

Structural and optical properties of sol-gel derived Cr-doped ZnO diluted magnetic semiconductor nanocrystals: an EXAFS study to relate the local structure

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Supplementary Document

Table-S1: Best fit results of the EXAFS measurements on Cr doped ZnO samples at Zn K edge:
(Typical uncertainty for CN $\sim \pm 10\%$; R $\sim \pm 0.02$ Å; $\sigma^2 \sim \pm 0.001$ Å²).

		Cr 0	Cr 0.5	Cr 1	Cr 1.5	Cr 2	Cr 4	Cr 6
Zn-O	CN(4)	4.16	2.8	2.76	2.84	2.56	2.6	2.48
	R(1.97Å)	1.93	1.95	1.95	1.95	1.95	1.98	1.95
	σ^2 (Å ²)	0.008	0.004	0.001	0.002	0.002	0.002	0.002
Zn-Zn	CN(12)	11.8	11.04	10.86	11.52	11.76	11.05	10.82
	R(3.20Å)	3.22	3.23	3.22	3.23	3.22	3.21	3.23
	σ^2 (Å ²)	0.008	0.008	0.009	0.008	0.009	0.009	0.009
R-factor		0.002	0.001	0.002	0.002	0.002	0.004	0.001

Table S2: Fit parameters by assuming wurtzite ZnO structure with Cr at Zn sites.
(Typical uncertainty for CN $\sim \pm 10\%$; R $\sim \pm 0.02 \text{ \AA}$; $\sigma^2 \sim \pm 0.001 \text{ \AA}^2$).

		Cr 1	Cr 2	Cr 4	Cr 6
Cr-O	CN(4)	2.96	5.2	3.24	3.69
	R(1.97 $\text{\AA}$)	1.96	1.96	1.96	1.96
	$\sigma^2 (\text{\AA}^2)$	0.005	0.003	0.001	0.002
Cr-Zn	CN(12)	1.54	8.1	6.7	5.04
	R(3.20 $\text{\AA}$)(3.25 $\text{\AA}$)	2.94	2.96	2.9	2.95
	$\sigma^2 (\text{\AA}^2)$	0.001	0.005	0.005	0.005
R-factor		0.003	0.002	0.003	0.003

Table-S3: Fit parameters by assuming Cr₂O₃ structure.
(Typical uncertainty for CN $\sim \pm 10\%$; R $\sim \pm 0.02 \text{ \AA}$; $\sigma^2 \sim \pm 0.001 \text{ \AA}^2$).

		Cr 1	Cr 2	Cr 4	Cr 6
Cr-O	CN(6)	5.64	6.48	6.48	6.06
	R(1.97 $\text{\AA}$)	2.01	2.00	2.03	2.02
	$\sigma^2 (\text{\AA}^2)$	0.018	0.005	0.017	0.014
Cr-Cr/Zn	CN(2)	1.81	1.99	1.96	1.90
	R(2.58 $\text{\AA}$)	2.51	2.46	2.51	2.52
	$\sigma^2 (\text{\AA}^2)$	0.008	0.004	0.001	0.005
Cr-Cr/Zn	CN(2)	4.16	4.12	4.06	4.0
	R(2.88 $\text{\AA}$)	2.94	3.01	3.01	3.00
	$\sigma^2 (\text{\AA}^2)$	0.02	0.001	0.007	0.009
R-factor		0.006	0.002	0.002	0.008

Table-S4: Observed Raman peaks of $\text{Zn}_{1-x}\text{Cr}_x\text{O}$ ($0 \leq x \leq 0.06$) nanoparticles and their symmetry assignments.

Vibration frequency (cm^{-1})							Assignments	Process
Cr0	Cr0.5	Cr1	Cr1.5	Cr2	Cr4	Cr6		
329	328.71	327.58	328.71	329.84	328.71	329.56	$\text{E}_{2\text{H}}-\text{E}_{2\text{L}}$	Second order
378	377.32	379.21	377.44	377.37	380.12	384.30	$\text{A}_1(\text{TO})$	First order
408	409.58	411.86	413.18	414.31	413.20	418.28	$\text{E}_1(\text{TO})$	First order
434	434.59	433.46	434.59	434.59	433.46	434.68	$\text{E}_{2\text{H}}$	First order
-----	480.78	477.34	476.43	477.44	470.94	472.96	-----	NM1
-----	523.38	529.01	530.18	529.39	530.37	536.60	-----	NM2
575	578.76	575.38	576.51	577.63	575.38	578.29	$\text{A}_1(\text{LO})$	First order
585	-----	-----	-----	-----	-----	-----	$\text{E}_1(\text{LO})$	First order
658	655.73	660.01	668.52	672.11	686.89	684.36		Second order
-----	852.46	856.93	853.56	852.26	851.59	850.80	-----	-----
1142	1149.8	1144.1	1147.5	1143	1144.1	1147.5		Second order

Table-S5: Different vibrational modes obtained from FTIR study of $\text{Zn}_{1-x}\text{Cr}_x\text{O}$ nanocrystals.

Sample	Zn-O bond (cm^{-1})	New band	Citrate Precursor (cm^{-1})	Asymmetric C=O stretching mode of Zinc citrate (cm^{-1})	Symmetric stretching of C=O in Zinc citrate (cm^{-1})	CO_2 molecules in Air (cm^{-1})	C-H bond (cm^{-1})	O-H bond (cm^{-1})
ZnO	437	649	874	1385	1620	2345	2927	3468
$\text{Zn}_{0.995}\text{Cr}_{0.005}\text{O}$	427	645	889	1384	1604	2343	2923	3456
$\text{Zn}_{0.99}\text{Cr}_{0.01}\text{O}$	431	640.	898	1384	1602	2347	2923	3447
$\text{Zn}_{0.985}\text{Cr}_{0.015}\text{O}$	438	635	895	1384	1602	2347	2926	3439
$\text{Zn}_{0.98}\text{Cr}_{0.02}\text{O}$	444	638	902	1384	1615	2341	2931	3447
$\text{Zn}_{0.96}\text{Cr}_{0.04}\text{O}$	455	641	904	1384	1612	2347	2931	3442
$\text{Zn}_{0.94}\text{Cr}_{0.06}\text{O}$	438	644	920	1384	1612	2347	2924	3440

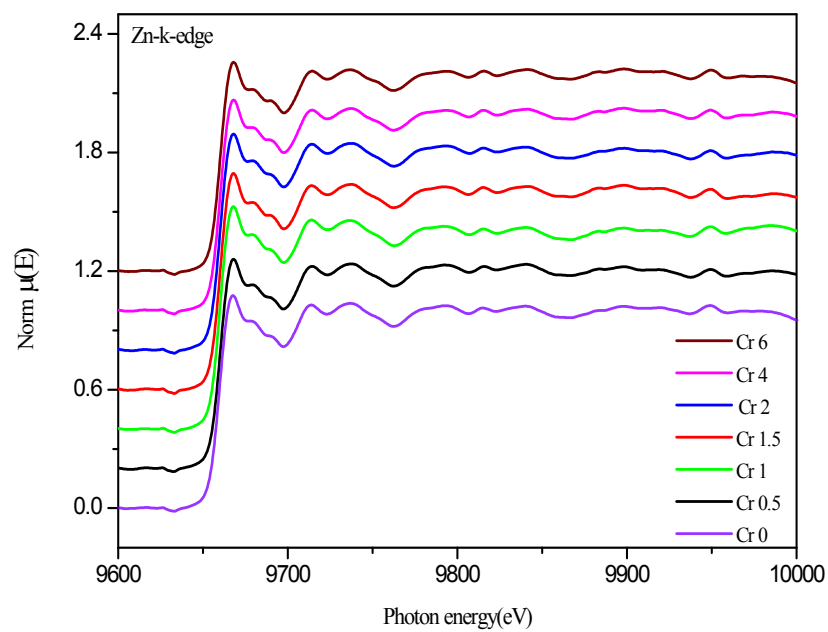


Figure S1: Normalized experimental Zn K-edge EXAFS ($\mu(E)$ versus E) spectra of undoped and Cr doped ZnO nanocrystals.

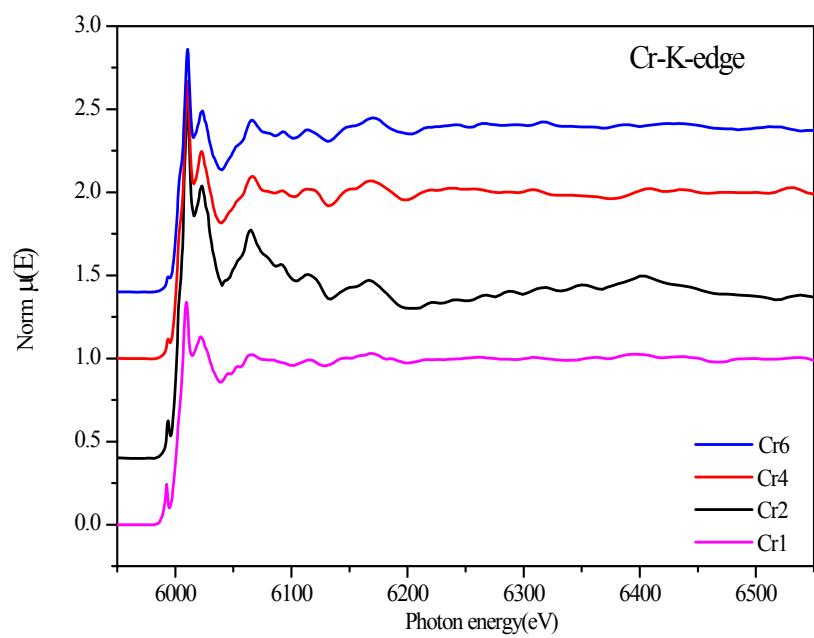


Figure S2: Normalized experimental Cr K-edge EXAFS ($\mu(E)$ vs E) spectra of Cr doped ZnO nanocrystals.