

Supplementary Information for the Manuscript

Size-dependent photoluminescence of zinc oxide quantum dots through organosilane functionalization

Viorica Muşat,^{,a} Aurel Tăbăcaru,^a Bogdan Ştefan Vasile,^b Vasile-Adrian Surdu^b*

*Corresponding author

E-mail address: viorica.musat@ugal.ro; telephone: +40-757070613.

Synthesis of ZnO QDs grafted with MPS

ZnO QDs were synthesized according to a slightly modified precipitation method reported in the literature.¹ For the sake of completeness, we give the detailed synthetic procedure, as follows: in 10 mL of methanol heated in a 100 mL round bottomed flask until 55 °C, different amounts of 3-(trimethoxysilyl)propylmethacrylate (MPS) were added in order to reach the Si/Zn molar ratio of 0, 2, 5 and 10%. After a further heating to 60 °C for 10 min, zinc acetate dihydrate was added in the reaction vessel. A basic solution of 1.25 g of potassium hydroxide, separately dissolved in 5 mL of methanol, was added dropwise. The white suspensions so obtained were stirred for 3 hours under reflux, centrifuged (9000 rpm, 5 min), washed with three portions of methanol (10 mL), and finally dried in air at 100 °C for three hours.

Table S1. Relevant crystallographic data for the unmodified ZnO and MPS-grafted ZnO QDs

	ZnO	ZnO-MPS 2%	ZnO-MPS 5%	ZnO-MPS 10%
Crystal System	Hexagonal	Hexagonal	Hexagonal	Hexagonal
SPGR, Z	<i>P6₃mc</i> , 2	<i>P6₃mc</i> , 2	<i>P6₃mc</i> , 2	<i>P6₃mc</i> , 2
a, Å	3.250083447	3.250510216	3.24973011	3.249323368
b, Å	3.250083447	3.250510216	3.24973011	3.249323368
c, Å	5.206603527	5.207901001	5.209373951	5.212234497
α, °	90	90	90	90
β, °	90	90	90	90
γ, °	120	120	120	120
V, Å³	47.6293	47.65368	47.64428	47.65835
Mean crystallite size (nm)	7.569	5.24	4.342	4.189
T, K	298	298	298	298
R_p, R_{wp}	5.8606, 7.5951	6.7876, 8.3636	7.1158, 8.5534	7.2465, 8.8305
R_{expected}	5.5439	5.5114	5.5391	5.3924
GoF	1.8768	2.3028	2.3845	2.6817

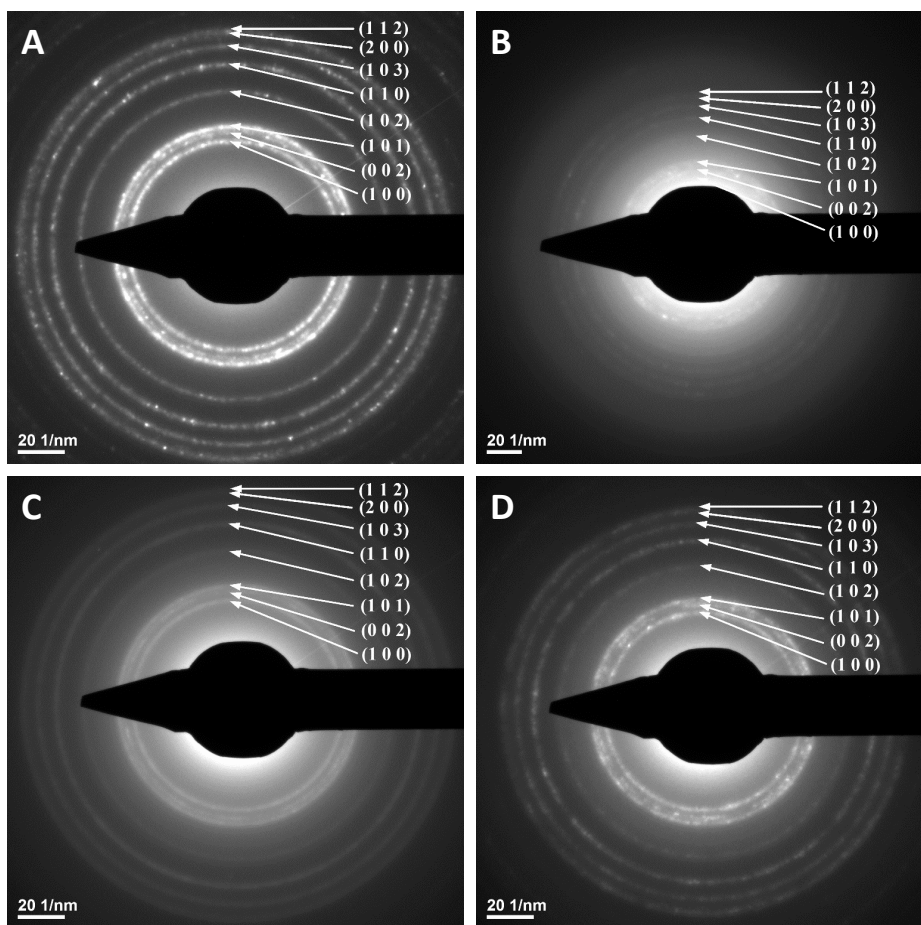


Figure S1. Electron diffraction patterns of unmodified ZnO (A), ZnO-MPS 2% (B), ZnO-MPS 5% (C) and ZnO-MPS 10% (D).

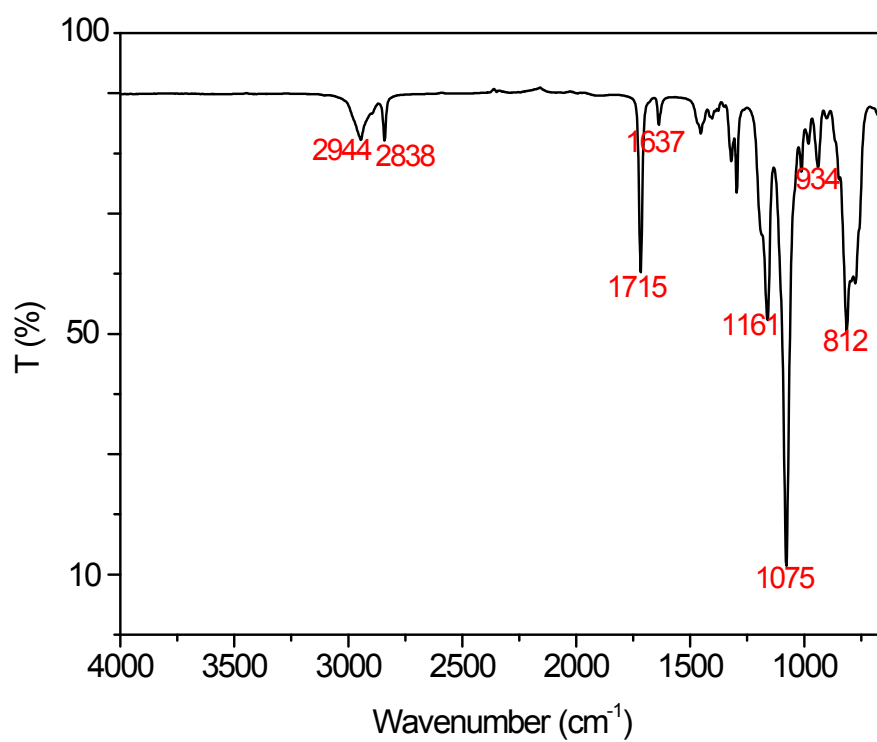
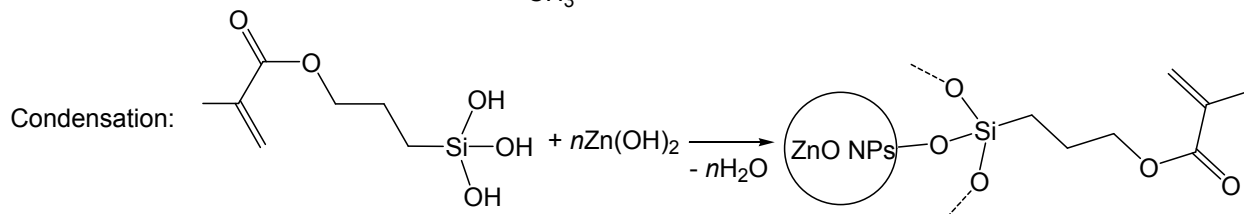
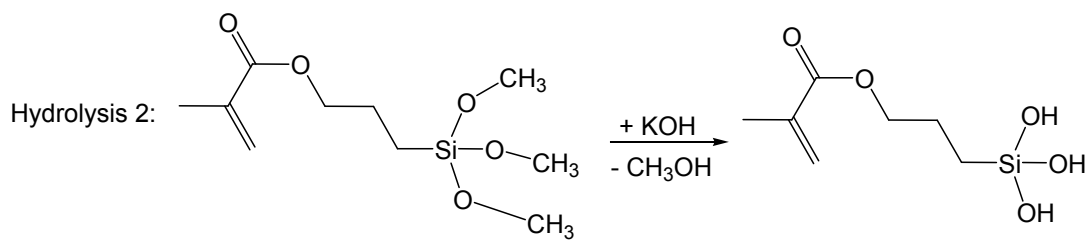


Figure S2. Infrared spectrum of free MPS



Scheme S1. Reaction schemes for MPS grafting of ZnO QDs

Table S2. Proposed stoichiometric formulae of unmodified ZnO and MPS-modified ZnO QDs

Sample	Proposed formula	Elem. Anal. (found)		Elem. Anal. (calcd.)	
		C (%)	H (%)	C (%)	H (%)
ZnO	$(\text{ZnO})_{25}\text{Zn}_2(\text{OH})_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2$	2.089	0.485	2.041	0.513
ZnO-MPS 2%	$(\text{ZnO})_{31}\text{Zn}_2(\text{OH})_4(\text{CH}_3\text{COO})(\text{C}_7\text{H}_{11}\text{O}_5\text{Si})(\text{H}_2\text{O})_2$	3.567	0.746	3.579	0.734
ZnO-MPS 5%	$(\text{ZnO})_{33}\text{Zn}_3(\text{OH})_7(\text{CH}_3\text{COO})(\text{C}_7\text{H}_{11}\text{O}_5\text{Si})_2(\text{H}_2\text{O})_2$	5.434	1.037	5.487	1.036
ZnO-MPS 10%	$(\text{ZnO})_{41}\text{Zn}_4(\text{OH})_{10}(\text{CH}_3\text{COO})(\text{C}_7\text{H}_{11}\text{O}_5\text{Si})_3(\text{H}_2\text{O})_3$	6.111	1.151	6.151	1.167

REFERENCES

-
- ¹ M. Kotecha, W. Veeman, B. Rohe, M. Tausch, *Microporous and Mesoporous Materials* 2006, **95**, 66.