

Luminescence blinking in Eu^{3+} doped yttrium oxysulfide ($\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$) quantum-dot ensembles: Photo-assisted relaxation of surface state(s)

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Abstract

Ensembles of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ widegap semiconductor nano-crystals exhibit ON–OFF fluorescence blinking phenomenon, which mimic II–VI semiconductor quantum-structures. Attempt has been made to explain this phenomenon under the ambit of diffusion controlled electron transfer (DCET) model. Insights derived using opto-impedance technique in conjunction with the DCET model clearly establish the relaxation of surface state(s) through a diffusion process. Ensembles of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nano-crystals, the insulating counterpart investigated for comparison does not show such fluorescence blinking.

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1. Introduction

Nano-scale semi-conducting luminescent quantum-structures have attracted considerable interest owing to their potential for application in luminescent markers(labels) for single biological molecules [1], single-photon light sources for quantum information processing [2], lasers systems [3], optical switches [4] and optical memory [5]. Research concerning luminescence blinking in quantum-structures so far has been focussed mainly on undoped II–VI type quantum-structures [6–8]. Luminescence blinking showing ON–OFF intermittence followed by prolonged dark-time limits the scope of these luminescent quantum-structures for applications in devices. In a luminescent nano-crystalline system, the role of surface states can be multifarious and can determine the blinking phenomenon and its kinetics. We report here on the luminescence blinking phenomenon observed in a large collection of trivalent europium doped yttrium oxysulfide ($\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$, labeled as YOS for brevity) quantum-dots (quantum-dot ensembles), a new luminescent nano-crystalline system showing

several intriguing opto-electronic properties [9–11]. In an Eu^{3+} doped luminescent system the metal \rightarrow ligand ($\text{Eu}^{3+}-\text{O}^{2-}/\text{S}^{2-}$) electron transfer transition can be described as Eu^{2+} center with a weakly coupled exciton represented by the electron configuration $4f^7 2p^{-1}$, a situation comparable to undoped II–VI quantum-structures under band edge excitations. Experimental results derived from quantum-ensembles can be used to extract phenomenological parameters related to single QD statistical model(s). This becomes more powerful when experiment(s) on collections of QD's can access regimes, such as long effective time traces or low laser flux intensities that are inaccessible with single QD experiments [8]. For comparison purposes, europium doped yttrium oxide nano-crystals $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, (labeled as YOX), the insulating counterpart having a band-gap value of $E_g \sim 5.6$ eV was also investigated. We extend the scope of the present study using a novel opto-impedance method [12,13].

2. Experimental

The experimental procedure related to the syntheses of samples and characterization such as XRD, optical characteristics, TEM and opto-impedance measurements were the

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same as described before [9–13]. YOS nano-samples used in this study had a crystallite size of ~ 7 nm while YOX nano-samples had a size of 5 nm. Transmission electron microscope image(s) and the corresponding selected area electron diffraction (SAED) pattern consistent with the target phase under investigation are given in Fig. 1 inset. For recording ‘ON–OFF’ blinking events, a digital camera (Olympus Version 1.1) equipped with a CCD detector operated in multiple flash modes was used. The blinking images were recorded while the samples being continuously excited using UV radiation with wavelength(s) corresponding to respective fundamental band-edge, charge transfer band

regions of YOS and YOX samples as mounted in the fluorescence spectrophotometer.

3. Results and discussion

3.1. ON–OFF fluorescence intermittence in oxysulfide quantum-dot ensembles

Similar Stark splitting patterns of photo-luminescence emission spectra for the bulk and nano-YOS samples confirm identical chemical surroundings for the Eu^{3+} center. Whilst the diffuse reflectance spectra (Fig. 1) corresponding

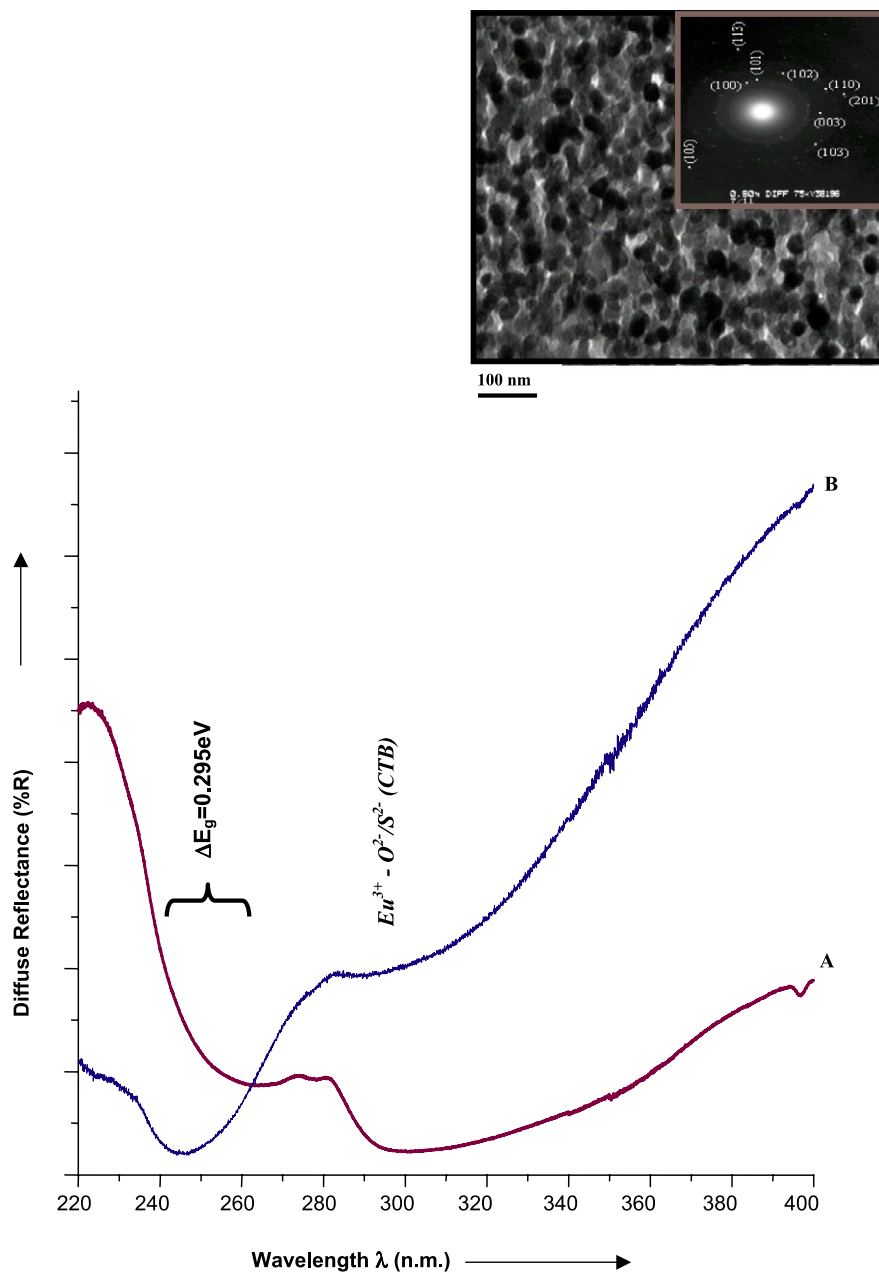


Fig. 1. Diffuse reflectance spectra of bulk (A) and nano-crystalline (B) $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ samples. Inset: Transmission electron microscope image of yttrium oxysulfide nano-crystals ($\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$) and the corresponding SAED pattern.

to the fundamental absorption edge (~ 260 nm) of the host-matrix shows a significant blue shift of ~ 0.3 eV. This indicates a Bohr exciton size of 5.3 nm much comparable to the crystallite size in suggesting a strong quantum confinement [11] while for yttrium oxide:Eu³⁺ nano-crystals these shifts/features are not observable or appreciable.

For the YOS nano-crystalline ensembles when being excited continuously using UV radiation the fluorescence intensity goes ON–OFF (Fig. 2a) resembling luminescence blinking reported in other II–VI compounds [4,6,14]. The luminescence intensity variation between the dark and bright events (referred as dynamic range) is very moderate limited to about 2–3 folds. However, this convincing difference in intensity scales between bright and dark periods can be ascribed to luminescence blinking mechanism in a similar fashion as observed in InGaAs/GaAs quantum-dots

[15]. The moderate dynamic range observed may be attributed to a low time resolution of the experimental set-up used. Also the large collection of quantum-dots in the sample configuration may lead to poor ON–OFF time averaging moments. Whilst YOX nano-crystals do not show any such fluorescence blinking (Fig. 3a).

The relative intensities of ON–OFF events determined with respect to time and number of events/occurrences, especially the latter follow a Gaussian pattern(s) (Fig. 2 insets b–c). Because photo-luminescence efficiencies of YOS and YOX systems differ considerably, there is a significant difference in the luminescent intensity scales for fixing position(s) or limit(s) of the ON–OFF switching pattern(s).

The blinking phenomenon observed in the YOS quantum-structure can be explained using a four level scheme known as diffusion controlled electron transfer (DCET)

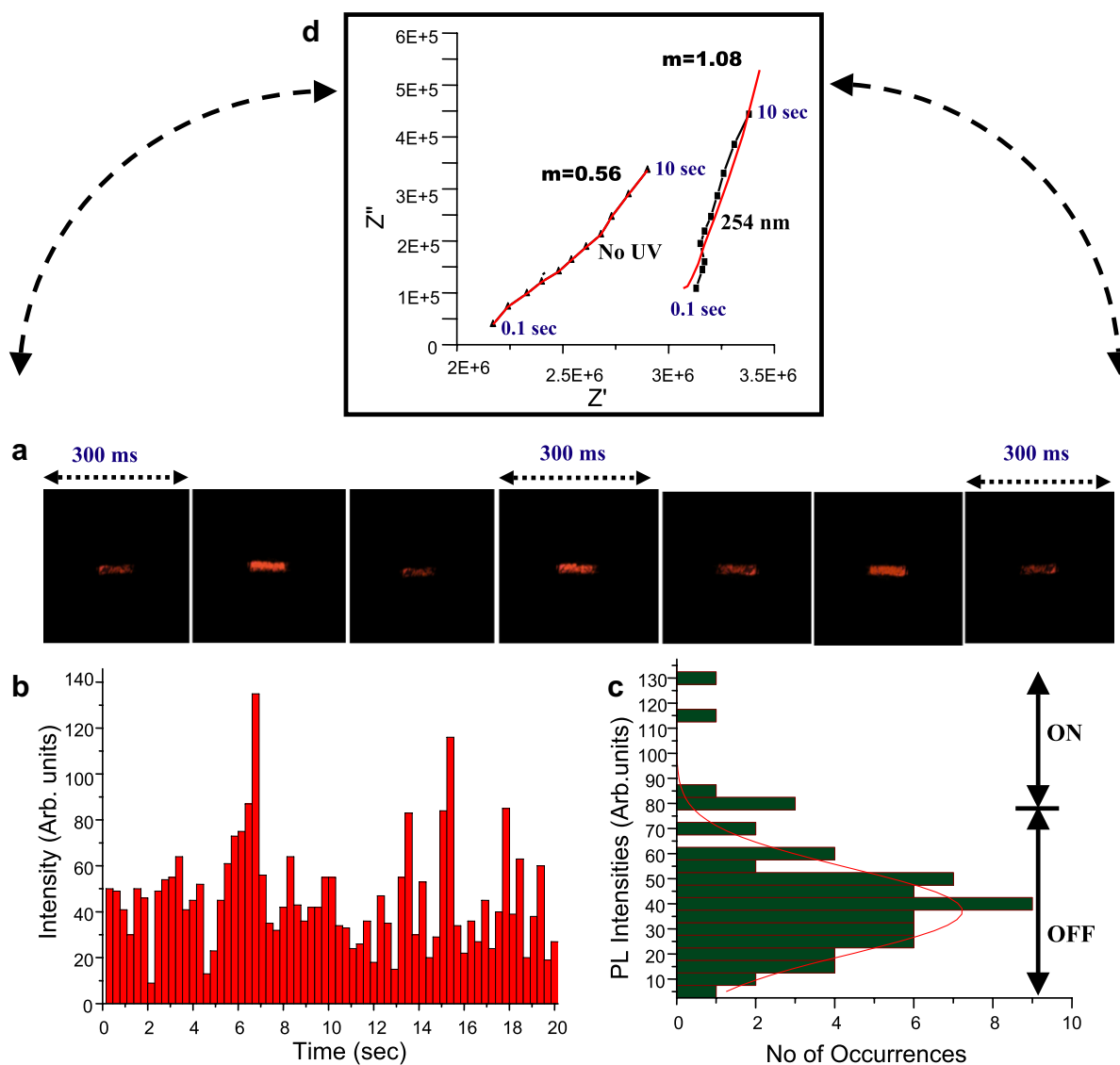


Fig. 2. (a) Photograph images of successive frames showing ON–OFF blinking in Y₂O₂S:Eu³⁺ nano-crystals, (b) corresponding fluorescence intensity versus time plot. (c) histogram showing the PL intensity versus number of ON–OFF occurrences fitted under single Gaussian. Using PL intensity scales ‘ON’ and ‘OFF’ states are identified as marked. Also (d) opto-impedance data corresponding to Warburg impedance part (diffusion process) on Y₂O₂S:Eu³⁺ nano-crystals showing variation in slope (m) upon UV shining in a comparable time scale as the blinking is indicated.

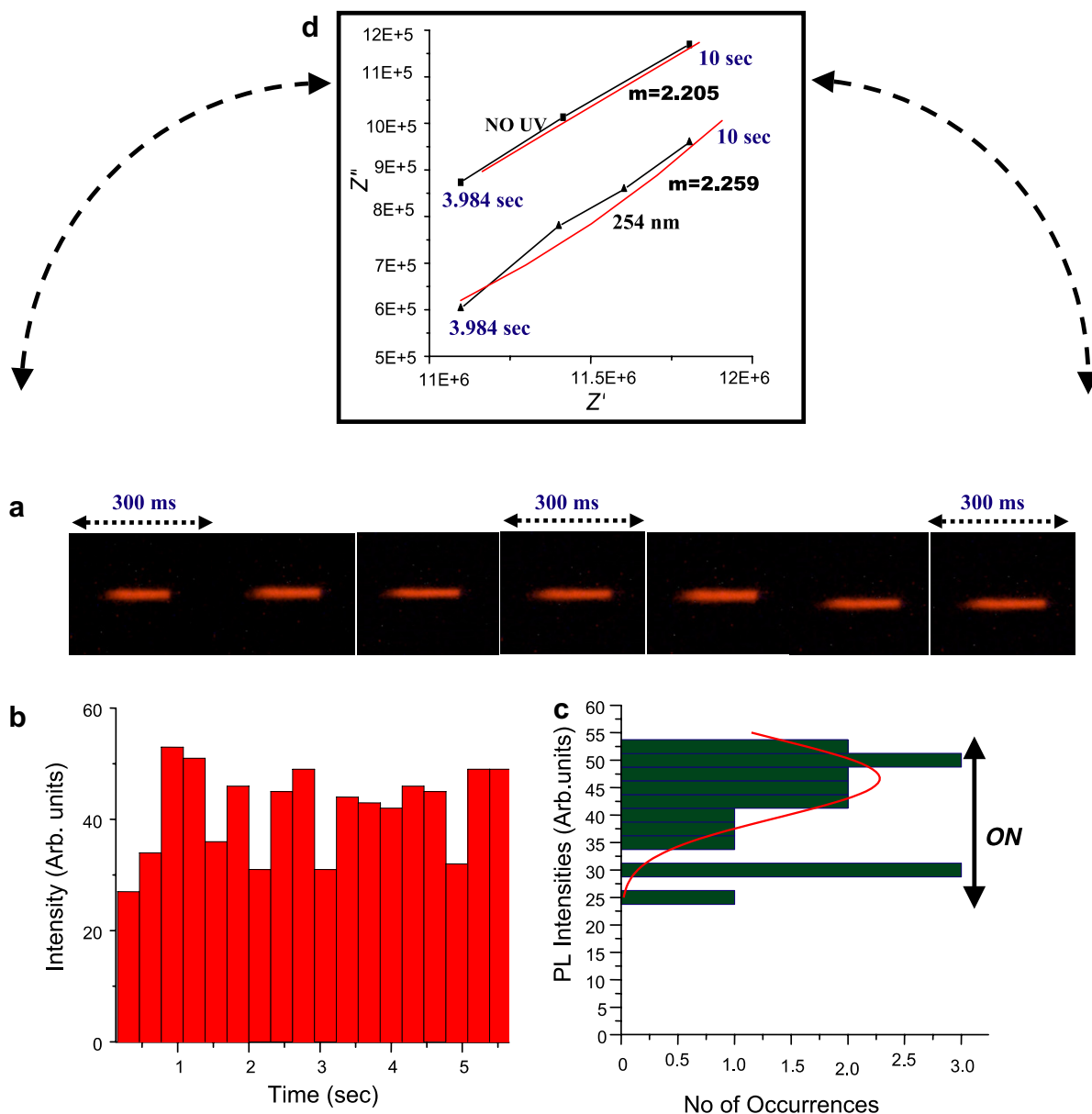


Fig. 3. (a) Photograph images of successive frames showing the absence of any blinking phenomenon in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nano-crystals. Based on emission intensity of events/frames can be considered to represent ON events only (b) corresponding fluorescence intensity versus time plot (c) histogram showing the PL intensity versus number of ON occurrences fitted under single Gaussian. Also (d) opto-impedance data corresponding to Warburg impedance part on $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nano-crystals showing no variation in slope (m).

model proposed by Tang and Marcus [14]. In this model, a back and forth spectral diffusion process between two tracks comprising four states *viz.*, light (neutral-quantum-dot) and dark quantum-dots (charge separated states-CSS) is considered. In a similar way, the presence of large ensemble of two kinds of YOS quantum-dots *viz.*, neutral and dark dots are possible here. The latter may be attributed to the presence of innumerable optically induced surface states especially in the vicinity of conduction band and charge separated state. Optical pumping can hasten the relaxation of surface states or the release of captured electrons to feed the luminescence transitions *via* the excited CTS through a resonance process as schematized in

Fig. 4. The charge transfer state (CTS) of europium in yttrium oxysulfide lying near the vicinity of the band-edge can be analogized to the situation of an exciton weakly coupled to divalent europium species. Upon size miniaturization these CTS states may get ruptured leading to a situation similar to that of charge separated state of the DCET model. Upon optical pumping the exciton trapped at the surface-states will get relaxed *via* localized f-f levels of europium, in particular $^5\text{D}_0 \rightarrow ^7\text{F}_J$ levels of europium thereby explaining the blinking observed. This means that photo-induced surface state relaxation may generate an electron transfer process between charged and neutral quantum-dots. The electron transfer between the two states

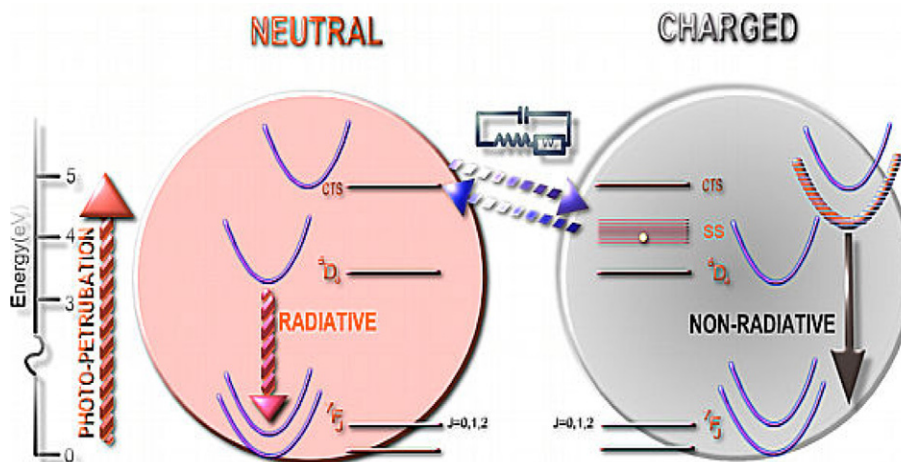


Fig. 4. Schematic diagram to illustrate the blinking mechanism in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ nano-crystals following diffusion assisted charge transfer between neutral and charge separated states (CSS). E_{FS} and E_{CTS} are the Fermi level of surface states and Eu^{3+} – ligand charge transfer states in YOS nano-crystals.

has been established to follow a one-dimensional back and forth diffusion process explained by the potential cross-over model [16]. As will be seen in the subsequent sections, our results based on opto-impedance study corroborate the presence of a diffusion regulated electron transfer process.

In the case of insulating $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nano-crystals, the weak quantum confinement will facilitate the direct feeding of the CTS level which in turn can feed f–f luminescence transitions of Eu^{3+} in the same fashion as its bulk counterpart resulting in the absence of quantum blinking. This insulating system having a larger band-gap will have little scope for the ruptured CSS to relax radiatively *via* f–f level and instead the exciton will follow an Auger process. The constant intensity level observed in this case can be explained in terms of direct photo-luminescence.

3.2. Photo-chemical processes and surface state relaxation

Impedance spectroscopy is an excellent tool for studying charge exchange between core state(s) (conduction/valence band) and charges trapped at the surface state(s) [17]. Relaxation of surface states (SS) with the combination of electric-field resonance and optical excitation generating pairs of neutral and charged quantum-dots [18] and their role in augmenting various photo-chemical properties such as luminescence, and solar cells have been well demonstrated [19]. In semiconductor nano-crystals, there exists two kind(s) of surface states *viz.*, neutral SS (having no net-charge) and charged SS^+ (with charge carriers released/captured by the intrinsic surface states).

Total surface states density is given by the sum of the concentrations of these two states

$$N_{\text{SS}} = [\text{SS}] + [\text{SS}^+] = n_{\text{SS}} + p_{\text{SS}} \quad (1)$$

In a photo-irradiated quantum ensemble, there is considerable probability of finding both neutral and charged surface states.

Upon UV shining on the YOS sample, the Nyquist type complex impedance plot comprising three parts (marked I,

II, III in Fig. 5) undergoes significant modification. The semi-circular region I in the high frequency side (1 MHz–60 Hz) can be attributed to a space-charge build-up across the dielectric medium by considering a parallel resistor-capacitance combination [20]. Whilst the second semi-circular region marked II in the middle frequency (60–10 Hz) would correspond to relaxation of surface states. Different models have been proposed for explaining contribution from surface state(s) on the impedance spectra for several semi-conductor electrode systems [21–23]. Of these, the most viable equivalent circuit fixed for this contribution is a resistor (R) and capacitor (C) components in parallel combination [23]. The third region (region marked III) comprising a linear portion having profound dependence on excitation energy on the slope would correspond to an electron/charge transfer process between core and surface state(s) in the vicinity of conduction band-edge and subsequent relaxation through diffusion of charge carriers/defects. It should be noted that the photo-relaxation kinetics of these processes differ in time-scale by several orders.

Also the magnitude of charge carriers, (i.e. the total charge) associated with surface states as reflected in the opto-impedance data (having direct impact on the blinking rate) can be obtained from the relation.

$$e_o N_{\text{SS}} = Q_{\text{SS}} = \int_{V_0}^{V_1} C_{\text{SS}} dV \quad (2)$$

From Table 1 we have that optical excitation causes substantial increase in both R_{SS} and C_{SS} values corresponding to the resistance and capacitance values of surface-states suggesting significant increase in the photo-generated carriers. This may stem from photo-induced relaxation of surface states, in particular SS^+ (charged surface states). As a consequence we can observe a twofold increase in capacitance, hence the charge associated Q_{SS} . Based on these results we can surmise a twofold increase in the total surface state density N_{SS} implying a pronounced increase in the

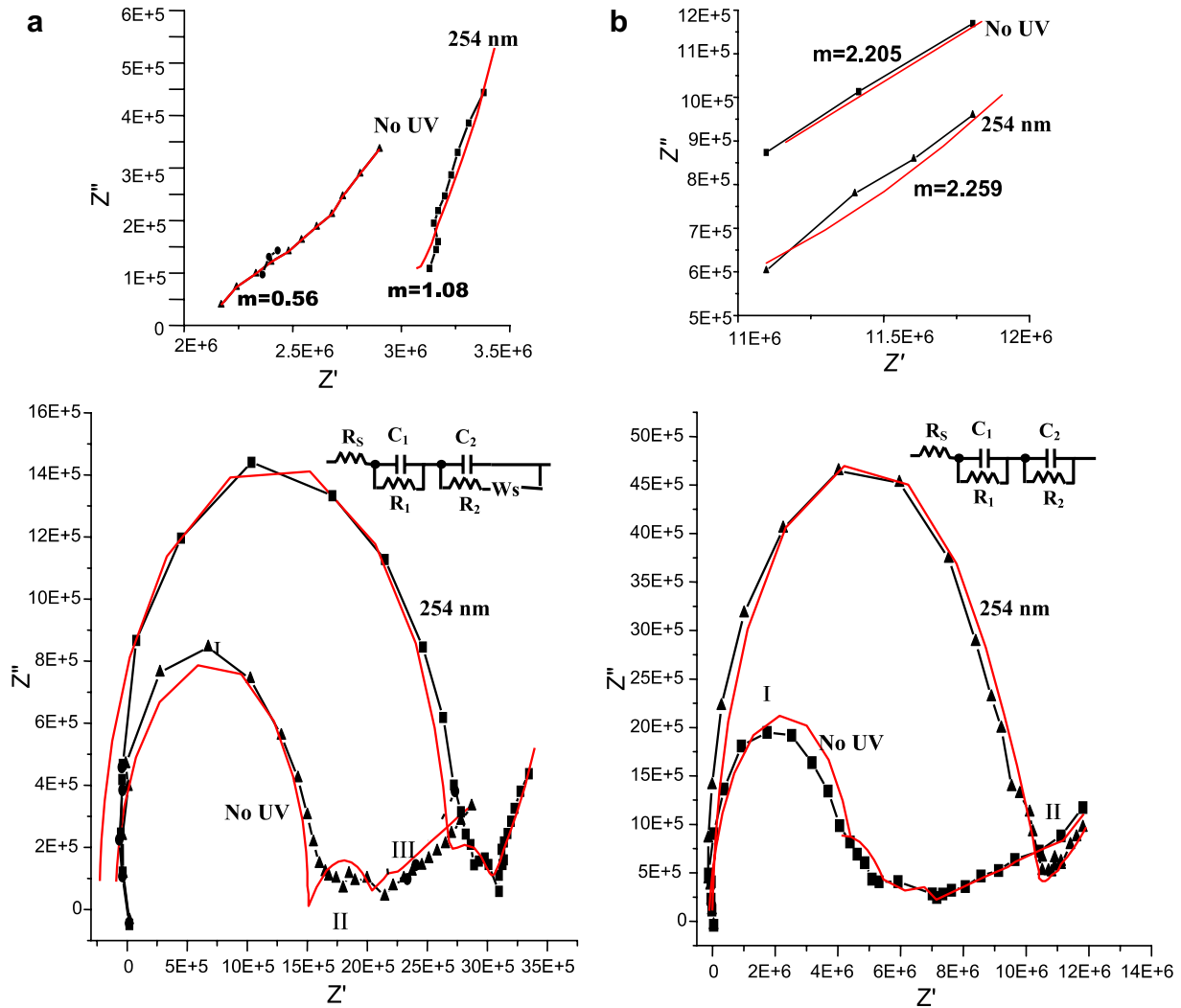


Fig. 5. Nyquist impedance fitted plot for (a) $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ and (b) $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nano-crystals under dark and UV excitation conditions and the corresponding electrical-impedance equivalent circuits. Insets: expanded portion of Warburg impedance pattern with variation in slope (m) upon UV shining and absence of any variation in the respective cases.

Table 1

Fitted parameters corresponding to semi-circular portion of the impedance spectrum following photo-chemically induced space-charge region and surface states relaxation and photo-chemically induced diffusion process of surface state relaxation

System	R_{sc} (Ω)	C_{sc} (μF)	R_{SS} (Ω)	C_{SS} (μF)	$WsR \times 10^6$ ($\Omega \text{ cm}^2$)	WsT (s)	WsP
NYOS (254 nm)	2.93E6	1.76E-11	313700	1.58E-8	2.48	23.06	0.4774
NYOS (no UV)	1.61E6	2.07E-11	285350	7.44E-9	–	–	–

Different Warburg parameters WsR (Ω), WsT (s), WsP indicate bulk (ohmic) resistance, Warburg resistance, Warburg time constant and order of the process, respectively.

concentration of charge separated states (CSS). It is reasonable to expect that this significant increase will set-in an electron transfer process between charged and neutral quantum-dots so as to achieve equalization of charge carriers.

In the opto-impedance behavior of oxysulfide quantum-ensembles investigated, the most important point that merits a detailed explanation would be the variation in slope of the straight-line observed in the region III at the low frequency side (0.1–10 Hz) indicated by m in Fig. 5a-inset which can be fixed to motion of charge carriers. In an

impedance spectrum, a straight-line spectrum having a slope $m = 1$ would indicate a diffusion mediated process referred as Warburg impedance [24]. The value of slope of the linear portion approaching unity indicates a clear diffusion process attributed to the transport of charge carriers (electrons in the present case) through a diffusion process. This can be represented by the equation

$$Z = R^* \tanh([I^* T^* w] \wedge P) / (I^* T^* w) \wedge P. \quad (3)$$

From Table 1, it turns out that for the YOS nano-system upon UV shining there is a substantial change in various

Warburg impedance parameters. Although there is only a moderate increase in Warburg Resistance (W_sR), there is about twofold increase in the values of Warburg parameters corresponding to kinetic processes such as W_sT , W_sP . It is pertinent to note that Warburg impedance is known to have frequency dependence [25]. The emergence of a clear Warburg regime with slope $m = 1$ upon optical pumping on YOS quantum-ensembles is a convincing proof for the verification of DCET model. It should also be mentioned that the DCET model has been proposed on the basis of photo-induced electron transfer through a diffusion process from neutral to charged quantum-dots [14]. Furthermore, we observe that there is a reasonable comparison between the time-scale corresponding to diffusion of charge carriers reflected in the opto-impedance data and the blinking kinetics.

Turning to explain the absence of luminescence blinking in nano-YOX system: the respective impedance spectra show relatively simple impedance spectrum comprising a semi-circle and a line without any spectacular change in the opto-impedance pattern (Fig. 5b). However, there is a convincing change in the impedance value (region I) representing the space-charge build-up of the dielectric medium of the material. This indicates the absence of any contribution from surface states (corresponding to the region II of YOS system). More important, there is not any obvious photo-induced change in the slope for the linear-portion (region III) consistent with the absence of any luminescence blinking. This lends support to our hypothesis that the regions II and III of the opto-impedance spectrum for YOS nano-ensembles respectively represent surface charges and their relaxation kinetics in the same time scale as does the luminescence blinking.

4. Conclusions

The ON–OFF luminescence blinking observed in YOS nano-crystals follows a diffusion regulated electron transfer process between the neutral and charge separated quantum-dots. This is revealed through the occurrence of fluorescence blinking and the Warburg opto-impedance profile corresponding to photo-induced electron diffusion

processes of nearly comparable time-scales in a good agreement with the DCET model.

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