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Controlled size and high stability SiO_2@ZnO QD's with high green emission obtained by a simple colloidal route.

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Abstract

In this work the synthesis of visible ZnO quantum dots (QDs) functionalized/stabilized with oleic acid and core-shelled with SiO_2 is presented. A colloidal route was followed to synthesize ZnO QDs with 5 nm average size. Several characterizations were done to identify and assure the core, the stabilization, grain size and QDs emission characteristics. Techniques like FT-IR, XRD, TEM, SEM, UV-Vis, PL and an UV lamp were used to test composition, structural, morphological and emission of the as obtained quantum dots. After the structural and morphological characterization of the particles, they were functionalized with (3-aminopropyl) trimethoxysilane (APTMS). It was observed that the size and morphology are unchanged but the stability depends directly on the APTMS oversaturation which is due to the formation of a thick SiO_2 layer. From the PL characterization results it was noticed that the strong green emission is related to the APTMS content and directly related to the shell formation, this emission decreases as the core-shell thickness increases.

Keywords. Zinc Oxide, Quantum dots, core-shell, stabilization, green emission.

Introduction.

Quantum dots (QDs) are useful for devices such as: energy storage, energy conversion, communications, sensors, optoelectronic, cosmetics and photonics, etc. Versatility of materials applications is directly related to the main properties presented; those properties are mainly correlated to the crystallite size, involving optic and electronic characteristics. On this quantum sized materials, the carrier (electron) moves through the band gap to localized bands these move between bands can let a visible emission happens. Albeit at this size range the carriers radiative lifetime increases from picoseconds to nanoseconds at the same time the emission in the visible region can be tuned from blue to yellow easily, etc. [1].

ZnO QDs have attracted attention due to the direct band gap (3.37 eV) and the exciton binding (60 meV) at room temperature that are useful for optics and electronics. Due to its quantum efficiency it has been proposed to be used in light emitting diodes, photodetectors, solar cells, chemical-biological markers, drug delivery, and as active catalytic materials [2-6].

Many studies from photoluminescence characteristics have demonstrated that the QDs shows two main bands: a narrow in the UV region and wide one in the visible, respectively. The UV emission is related to the radiative exciton recombination and the visible to recombination centers assigned to the oxygen vacancies and zinc interstitial mainly.

Recently, several researchers have suggested and demonstrated that the visible emission can be tuned from blue to yellow when the particle size is modified. Dijken et al. explains the ZnO QDs behavior, they mentioned that it is presented when the carriers (electrons) are promoted from the conduction band to deep recombination levels (when an electron is trapped and recombines with double charge oxygen vacancies $V_O^{\circ\circ}$)[7], albeit, Zhang et al. assigned the visible QDs emission to the holes promotion from the valence band to a deep donor level (single charge oxygen vacancies V_O°) [8], but not only the localized energy levels contributes to the emission, there is a contribution from deep levels correlated directly with surface defects, this defects are huge since the crystal size is too small the volume-surface relation increases and affects the luminesce [9].

On the other hand, there are many efforts to synthesize ZnO QDs by physical and chemical techniques with homogeneous size, high visible emission and pure, but it is still a challenge [10-12]. A technique that has been considered as “bottom up” is the colloidal synthesis, this process is cheap and possesses good reproducibility, the size and shape of particles can be controlled easily [13,14]. But an intrinsic disadvantage from nano-sized particles is the high free surface energy, presented when they are obtained through this method. When they are dispersed in the solution there exist an inter-particle interaction allowing the aggregation, ripening and precipitation: if this process occurs, the nature emitting and electric properties are lost and reduce the application possibilities [15]. A good process to follow in order to preserve the quantum properties is the particle surface passivation like building a shell over the surface commonly known as core-shell system. This process is mainly a chemical addition of a specific material (organic or inorganic) bonded over the QDs surface which permits to retain and preserve the quantum emission characteristics and block in the either way the particle-particle interactions increasing the dispersion stability suppressing the agglomeration [16,17].

In this research, we report the ZnO QDs synthesis, purification, passivation and core-shell formation following a colloidal route. These QDs were purified and modified using oleic acid before the functionalization with (3-aminopropyl) tri-methoxysilane (AMPTS). Finally, to obtain a core-shell of ZnO@SiO_2, after shell formation a purification process was done to remove all the byproducts presented. Several characterizations were done, from the results we observed an increase in stability, particle size control and unaltered emission properties. But also, there is something important to mention, this process reach a limit with the passivation or shell concentration that affects directly the ZnO quantum properties. Moreover, we report high visible emitting quantum dots with core-shell with long last stability that could be applied in many research areas.

Experimental

QD’s synthesis

The ZnO QD’s synthesis were prepared using zinc acetate dihydrate 0.04 M (≥98%, Sigma-Aldrich) with the use of methanol as solvent and KOH 0.08 M (≥85%, Merk). The reaction was done at 60 °C for 120 minutes under continuous stirring and reflux. After the synthesis the clear solution was reduced following the QD’s precipitation using hexane and isopropyl alcohol (IPA) 1:5:1 QD’s [13]

QD´s Purification and oleic stabilization process

After synthesis the QD’s were purified using the same solution mentioned previously, 3 times to remove the byproducts and the unreacted precursors [13]. Immediately the QD’s were dispersed in methanol followed by the stabilization in oleic acid 5:2 M (90%, Sigma-Aldrich) at 50 °C for 60 minutes.

QD’s-oleic purification and SiO_2 core shell formation

Prior the shell formation the ZnO QD´s-oleic were purified using methanol as solvent in a centrifuge (4,000 rpm) for 15 minutes three times to remove the oleic acid. Then the pure QD’s were dispersed in toluene anhydrous (99,8%) and 3-aminopropyl trimethoxysilane (97%, Sigma-Aldrich) (APTMS) at 10-80 wt% respectively was added obtaining a clear solution, this solution was stirred for 10 min at room temperature under nitrogen atmosphere. After the stir process 2 ml of 0.1 M tetrabutylammonium (TBAH) was added to the solution and heated for 15 minutes at 85 °C.

QD’s ZnO@SiO_2 purification

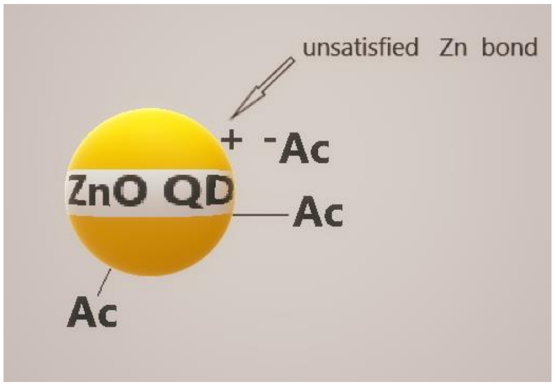
The obtained colloidal solution ZnO@SiO_2 was purified using toluene under centrifugation (4,000 rpm) for 15 minutes three times, then the functionalized QD’s were dispersed and heated (85 °C, 15 min.) in toluene/TBAH (10:2 v:v) to assure the complete crosslinking [18]. The purification process was carried out using methanol and a centrifuge (4,000 rpm) three times 15 minutes each. After this step the QD’s were dispersed on deionized water to be characterized.

Results and discussion

1. ***QDs characterization***

Fourier Transform Infrared (FT-IR)

QDs FT-IR characterization is shown in figure 1a) Bare ZnO QDs after purification process, 1b) ZnO QDs-Oleic, 1c) ZnO@SiO_2 core-shell at 10 wt% APTMS concentration, 1d) ZnO@SiO_2 core-shell at 80 wt% APTMS. From the spectra analysis the Zn-O characteristic vibrational mode is observed at 450 cm^{-1} [19]. The OH stretching modes related to the alcohol physisorbed due to the nature of the solution that still attached to ZnO surface are shown at 2950-3670 cm^{-1} [20]. After the washing process some byproducts such as COO^- still appear at 1577 and 1400 cm^{-1}, this byproduct is related to the residual acetate (see scheme 1). D. Sun and coworkers has reported KAc (potassium acetate) byproduct removing, it was reported that after 2 washing process steps this compound is reduced but this purification process has a limit that is reached at 4 cycles and only 48 % of K^+ is removed from the solution, they concluded that this limit efficiency is proportional to the dynamic equilibrium between the ion K^+ and Ac^-, that cannot be removed from the QDs, because they are strong attached to the particles surface [21]. In their research the QDs were purified and characterized through TGA, it was observed that the particles lose 6% in mass weight, this loss in weight is due to the washing process that results effective at removing KAc byproduct [21], they also mentioned that after an annealing treatment under 150 °C, was not enough to decompose the acetate compound and only 0.4 % wt content was reduced, this weight loss is related to the solvent dissociation (methanol and water) from the QDs surface. Is easy to suppose that all the remaining Ac anions (5.6 %) are strong linked over the QDs surface and it is hard to remove just with the washing process. In addition, at 1016, 929 and 678 cm^{-1} vibrational modes are related to the CH_2-OH, belonging to methanol and isopropyl alcohol and were not removed efficiently after the drying process [22].



Scheme 1.- ZnO quantum dots interacting with Acetate byproducts.

Figure 1b) shows ZnO QDs-oleic characteristic spectra, where the COO-Zn stretching vibrations modes ones appear at 1577 and 1400 cm^{-1} this is related to the oleic acid that still attached over the QDs surface [23]. Furthermore, at 2926 and 2854 cm^{-1} CH_2^- symmetric and asymmetric modes are presented due to the elemental oleic acid composition [23]. Afterwards, the FT-IR analysis from QDs functionalized core shell spectra figure 1c) $ZnO@SiO_2$ 10 wt% and 1d) $ZnO@SiO_2$ 80 wt% where the N-H_2 deformation vibrational amine group mode at 1650-1580 cm^{-1} is presented even this kind of modes are shifted to higher frequencies for this research the hydrogen bonding does not present this effect. Furthermore, the -CH_2 characteristic modes are located at 2926 and 2854 cm^{-1} which corresponds to the propyl chains that belongs to the APTMS attached to the QDs surface, in addition the bonding Zn-O-Si modes are shown at 970 and 870 cm^{-1} [20, 22].

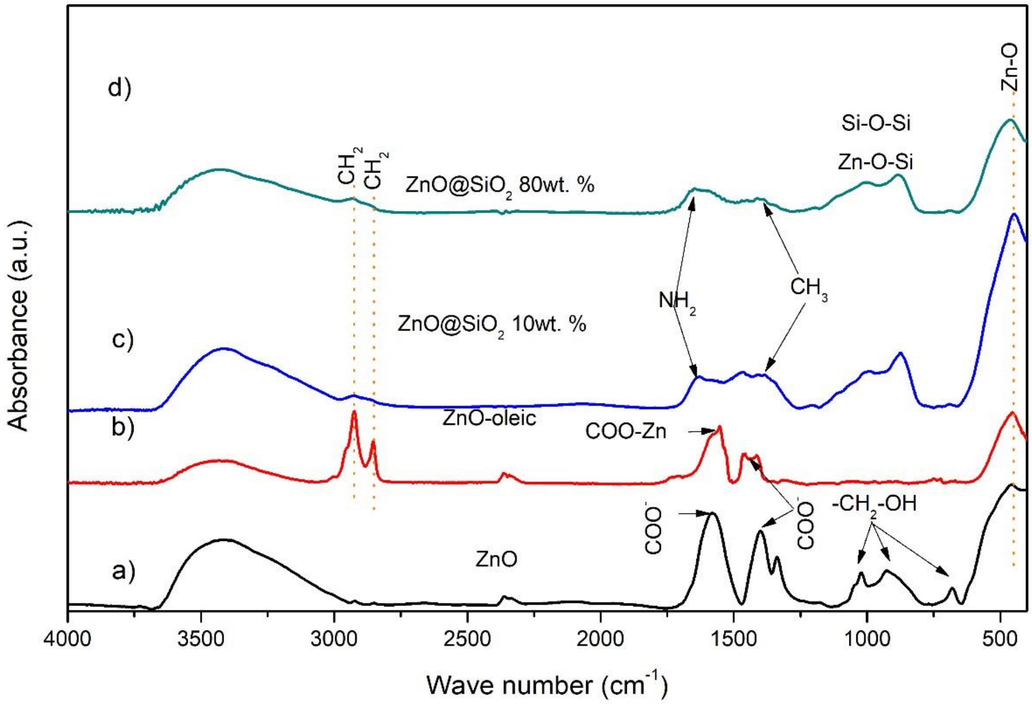


Figure 1. FT-IR QDs Spectra a) bare ZnO, b) ZnO QDs-oleic, c) ZnO@SiO_2 10 wt% and d) ZnO@SiO_2 80 wt%.

X ray diffraction (XRD)

In figure 2 XRD patterns from QDs functionalized and non-functionalized are presented all the patterns exhibit all ZnO planes which corresponds to the wurtzite ZnO polycrystalline (ICDD PDF No. 036-1451), from the XRD pattern is observed the FWHM (Full Width at the High Maximum) that are mainly different for those reported for bulk ZnO [19,24], so with this, can be assured that there exist a crystal size decrease, also the peaks decreases in intensity when the APTMS concentration increases, this change could be due to the core-shell that surrounds each QDs increasing its thickness.

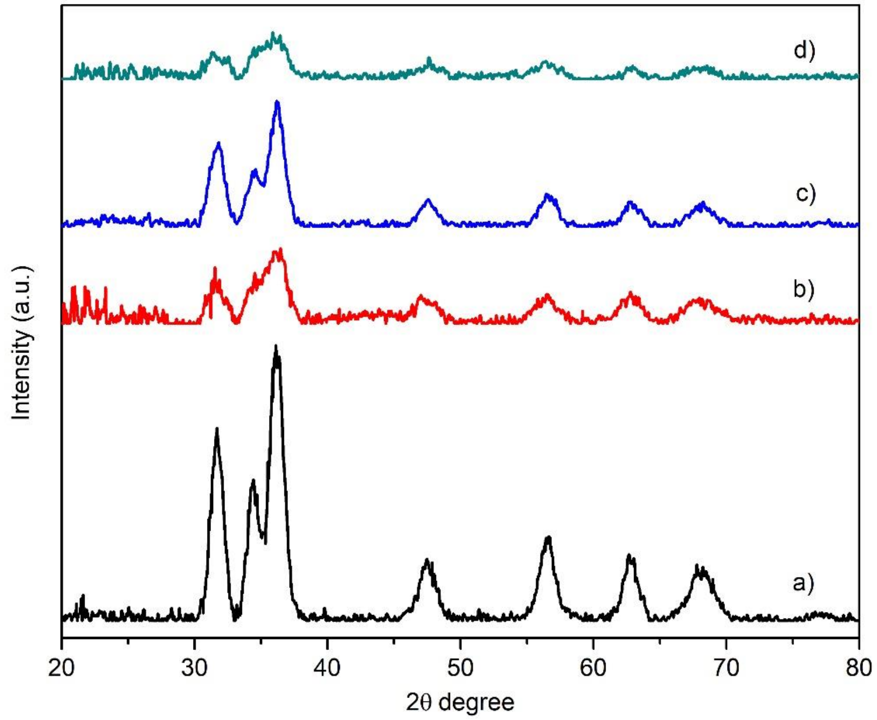


Figure 2 XRD patterns a) bare ZnO QDs, b) ZnO QDs-Oleic, c) ZnO@SiO_2 10wt% and d) ZnO@SiO_2 80 wt%.

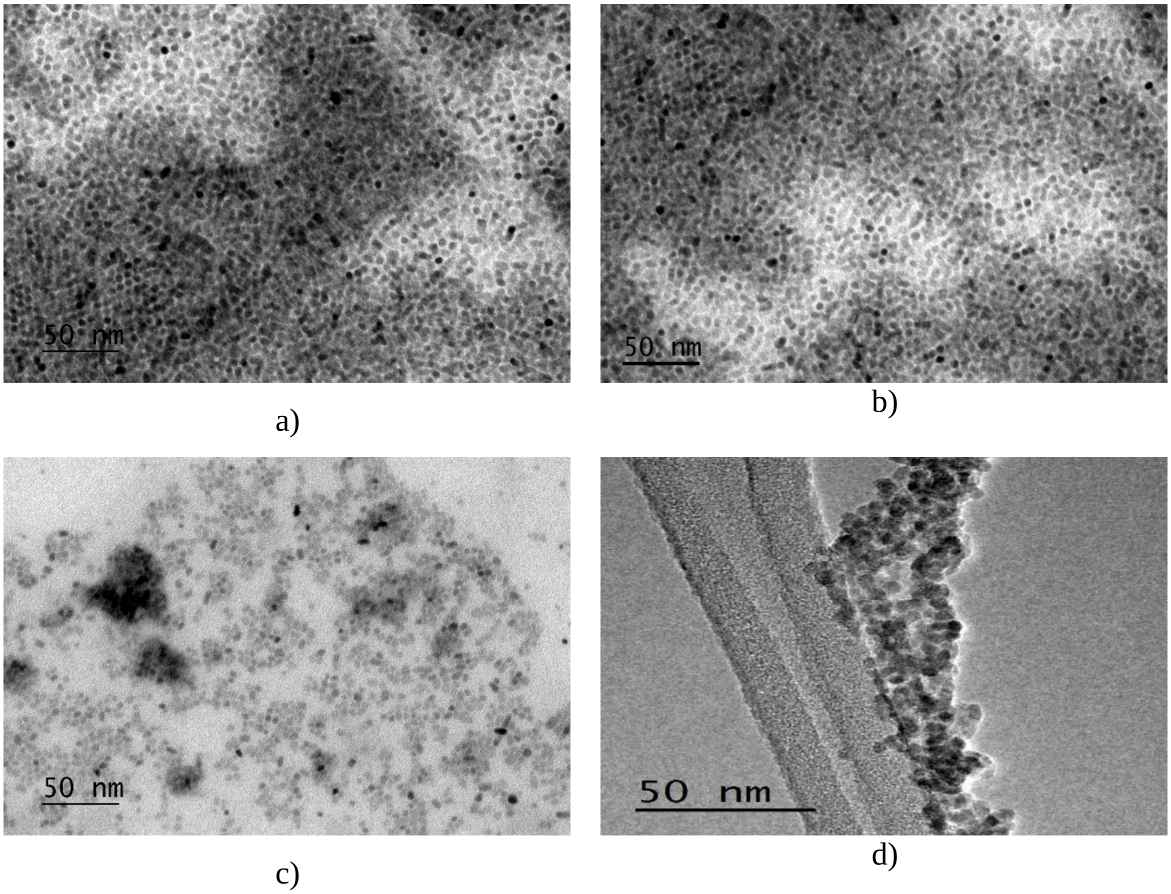
Crystallite average size was obtained using Scherrer formula as follow [25];

$$D = \frac{k\lambda}{\beta\ (cos\theta)} \qquad 1$$

Where D is defined as the crystal size, K a constant, λ as the x-ray wavelength (0.1548), β is the full wide of the half maximum and θ is defined as Bragg diffraction angle. From this formula an average size was obtained that was around 5 nm for those QDs without functionalization, ZnO QDs-oleic and ZnO@SiO_2 core-shell at 10 wt% but respect the ones with 80 wt% it was not possible to calculate due the pattern was not defined clearly so there was no chance to determine the FWHM but from TEM analysis it can be seen that the size is maintained (see TEM section). All the calculus from XRD are correlated with those ones observed and measured by TEM analysis (see fig. 3), so with this technique used to synthesize the ZnO is easy to obtain QDs with well controlled and homogeneous particle size, whereas there were no byproducts or intermediate like (Zn-LDH) presented on the patterns assuring that this synthesis after the purifying process is efficient enough.

TEM (Transmission Electron Microscopy)

To follow the stability and compare the crystallite size obtained from XRD patterns, a batch of solutions with well dispersed particles were characterized by TEM, from the micrographs is clearly seen that the dispersion and size is directly affected to the APTMS content and the core formation as showed in figure 3. Where a) is for bare ZnO particles (as it was obtained), the particle size distribution is around 5 nm that is according to the XRD results. When the particles are re-dispersed in oleic solution (fig. 3b), after the purification process the dispersion and size remain similar, but when the core is generated after APTMS addition (fig. 3c) particles remain homogeneous but the stability start being affected, it could be due to the SiO_2 interactions in between ZnO particles and increases as the APTMS concentration is oversaturated fig. 3d) ZnO 80 wt%. It has been observed that, when there is a solution with high SiO_2 precursor concentration there exist an incomplete SiO_2 formation and non-uniform shelled particles start interacting each other forming the Ostwald ripening effect where strong agglomerated particles are formed [26]. That can be explained through the photographs and the photoluminescence spectra in the QDs emission that it is reduced drastically with the APTMS concentration as it will be explained in PL section (see fig. 7 and 8).



a)

b)

c)

d)

Figure 3. ZnO QDs, a) Bare, b) ZnO QDs-oleic, c) ZnO@SiO_2 10 wt% and d) ZnO@SiO_2 80 wt%

All the samples maintain the spherical shape with 5 nm in average size. Comparing the results from those ones that are functionalized there is no increase on the average diameter due to SiO_2 shell this is reasonable the dispersion is better when a passivation is formed at QDs surface when oleic acid and APTMS at 10 wt%, it could explain the stability observed from the photographs taken the first day and after 30 days, figure 4.

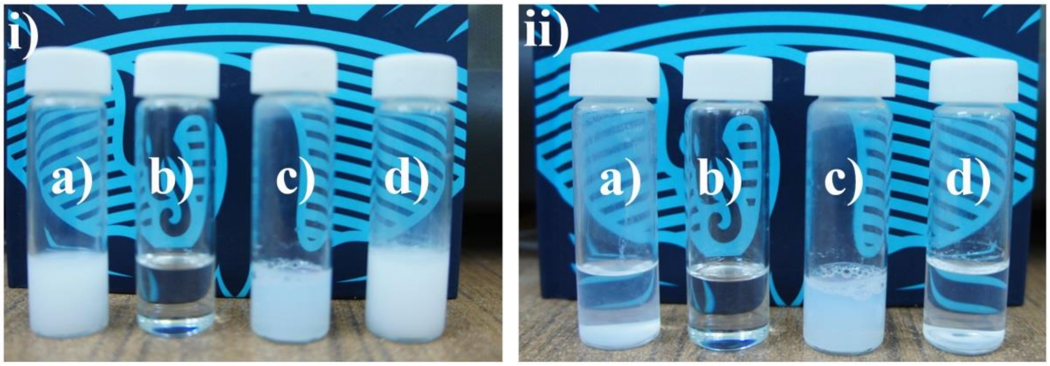


Figure 4 colloidal solution a) bare ZnO, b) ZnO QDs-oleic, c) ZnO@SiO_2 10 wt% and d) ZnO@SiO_2 80 wt%, i) day one and ii) after a month aged solution.

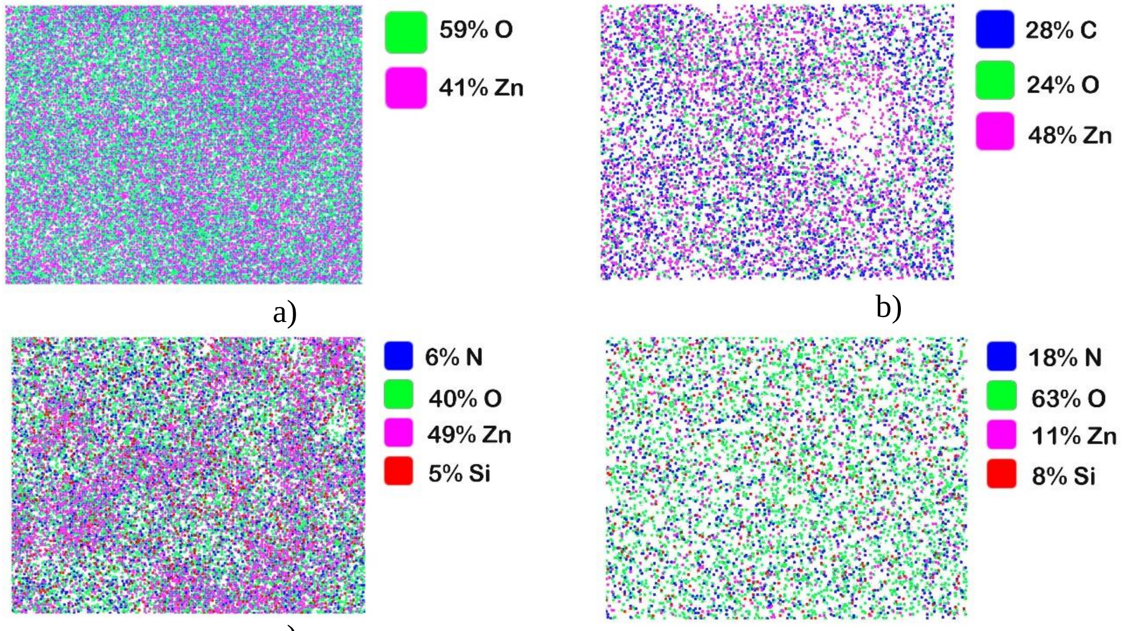
Electron dispersion spectroscopy (EDS)

Table 1 and figure 5 is refers to the EDS ZnO QDs fundamental compositional film images (5 layers) deposited by spin coating over silicon substrates with no annealing treatment, the solvent evaporation was carried out at 80 °C, this temperature is to assure no re-crystallization process. The fundamental composition was obtained for the full batch of solution. The analysis corresponds directly to the elements presented in the QDs surface for the bare QDs (purified) and no byproducts were detected (fig. 5a), but for those particles dispersed in oleic solution a certain carbon concentration (28%) was determined which correspond to the main oleic composition that surround the particles making them stable conserving the shape and size (fig. 5b), but when we add 10 wt% to 80 wt% APTMS silicon and nitrogen concentrations start being important, the specific concentration of Si and N at 10 wt% makes the shell formation thus the stabilization still being good it could be due to the specific charges formed around the QD's due to the shell it could be the coulombic forces were an specific charge is presented in a particle but when this particles are charged similarly, the particles shows repulsion and not allow the agglomeration or secondary growth [27]. But when the medium is oversaturated with the APTMS solution these shells are incomplete and forms a disordered Si-O bonds. This unstable quasi shell permits the interaction (attraction) between the particles letting the formation of strong agglomerated particles known as the Ostwald ripening effect [27].

Table 1 shows the elemental composition obtained by EDS.

Sample	Zn (%)	O (%)	C(%)	Si (%)	N(%)
ZnO	51	49	0	0	0

ZnO QDs-Oleic	48	24	28	0	0
ZnO 10 wt%	49	40	0	5	6
ZnO 80 wt%	11	63	0	8	18



a) b) c) d)

Figure 5. EDS ZnO QDs images, a) Bare, b) ZnO QDs-oleic, c) ZnO@SiO_2 10 wt% and d) ZnO@SiO_2 80 wt%

OPTICAL CHARACTERIZATION

Ultra Violet Visible characterization (UV-Vis).

Figure 6 shows UV-Vis spectrum for the whole batch of QDs ZnO from bare to 80 wt% functionalized. In figure 6d there is a change on the absorbance part, it happens when the QDs are totally covered with the shell. From the UV-Vis absorption it is clearly observed that there exists a main absorbance localized at 355 nm for particles bare to those shelled. Absorbance characterization from those particles without any functionalization were dispersed in methanol, for QDs-oleic they were dispersed on toluene, water was used as dispersing agent for QDs@ SiO_2 (10 wt% and 80 wt%). According to UV-vis results it is clearly seen that ZnO@SiO_2 synthesized through colloidal technique are totally shelled by SiO_2, and the sample with 10 wt% APTMS concentration does not present a redshift in wavelength compared to the ones that has no functionalization, also there is another characteristic after functionalization where the particles are totally stable, no aggregation, coalescence or secondary growth is observed. Whereas those particles that are 80 wt%, the absorbance is lower and could be governed by 2 different factors i) could be that the shell formed by SiO_2 is thicker and provokes a lower absorbance emission but after a magnification of the spectra between 350-375 nm it could be observed a contribution at 360 nm fig. 6d, ii) also could be related to a direct cross-linking due to the high APTMS concentration and there is no shell formed around QDs, so a precipitation is formed and the signal is weak compared to that one with 10 wt% [26, 28].

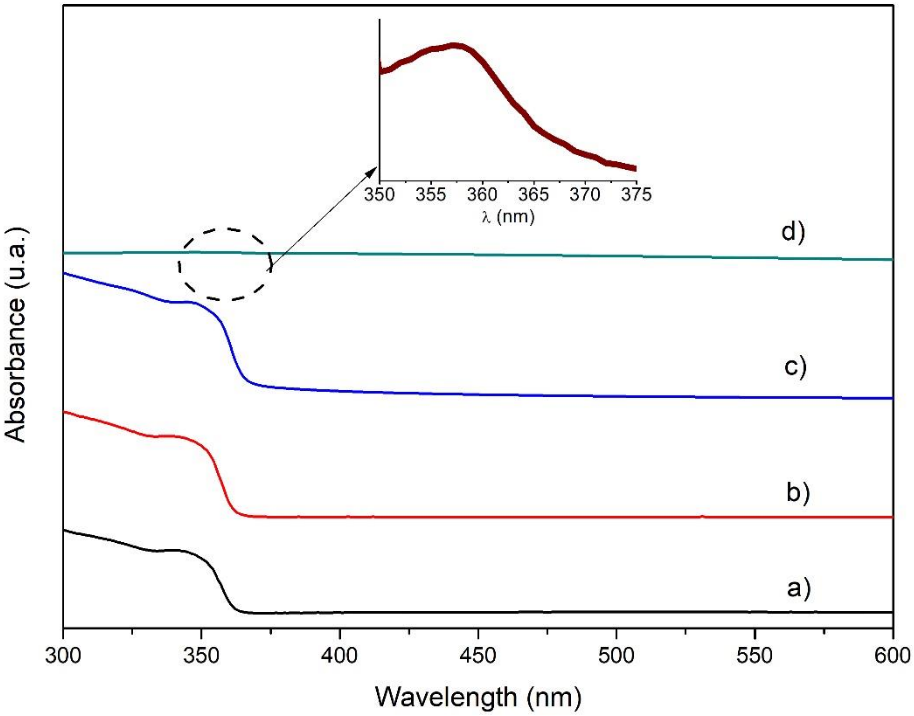


Figure 6. UV/Vis spectra a) bare ZnO QDs, b) ZnO QDs-Oleic, c) ZnO@SiO_2 10 wt% and d) ZnO@SiO_2 80 wt%.

But is important to notice that most of the samples are shifted to the blue region (355 nm) at room temperature and it can be related to the quantum effects. Using the UV-Vis spectra the optical band gap has been calculated from absorption onset demonstrating that all the values are different from that value reported to the bulk ZnO (3.33 eV) [29], see table 2.

Table 2. Eg value calculated from UV-Vis for different samples.

Sample	Absorption onset (nm)	Eg (eV)

ZnO	355	3.5
ZnO-oleic	355	3.5
ZnO@SiO_2 10wt. %	355	3.5
ZnO@SiO_2 80wt. %	360	3.44

Photoluminescence (PL)

From spectra analysis we can observe an intense green emission at 550 nm (2.25 eV) related to recombination centers donor-acceptor [7-9]. This emission could be assigned to the hole transition from the valence band to the deep donor energy level (singly ionized oxygen vacancies) at 2.2 eV above balance band [8]. PL intensity increases when the QDs are functionalized with oleic acid, however, when them are shelled with SiO_2 at 10 and 80 wt% this intensity decreases becoming even lower than those bare QDs. This effect occurs under certain conditions, i) there exist a random coalescence producing clusters in an oriented crystalline direction this could reduce the visible emission, but as is it shown in this work the coalescence could be suppressed with the oleic acid when is attached to the QD's surface (fig.7b), working as a surface passivation suppressing the secondary growth and particle interaction thus the agglomeration will not occur suddenly and a well dispersed solution is obtained exhibiting an intense luminescence compared to those particles with no passivation layer (fig 7a) . [15,16,20], ii) by the second case the ionization energy plays an important role at the colloidal solution. X. Zhang et al., showed that the ZnO QDs dried exhibit a high UV emission, however, the visible emission never occurs, because the ionization energy was completely suppressed [13], The colloidal ZnO QDs dispersed in a highly polar solvent leads to an excess surface charge and electrostatic repulsion between particles which allows the ZnO QDs to be individually dispersed until the repulsion between particles is overcome by the van der Waals attraction (dry ZnO QDs) [27]. So, after the QD's are shelled with SiO_2 there is an ionization suppress due to the excess Si-O-Zn bonds (fig. 7c and 7d) provoking a self-condensation allowing an aggregation and finally forming clusters after several days as it is observed in TEM images.

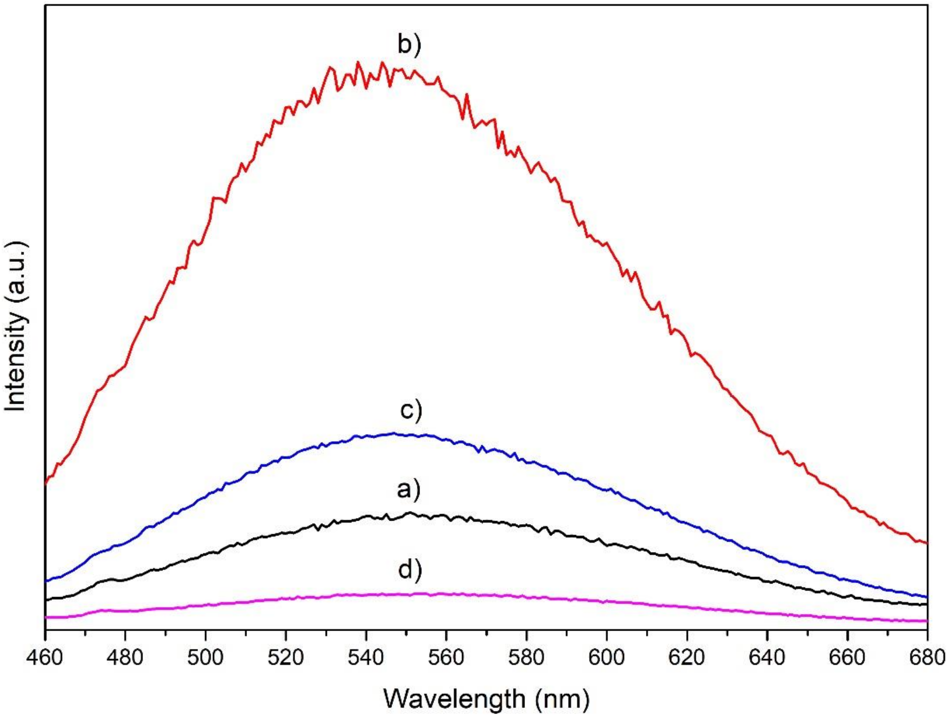


Figure 7. PL characteristic emission spectra a) bare ZnO, b) ZnO QDs-oleic , c) ZnO@SiO_2 10 wt% and d) ZnO@SiO_2 80 wt%.

QDs UV light emission

The QDs emission were observed under common UV lamp illumination i) first and ii) after 30 days aged solutions (see fig. 8), the same label as the previous ones were used to identify the flasks, we can observe a high green emission due to the size effect as a multi-excitonic in the quantum range due to the defects related to the oxygen vacancies

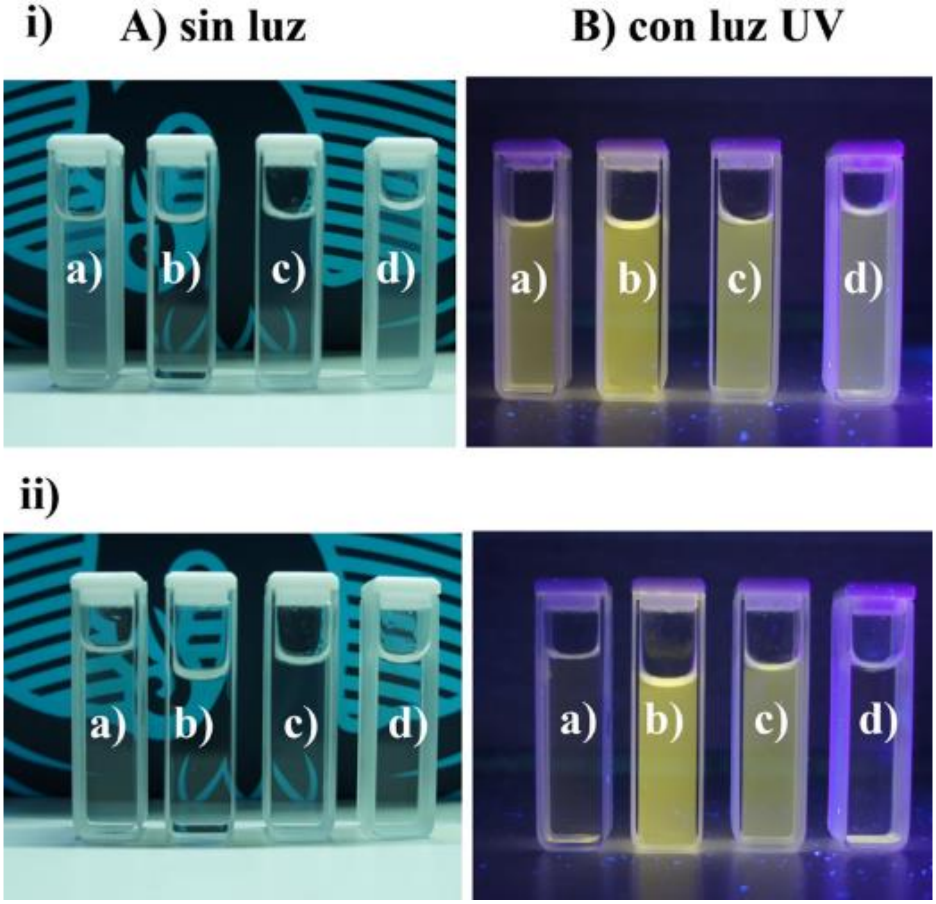


Figure 8. i) first day and ii)30 days aged solution a) bare ZnO, b) ZnO QDs-oleic , c) ZnO@SiO_2 10 wt% and d) ZnO@SiO_2 80 wt%

Conclusion

In this work we obtained a high stable QDs solution without any surfactant addition, from the structural and optical characterization the size and morphology were identified, ZnO wurtzite polycrystalline was successfully synthesized with the results analysis we conclude that the emission depends on the stabilization and the APTMS content these factors also affects directly on the particle size. A strong green emission was observed through the UV irradiation and from PL results the oxygen vacancies were assigned to be responsible. The solution also plays an important role in the emitting and stabilization process, with this report we can assure the use of this method to obtain multi-excitonic QD's for future photoemission devices even with the SiO_2 shell formation.

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