Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information

Synthesis and cathodoluminescence properties of CdSe/ZnO hierarchical nanostructures

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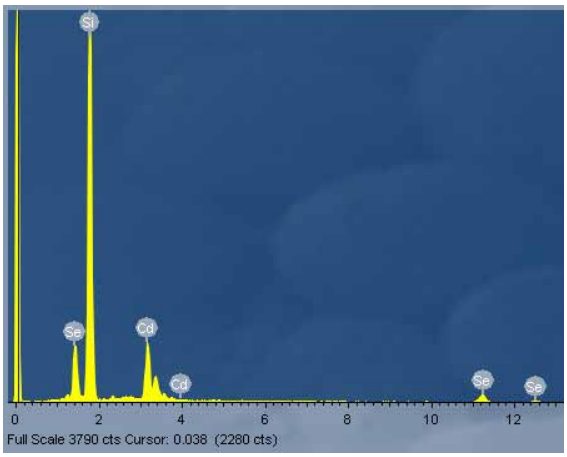
SI_1a: Calculation of lattice mismatch (LM) between hexagonal (hex) ZnO and hexagonal CdSe using their bulk JCPDS data are given below.

$$LM = \frac{difference(a_c, a_b)}{average(a_c, a_b)}$$

	Structure	a	b	c	a-a%	b-b%	c-c%	a-c%
CdSe (core)	**Hex.**	4.30	4.30	7.01				
ZnO (branch)	**Hex.**	3.25	3.25	5.21	27.82	27.82	29.54	19.07537

SI_1b: EDX spectrum and elemental composition of as-grown CdSe nanorods grown by electrochemical deposition at room temperature.



Element	App	Intensity	Weight%	Weight%	Atomic%	
	Conc.	Corrn.		Sigma		
Se L	2.05	0.5974	39.35	1.32	48.02	
Cd L	4.68	0.8839	60.65	1.32	51.98	
Totals			100.00			

SI_2: Structural parameters of the ZnO NHs grown CdSe NR cores in a reaction time of 10 hours is given below with the standard data of ZnO (JCPDS: 01-089-1397).

2θ	Observed d-value (nm)	Standard d-value (nm)	Miller Indices
28.75	0.3103	0.3135	Si (111) (sub)
34.56	0.2595	0.2607	(002)
36.23	0.2477	0.2476	(101)
56.40	0.1631	0.1627	(110)

SI_3: Elemental composition of CdSe/ZnO heterostructures obtained from EDX-ESEM:

Element	**App Conc.**	**Intensity Corrn.**	**Weight%**	**Atomic%**	**Weight% Sigma**	**Atomic ratio**
O K	1.05	0.4351	6.99	26.09	0.76	
Zn K	8.3	1.0196	29.88	27.28	0.74	1.05
Se L	3.29	0.4403	24.68	22.12	0.67	
Cd L	10.39	0.8485	38.45	24.26	0.76	1.10
				100		

SI_4: Roughly estimated dimensions of ZnO NHs grown on CdSe cores from ESEM studies:

Parameter\RT (s)*	**5**	**30**	**60**	**120**	**180**
AD (nm)	13	19	27	32	36
AL (nm)	24	67	90	135	143
ρ (NHs/μm^2)	447	467	573	667	750
TNNHs in 1 μm length	413	431	529	615	691

RT*-reaction time, AD- average diameter, AL- average length, r- density of NHs, TNNHs- total number of nanohairs in 1 micro meter length.

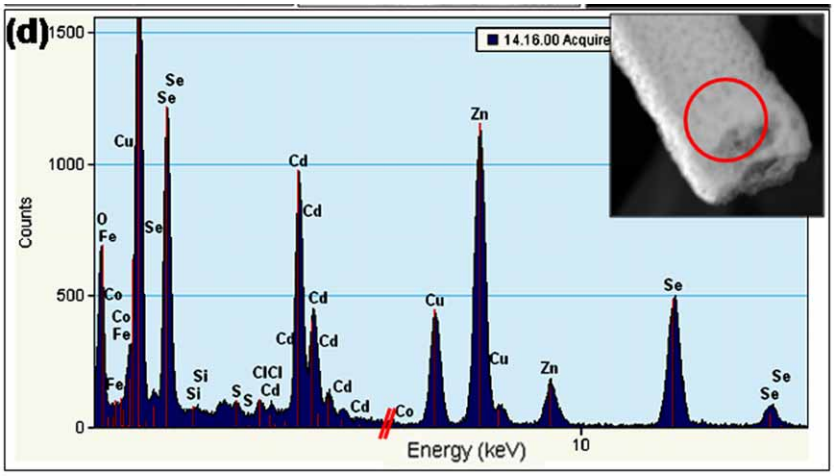
SI_5: Structural parameters of ZnO/CdSe nanostructures evaluated from XRD studies.

RT (minutes)	**ZnO (002)**	
	Height (a.u.)	**FWHM (degrees)**
30	414	0.336
60	638	0.133
120	1716	0.128
240	2796	0.115

SI_6a: The data obtained from the FFT analysis of Figure 6b:

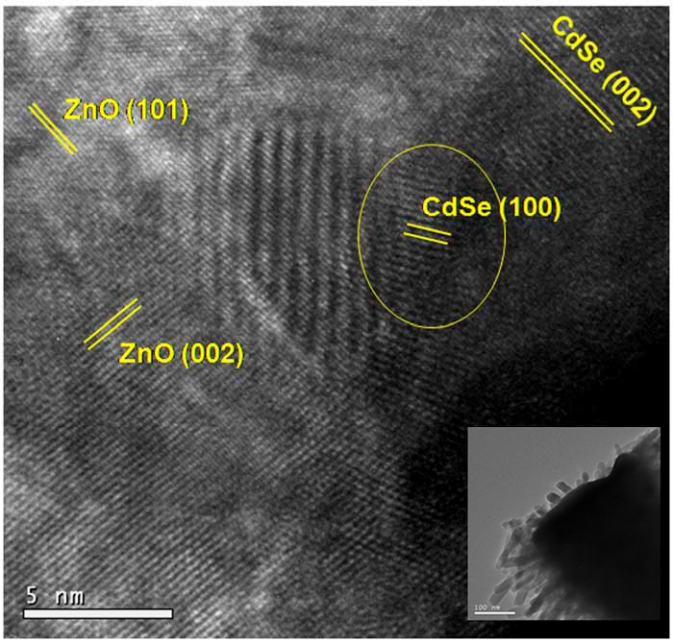
Spot#	d-Spacing (nm)	Rec. Pos. (1/nm)	Degrees to Spot 1	Degrees to x-axis	Amplitude	Identified Phase
1	0.3701	2.702	0.00	139.83	2678.00	CdSe(100)
2	0.3524	2.838	177.58	95.6	13308.00	CdSe(002)
3	0.2157	4.636	25.68	114.15	1749.00	CdSe(110)
4	0.1913	5.226	50.79	89.04	1351.00	ZnO (102)
5	0.1427	7.007	39.89	99.94	922.00	ZnO (200)
6	0.1283	7.795	50.52	89.31	810.00	ZnO (004)

SI_6b: Elemental composition of CdSe/ZnO heterostructures obtained from EDS-STEM:

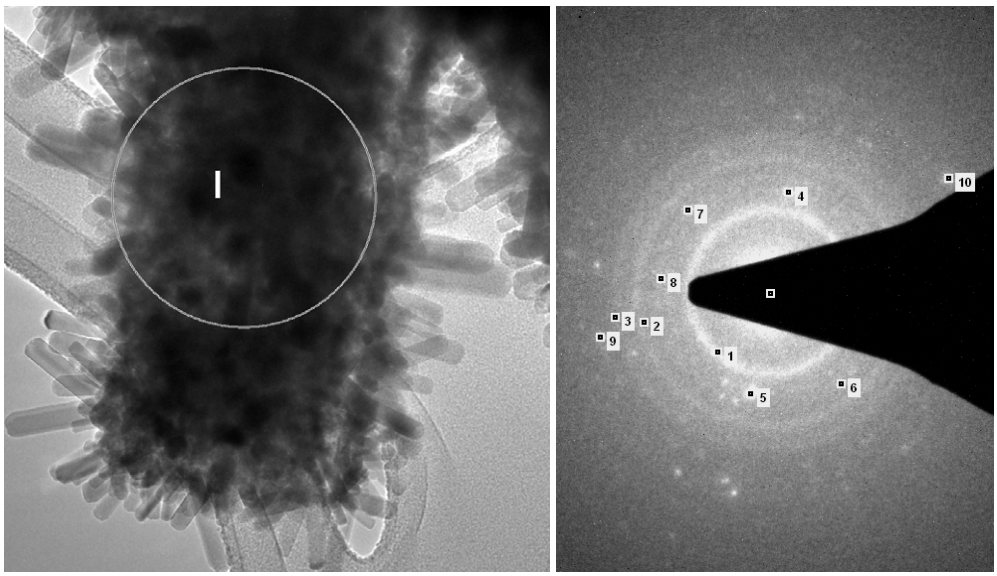


Element	Weight %	Atomic %	Uncert. %	Correction	k-Factor	Atomic ratio
O(K)	6.90	25.80	0.12	0.49	1.94	
Zn(K)	29.70	27.12	0.19	0.99	1.74	1.05
Se(K)	24.02	19.13	0.18	1.00	2.42	
Cd(K)	36.24	22.12	0.45	0.97	7.12	1.16
S(K)	1.88	3.80	0.05	0.92	1.016	
Cl(K)	1.24	2.09	0.03	0.95	1.057	

SI_7: HRTEM image of CdSe/ZnO hierarchical nanostructures:



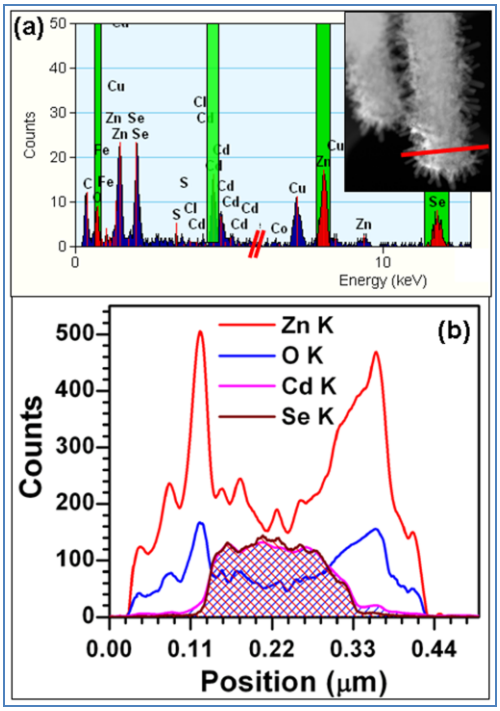
SI_8a: SAED image of CdSe/ZnO heterostructures grown in a reaction time of 60 minutes taken on the marked area in the left TEM image.



Spot#	d-Spacing (nm)	Rec. Pos. (1/nm)	Degrees to Spot 1	Degrees to x-axis	Amplitude	Identified phases
1	0.3692	2.709	0.00	-131.13	185.00	CdSe (100)
2	0.2146	4.659	35.65	-166.79	138.00	CdSe (110)

3	0.1863	5.368	39.84	-170.98	141.00	CdSe (200)
4	**0.2834**	**3.528**	**149.43**	**79.44**	**317.00**	**ZnO (100)**
5	0.2513	3.979	79.30	-51.84	236.00	CdSe (102)
6	**0.2499**	**4.002**	**94.35**	**134.52**	**220.00**	**ZnO (101)**
7	**0.2658**	**3.762**	**56.41**	**172.45**	**200.00**	**ZnO (002)**
8	0.1663	6.012	34.20	-165.33	232.00	CdSe (202) /ZnO (110)
9	0.1368	7.309	163.84	32.70	261.00	CdSe (211) /ZnO (112)

SI_8b: (a) EDS spectrum (inset is the STEM images where the EDS were recorded) and (b) line-scanning elemental mappings of CdSe/ZnO heterostructures.



SI_9: Theoretically evaluated optical band gap of the ZnO nanostructures grown on CdSe NRs at different reaction times (based on the diameter of the as-grown ZnO nanohairs). Here we used the following equation reported elsewhere [x],

$$E_g^* = E_g + \left(\frac{\hbar^2 \pi^2}{2\mu R^2}\right) - \left(\frac{1.8e^2}{\varepsilon R}\right)$$

where E_g^* is the effective band gap, E_g - the band gap of the bulk material, h - Planck's constant, μ - the reduced mass of the carriers, R- radius of the nanostructure, e - charge of the electron, and ε - dielectric constant. To calculate the effective band gap of the nanostructures we used the data reported in the literature as follows:

For ZnO [y]: $E_g \sim 3.4$ eV, h ~ 6.602×10^{-34} Js, μ ~ 0.194 m_o ($1/\mu = 1/m_e^* + 1/m_h^*$; $\therefore m_e^* \sim 0.318\ m_o$, $m_h^* \sim 0.5\ m_o$), m_o - rest mass of the electron, R - from SI3, e - 1.602×10^{-19} C and $\varepsilon \sim \varepsilon_r\varepsilon_o \sim (8.12 \times 8.85 \times 10^{-12}\ C^2/Nm)$.

For CdSe [z]: $E_g \sim 1.75$ eV, h ~ 6.602×10^{-34} Js, μ ~ 0.088 m_o ($1/\mu = 1/m_e^* + 1/m_h^*$; $\therefore m_e^* \sim 0.11\ m_o$, $m_h^* \sim 0.45\ m_o$), m_o - rest mass of the electron, R ~ 60 nm, e - 1.602×10^{-19} C and $\varepsilon \sim \varepsilon_r\varepsilon_o \sim (10.2 \times 8.85 \times 10^{-12}\ C^2/Nm)$.

Table-I ZnO related data:

Parameter\RT (minutes)*	**For ZnO nanostructures Reaction time (minutes)**					
	5	**30**	**60**	**120**	**180**	**240**
Cal. Eg* (eV)	3.461	3.423	3.411	3.410	3.406	3.405
Observed Eg* (eV)			3.543			3.543
	For ZnO nanostructures (~7 nm diameter)					
Cal. Eg* (eV)	3.559					

Table-II CdSe related data:

Diameter (nm)	**Add factor (eV)**	**Eg* (eV)**	**Diameter (nm)**	**Add factor (eV)**	**Eg* (eV)**
3	1.9047	3.655	20	0.0429	1.793
4	1.0714	2.821	25	0.0274	1.777
5	0.6857	2.436	30	0.0190	1.769
6	0.4762	2.226	35	0.0140	1.764
7	0.3498	2.100	40	0.0107	1.761
8	0.2678	2.018	45	0.0085	1.758
9	0.2116	1.962	50	0.0069	1.757
10	0.1714	1.921	100	0.0017	1.752
15	0.0762	1.826	200	0.0004	1.750

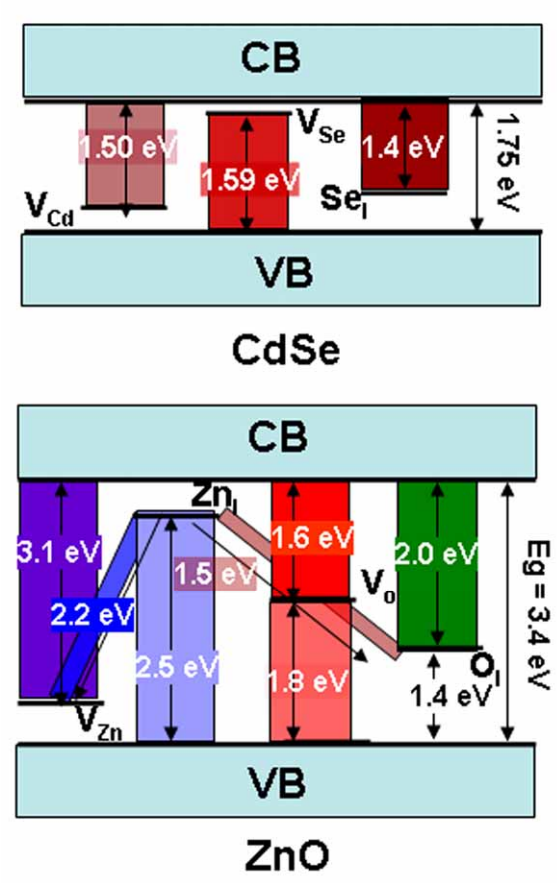
T*-reaction time

[x] L. Brus, J. Phys. Chem. **90**, 2555 (1986).

[y] (a) A. Ohtomo, K. Tamura, K. Saikusa, K. Takahashi, T. Makino, Y. Segawa, H. Koinuma, and M. Kawasaki, Appl. Phys. Lett. **75**, 2635 (1999). (b) D. L. Rode, Semicond. Semimet. **10**, 1 (1975). (c) O. Medelung (Ed.) and Landolt-Bornstein, Semiconductors, Springer, Berlin **III-17**, 35-115 (1998).

[z] A. Urbieta, P. Fernández, and J. Piqueras, J. Appl. Phys., Vol. 96, 2004, 2210.

SI_10: Schematic representation of energy level band diagram of CdSe [x, y] and ZnO with its impurity levels, respectively.

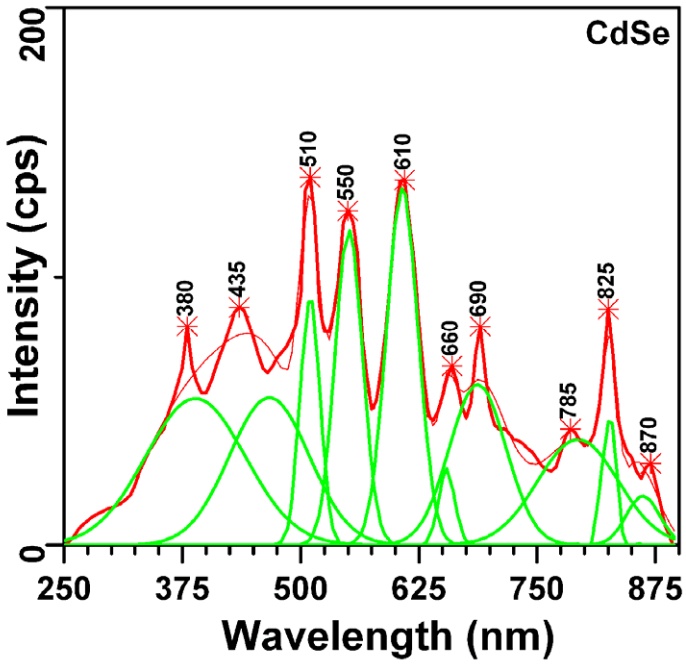


[x] A. Urbieta, P. Fernández, and J. Piqueras, J. Appl. Phys., Vol. 96, 2004, 2210.

[y] A. Urbieta, P. Fernández, and J. Piqueras, Appl. Phys. Lett., Vol. 85, 59687, 2004.

SI_11: De-convoluted CL images of CdSe, CdSe/ZnO grown in 1 hour and CdSe/ZnO grown in 4 hours and the obtained data are given below. The equation used to calculate the peak intensity ratio and percentage of improvement in their intensities are also state bellow.

For CdSe:



[30/12/2009 16:59 "/Graph1" (2455195)]

Gauss(10) fit to Smoothed23_Book1M:

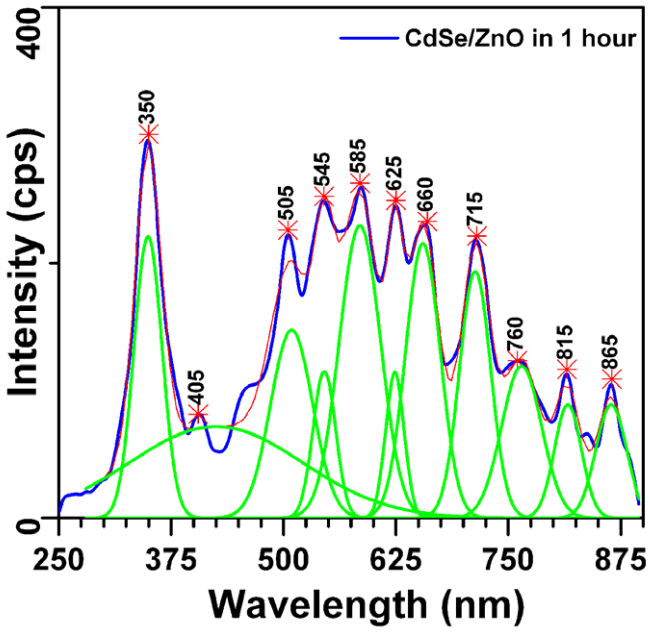
Chi^2/DoF 37

R^2 1

Peak	Area	Center	Width	Height	
1	7174.3	388.76	104.97	54.532	
2	5802.9	466.89	84.334	54.901	
3	**2424.1**	**509.90**	**20.684**	**93.512**	**(peaks matched with**
4	**4277.7**	**550.88**	**28.991**	**117.73**	**other structures)**
5	5569.7	607.39	33.382	133.12	
6	**596.23**	**659.32**	**16.762**	**28.380**	
7	**4489.1**	**687.16**	**59.990**	**59.707**	**(CdSe NBE peak)**
8	4204.6	793.18	85.246	39.354	
9	871.88	825.69	13.053	53.294	
10	**805.36**	**870.71**	**35.170**	**18.271**	

Y offset = 0

For CdSe/ZnO: grown in 1 hour reaction time:



[03/01/2010 12:15 "/Graph1" (2455199)]

Gauss(11) fit to Smoothed24_Book1D:

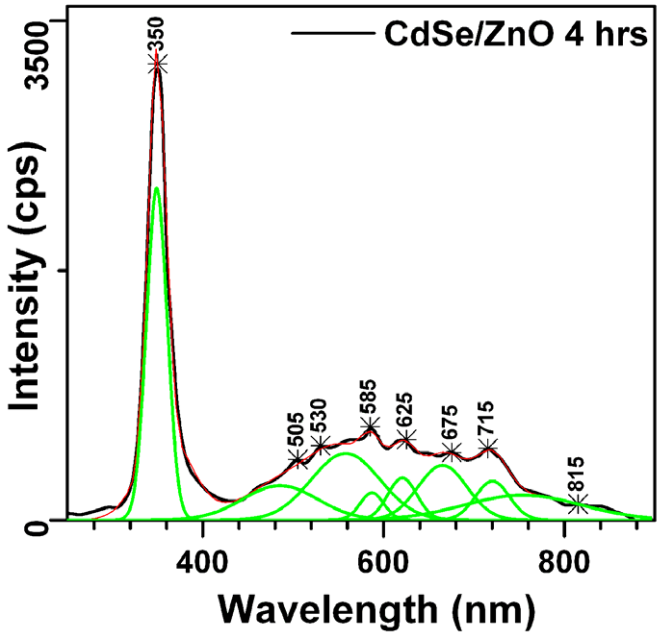
Chi^2/DoF 132

R^2 1

Peak	Area	Center	Width	Height	
1	**8653.4**	**349.31**	**28.818**	**239.59**	**(ZnO NBE peak)**
2	17237	424.87	191.78	71.713	
3	**8619.6**	**505.06**	**45.199**	**152.16**	
4	**3613.0**	**545.36**	**21.983**	**131.13**	
5	13164	584.90	44.182	237.73	
6	2928.2	623.78	16.808	139.01	
7	**10400**	**654.97**	**36.607**	**226.68**	
8	8403.5	715.07	32.468	206.52	
9	6605.0	764.75	42.702	123.41	
10	3339.4	816.22	27.565	96.661	
11	**3800.9**	**864.38**	**32.034**	**94.669**	

Y offset = 0

For CdSe/ZnO: grown in 4 hours reaction time:



[03/01/2010 12:40 "/Graph1" (2455199)]

Gauss(9) fit to Smoothed25_Book1G:

Chi^2/DoF 2180

R^2 1

Peak	Area	Center	Width	Height	
1	**66547**	**349.31**	**19.172**	**2769.5**	**(ZnO NBE peak)**
2	**25037**	**485.50 (505)**	**82.245**	**242.89**	
3	**44553**	**558.08 (530)**	**75.257**	**472.35**	
4	6290.4	584.91	22.973	218.47	
5	11845	624.77	29.521	320.15	
6	25959	669.15 (675)	52.813	392.18	
7	12787	715.28	35.373	288.44	
8	28166	753.81 (816)	128.50	174.90	

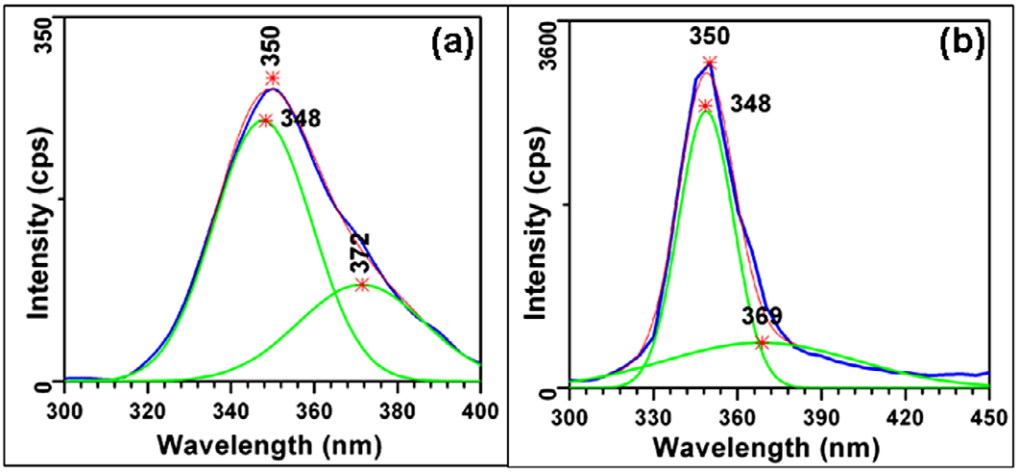
Y offset = 0

*number given in brackets indicates its actual peak position.

Intensity ratio = CdSe/ZnO peak intensity/bare CdSe peak intensity

Improvement percentage in emission intensity = (CdSe/ZnO intensity - bare CdSe intensity)*100/(CdSe/ZnO intensity + bare CdSe intensity)

SI_12: CL spectra of CdSe/ZnO hierarchical nanostructures grown in a reaction time of (a) 1 and (b) 4 hours, which are divided into two bands by Gaussian fitting of the QCUV peak.



The data obtained from Gaussian fit of the above curves:

1. CdSe/ZnO structures grown in a reaction time of 1 hour

Peak	Center (nm)	FWHM (nm)	Height (cps)
1	**347.64**	**23.228**	**249.71**
2	**370.97**	**29.660**	**93.084**

2. CdSe/ZnO structures grown in a reaction time of 4 hour

Peak	Center (nm)	FWHM (nm)	Height (cps)
1	**348.81**	**19.298**	**2768.4**
2	**368.33**	**68.220**	**443.25**

*FWHM – full width at half maximum

SI_13: CL measurements on the ZnO ALD-seeded CdSe NRs. From this CL spectrum, a clear QCUV peak related to ZnO nanoparticles, formed using Atomic Layer Deposition, on CdSe NRs with an average thickness of ~7 nm can be noticed (also, TEM measurements confirmed the presence of a dense nanoparticles layer formed by ALD at our particular deposition conditions, with a nanoparticle average diameter of 6-7nm). Apart from this, few additional peaks related to ZnO can be noticed. Thus, it is a clear that the observed QCUV peak from CdSe/ZnO hierarchical nanostructures is originated from ZnO nanoparticles, as well as nanohairs, having an average diameter of ~7 nm.