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Optical characterization of core–shell quantum dots embedded in synthetic saliva: Temporal dynamics

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ABSTRACT

The present work reports the spectroscopic and thermo-optical properties of CdSe/ZnS and CdSe/CdS core–shell quantum dots (QDs) embedded in synthetic saliva. Spectroscopy studies were performed applying nonfunctionalized CdSe/ZnS QDs (3.4, 3.9 and 5.1 nm cores) and hydroxyl group-functionalized ultrasmall CdSe/CdS core–shell quantum dots (1.6 nm core) suspended in artificial saliva at different potential of hydrogen (pH) values. Saliva was chosen because it is important in a variety of functions such as protecting teeth through the buffering capacity of the formed biofilm, hydration, and dental remineralization. Thermo-optical characterizations using the thermal lens (TL) technique were performed in QD-biofluids for different QD sizes and pH values (3.9–8.3) of the synthetic oral fluids. Transient TL measurements were applied to determine the fluorescence quantum efficiency (η) in QD-biomaterial systems. High η value was obtained for ultrasmall CdSe/CdS QDs. Fluorescence spectral measurements of the biomaterials support the TL results. In addition, for nonfunctionalized (3.4 and 5.1 nm) and hydroxyl group-functionalized QDs, the temporal behavior of the fluorescence spectra was accomplished about approximately 1200 h at two different biofluid pH values (3.9 and 8.3). The temporal fluorescence intensity result is dependent on the pH of the saliva in which the QDs were embedded, QD functionalization and QD sizes. The time for an approximately 50% decrease in the peak intensity fluorescence of CdSe/ZnS QDs (3.4 nm core) and ultrasmall CdSe/CdS QDs is respectively 25 h and 312 h at pH 3.9 and 48 h and 360 h at pH 8.3.

1. Introduction

Quantum dots (QDs) are inorganic nanocrystals that can be synthesized by standard chemical means [1]. These materials present properties of the semiconductor family, but unlike most semiconductors, they have characteristic absorption and emission spectra [2]. The optical properties of the QDs can be modified simply by varying the particle size [2], and QDs synthesized in aqueous solutions [3,4] with appropriate functionalizations [5,6] are required for biomedical applications. Nanoparticles are very chemically flexible in aqueous phases; this flexibility makes it possible to incorporate a wide variety of biomolecules, such as proteins, peptides and DNA [7]. In general, QDs and bio-conjugated QDs have been used for several applications as imaging markers of the following: microscopic cells, engineered tissues, cancer, and glycoprotein surfaces of bacteria, fungi and other microorganisms; these molecules have also been used for drug delivery, as well as for applications requiring biological detectors of pathogens and proteins [7–10]. Recently, studies showed the use of functionalized QDs as contrast agents in optical images of pancreatic cancer cells in vitro [7].

Core–shell QDs are formed by combining two different semiconductor molecular devices, one of which forms the core, which is covered by an outer layer containing another type of semiconductor. Such systems increase the quantum yield of fluorescence and also increase the stability of the nanocrystals. Additionally, the emission of these nanomaterials can be extended to a wide range of wavelengths given the proper choice of materials for the core and shell [11]. CdSe/ZnS and CdSe/CdS core–shell QDs are classified as type I QDs, where electrons and holes are both confined in the core region of the core–shell QDs [12,13]. The shell

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provides a physical barrier between the core and the surrounding environment, making the core less sensitive to environmental changes in the nanocrystals due to photo-oxidation [14] and improving the radiative quantum efficiency (η) by passivating the nonradiative recombination sites at the surface [15,16]. The η parameter can depend on the potential hydrogen (pH) value of the medium in which the QDs are immersed [1,17,18]. pH is capable of affecting the structure and activity of both molecules and nanoparticles. For example, CdSe/ZnS core–shell QDs have been used for a highly sensitive system for urea detection [19], for the quantitative determination of triglyceride content [20] and for lifetime-based pH nanosensors [21].

The present work reports the thermal characterization of CdSe/ZnS core–shell nanocrystals embedded in artificial saliva. The study was performed using different sizes of CdSe/ZnS QDs suspended in fluids with different pH values and using ultrasmall CdSe/CdS QDs that were functionalized with hydroxyl groups in aqueous solutions. The thermo-optical properties, such as the thermal diffusivity (D) and η, of the QD-biomaterial systems were determined using the thermal lens (TL) technique. The temporal dynamics of fluorescence spectra was measured for CdSe/ZnS nano-systems with both different pH values and different QD sizes and for ultrasmall CdSe/CdS QDs functionalized with hydroxyl groups. Saliva was used as biofluid because it is important and performs different functions in organisms in general, such as preparing food for digestion, protecting teeth during the formation of the acquired pellicle, providing buffering capacity, controlling the oral microbiota, providing lubrication and hydration, facilitating remineralization and aiding in sensory processes [22–24]. Currently, saliva is also widely used as an indicator of systemic diseases related to immune deficiencies, gastric cancer, liver function disorders, and infection and to monitor drug and hormone levels, dental caries and periodontal disease [25–27]. For example, in a healthy person, saliva has a pH value between 6 and 7, and this value depends on the salivary flow (5.3 for low flow and 7.8 for peak flow) [28,29]. In contrast, cancer patients present lower salivary pH levels [30]. The use of QDs as a pH-dependent sensor is a further possibility for applications of QDs embedded in biofluids because the pH of human saliva may vary in different disease states [17].

The saliva choice as the biofluid was not only due to its importance in the human body, but as the possibility to vary the pH to test the sensitivity of the QDs for applications in sensors, and also the QDs stability in biological applications as a function of time. For example, magic-sized CdSe QDs have been showed highly stable fluorescence even in HeLa cells after 36 h of incubation, it is an excellent tool to monitor biological processes or changes as a function of time [31]. In addition, the techniques used for metabolomics in biofluids studies are for example, nuclear magnetic resonance (NMR), gas chromatography–mass spectrometry (GC/MS) and liquid chromatography–mass spectrometry (LC/MS). For example NMR present to be an excellent technique for biofluids and complex solutions analyses, LC/MS technique has been applied in microseparation platform in metabolomics and disease diagnosis, and GC/MS technique can be applied in volatile compounds after derivatization [26,32]. In our work, QDs nonfunctionalized and functionalized were studied embedded in biofluids with different pH values and QD sizes to verify the sensor behavior and sensibility of fluorescence and TL techniques for detection as alternative lower cost methods.

2. Thermal lens (TL) technique theory

The TL effect [33–37] is caused when the laser energy that should be absorbed by a sample with a thickness L becomes dissipated heat due to nonradiative decay processes. The thermally induced distortion of the Gaussian laser beam that occurs when it passes through the sample is described by the optical path-length (S) change ($ds/dT = L^{-1}\, dS/dT$), which produces lensing at the sample. In the case of liquid samples, $ds/dT \approx dn/dT$, where dn/dT is the temperature coefficient of the refractive index. In the dual-beam mode-mismatched configuration [34,36], the presence of such a thermal lens is detected by its effect on the propagation of a probe beam that passes through the sample. The propagation of a probe laser beam through the TL is dependent on the temperature coefficients of the electronic polarizability, stress and thermal expansion of the sample [34,35].

The fraction of absorbed energy converted to heat generates a radial temperature profile $\Delta T(r, t)$ on the sample. The propagation of a probe beam through this TL results in a variation of its on-axis intensity, $I(t)$, which can be calculated using the diffraction integral [35]. In the cw regime, $I(t)$ is given by [34]:

$$I(t) = I(0)\left[1 - \frac{\theta}{2}\tan^{-1}\left(\frac{2mV}{[(1+2m)^2 + V^2]\tau_c/2t + 1 + 2m + V^2}\right)\right]^2 \quad (1)$$

where $I(0)$ is the on-axis intensity when t and/or θ are zero; $m = (w_p/w_e)^2$, with w_p and w_e as the probe and excitation beam radii at the sample, respectively; $V = z_1/z_o$, z_1 is the distance between the sample and the probe beam waist; and z_o is the Rayleigh range of the probe beam. $\tau_c = w_e^2/4D$ is the characteristic heat diffusion time, where $D = K/\rho C$ is the thermal diffusivity (cm^2/s), K is the thermal conductivity (W/cm K), ρ is the density (g/cm^3), and C is the specific heat (J/gK). The TL transient signal amplitude, θ, is approximately the phase difference of the probe beam between $r = 0$ and $r = \sqrt{2}\, w_e$, which is induced by the pump beam. The normalized phase shift, $\Theta = -\theta/P_e \alpha L_{eff}$, where P_e (W) is the excitation power, α (cm^{-1}) is the optical absorption coefficient at the excitation wavelength (λ_e), and $L_{eff} = (1 - e^{-\alpha L})/\alpha$ is the effective length, can be expressed as [34,37]:

$$\Theta = \frac{1}{K\lambda_p}\frac{dn}{dT}\left(1 - \eta\frac{\lambda_e}{\langle\lambda_{em}\rangle}\right) \quad (2)$$

where λ_p is the wavelength of the probe beam, η is the fluorescence quantum efficiency (or quantum yield), and $\langle\lambda_{em}\rangle$ is the average emission wavelength. The last term in the parenthesis of Eq. (2) is considered the fraction of absorbed energy that is converted into heat (or absolute nonradiative quantum efficiency).

3. Experimental procedure

3.1. Sample preparation

Three different sizes of CdSe/ZnS QDs suspended in aqueous solutions (Table 1) were purchased from NN-Labs at concentrations of 7.50 (QD_{Yellow}), 7.20 (QD_{Orange}) and 6.25 (QD_{Red}) $\times$ 10^{-6} mol/L. CdSe core ultrasmall QD coated with a CdS shell thickness of 0.83 nm (sample CdSe:7T) and functionalized with hydroxyl groups at a concentration of 9.3×10^{-6} mol/L have been

Table 1
Nomenclature, particle size and average emission wavelength $\langle\lambda_{em}\rangle$ of the studied core–shell QD samples.

Sample	QDs	Functionalization group	Size (nm)	$\langle\lambda_{em}\rangle$ (nm)
QD_{Red}	CdSe/ZnS	NF	(5.1 ± 0.9)	(629 ± 6)
QD_{Orange}	CdSe/ZnS	NF	(3.9 ± 0.7)	(596 ± 5)
QD_{Yellow}	CdSe/ZnS	NF	(3.4 ± 0.6)	(580 ± 4)
QD_F	CdSe/CdS	Hydroxyl	1.59 [38]	(522 ± 4)

NF is nonfunctionalized.
Average values for different pH values (3.9 and 8.3).