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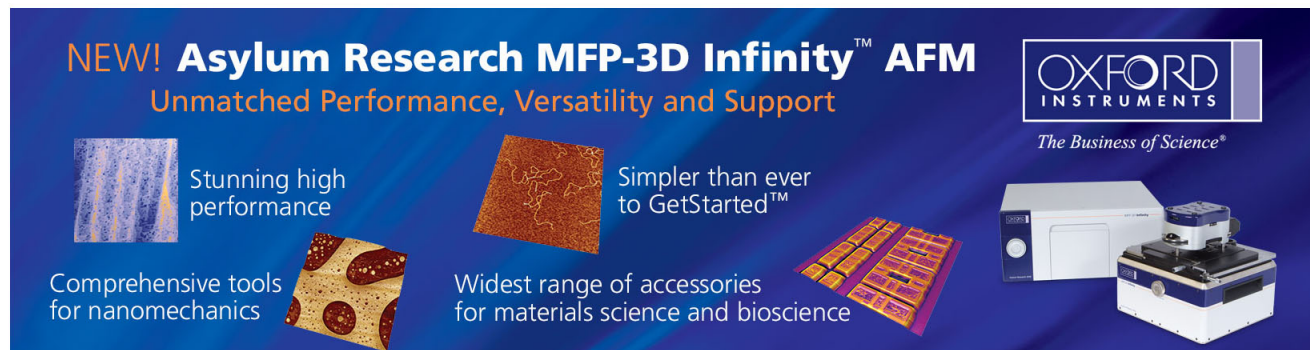
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## Photoinduced fluorescence enhancement in colloidal CdSeTe/ZnS core/shell quantum dots

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Photoinduced fluorescence enhancement (PFE) in colloidal CdSeTe/ZnS core/shell quantum dots (QDs) was investigated by monitoring ensemble fluorescence and single-QD fluorescence blinking behavior upon illumination. Ensemble fluorescence was increased in air and in vacuum with different enhanced factors. At the single-QD levels, fluorescence was also enhanced for some individual QDs. Relatively long on times, high quantum yields within the on times, and multilevel on states were found in fluorescence time traces. We suggest that the PFE origin *from single-QD viewpoint* is attributed to the contributions of surface passivation by photoinduced charged carriers and the formation of neutral core/charged shell QD states. © 2008 American Institute of Physics. [DOI: 10.1063/1.2921779]

Colloidal CdSe quantum dots (QDs) have attracted much attention due to excellent fluorescence (also called photoluminescence) properties, including high quantum yields (QY), size-dependent emission spectra, and good photostability.<sup>1,2</sup> The high surface to volume ratio makes fluorescence properties variable and sensitive to surface molecules,<sup>3</sup> local environments,<sup>4–6</sup> and light illumination.<sup>7–9</sup> Photoinduced fluorescence enhancement (PFE) for *ensemble* colloidal CdSe QDs has been observed under various conditions, such as in aqueous and organic solutions,<sup>7,8</sup> in aggregated QD monolayers,<sup>9</sup> in a polymer thin film,<sup>10</sup> or even just under exposure to ambient light (i.e., unintentionally illuminating by room light)<sup>11</sup> and has been extended to the single-QD levels.<sup>12</sup> Furthermore, the PFE phenomenon has been utilized to fabricate multilayer optical data storage.<sup>13</sup> The main proposed mechanism *from ensemble viewpoints* was attributed to surface-environmental effect, such as photoinduced surface passivation by water molecules,<sup>9</sup> photoinduced surface transformation,<sup>14</sup> and photoinduced oxidation.<sup>15</sup> On the

other hand, from the viewpoint of single QD, the emission efficiency is mainly influenced by the fluorescence blinking behavior.<sup>16</sup> The dark state is ascribed to the formation of charged QDs, which can considerably quench the fluorescence by efficient energy transfer from exciton annihilation to the excess charges within the QD.<sup>17,18</sup> Previous works have demonstrated that photoinduced ionization in single colloidal QDs can occur upon illumination by means of electrostatic force microscopy.<sup>19–22</sup> Some of the single QDs can exhibit a positive charge upon illumination. Therefore, fluorescence should be quenched rather than enhanced upon light illumination. This finding seems to be inconsistent with the ensemble PFE phenomenon. It also indicates that the photo-generation of charged carriers should play an important role in PFE phenomenon. Consequently, it is necessary to investigate the fluorescence properties down to single-QD levels.

In this work, PFE phenomenon has been studied by ensemble fluorescence and single-QD fluorescence blinking behavior with/without illumination. Fluorescence was in-

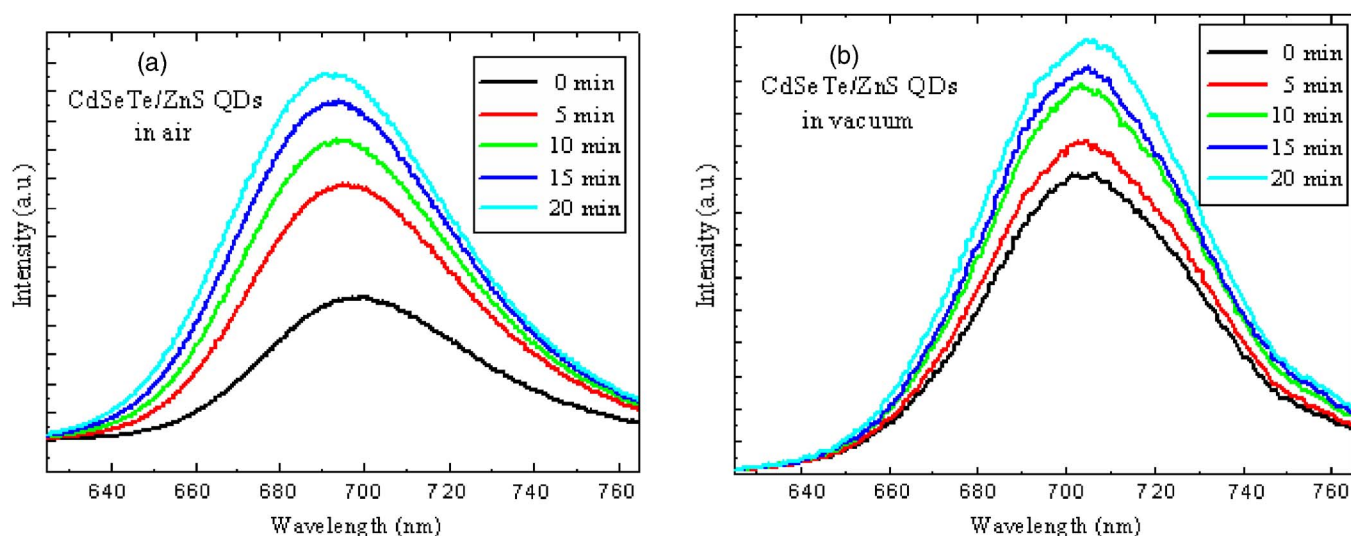


FIG. 1. (Color online) Fluorescence spectra of colloidal CdSeTe/ZnS QDs with various illumination times in air (a) and in vacuum (b).

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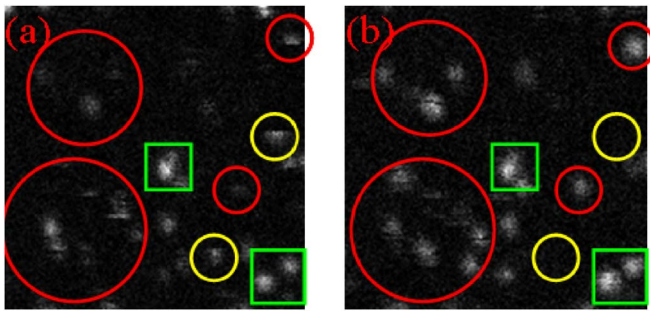


FIG. 2. (Color online) Fluorescence images without (a) and with 20 min illumination (b).

created by illumination either for ensemble QDs or for some of individual QDs. In particular, fluorescence blinking behavior was modified for individual PFE QDs.

Colloidal CdSeTe/ZnS core/shell QDs were purchased from Quantum Dot Corporation. Before fluorescence measurements, the samples were intentionally kept in dark for a few days (called unilluminated samples). For illumination, the samples were irradiated by 480 nm light. For the single-QD measurements, an extremely dilute QD solution was dispersed onto a clean glass coverslip by spin coating.<sup>23</sup> Single-QD fluorescence measurements were performed based on a laser scanning confocal microscope. The excitation pulses at 405 nm were focused to a nearly diffraction-limited spot by an oil-immersion objective. Fluorescence was collected and guided to a single photon avalanche photon diode after passing through a 50  $\mu\text{m}$  confocal pinhole.

Figure 1(a) shows the fluorescence spectra of ensemble colloidal CdSeTe/ZnS core/shell QDs in air with various illumination times. The fluorescence intensity monotonically increased accompanied with a blueshift in the emission peak with the illumination time. The enhancement of fluorescence is initially assigned to the surface passivation by surface oxidation.<sup>15</sup> This surface oxidation caused the blueshift of peak position due to the reduction in the effective core size. To eliminate the oxidation effect, we also performed the

fluorescence measurements in vacuum, as shown in Fig. 1(b). In general, the fluorescence intensity was decreased upon the evacuation of air.<sup>6</sup> Interestingly, the PFE behavior can still be observed, but with a smaller enhanced factor. It indicates that the surface oxidation is not the only origin of the PFE phenomenon.<sup>14</sup> Therefore, it is believed that the photoinduced charge carriers can play an important role in the PFE mechanism due to modifications of the single-QD fluorescence blinking behavior.

In order to unravel this PFE mechanism, fluorescence variations at the single-QD levels were also studied. Figure 2 displays the representative fluorescence images with  $4 \times 4 \mu\text{m}^2$  area without (a) and with 20 min illumination (b). Some of the individual QDs with initially weak emission can be enhanced by illumination (marked by red circles, hereafter referred to as PFE QDs). On the other hand, some of the individual QDs with initially strong emission maintain their original fluorescence intensity (green rectangles). Moreover, the fluorescence was quenched for a portion of single QDs (yellow circles). This work mainly focuses on these individual PFE QDs.

Figure 3(a) reveals the typical fluorescence time traces for a representative PFE QD. The inset shows the fluorescence time trace for a unilluminated QD for comparison. For unilluminated QDs, the blinking behavior exhibits the simple two-states (on/off) transition with very fast transition rates and with average counts of  $\sim 18/\text{bin}$ , as shown in Fig. 3(b). According to theoretical simulation by Verberk *et al.*<sup>24</sup> this fluorescence blinking feature is attributed to exciton emission from the true neutral core/shell QDs. In contrast, the fluorescence time traces of PFE QDs revealed relatively long on times and exhibited multilevel on-time states (marked by green solid line). The fluorescence intensity levels for PFE QDs either are higher or lower than the fluorescence intensity for true neutral QDs. This blinking behavior with relatively long on times is assigned to emission from neutral core/charged shell QD states.<sup>24</sup> It was also reflected on the histograms of fluorescence intensity in Fig. 3(c).

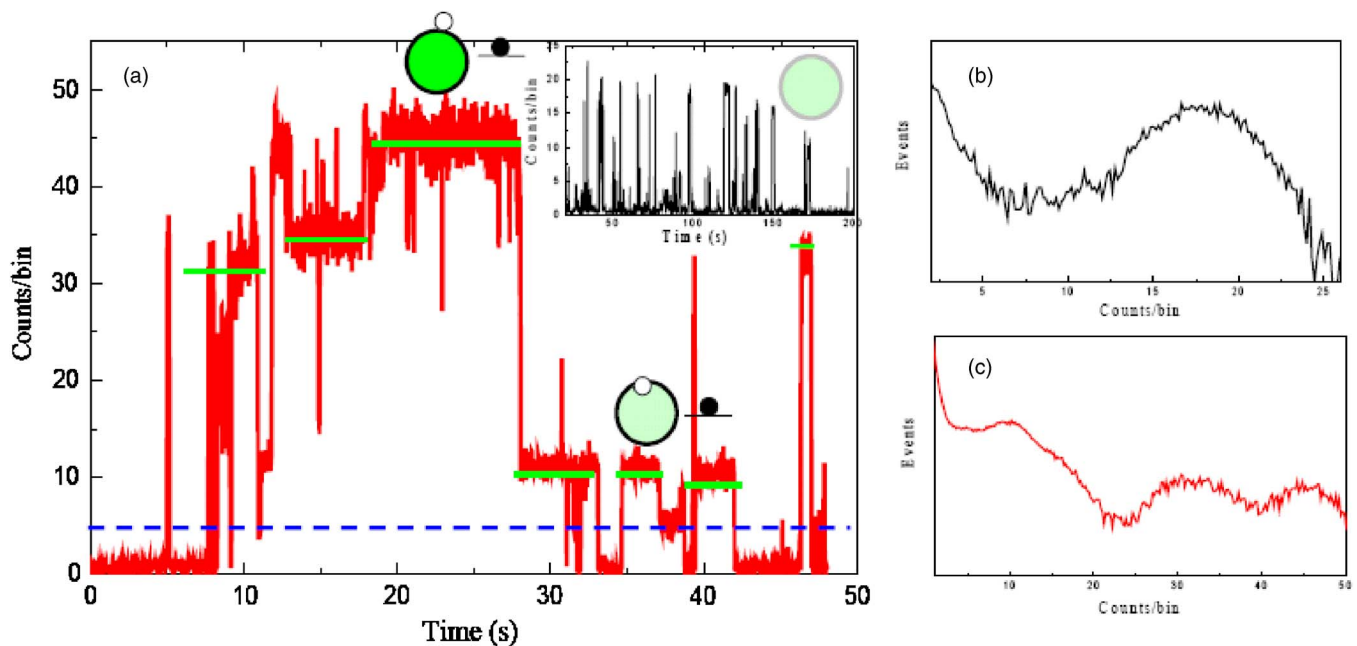


FIG. 3. (Color online) (a) Representative fluorescence time traces for single PFE QDs and unilluminated single QDs in the inset. (b) The distributions of events of fluorescence intensity for unilluminated QDs and (c) for PFE QDs.

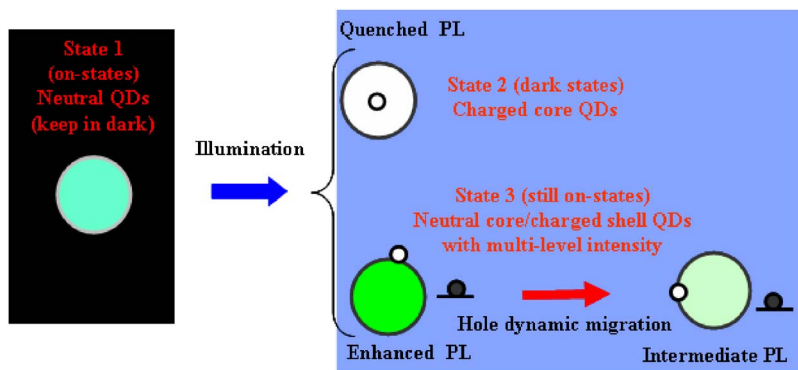


FIG. 4. (Color online) Schematic illustration for PFE origin from single-QD viewpoints.

Based on both ensemble and single-QD fluorescence measurements, a possible model from *single-QD viewpoints* was introduced to rationalize this PFE phenomenon. A previous report has demonstrated that photoinduced ionization in colloidal CdSe/ZnS QDs occurs after illumination. In this case, some of single QDs have a positive charge within the QDs.<sup>19–22</sup> This photoinduced ionization model is followed to elucidate our experimental observations. As illustrated in Fig. 4, upon illumination, photogenerated electrons can either passivate surface/interface trap states or was ejected to outside trap states in the surrounding matrix, to prevent further ionization process by Coulomb blockage.<sup>24</sup> The former was evidenced by enhanced fluorescence for either ensemble or individual QD samples. The latter was proved by relatively long on times in single-QD fluorescence time traces. On the other hand, counterpart holes either delocalized within the QD core to form the charged QD state (state 2, dark state) or trapped into the core/shell interface or on the shell surface (state 3, still on states). While the holes were delocalized within the QD core, it causes the quenched fluorescence in Fig. 2), marked by yellow circle in fluorescence images in Fig. 2). However, when the holes were localized on the surface far away from the core, the QDs can still emit fluorescence because of less wave function overlap between the delocalized exciton and the localized holes.<sup>24</sup> Actually, hole trap states were commonly observed in nanometer-size colloidal QDs because of their high surface to volume ratio. In previous studies, photogenerated holes which located on the surface or interface can migrate and cause the fluorescence intensity with multilevel states.<sup>25</sup> In this case, the fluorescence intensity could range a broad distribution, which depends on the distance from the trapped hole to the core and should be weaker than true neutral core states. However, the combination of both surface passivation and charged shell/neutral core QD states, single-QD fluorescence intensity in the fluorescence time traces may exceed the true neutral QD states. Therefore, we suggest that the origin of PFE phenomenon is attributed to the overall contributions of both photoinduced surface passivation by photogenerated charged carriers and the formation of neutral core/charged shell QD states.

In conclusion, PFE phenomenon was studied by means of ensemble and single-QD fluorescence measurements. At the single-QD levels, fluorescence intensity was increased for some of individual QDs upon illumination. For PFE QDs, relatively long on times, high QYs within the on times, and

multilevel on-time states were found. We proposed that the origin of PFE phenomenon is attributed to the both contributions of surface passivation by photoinduced charged carriers and the formation of neutral core/charged shell QD states.

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