Journal of Colloid and Interface Science 505 (2017) 528–536

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

Influence of surface states on blinking characteristics of single colloidal CdSe-CdS/ZnS core-multishell quantum dot

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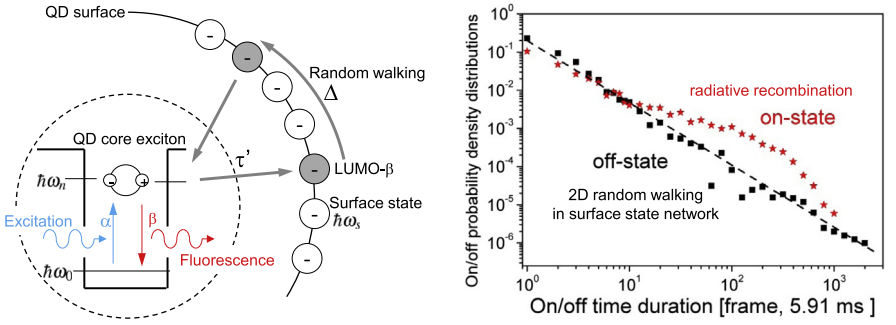
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 April 2017
Revised 14 June 2017
Accepted 14 June 2017
Available online 16 June 2017

Keywords:
Colloidal quantum dot
Fluorescence blinking
Surface state

ABSTRACT

We carefully characterized the fluorescence blinking of single colloidal CdSe-CdS/ZnS core-multishell quantum dots (QDs) with different surface modifications, including octadecylamine (ODA) coated QDs dispersed in chloroform, aqueous 3-mercaptopropionic acids (3MPA) coated QDs in HEPES solution treated by Ca^{2+} ions and ethylene glycol tetraacetic acid (EGTA, Ca^{2+} chelator), and aqueous 3MPA-QDs treated by glycerol. It was found that the on- and off-state probability density distributions displayed different rules. The off-state probability density distributions of all QDs complied well with the inverse power law, while the on-state probability density distributions bended upwards in log-log scale, and the degree of the upwards-bending correlated strongly with QD surface modification and fluorescence brightness of the single QD. Further autocorrelation analysis revealed that the fluorescence time series of a single QD was more random when the single QD showed a stronger fluorescence. Realistic numerical simulations with input parameters from quantum mechanical calculations showed that the QD exciton was first generated by an excitation photon; It radiatively recombined to give QD's fluorescence response, i.e., the on-state, which displayed the upwards-bended on-state probability density distribution profile; The electron and/or the hole of the photoexcited exciton in the QD core, after tunneling to the QD surface, randomly walked through the two-dimensional network of the QD surface states, resulting in the off-state probability density distribution profile of the inverse power law. Surface modification modified the QD surface-state network, in turn modifying the on/off probability density distribution profiles.

Our findings provide us with a novel highway of applying colloidal QDs to study microscopic physical, and chemical, processes in many fields including *in vivo* and *in vitro* imaging, sensing and labelling.

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http://dx.doi.org/10.1016/j.jcis.2017.06.046
0021-9797/

1. Introduction

Due to their extraordinary optical and electrical properties, colloidal semiconductor quantum dots (QDs) have been extensively studied and developed for various applications such as solar cells [1,2], light-emitting diodes [3,4], single photon sources [5,6], fluorescent biomedical probes [7–12]. At the single QD level, one extremely interesting phenomenon is its fluorescence blinking, which refers to stochastic fluorescence interruptions which occurs under constant or pulsed illumination. Despite tremendous efforts to seek the underlying physical mechanisms, see, e.g. [13–24], it remains a mystery to this day. For example, the bending tail, or exponential cutoff, has been widely studied especially for the on-state probability distribution, but remains strongly controversial [17,19,21,23]. In the work by Peterson and Nesbitt [19], the off-state statistics was shown to be dependent on the excitation laser power. They pointed out that the on-state distribution falloff (bending) should be attributed to low-probability biexciton formation followed by inefficient Auger ionization. Ko et al. [21] pointed out that the bending rate index was related to the activation energy of an electron charge transfer from a light state to a dark state shown by using agarose gel, which increased the activation energy of the electron charge transfer and suppressed the blinking phenomenon. In general, the proposed models are largely focused on interactions between the on- and off-state, e.g., Lévy-walk processes [25], diffusion-controlled electron transfer processes [26]. In multiple recombination center model (MRC model), the excited state in a QD is relaxed by trapping a hole to one of a number of recombination centers (RCs) followed by a slow nonradiative recombination of the trapped hole with the remaining electron [27]. A hierarchical sequence of the hole and electron trapping was proposed [28]. Surface-to-core charge switching mechanism was studied recently that included surface states [29].

It was reported that several electronic traps at the QD surface were extrinsic and detrimental to the fluorescence properties of QDs [30], which is closely related to many works demonstrating the modulation of the blinking and photobleaching effects of single QDs by surface passivation using different molecules [13,19,16,21,24,29,31,32]. β-mercaptoethanol (BME) was shown to be effective on modifying blinking [16], glycerol was used to passivate 3C-SiC nanocrystals [24], and mercaptoethylamine (MEA) was excellent in suppressing both blinking and photobleaching [32]. Recently, supporting media of different dielectric constants were used to probe the QD blinking [29].

For bioimaging applications, single QDs are highlighted mostly due to their fluorescence brightness and photostability, thus being highly applicable for single particle signal tracking [9]. Blinking is usually treated as an extremely adverse effect, hindering QD bioimaging applications in time-lapse experiments, e.g., single particle tracking, since the stochastic intermittence of fluorescence signal would cause the loss of the labelled target or, a flawed or incorrect signal trace. However, it can also be an advantage and even a necessity in super-resolution fluorescence microscopy, e.g., stochastic optical reconstruction microscopy (STORM) [11]. Therefore, it is of significance and urgency to understand, as well as to control the blinking characteristics.

In this work, we employed three groups of QDs, octadecylamine (ODA)-coated QDs with different shells, aqueous QDs treated by Ca^{2+} in 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid buffer solution (HEPES), and aqueous QDs treated by glycerol, to correlate the fluorescence blinking characteristics of single QDs to their surface states. We then propose a microscopic model with input parameters from quantum mechanical calculations to understand the blinking of single QDs as a function of QD surface states.

2. Materials and measurement

CdSe-CdS/ZnS based QDs were prepared using common chemical synthesis method described in detail before [33]. Three types of surface modifications, corresponding to the three QD groups listed in Table 1, were studied. Here the CdSe cores were the same for all the samples which differed only in their shell structures, surface ligands, and environmental conditions.

- **Oil-dispersible ODA-QDs.** The CdSe cores from one growth batch were coated with different shell structures: (A) one-monolayer CdS and 0.5-monolayer ZnS, denoted as CdSe-$(CdS)_1/(ZnS)_{0.5}$; (B) CdSe-$(CdS)_2/(ZnS)_{1.5}$. Their surface ligands were ODA and therefore dispersible in chloroform.
- **Ion-treated 3MPA-QDs.** Surface ligands of ODA-coated CdSe-$(CdS)_2/(ZnS)_{1.5}$ QDs were exchanged to 3-mercaptopropionic acids (3MPA) for water dispersion. (C) 3MPA-QDs (37 nM) were dispersed to a HEPES buffer solution of pH 7.2 (50 mM HEPES and 23 mM NaOH); (D,E) 3MPA-QDs in HEPES, with 2 mM Ca^{2+} added; (E) 3MPA-QDs in HEPES, with 2 mM Ca^{2+} added, with the further addition of 5 mM ethylene glycol tetraacetic acid (EGTA). Detailed preparation protocols of these samples were reported before [34]. Monitoring Ca^{2+} in live cell is critical in biological research. Moreover, we notice that a Ca^{2+} ion chelator, EGTA is able to specifically capture free Ca^{2+} ion, usually in a one-to-one relationship. Thus, Ca^{2+}-EGTA interaction provides an excellent tool to study the dynamic reversible effects of QD surface modification by Ca^{2+}.
- **Glycerol-treated 3MPA-QDs.** The QDs were water-dispersible CdSe-$(CdS)_2/(Cd_{0.5}Zn_{0.5}S)_1/(ZnS)_{1.5}$. (F) QDs (2 nM) dispersed in Milli-Q water; (G) QD solution added with 2% glycerol (volume percent); (H) 10% glycerol.

A drop of each QD solution was deposited into a circular area formed by nail polish on a microscope slide, then covered by a coverslip and mounted on a fluorescent light microscope. Solvent was enclosed in order to study the dynamic effects of Ca^{2+}, EGTA and glycerol. The non-volatile part of nail polish is mostly nitrocellulose, which will not interact with the ODA molecules on the surfaces of ODA-coated QDs dispersed in chloroform under our blinking experimental conditions, it is also insoluble in water so it will neither interfere with the water-dispersible 3MPA-QDs. Imaging series of the fluorescence trajectory of single QDs, which transiently sedimented on the microscope slide surface due to gravity, consisting of 10,000, 20,000, 50,000, and 100,000 frames, were recorded using an AxioObserver.D1 microscope (Carl Zeiss) equipped with a mercury lamp (HBO 100, Carl Zeiss), a filter set (Exciter: FF02-435/40-25, Dichroic: FF510-Di02-25 × 36, Emitter: FF01-500/LP-25, Semrock), an EMCCD camera (Andor), and a plan-apochromat 63 × /1.4 N.A. oil immersion objective (Carl Zeiss). QDs were excited by the spectral line of 415–455 nm

Table 1
QD samples under investigation.

	Structure	Ligands	Solution
A	CdSe-$(CdS)_1/(ZnS)_{0.5}$	ODA	Chloroform
B	CdSe-$(CdS)_2/(ZnS)_{1.5}$	ODA	Chloroform
C	CdSe-$(CdS)_2/(ZnS)_{1.5}$	3MPA	HEPES
D	CdSe-$(CdS)_2/(ZnS)_{1.5}$	3MPA	HEPES + Ca^{2+}
E	CdSe-$(CdS)_2/(ZnS)_{1.5}$	3MPA	HEPES + Ca^{2+} + EGTA
F	CdSe-$(CdS)_2/(Cd_{0.5}Zn_{0.5}S)_1/(ZnS)_{1.5}$	3MPA	Milli-Q water
G	CdSe-$(CdS)_2/(Cd_{0.5}Zn_{0.5}S)_1/(ZnS)_{1.5}$	3MPA	2% v/v glycerol
H	CdSe-$(CdS)_2/(Cd_{0.5}Zn_{0.5}S)_1/(ZnS)_{1.5}$	3MPA	10% v/v glycerol