g. better passivation of NCs if there is only a weak ionic double layer formed. The reason is that the free charge carriers around the QDs screen the exciton in the QDs strongly. If the screening is enhanced the exciton binding energy lowers [3].

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