

Synthesis of multi-color luminescent ZnO nanoparticles by ultra-short pulsed laser ablation

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Abstract

Crystalline ZnO nanoparticles (NPs) are synthesized by ultra-short femtosecond (fs) pulsed laser ablation (PLA) of a zinc plate in deionized water, and are investigated by optical absorption and time resolved luminescence spectra in combination with the morphology and structure analysis. The comparison with previous experiments based on short nanosecond (ns) PLA highlights that pulse duration is a crucial parameter to determine the size and the optical properties of ZnO NPs. While short PLA generates NPs with average size $\bar{S}$ of ~ 30 nm, ultrashort PLA allows to achieve much smaller NPs, $\bar{S} \leq 10$ nm, that evidence weak quantum confinement effects on both the absorption edge and the UV excitonic emission. Moreover, the defective nature of synthesized ZnO NPs gives rise to two visible photoluminescence bands: the first, centered around 2.3 eV and commonly associated with oxygen vacancies, unexpectedly blue-shifts on decreasing the NPs size; the second, peaked at 2.8 eV, shows a Lorentzian shape characteristic of a mobile exciton. Overall, these results demonstrate that PLA is a successful method to synthesize ZnO NPs with controlled luminescence properties, thus increasing their application in lighting technologies.

Keywords:

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9 Ultrashort pulsed laser ablation; ZnO nanoparticles; quantum confinement
10 effects; time resolved luminescence; atomic force microscopy; transmission
11 electron microscopy
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14 15 **1. Introduction**

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18 Nowadays, zinc oxide nanoparticles (ZnO NPs) are a versatile platform for
19 several nanotechnology applications (biomedical imaging, drug delivery, photo-
20 catalysis) exploiting some of their intrinsic characteristics related to the chemical
21 composition and structure, such as low toxicity, biodegradability, direct bandgap
22 ($E_g \approx 3.4$ eV in the bulk form), and large exciton-binding energy (≈ 60 meV)
23 [1, 2, 3, 4, 5, 6]. Further advances in specific fields require the ability of deliber-
24 ately introducing defects in the ZnO network as a route to engineer the optical
25 properties. Indeed, localized defect states within the forbidden band originate
26 photoluminescence (PL) transitions falling in the visible range, in addition to
27 the exciton related UV emission [7, 8, 9, 10]. Usually, the most common defect-
28 related emissions include a yellow-orange band centered at 2.0-2.1 eV, a green
29 band at 2.2-2.4 eV, and a blue band at 2.7-2.8 eV. The observation of these
30 PL bands strongly depend on the production methods of ZnO NPs and on
31 external treatments (heating, loading with atoms or molecules), so that their
32 origin has not been conclusively established. The yellow and blue emissions have
33 been observed in samples produced in oxygen-rich [11, 12, 13, 14] and zinc-rich
34 [15] environments, respectively, and associated with intrinsic defects: O excess
35 (yellow band), Zn excess (blue band). The origin of the green band is more con-
36 troversial and its correlation with a specific defect structure is widely debated
37 [5, 16, 17, 18].
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50 The choice of synthesis processes is crucial to determine the relative weight of
51 these emissions and, as a fundamental objective, to identify the exact structure
52 of luminescent defects. To this purpose, pulsed laser ablation (PLA) offers a
53 simple and versatile top-down route to synthesize a wide variety of luminescent
54 NPs [15, 19, 20, 21]. In fact, PLA of a metal zinc target immersed in aqueous so-
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lution produces ZnO NPs of extremely high purity by a many steps process that starts from the formation of Zn NPs and, after their oxidation in water, leads to the growth of ZnO with wurtzite crystalline structure [22]. In general, the laser characteristics strongly affect the physical processes involved during the synthesis [21, 23, 24]. When the laser beam interacts on a conducting material, free electrons directly absorb the photon energy and form a hot electron-hole plasma [25]. Therefore, a key laser parameter is the pulse length τ_{laser} compared with the electron cooling time, that is the electron-phonon thermalization processes occurring in $\tau_{therm} \sim 10^{-11}$ - 10^{-12} s: i) if $\tau_{laser} < \tau_{therm}$, ultra-short (fs) pulse, during the laser exposure any thermal conduction can be neglected, the lattice remains at its temperature and a large number of excited electrons can leave the solid (non-thermal ablation); ii) if $\tau_{laser} > \tau_{therm}$, short (ns) or long (μ s-ms) pulse, the energy of excited electrons relaxes within the laser exposure and the temperature at the target surface increases (thermal ablation). Macroscopically, non-thermal and thermal ablation induce different effects on the target: under ultra-short PLA, the ablated area closely matches the laser spot and has sharp borders; under short and long PLA, the ablated area exceeds the laser spot, due to the heat transfer from the irradiated region to surrounding. From the microscopic viewpoint, the influence of pulse duration on the morphology and structure of the produced NPs is not well clarified, also due to the lack of systematic studies on a wide typology of materials.

As concerns ZnO NPs, so far several of PLA experiments in water have used ms- and ns-pulsed lasers ($\tau_{laser} > \tau_{therm}$) and have evidenced that their luminescence mainly consists of UV exciton-related and visible defect-related bands [23, 26, 27, 28, 29]. By in-situ experiments [22], we have demonstrated that green luminescent defects are produced by an incomplete oxidation process of Zn materials, this finding corroborates the hypothesis that this emission is associated with the recombination between a hole in the valence band (VB) and an electron trapped in an ionized oxygen vacancy [5]. In contrast, ZnO NPs produced by ultrashort laser ($\tau_{laser} < \tau_{therm}$) have been investigated in few experiments using ps- [30, 31] and fs-pulses [32], this is a limit to the thorough

understanding of the potentialities of PLA to control the optical properties of these nanomaterials. To this end, in this work we investigate ZnO NPs produced by using Ti:Sapphire laser pulses (50 fs) at various pulse energies (75-350 μ J). Our experimental approach is mainly based on the use of time-resolved luminescence in combination with complementary techniques, atomic force microscopy (AFM) and transmission electron microscopy (TEM), that allow us to relate the observed emission bands to the morphology and structure of the produced NPs. The results here reported, and their comparison with those obtained by longer pulse duration, highlight relevant peculiarities associated with the ultrashort PLA synthesis. Mostly, fs ablation provides a route to finely control the morphology of the produced NPs, their sizes depend on laser ablation parameters and are smaller than those produced by ns ablation. In these conditions, ZnO NPs display clear quantum confinement (QC) effects on the optical bandgap due to the NPs sizes comparable to the excitonic Bohr radius.

2. Experimental Methods

ZnO NPs were produced by PLA of a zinc plate (thickness of 0.5 mm, 99.9% trace metals basis) provided by Sigma-Aldrich [33], placed at the bottom of a graduated 50 mL becher containing deionized water. The laser beam was generated by an amplified Ti:Sapphire system (Spectra Physics Solstice), $\lambda=800$ nm and pulse duration of 50 fs, and it was focused by a parabolic mirror to achieve a spot size of ≈ 100 μ m) on the Zn target. The repetition rate was selected at 1 kHz to avoid the spatial overlap between the laser pulse and the previously created cavitation bubble (bubble lifetime ~ 100 μ s). The Zn target was continuously moved via a rotator plate to prevent the laser beam from hitting the same area thus forming craters. Preliminary, we changed the water volume to optimize the ablation efficiency. In fact, we noted that the amount of generated ZnO NPs critically drops down when the height of liquid above the zinc target exceeds ≈ 2 mm; this finding can be attributed to laser pulse degrada-

tion, such as self-focusing, that reduces the laser intensity on the target [20]. We performed different synthesis on varying the pulse energy (E_{pulse}) and the corresponding fluence (ϕ): 1) $E_{pulse} = 75 \mu\text{J}$ ($\phi = 0.95 \text{ J/cm}^2$); 2) $E_{pulse} = 150 \mu\text{J}$ ($\phi = 1.90 \text{ J/cm}^2$); 3) $E_{pulse} = 350 \mu\text{J}$ ($\phi = 4.43 \text{ J/cm}^2$), the irradiation times were set at 900 s, 450 s and 193 s, in order to maintain the same total power density of 855 kJ/cm^2 on the zinc target.

Optical absorption (OA) and PL properties were investigated on the PLA induced colloidal solution put in a quartz cuvette (1 cm optical path). UV-Visible OA spectra were recorded by a double beam spectrometer (JASCO V-560) with bandwidth of 2 nm and were corrected by subtracting the contribution of the cuvette with deionized water alone. Time resolved PL spectra were carried out under a tunable laser excitation, provided by an optical parametric oscillator (VIBRANT OPOTEK) pumped by the third harmonic (3.49 eV) of a Nd:YAG laser (pulse width $\approx 5 \text{ ns}$, repetition rate 10 Hz). The emitted light was analyzed by a monochromator equipped with a grating of 150 lines/mm and blaze wavelength 300 nm, and acquired by an intensified CCD camera driven by a delay generator (PIMAX Princeton Instruments) setting the acquisition time window, T_W , and the delay, T_D , with respect to the arrival of laser pulses. All the emission spectra were detected with a bandwidth of 3 nm and corrected for the monochromator dispersion.

AFM measurements were done on dried droplets of the ablated solution ($\sim 50 \mu\text{L}$) by a Bruker FASTSCAN microscope working in soft tapping mode and using a FAST-SCAN-A probe ($27 \mu\text{m}$ long triangular silicon nitride cantilever) with the following characteristics: 1400 kHz resonant frequency, 17 N/m force constant, and $\approx 5 \text{ nm}$ apical radius. All the AFM images were acquired in air on specimens deposited onto a mica substrate by a scan window of $2 \mu\text{m} \times 2 \mu\text{m}$; the morphology of the system was determined by evaluating the heights of the NPs. Then, the solution was properly diluted in order to leave on the substrate a large number of isolated NPs and a limited number of aggregates, in order to reduce the overlapping of NPs that may give wrong heights [34].

High-resolution (HR) TEM experiments were carried out on an aberration-

corrected FEI Titan 80-300 microscope at 300 keV electron energy. TEM samples were prepared at room temperature in air by drop-casting of a diluted suspension of ZnO NPs dispersed in ethanol onto a commercial holey ultrathin amorphous carbon film (3 nm) on Lacey support mounted on 400 μm mesh Cu grid (Plano 01824). Crystal structure analyses were performed by selected-area electron diffraction (SAED). High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) in combination with energy-dispersive X-ray spectroscopy (EDXS) carried out on an FEI Osiris ChemiS-TEM microscope at 200 keV electron energy, was used for chemical analyses. EDXS spectra were quantified with the FEI software package TEM imaging and analysis (TIA) version 4.7 SP3. Element concentrations were calculated on the basis of a refined Kramers law model, which includes corrections for detector absorption and background subtraction. For this purpose, standard-less quantification, i.e. by means of theoretical sensitivity factors without thickness correction, was applied.

3. Results and Discussion

Electron microscopy makes clear the structure and chemical composition of the produced NPs. Fig. 1 (a) displays a typical HRTEM image of three agglomerated NPs with sizes of about 3 nm, 5 nm and 10 nm. These NPs have a crystalline structure and grew together by oriented attachment. This is well observed by the magnified image of the interface region between two NPs, that have adjusted their positions in order to reach an almost perfect lattice match. Fig. 1 (b) shows the histogram of the size distribution calculated by using about 600 ZnO NPs located on HRTEM images recorded with different magnifications. The presence of lattice fringes extended through the whole NP was used as criteria to decide its mono-crystallinity. We found that the distribution is peaked around 7 nm (primary monocrystalline NPs) and shows a long tail that extends from about 20 to 80 nm (polycrystalline NPs).

Fig. 2 (a) shows the SAED pattern of a NP ensemble, where all observed

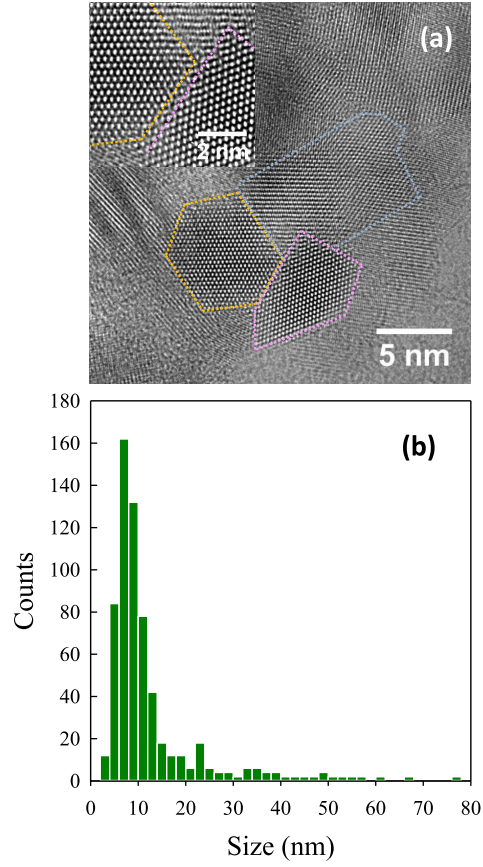


Figure 1: (a) HRTEM images of some typical ZnO NPs, with marked contours, synthesized by fs Ti:Sapphire Laser with $E_{pulse}=75 \mu\text{J}$, the zoom highlights the interface region between two NPs; (b) histogram of the NPs size distribution calculated from HRTEM images.

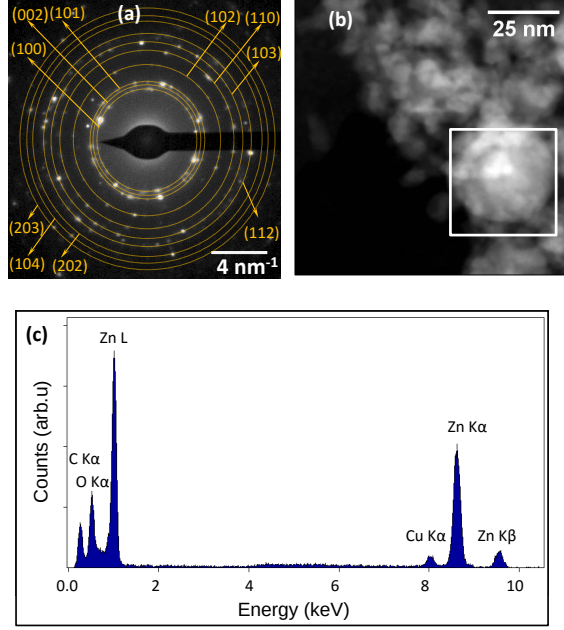


Figure 2: (a) indexed SAED pattern of an ensemble of agglomerated ZnO NPs with Miller indices corresponding to the bulk hexagonal ZnO; (b) HAADF-STEM image of NPs with the white frame used for the EDXS analysis; (c) EDX spectrum, in which the characteristic X-ray lines are indicated.

Debye-Scherrer rings can be attributed to reflections of ZnO crystallites with hexagonal structure (space group P63/mc, space group number 186) and lattice parameters $a = 0.3250 \text{ nm}$ and $c = 0.5207 \text{ nm}$. Fig. 2 (b) shows a HAADF-STEM image of agglomerated NPs. By scanning with the electron beam the region indicated by the white square, the EDX spectrum shown in Fig. 2 (c) was acquired to analyze the NPs composition. It reveals the characteristic Zn-K, Zn-L and O-K X-ray lines, together with the C-K lines from the amorphous C-film substrate and Cu-K lines that are an artifact from the Cu grid. Quantification of the Zn and O content yields an average chemical composition of $\text{Zn}_{0.51 \pm 0.53} \text{O}_{0.49 \pm 0.47}$ which is in agreement with the expected proportion considering the accuracy of quantitative EDXS analyses of about $\pm 5\%$. The comparison with previous experiments based on ultrashort pulsed laser ablation [30, 31, 32] highlights a good

agreement as concerns the crystalline structure of produced ZnO NPs. On the other hand, those works have also evidenced that the sizes measured by electron microscopy follow a bimodal distribution, most likely related to monocrystalline and polycrystalline composition structure of NPs. As reported in [30], ps-laser ablation in organic solvent produces primary particles with diameter of 7 nm and big particles of 100 nm, while in [32] it is shown that fs-laser ablation in ethanol produces small NPs of 2-4 nm and larger NPs of 15-20 nm.

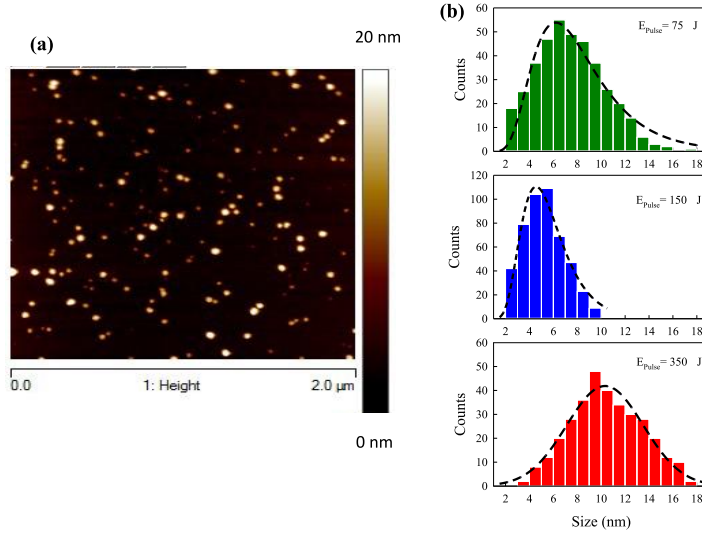


Figure 3: (a) $2 \times 2 \mu m^2$ AFM image of the dried colloidal solution of ZnO NPs produced by PLA of a zinc plate in water using a fs Ti:Sapphire Laser with $E_{pulse}=75 \mu J$; (b) size distribution calculated from AFM images of ZnO NPs produced with $E_{pulse}=75 \mu J$, $E_{pulse}=150 \mu J$ and $E_{pulse}=350 \mu J$, dashed lines are the best-fit curves.

The morphological properties of ZnO NPs, synthesized in the present work by 50 fs Ti:Sapphire pulsed laser, have also been investigated by AFM, especially to highlight the influence of laser pulse energy. Fig. 3 (a) shows the AFM image of ZnO NPs produced by PLA with $E_{pulse}=75 \mu J$ and reveals that they consist of spherical-like particles. As evidenced in Fig. 3 (b), the sizes, calculated by using about 400 ZnO NPs, are dependent on laser pulse energy: the sharpest distribution ranging from 2 to 10 nm with average size $\bar{S} \approx 5.2$ nm is

observed with $E_{pulse}=150 \mu\text{J}$; a distribution from 3 to 18 nm and $\bar{S}\approx 10.5$ nm is obtained with $E_{pulse}=350 \mu\text{J}$; a distribution from 2 to 17 nm and $\bar{S}\approx 7.4$ nm is obtained with $E_{pulse}=75 \mu\text{J}$. Combining these results with HRTEM analysis, we infer that the size distributions extracted from AFM images refer to primary monocrystalline ZnO NPs. Fig. 3 (b) also evidences that the distribution lineshape is asymmetric for $E_{pulse}=75 \mu\text{J}$ and $E_{pulse}=150 \mu\text{J}$, whereas it is symmetric for $E_{pulse}=350 \mu\text{J}$. In agreement with literature data [29, 35], the asymmetric and symmetric curves are fitted by Log-Normal and Gaussian functions, respectively. In those works, it is proposed that the size distribution is influenced by two competitive growth processes of NPs, diffusion and drift: it follows a Log-Normal shape when diffusion is the main process; it tends to a Gaussian shape when the drift grows and becomes prevalent. At the moment, the understanding of the dependence of size distribution on pulse energy remains an open question. However, it is worth noting that, differently from previous PLA experiments performed with ms and ns lasers [23, 24, 26, 27, 28, 29], in the present work we synthesized smaller NPs with average radii only slightly larger than the excitonic Bohr radius ($a_0\approx 2.23$ nm), this finding will be useful to highlight QC effects on the ZnO NPs optical properties.

The optical properties of ZnO NPs dispersed in water are shown in Fig. 4 and clearly evidence a size-dependence. Under the hypothesis of direct band-gap, we report in Fig. 4 (a) the Tauc plot of the OA spectra [36], from which we extrapolate the linear region that intersects the energy axis at E_g . In fact, the UV absorption edge characteristic of crystalline ZnO is located at different spectral positions for the three samples; thereby, we estimate E_g of 3.41 ± 0.01 eV, 3.45 ± 0.03 eV and 3.50 ± 0.02 eV for ZnO NPs with $\bar{S}$ of 10.5, 7.4 and 5.2 nm, respectively. These values are larger than the known E_g for bulk wurtzite ZnO (3.37 eV) [37], thus revealing a QC effect on the ZnO NPs produced by fs laser pulses. Fig. 4 (b) displays the normalized UV emission of the three solutions under excitation at 4.66 eV and acquired with $T_W=10$ ns and $T_D=0$ ns. All the samples exhibit a PL band with an almost Lorentzian shape, that is well associated with the exciton radiative recombination occurring in a sub-nanosecond

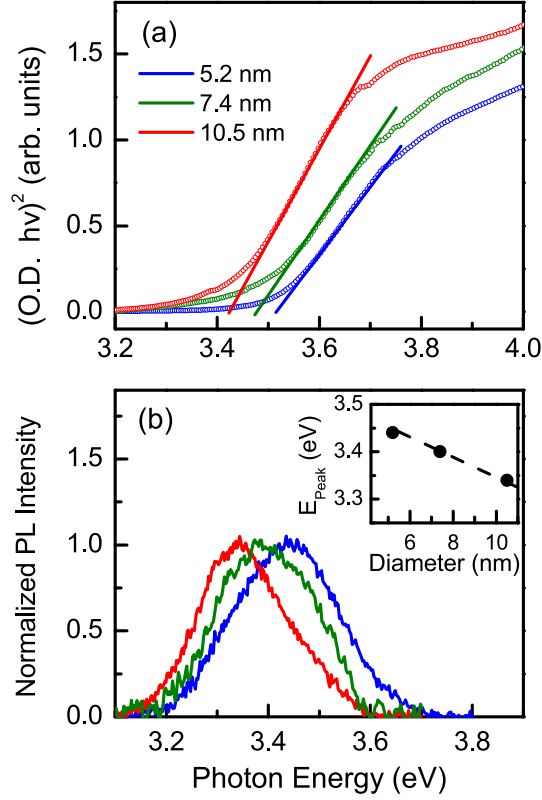


Figure 4: (a) Tauc plot of the absorption spectra recorded from the colloidal solutions of ZnO-NPs with different average sizes. Solid lines refer to the linear range from which the optical band-gap E_g is extrapolated; (b) Exciton-related PL spectra acquired under excitation at 4.66 eV. The inset shows the emission peak as a function of the average diameter of ZnO NPs, dashed line is an eye guide.

timescale [38, 39]. The spectral properties of the exciton-related PL band as well depend on NPs size. The peak position is estimated to be 3.34 ± 0.01 eV ($\bar{S} \approx 10.5$ nm), 3.39 ± 0.02 eV ($\bar{S} \approx 7.4$ nm) and 3.43 ± 0.01 eV ($\bar{S} \approx 5.2$ nm). Interestingly, these emission values are about 60 meV below the optical band-gap measured from Fig. 4 (a), thus matching the known exciton binding energy E_{ex} of ZnO in all three cases. Moreover, the full width at half maximum (FWHM) broadens from 0.21 eV to 0.27 eV on decreasing the NPs diameter.

It is worth noting that the size-dependent effects on the absorption edge and

the excitonic PL band of ZnO NPs produced by ultrashort laser pulses agree with previous PLA experiments performed in high pressure (up to ~ 30 MPa) water [40, 41] and chemical synthesis [42, 43], and are relevant to point out the QC regime. Generally, quantum dots (QD) experience a weak confinement if their sizes are comparable with the excitonic Bohr radius (a_0); instead, if the sizes are smaller than a_0 , the electron-hole pairs are strongly confined thus preventing the formation of excitons [44]. Therefore, our data support the hypothesis of weak confinement so that the excitonic emission peak is expected to depend on the average size $\bar{S}$ of ZnO NPs in agreement with the equation:

$$E = E_g^{bulk} + \frac{\hbar^2 \pi^2}{2Me\bar{S}^2} - E_{ex}, \quad (1)$$

where $M=0.69m_0$ is the translational mass of exciton expressed in terms of the free electron mass m_0 , $E_g^{bulk} = 3.37$ eV and $E_{ex}=59$ meV for ZnO in bulk form [45]. Table 1 reports the comparison between the energy gap obtained by Tauc plot of Fig. 4(a), the measured parameters of PL excitonic curves reported in Fig. 4(b) and those obtained by Eq. 1 as a function of NPs size measured by AFM analysis.

<i>NPs size</i> (nm)	E_g (eV)	<i>Peak pos.</i> (eV)	<i>FWHM</i> (eV)	<i>Calc. Peak pos.</i> (eV)
5.2	3.50 $\pm$ 0.02	3.43 $\pm$ 0.01	0.27 $\pm$ 0.01	3.44
7.4	3.45 $\pm$ 0.03	3.39 $\pm$ 0.02	0.24 $\pm$ 0.02	3.37
10.5	3.41 $\pm$ 0.01	3.34 $\pm$ 0.01	0.21 $\pm$ 0.01	3.34
~ 30	3.38 $\pm$ 0.01	3.32 $\pm$ 0.01	0.20 $\pm$ 0.01	3.32

Table 1: Optical parameters of ZnO NPs produced by ablation with fs laser pulses. Data reported in the last row are extracted from [27] and refer to ZnO NPs produced by ns pulses.

The calculated excitonic peak positions are consistent with those obtained by PL curves and, considering E_{ex} , with the optical band-gap extrapolated by Tauc plot. Moreover, the increasing broadness of the excitonic band on decreasing the NPs size can be attributed to the fact that smaller NPs are more affected by QC, thus their size distribution leads to an overlap of excitonic curves peaked

at different energy values. For the sake of comparison, in the last row we report the optical parameters for ZnO NPs synthesized by ablation with Nd-YAG ns pulsed laser [27]; the sizes are ~ 30 nm so that QC effects are negligible and the energy gap agrees with that of bulk material.

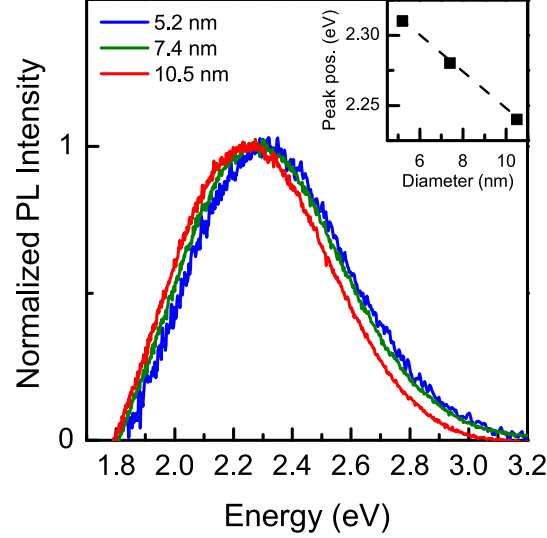


Figure 5: Normalized green PL excited at 4.66 eV and recorded in the colloidal solutions containing ZnO NPs with different dimensions. Inset shows the emission peak as a function of the NPs diameter, dashed line being an eye guide.

In order to complete the optical characterization, we have investigated the visible emissions related to point defects. ZnO NPs, here produced by fs PLA, emit a green and a blue band. The green PL shows approximately the same features observed in ZnO NPs produced by ns PLA [22, 27]: emission peak around 2.3 eV, $\text{FWHM} \approx 0.6$ eV, PLE spectrum with a sharp threshold near E_g (~ 3.5 eV) that appears almost flat at higher energies thus indicating a band-to-band transition, decay kinetics that follows a power law consistent with the tunnelling of trapped electrons to recombination centers. It is worth noting that these spectroscopic features related to the green band are common to a wide range of ZnO-based nanostructures including nanorods of 50-100 nm produced by ms PLA [28] or Zn/ZnO NPs synthesized by gaseous PLA [46]. Fig. 5

reports the normalized green band acquired in our samples upon excitation at 4.66 eV and with $T_W=10$ ms and $T_D=20$ ns. These spectra well evidence a blue-shift on decreasing the NPs size; in detail, the peak position is estimated to be 2.24 ± 0.02 eV, 2.28 ± 0.02 eV and 2.31 ± 0.02 eV for the ZnO NPs having average sizes of 10.5, 7.4 and 5.2 nm, respectively. This trend is shown in the inset and agrees with the optical energies reported in Table 1, it is therefore consistent with a QC effect. This is quite a surprising result considering that this emission is related to point defects, rather to an intrinsic band-to-band recombination. Assuming that the green band originates from ionized oxygen vacancies [5], we infer that the excited state, associated with the trapped electron, is about 1.2 eV below the bottom of conduction band (CB) regardless of the ZnO NPs size, so that the QC effect is due to the placement of the hole tightly linked to the VB; see further details in the energy levels scheme of Fig. 7.

The blue emission is peculiar to ZnO NPs produced by non thermal ablation with fs pulses; it was not observed in our previous experiments based on thermal ablation with ns pulses [27]. This finding is not ascribable to specific structural properties since both syntheses produce wurtzite ZnO nanocrystals, the main difference is related to the morphology: fs pulses produces smaller NPs than those produced by ns pulses. Fig. 6 reports the main spectroscopic features of the blue emission recorded in our samples. As evidenced in Fig. 6 (a), its PL spectrum, excited at 3.76 eV and detected with $T_W=20$ ns and $T_D=0$ ns, does not depend on the ZnO NPs size. In fact, it shows a Lorentzian shape centered at 2.80 ± 0.02 eV with $\text{FWHM}=0.80\pm0.05$ eV, which suggests its attribution to an excitonic-like emission, although of a different type with respect to the main exciton-related UV emission displayed in Fig. 4. The PLE spectrum, reported in the inset, reveals that the blue band is only excited by photon energy larger than the optical band-gap, the efficiency reaches a maximum at 3.8 eV and then drops to zero giving rise to a bell shaped curve with a $\text{FWHM}\approx0.75$ eV. The decay curve is plotted in Fig. 6 (b), it agrees with a bi-exponential law with lifetimes $\tau_1=1.0\pm0.2$ ns and $\tau_2=6.0\pm0.2$ ns, consistently with an excitation/emission pathway driven by different processes or with the existence of two

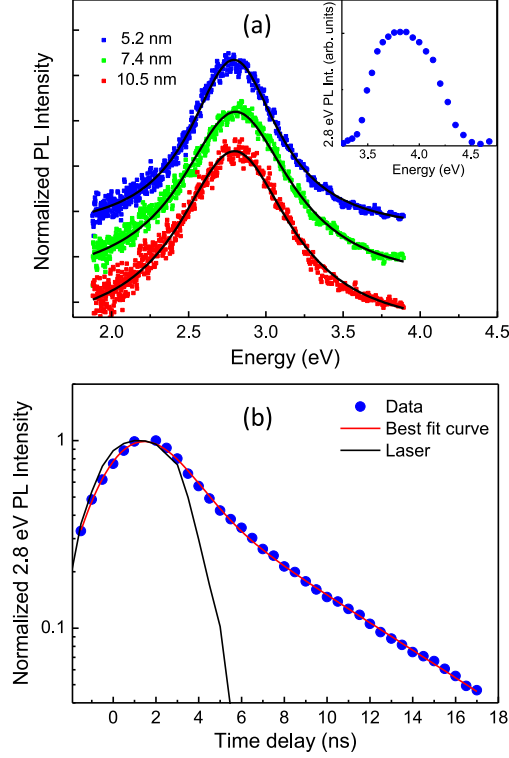


Figure 6: (a) Normalized blue PL observed under excitation at 3.75 eV in the ZnO samples with different dimensions, solid lines are the Lorentzian best fit curves. Inset reports the PLE spectrum obtained monitoring the emission intensity at 2.8 eV in ZnO NPs with average size of 5.2 nm. (b) Decay kinetics of the PL at 2.8 eV, red solid line represents the best fit curve. The temporal shape of laser pulse is also plotted by the black solid line.

variants of the same center. It is worth noting that nanosecond lifetime has been interpreted as due to the free excitons recombination in bulk ZnO [47] and in ZnO microstructures [48], this supports the excitonic origin of the blue band observed in ZnO NPs produced by fs pulses. Under this hypothesis, we infer that the Stokes shift (0.6-0.7 eV), much larger than the exciton binding energy for ZnO materials (≈ 60 meV), measures the energy amount transferred in an exciton trapping at defect states. For the sake of completeness, we acknowledge that a blue-violet emission at 2.8-3.0 eV has been observed by Zeng et al. [7, 49] in ZnO NPs produced by laser ablation of a Zn plate in liquid environments

favouring zinc-rich annealing, and associated, therefore, with interstitial zinc (Zn_i). In contrast with our results, the PLE spectrum reported in those works exhibits a peak below the band-gap, thus indicating a preferential excitation in an intra-gap state consistent with the shallow donors nature of Zn_i for ZnO.

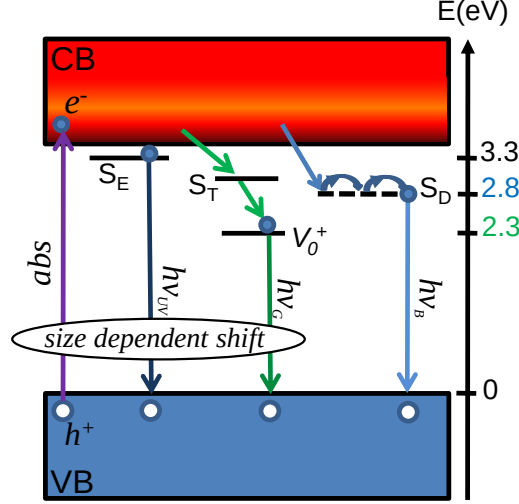


Figure 7: Photoluminescent processes suggested for the UV, green and blue bands of ZnO NPs produced by fs PLA.

The energy level scheme accounting for by the multi-color luminescence observed in ZnO NPs is depicted in Fig. 7. After band-to-band excitation, if the electron-hole pair has enough energy, the exciton (its energy state S_E being ~ 60 meV below the bottom of CB) can freely travel through the NP leading to the UV excitonic emission at $h\nu_{UV} \sim 3.3-3.4$ eV; otherwise the recombination occurs between a hole in the VB and an electron deeply trapped in a singly ionized oxygen vacancy (V_0^+) giving the green PL at $h\nu_G \sim 2.2-2.3$ eV. Both the UV and green PL shift towards higher energies on decreasing the NPs size because of a QC effect. The blue band is due to a photo-generated electron temporarily trapped in defect states S_D from which it recombines with a hole in the VB with a PL emission peaked at $h\nu_B = 2.8$ eV. Since it is observed only after excitation

in a limited energy range above the bottom of CB, we infer that only free electrons with low kinetic energy (< 1 eV) can be trapped in S_D . Then, they jump from one state to another, thus keeping the mobile nature of exciton so that a Lorentzian shape with homogeneous broadening prevails [50]. The observation that the blue peak position is independent of NPs size demonstrates that the S_D states are not influenced by any QC effect, therefore, they might be located at the surface of ZnO NPs.

4. Conclusions

We have demonstrated that non-thermal PLA of a zinc plate in deionized water, by using a fs pulsed Ti:Sapphire laser, produces wurtzite crystalline ZnO NPs emitting multi-color bands in UV and visible range. Results reported here point out significant differences with previous experiments based on thermal ablation by ns laser, able to produce ZnO NPs with sizes of ~ 30 nm. Samples synthesized by fs PLA have a size of the order of the excitonic Bohr radius (< 10 nm), this characteristic is relevant to evidence weak QC effects on the optical transitions. Indeed, both the absorption edge and the excitonic PL peak shift towards higher energies on decreasing the NP size. A green luminescence centered around 2.3 eV is associated with the presence of oxygen vacancies, because of the incomplete Zn oxidation during the PLA synthesis; this emission exhibits as well a blue-shift on decreasing the NP size. A further visible luminescence, with a spectrum of Lorentzian shape peaked in the blue region at 2.8 eV, is peculiar to non-thermal ablation with fs pulsed laser. We propose that the blue emission originates from a recombination mechanism involving a photo-generated electron temporarily trapped in a manifold of electronic states S_D , among which it can jump thus keeping its mobile nature. Overall, our findings underscore the possibility of controlling the spectral position of both the UV excitonic and green emissions by QC effect. The further blue luminescence enriches the spectral emission range thus increasing the potentiality of ZnO NPs with respect to their use in lighting applications.

Acknowledgments

We express our gratitude to the group of the Laboratory R. Boscaino of Advanced Materials (Palermo University, <http://www.unipa.it/lamp/>) for the valuable and stimulating discussions, and G. Napoli and G. Tricomi for their technical assistance. Advanced Technologies Network (ATeN) Center (Palermo University, <http://www.atencenter.com/it/>) is acknowledged for the Ti:Sapphire laser and AFM equipment use. This research received support from the QualityNano Project <http://www.qualitynano.eu/> financed by European Community Research Infrastructure Action under the FP7 "Capacities" Program.

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Figure1

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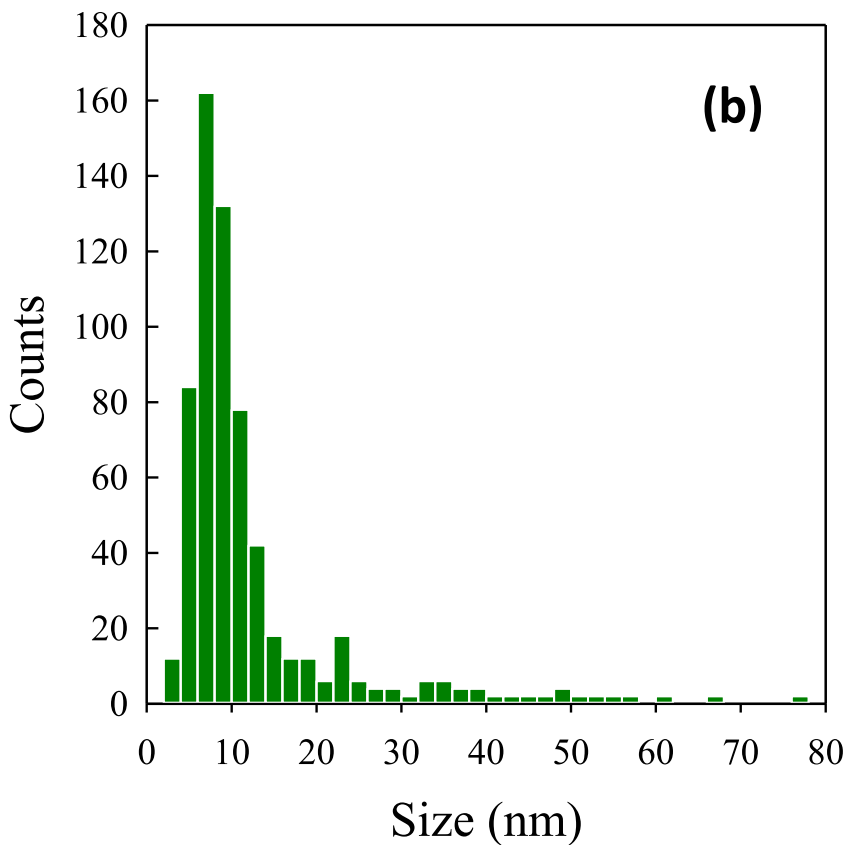
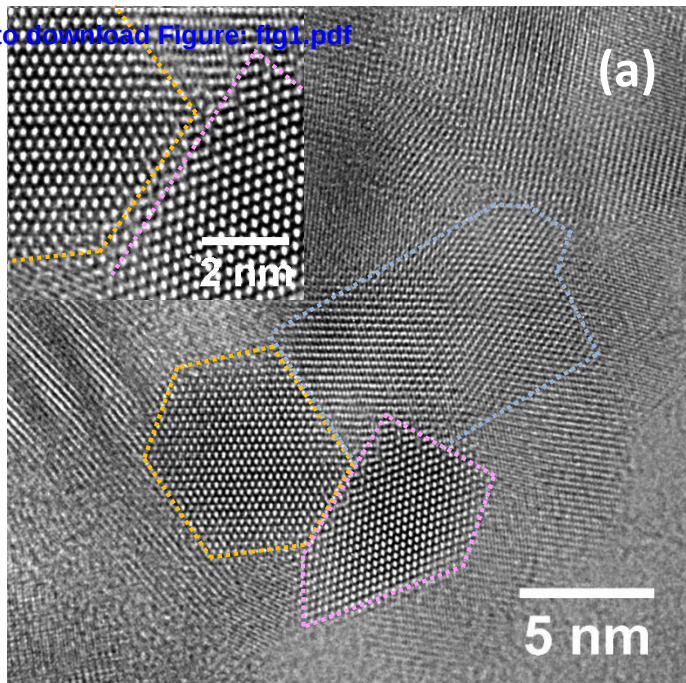


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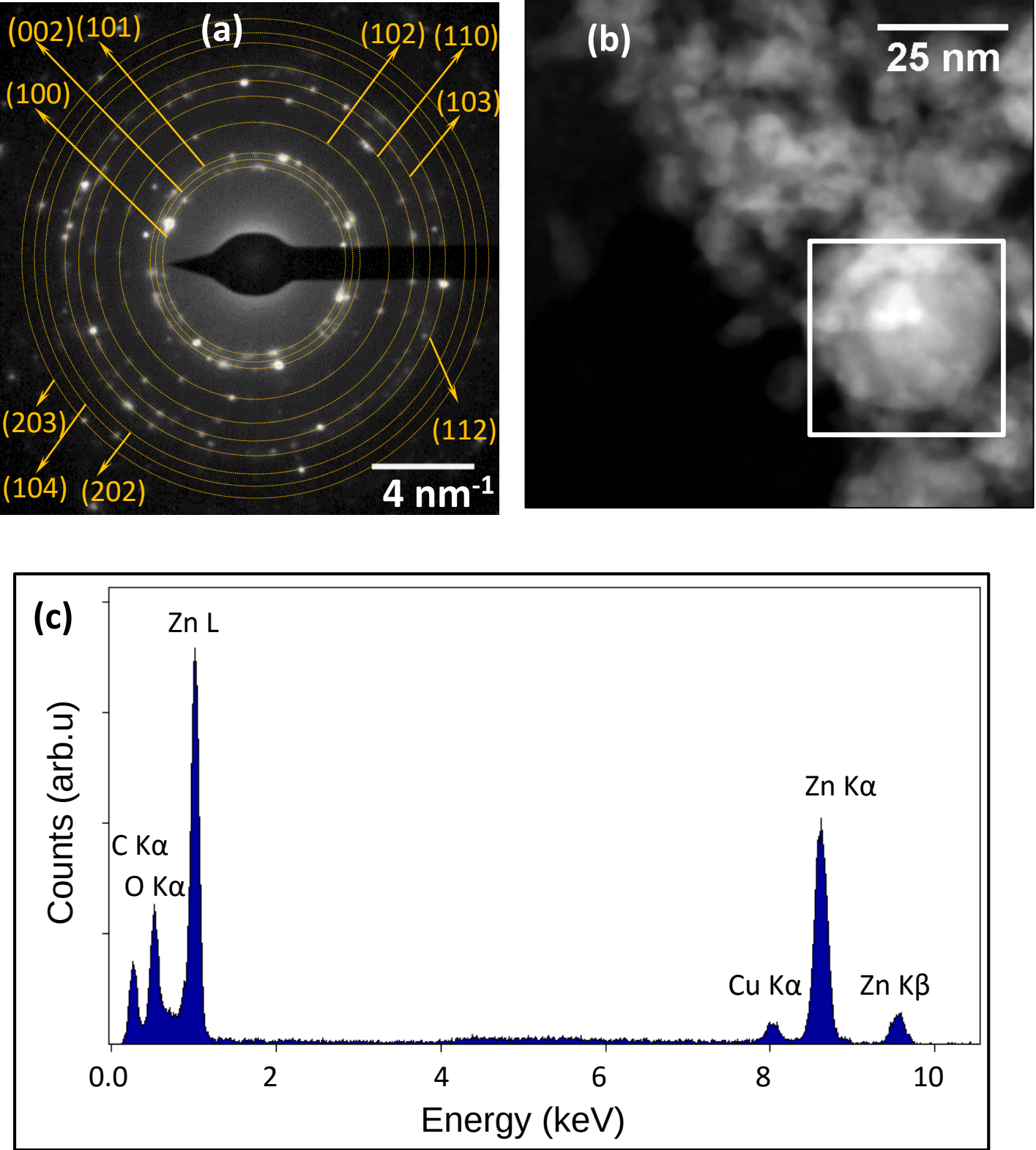
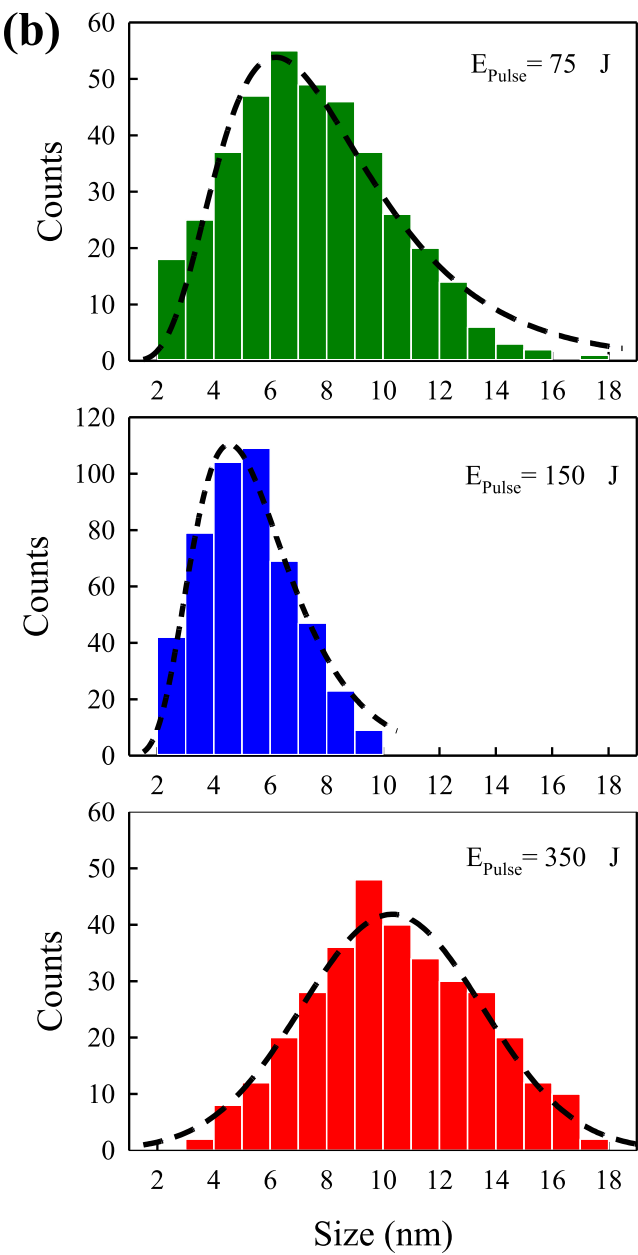
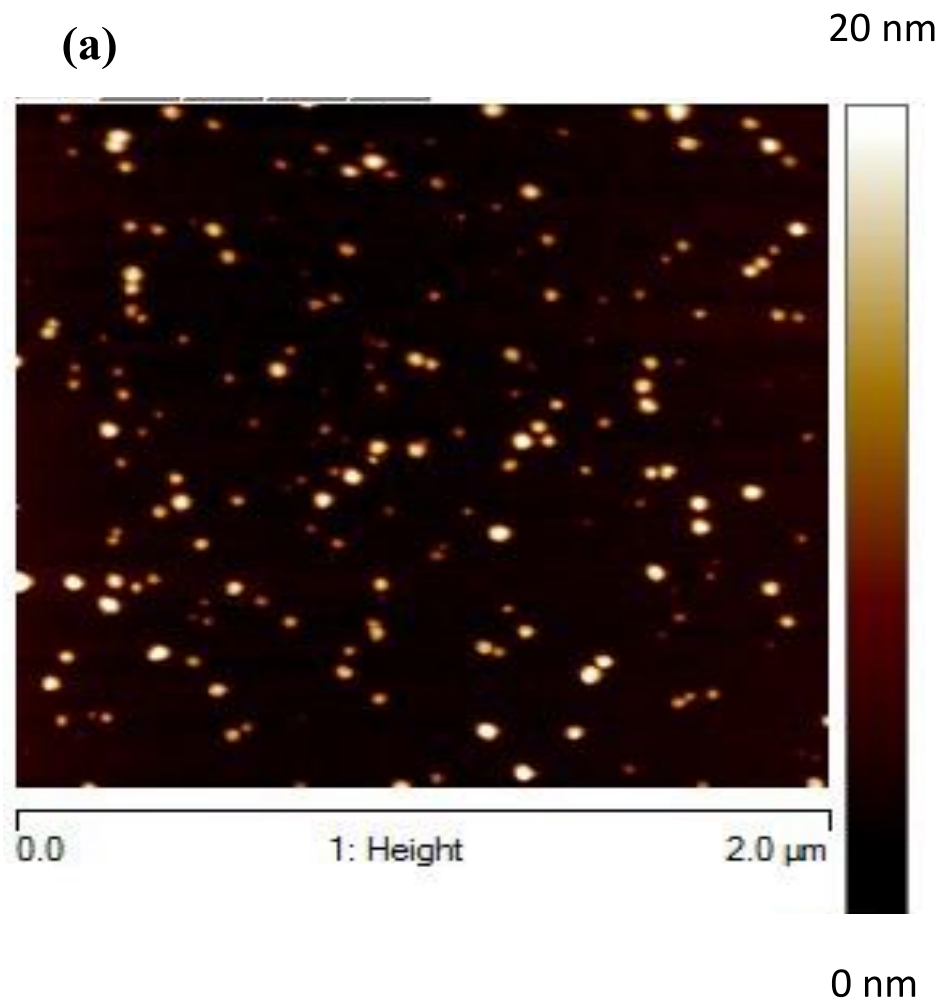
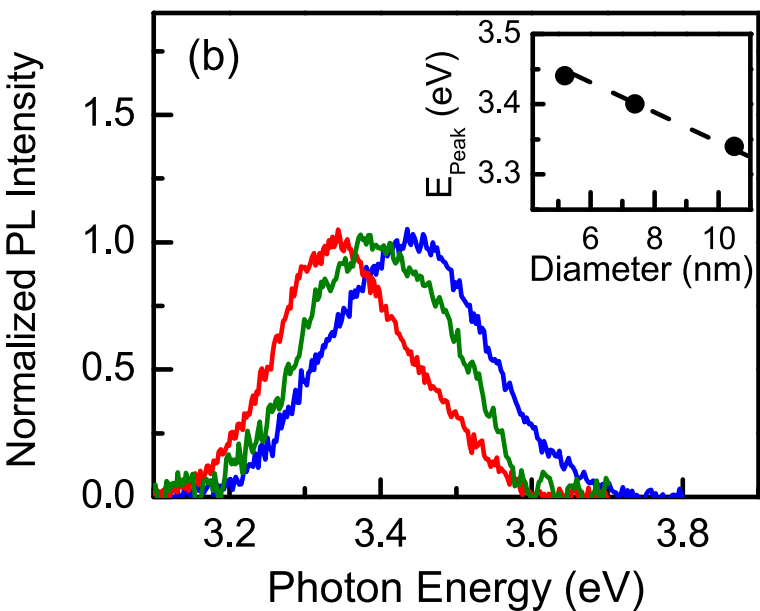
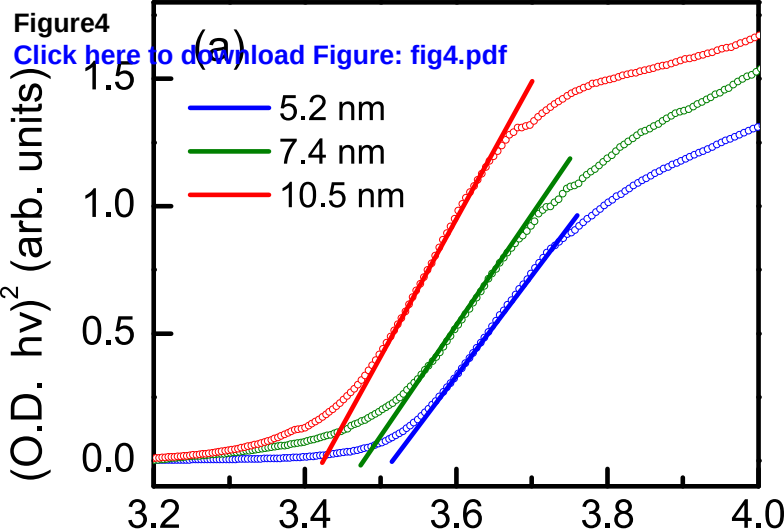


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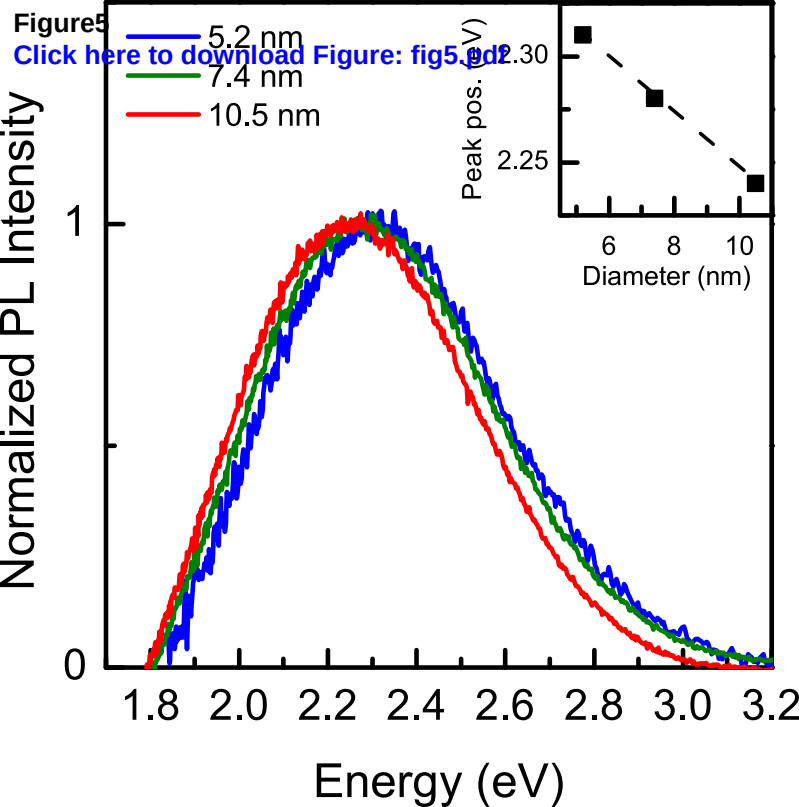


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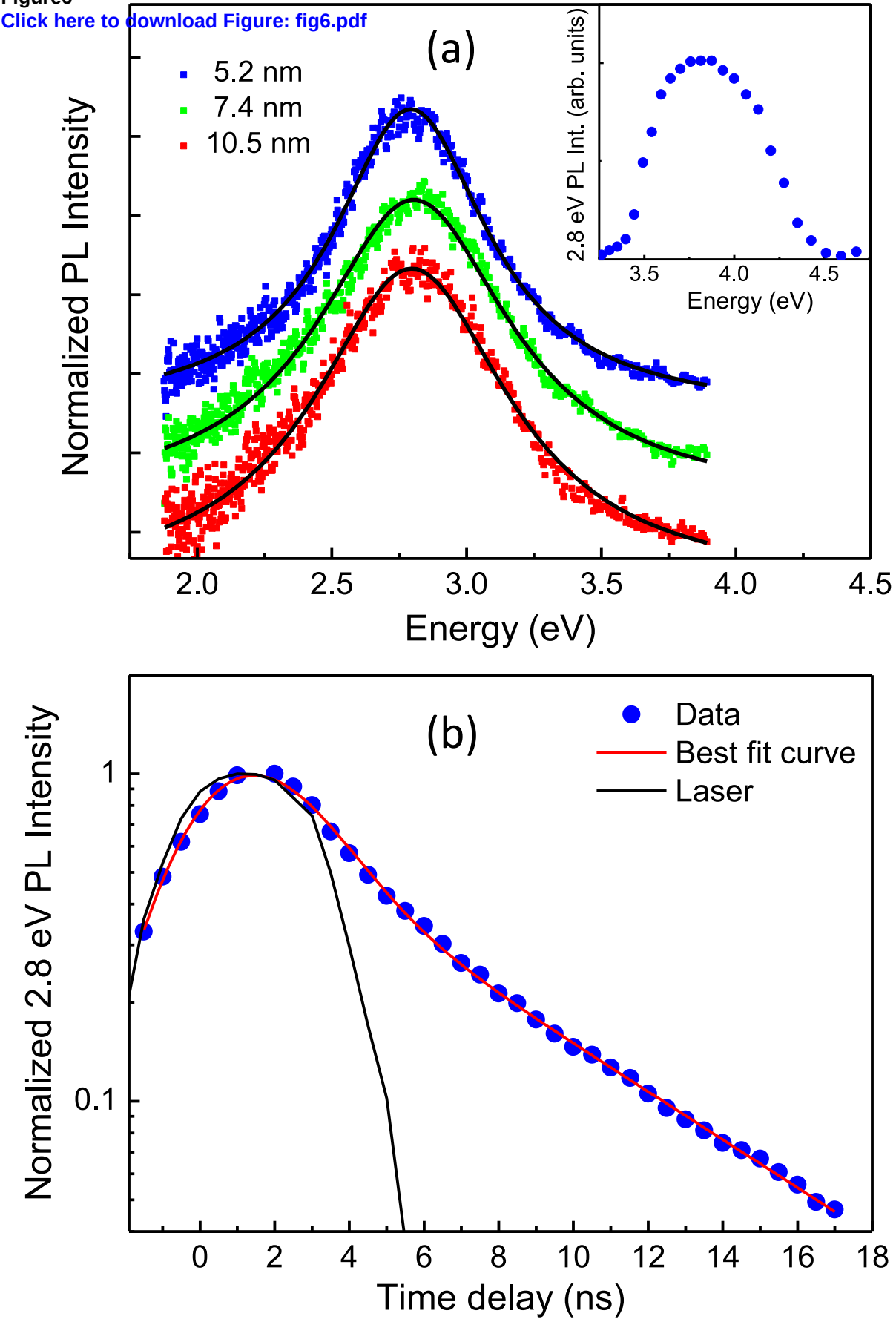
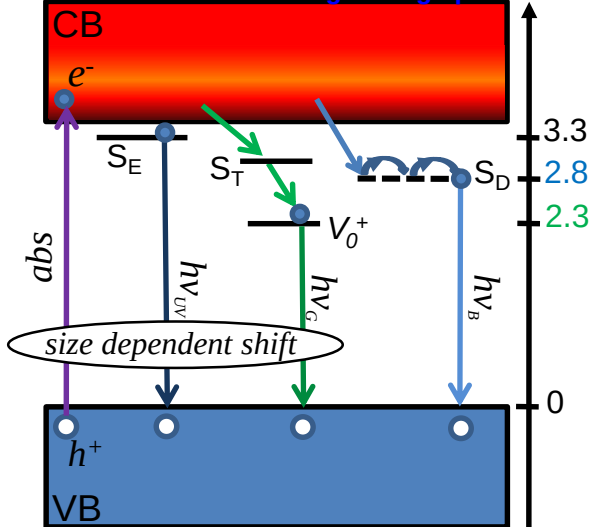


Figure7

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