Supporting Information

Colloidal fluorine-doped ZnO quantum dots: the synergistic action of atomic doping and growth conditions directs fluorescence and photoactivity

Noemi Gallucci[1,2], Alessandro Cangiano[1,2], Simone Russo[3], Giulio Pota[3], Rocco Di Girolamo[1], Eugénie Martinez[4], Nicolas Vaxelaire[4], Luigi Paduano[1,2] and Giuseppe Vitiello[2,3]*

[1] Department of Chemical Sciences, University of Naples Federico II, Via Cintia 4, 80126 Naples, Italy.

[2] CSGI -Center for Colloid and Surface Science, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy.

[3] Department of Chemical, Materials and Production Engineering, University of Naples Federico II, P.le Tecchio 80, 80125 Naples, Italy.

[4] University of Grenoble Alpes, CEA-LETI, 17 Av. des Martyrs, 38054 Grenoble, France.

*Corresponding author: Giuseppe Vitiello, email: giuseppe.vitiello@unina.it

Table S1. Amounts of reagents used in the synthesis of bare and doped ZnO-QDs under wet conditions.

Sample	ZAD ± 0.0001 g	MeOH for ZAD ± 0.0001 g	KOH ± 0.0001 g	MeOH for KOH ± 0.0001 G	NH_4HF_2 ± 0.0001 g
F0/ZnO-QDs	1.2342	39.8270	0.6038	27.7106	
F1/ZnO-QDs	2.6402	83.9602	1.3202	47.3301	0.0034
F2.5//ZnO-QDs	2.6402	83.9602	1.3202	47.3301	0.0085
F5//ZnO-QDs	2.6402	83.9602	1.3202	47.3301	0.0171
F7.5//ZnO-QDs	2.6402	83.9602	1.3202	47.3301	0.0256
F10//ZnO-QDs	2.6398	83.9605	1.3202	47.3298	0.0342
F15//ZnO-QDs	2.6401	83.9598	1.3201	47.3302	0.0513
F20//ZnO-QDs	2.6402	83.9960	1.3198	47.3301	0.0684

Table S2. Doping salt content used for the synthesis of ZnO-NCs under solvothermal conditions.

Sample	NH$_4$HF$_2$ ± 0.00001 g
F0/ZnO-NCs	
F1/ZnO-NCs	0.00068
F2.5/ZnO-NCs	0.00171
F5/ZnO-NCs	0.00342
F7.5/ZnO-NCs	0.00513
F10/ZnO-NCs	0.00684
F15/ZnO-NCs	0.01026
F20/ZnO-NCs	0.01368

Table S3. Average dimension obtained from the statistical analysis of TEM images and hydrodynamic radius of colloidal nanosystems obtained from DLS analysis for undoped and F-doped ZnO as synthesized through the wet-precipitation method (QDs) and solvothermal method (NCs).
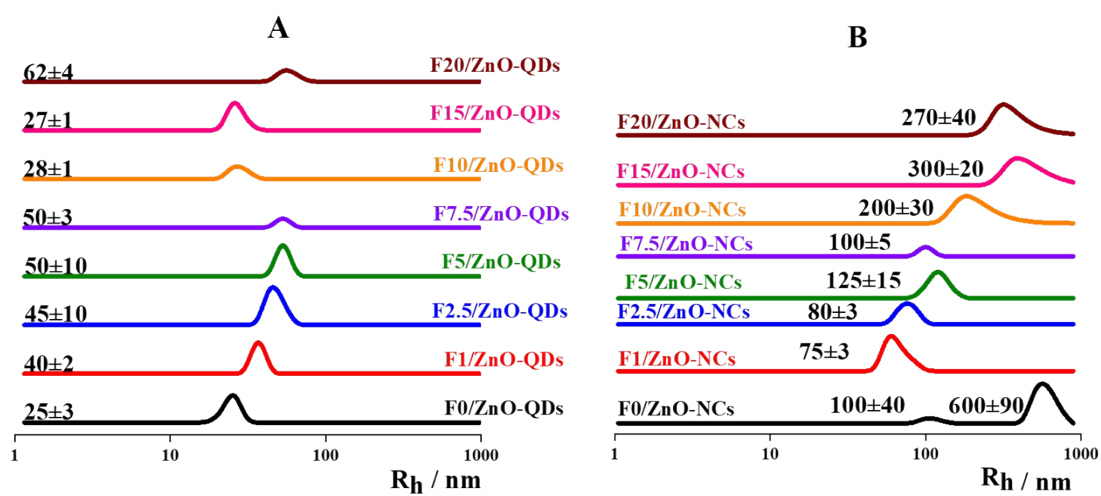
Sample	<R> / nm	<L> /nm	R$_h$ / nm
wet-precipitation synthesis			
F0/ZnO-QDs	3 ± 1		25 ± 3
F1/ZnO-QDs	2.5 ± 0.3		40 ± 2
F2.5/ZnO-QDs	3 ± 1		45 ± 10
F5/ZnO-QDs	3.0 ± 0.8		50 ± 10
F7.5/ZnO-QDs	3.5 ± 0.1		50 ± 3
F10/ZnO-QDs	3.4 ± 0.6		28 ± 1
F15/ZnO-QDs	2.7 ± 0.5		27 ± 1
F20/ZnO-QDs	3.3 ± 0.6		62 ± 4
solvothermal synthesis			
F0/ZnO-NCs		50 ± 30	100 ± 40 and 600 ± 90
F1/ZnO-NCs	28 ± 6		73 ± 3
F2.5/ZnO-NCs	11 ± 2		80 ± 3
F5/ZnO-NCs	11 ± 2		125 ± 15
F7.5/ZnO-NCs	12 ± 3		100 ± 5
F10/ZnO-NCs		26 ± 7	200 ± 30
F15/ZnO-NCs		30 ± 5	300 ± 20
F20/ZnO-NCs	50 ± 10		270 ± 40

Table S4. Experimental values of the diffraction angles (2θ, deg), corresponding Miller indices (hkl), and the cell dimensions of diffraction peaks.

Sample	(100)	(002)	(101)	(102)	(110)	(103)	(200)	(112)	(201)	a /Å	b /Å	c /Å	α/°	β/°	γ/°
F0/ZnO-QDs	31.56°	34.16°	36.21°	47.31°	56.43°	62.80°	66.43°	67.85°	68.86°	3.52	3.52	5.21	89.93	89.91	119.99
F1/ZnO-QDs	31.56°	34.07°	36.21°	47.22°	56.43°	62.80°	66.27°	67.85°	69.03°	3.27	3.28	5.21	90.70	89.49	120.66
F2.5/ZnO-QDs	31.64°	34.32°	36.21°	47.30°	56.50°	62.80°	66.35°	67.77°	69.03°	3.26	3.28	5.21	90.77	89.64	120.77
F5/ZnO-QDs	31.54°	34.32°	36.05°	47.22°	56.59°	62.80°	66.43°	67.85°	69.11°	3.25	3.27	5.21	90.67	89.30	120.33
F7.5/ZnO-QDs	31.54°	34.24°	36.13°	47.28°	56.51°	62.80°	66.43°	67.85°	69.11°	3.24	3.27	5.20	90.48	89.58	120.05
F10/ZnO-QDs	31.64°	34.32°	36.30°	47.28°	56.59°	62.80°	66.35°	67.92°	69.11°	3.25	3.24	5.20	89.81	90.12	119.93
F15/ZnO-QDs	31.54°	34.32°	36.21°	47.30°	56.51°	62.80°	66.51°	67.92°	69.11°	3.25	3.25	5.20	90.07	89.90	120.16
F20/ZnO-QDs	31.72°	34.32°	36.29°	47.28°	56.59°	62.88°	66.43°	67.92°	69.11°	3.25	3.25	5.20	90.01	90.04	120.05
F0/ZnO-NCs	31.63°	34.30°	36.13°	47.48°	56.48°	62.82°	66.09°	67.84°	68.99°	3.24	3.25	5.20	89.97	89.93	119.79
F1/ZnO-NCs	31.70°	34.30°	36.20°	47.56°	56.48°	62.74°	66.32°	67.84°	68.99°	3.25	3.25	5.21	89.98	89.91	119.94
F2.5/ZnO-NCs	31.63°	34.38°	36.20°	47.56°	56.48°	62.83°	66.17°	67.77°	69.07°	3.26	3.26	5.21	89.99	89.63	120.38
F5/ZnO-NCs	31.70°	34.38°	36.20°	47.42°	56.57°	62.88°	66.20°	67.92°	68.99°	3.25	3.25	5.21	89.93	89.91	119.99
F7.5/ZnO-NCs	31.63°	34.38°	36.20°	47.56°	56.57°	62.81°	66.24°	67.84°	68.91°	3.25	3.25	5.21	90.09	89.90	120.02
F10/ZnO-NCs	31.71°	34.38°	36.20°	47.48°	56.57°	62.82°	66.55°	67.92°	69.07°	3.26	3.26	5.22	88.87	90.69	120.21
F15/ZnO-NCs	31.71°	34.45°	36.27°	47.56°	56.57°	62.89°	66.55°	67.84°	69.99°	3.25	3.25	5.21	89.99	90.00	120.01
F20/ZnO-NCs	31.63°	34.53°	36.28°	47.44°	56.48°	62.97°	67.09°	67.92°	69.22°	3.25	3.25	5.21	89.99	90.00	120.03
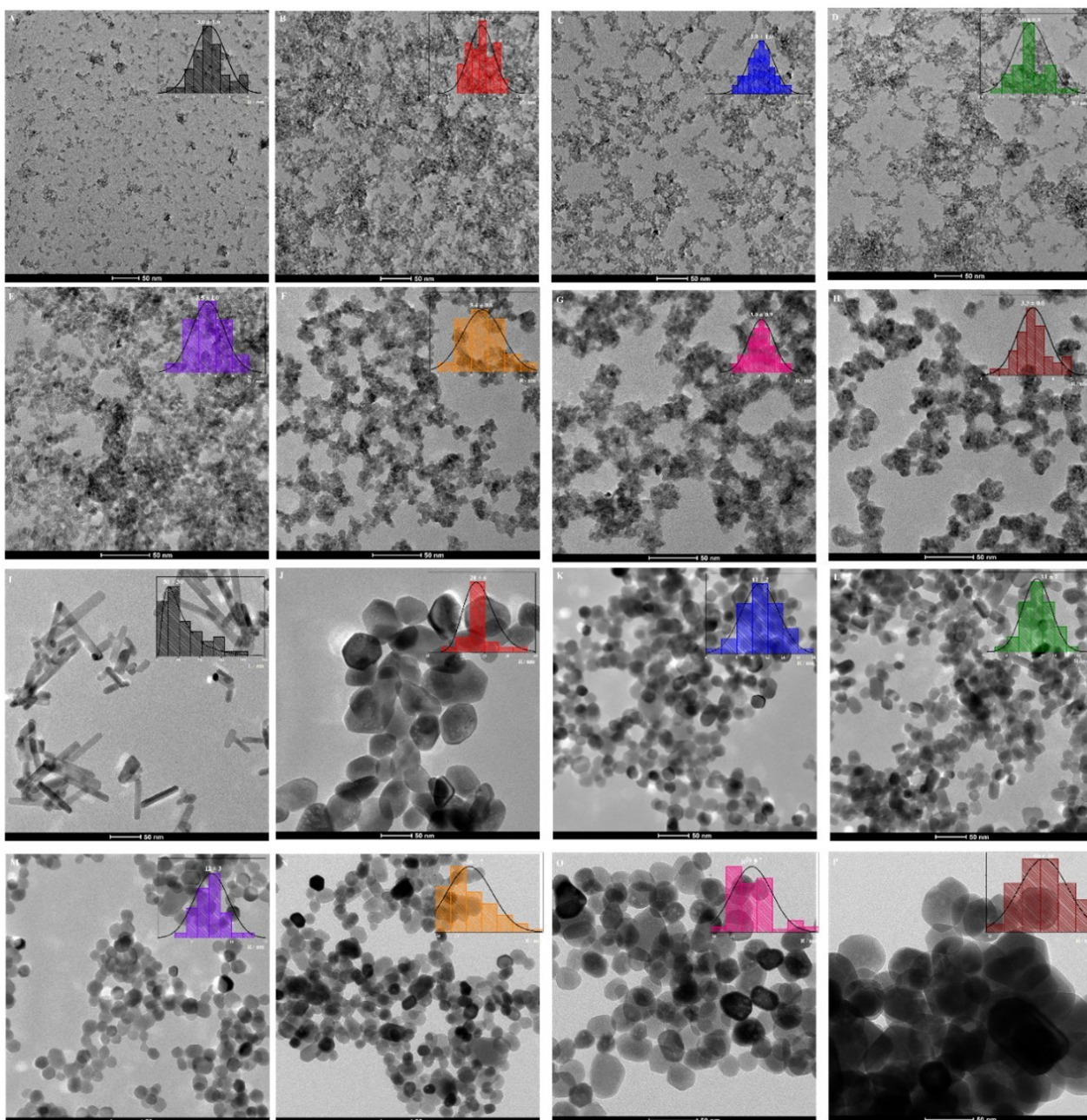
Figure S1. TEM images of undoped and F-doped ZnO were obtained through the two synthetic approaches: F0/ZnO-QDs **(A)**, F1/ZnO-QDs **(B)**, F2.5/ZnO-QDs **(C)**, F5/ZnO-QDs **(D)**, F7.5/ZnO-QDs **(E)**, F10/ZnO-QDs **(F)**, F15/ZnO-QDs **(G)**, F20/ZnO-QDs **(H)**, F0/ZnO-NCs **(I)**, F2.5/ZnO-NCs **(K)**, F5/ZnO-NCs **(L)**, F7.5/ZnO-NCs **(M)**, F10/ZnO-NCs **(N)**, F15/ZnO-NCs **(O)** and F20/ZnO-NCs **(P)** (scalebar: 50 nm).

A

62±4 — F20/ZnO-QDs
27±1 — F15/ZnO-QDs
28±1 — F10/ZnO-QDs
50±3 — F7.5/ZnO-QDs
50±10 — F5/ZnO-QDs
45±10 — F2.5/ZnO-QDs
40±2 — F1/ZnO-QDs
25±3 — F0/ZnO-QDs

R_h / nm

B

F20/ZnO-NCs — 270±40
F15/ZnO-NCs — 300±20
F10/ZnO-NCs — 200±30
F7.5/ZnO-NCs — 100±5
F5/ZnO-NCs — 125±15
F2.5/ZnO-NCs — 80±3
F1/ZnO-NCs — 75±3
F0/ZnO-NCs — 100±40   600±90

R_h / nm

Figure S2. Hydrodynamic radius distribution of F/ZnO-QDs as synthesized through the wet method (in methanol, panel **A**) and through the solvothermal method (in ethanol, panel **B**).
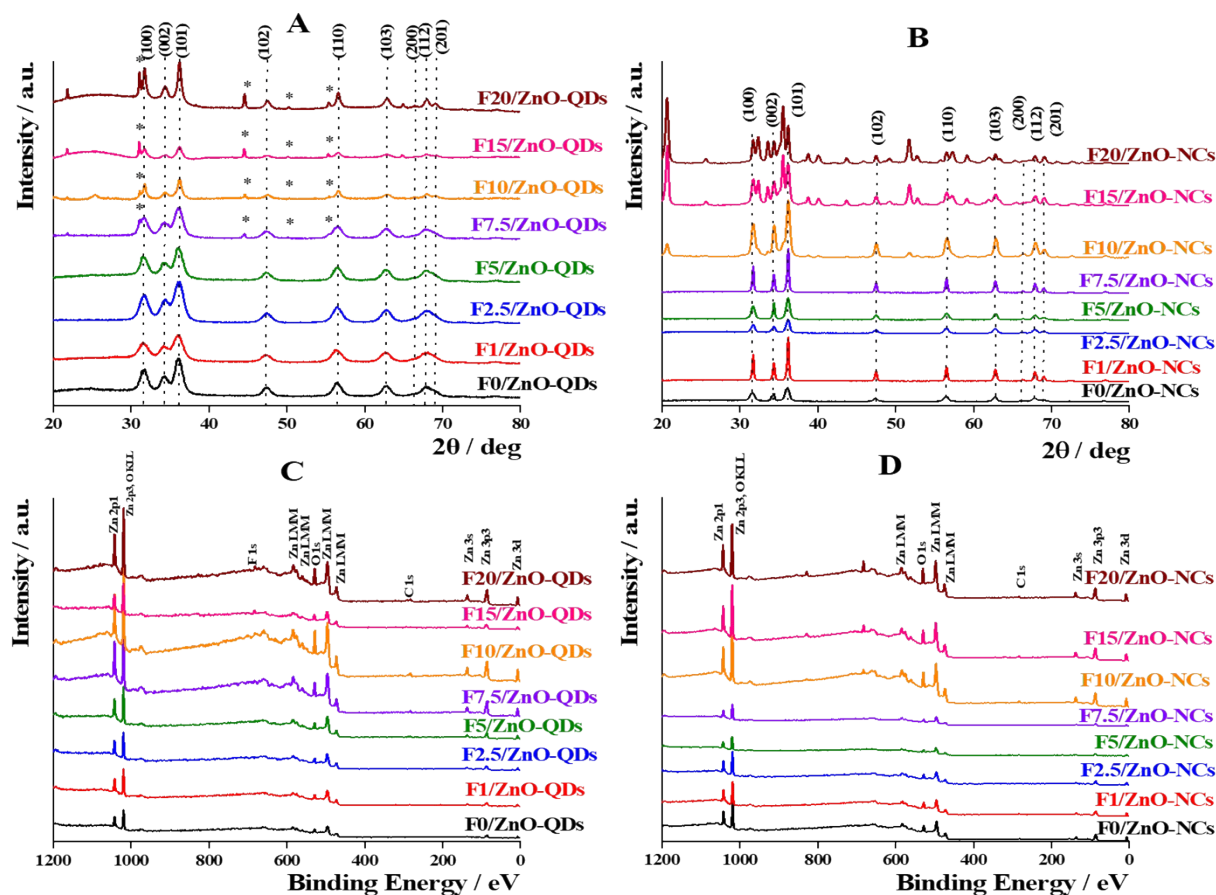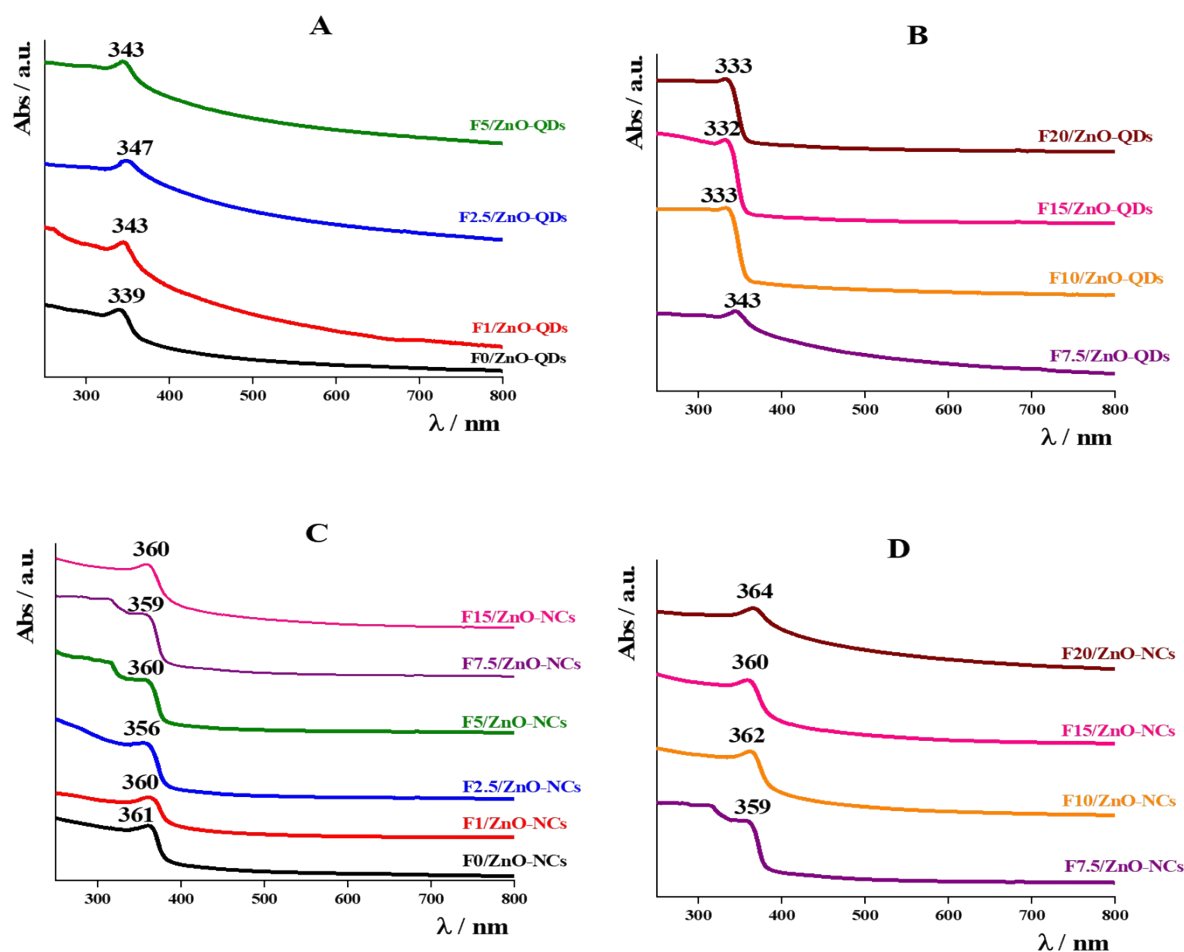
Figure S3. XRD patterns of undoped and F-doped ZnO-QDs as synthesized through the wet method (panel **A**) and of undoped and F-doped Zn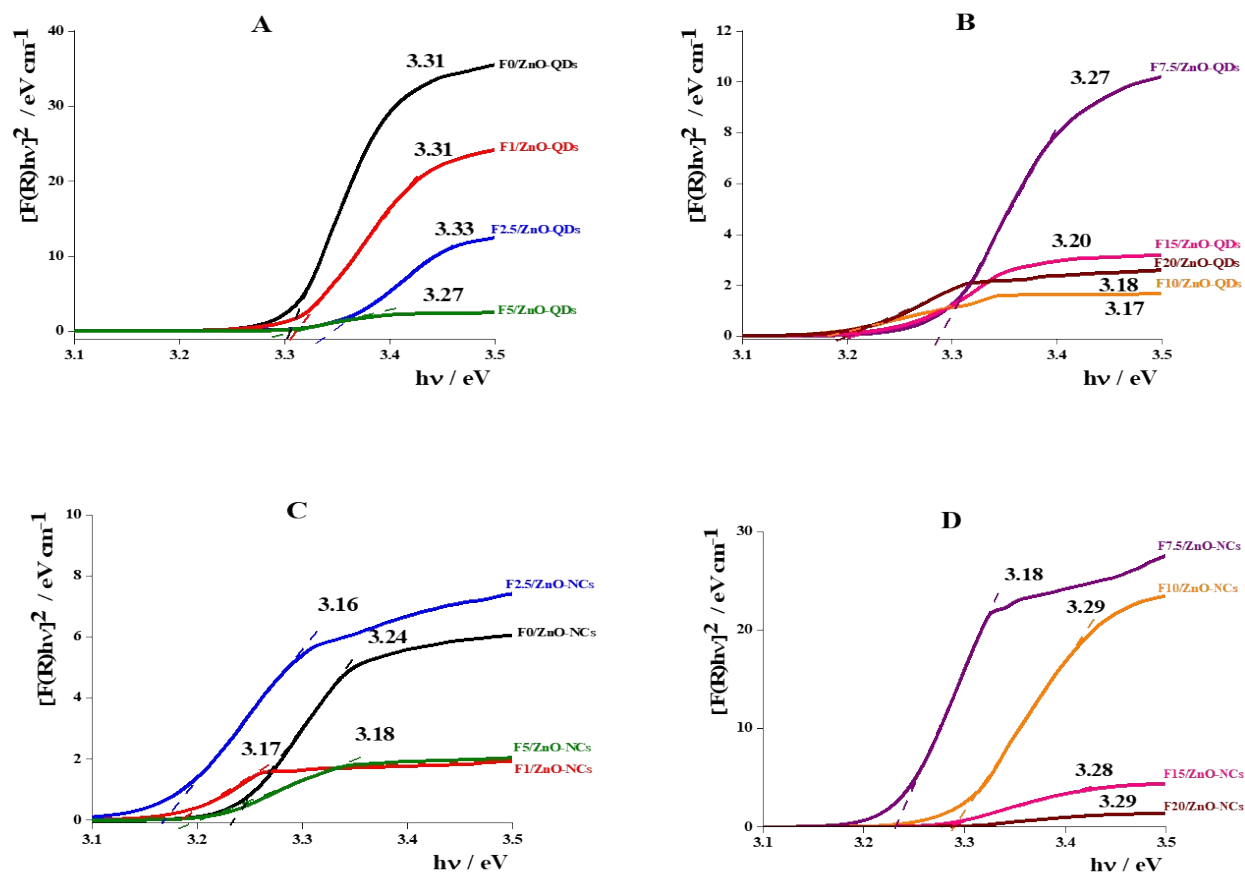O-NCs as synthesized through the solvothermal method (panel **B**). Dot lines indicate ZnO peaks, while stars indicate the ZnF_2 ones; and XPS patterns of undoped and F-doped ZnO-QDs as synthesized through the wet method (panel **C**) and undoped and F-doped ZnO-NCs as synthesized through the solvothermal method (panel **D**).
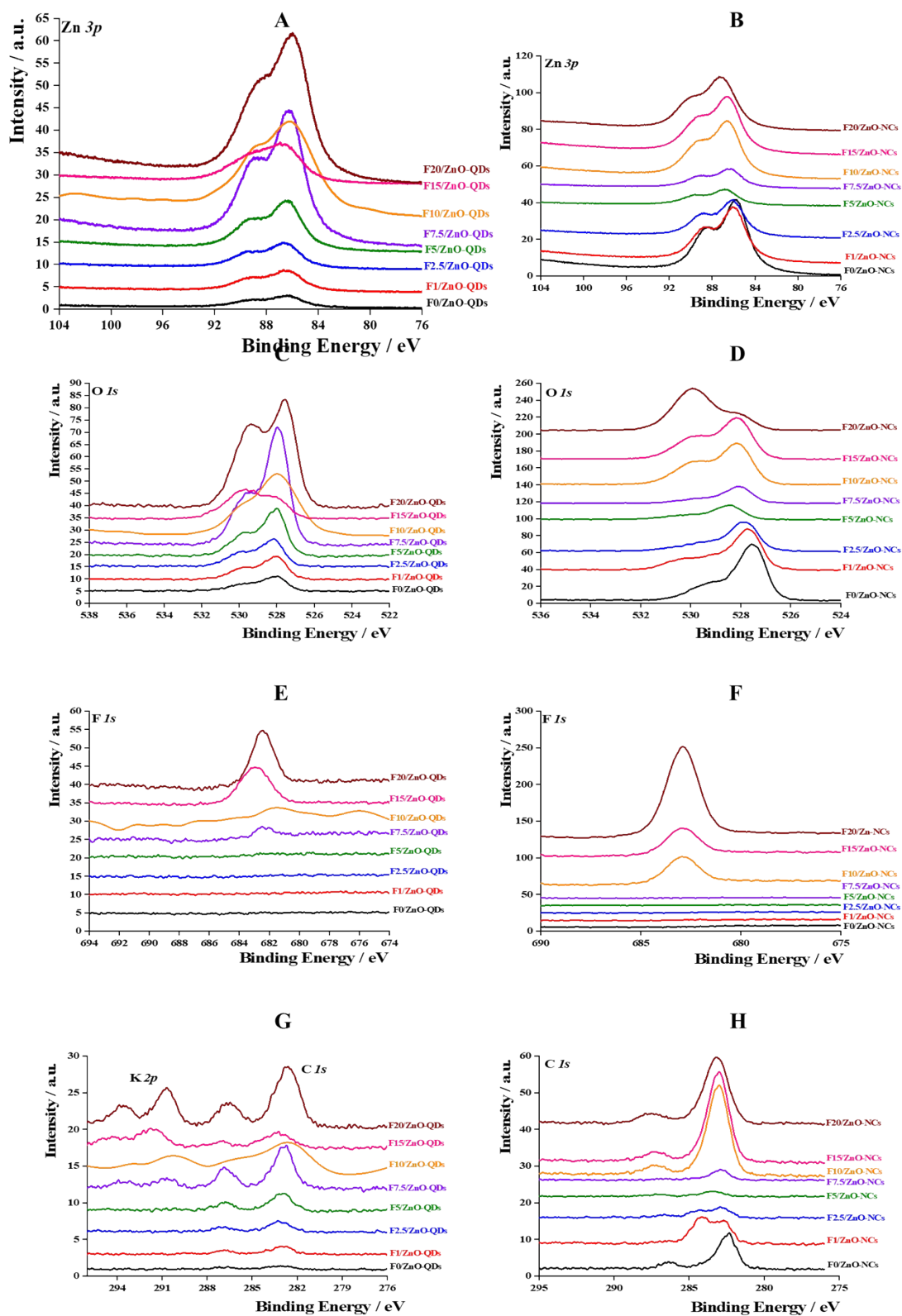
Figure S4. Zn *3p* **(A, B)**, O *1s* **(C, D)**, F *1s* **(E, F)**, and C *1s* **(G, H)** XPS spectra of undoped and F-doped ZnO-QDs as synthesized through the wet method (column on the left) and the solvothermal method (column on the right).
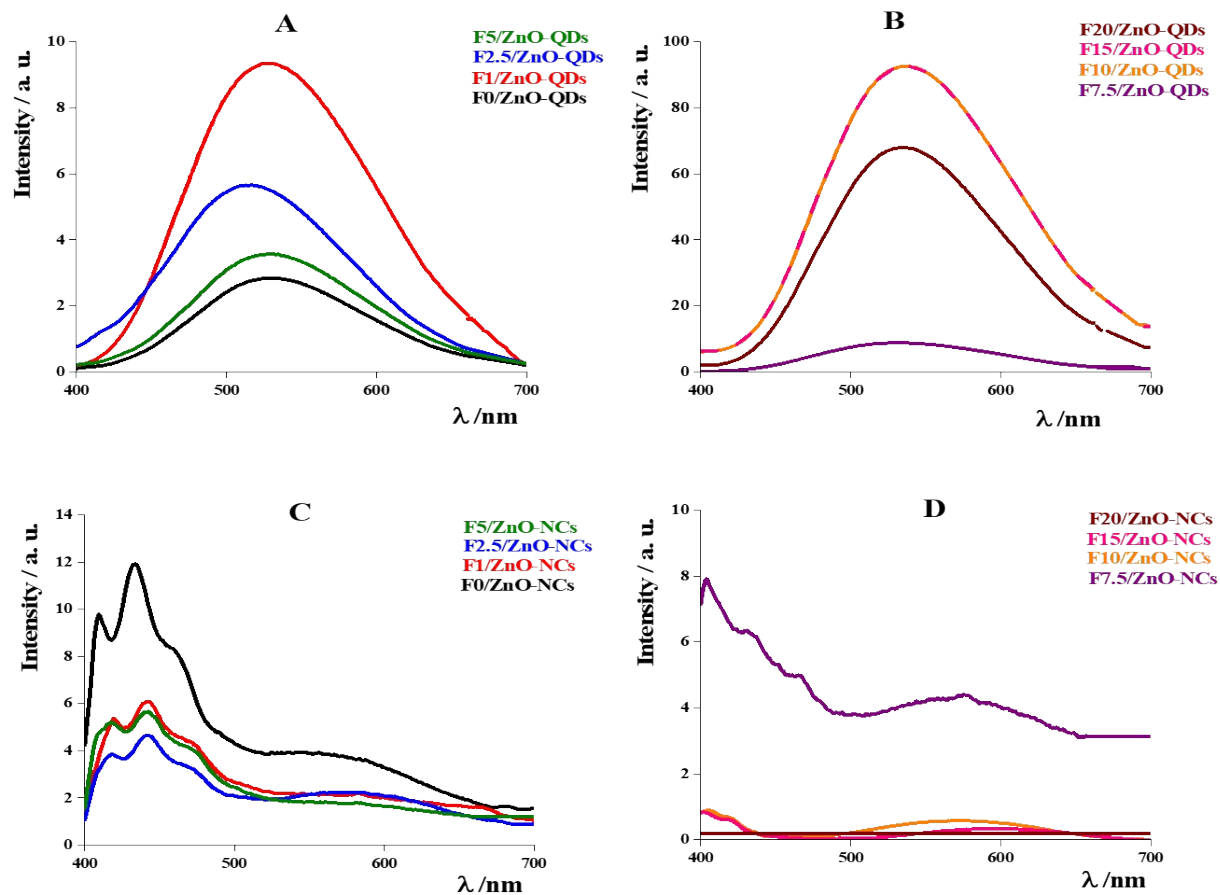
Figure S5. UV-visible spectra of undoped and F-doped ZnO-QDs as synthesized through the wet method (panels **A** and **B**) and the solvothermal method (panels **C** and **D**).
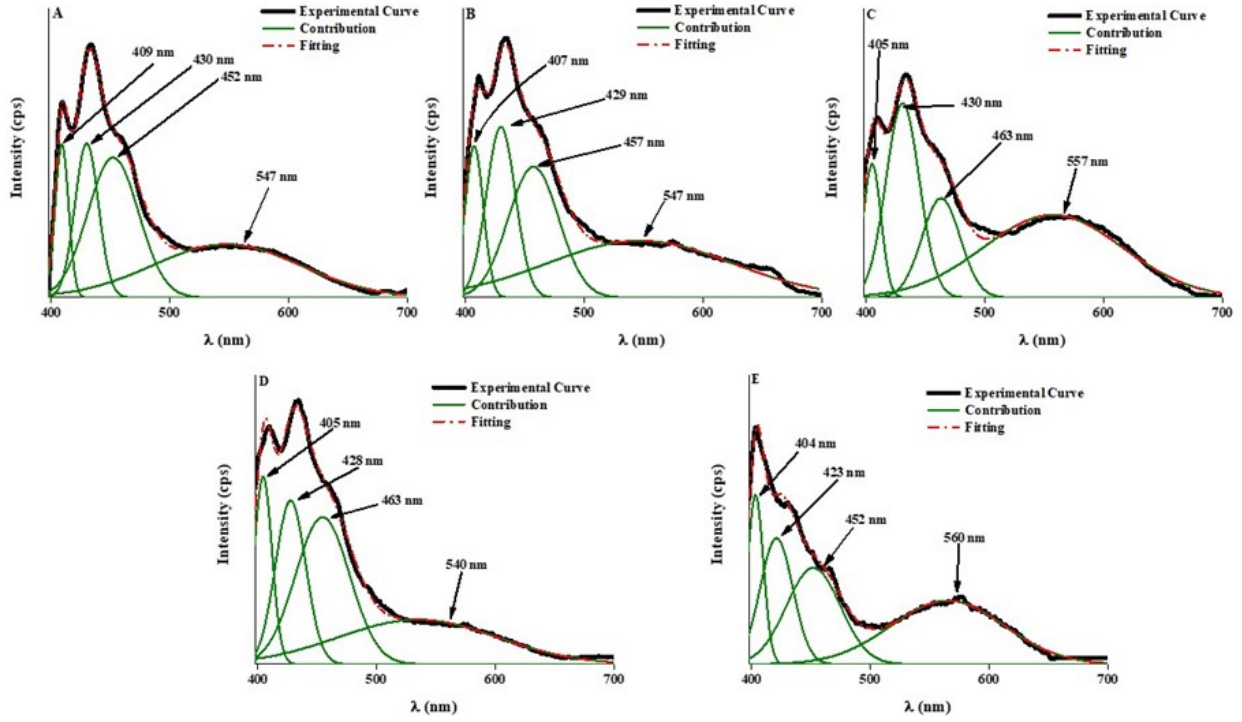
Figure S6. Tauc plot of undoped and F-doped ZnO-QDs as synthesized through the wet method (panels **A** and **B**) and the solvothermal method (panels **C** and **D**).

Figure S7. Fluorescence spectra of undoped and F-doped ZnO-QDs as synthesized through the wet method (panels **A** and **B**) and the solvothermal method (panels **C** and **D**).

Figure S8. Fluorescence spectra deconvolution of F0/ZnO-NCs **(A)**, F1/ZnO-NCs **(B)**, F2.5/ZnO-NCs **(C)**, F5/ZnO-NCs **(D)**, and F7.5/ZnO_NCs **(E)**.

Relative quantum yield calculations

To quantitatively estimate the changes in fluorescence emission, the relative quantum yield (Φ) was determined. Considering the absorption and emission bands of all synthesized nanocrystals, quinine sulfate monohydrate was chosen as an appropriate standard for calculating Φ. Specifically, the quantum yield Φ for F/ZnO-QDs of the wet-precipitation set was calculated as:

$$\Phi = \left(\frac{A_S}{A}\right)\left(\frac{F}{F_S}\right)\left(\frac{n}{n_S}\right)^2 \phi_s \tag{1}$$

where A_s is the absorption of the standard, A is the absorption of the sample, F is the integral of the area below the fluorescence peak of the sample, F_s is the integral of the area below the emission peak of the standard, n, and n_s are the reflective indices of the solvent in which the sample and the standard are solubilized, respectively, and ϕ_s is the quantum yield of the standard ($\phi_s = 0.59$). On the other hand, for the F/ZnO-NCs of the solvothermal set, the relative quantum yield was calculated using the following equation:

$$\Phi = \left(\frac{m}{m_s}\right)\left(\frac{n^2}{n^2_S}\right)\phi_s \tag{2}$$

where m and m_s are the slope obtained from the linear fitting of the graph area of the fluorescence peaks versus absorbance of the sample and the standard, respectively, where the intercept is q=0. In this case, the Φ was calculated considering two emission peaks of these nanocrystals: the first one at 430 nm and related to the zinc-based defects; and the second one at 550 nm and related to the oxygen defects (**Table 3**).