Electronic Supplementary Material (ESI) for Nanoscale.

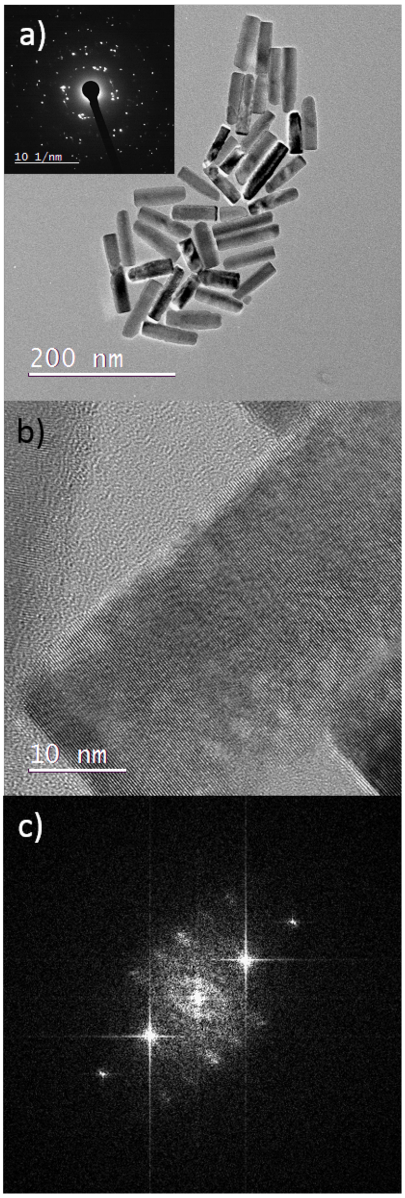
Nanoparticle Shape Anisotropy and Photoluminescence Properties: Europium containing ZnO as a Model Case

Melanie Gerigk,[a] Philipp Ehrenreich,[a] Markus. R. Wagner,[b] Ilona Wimmer,[a] Juan Sebastian Reparaz,[b] Clivia M. Sotomayor Torres,[b,c] Lukas Schmidt-Mende,[a] and Sebastian Polarz[a*]

Electronic Supplementary Information

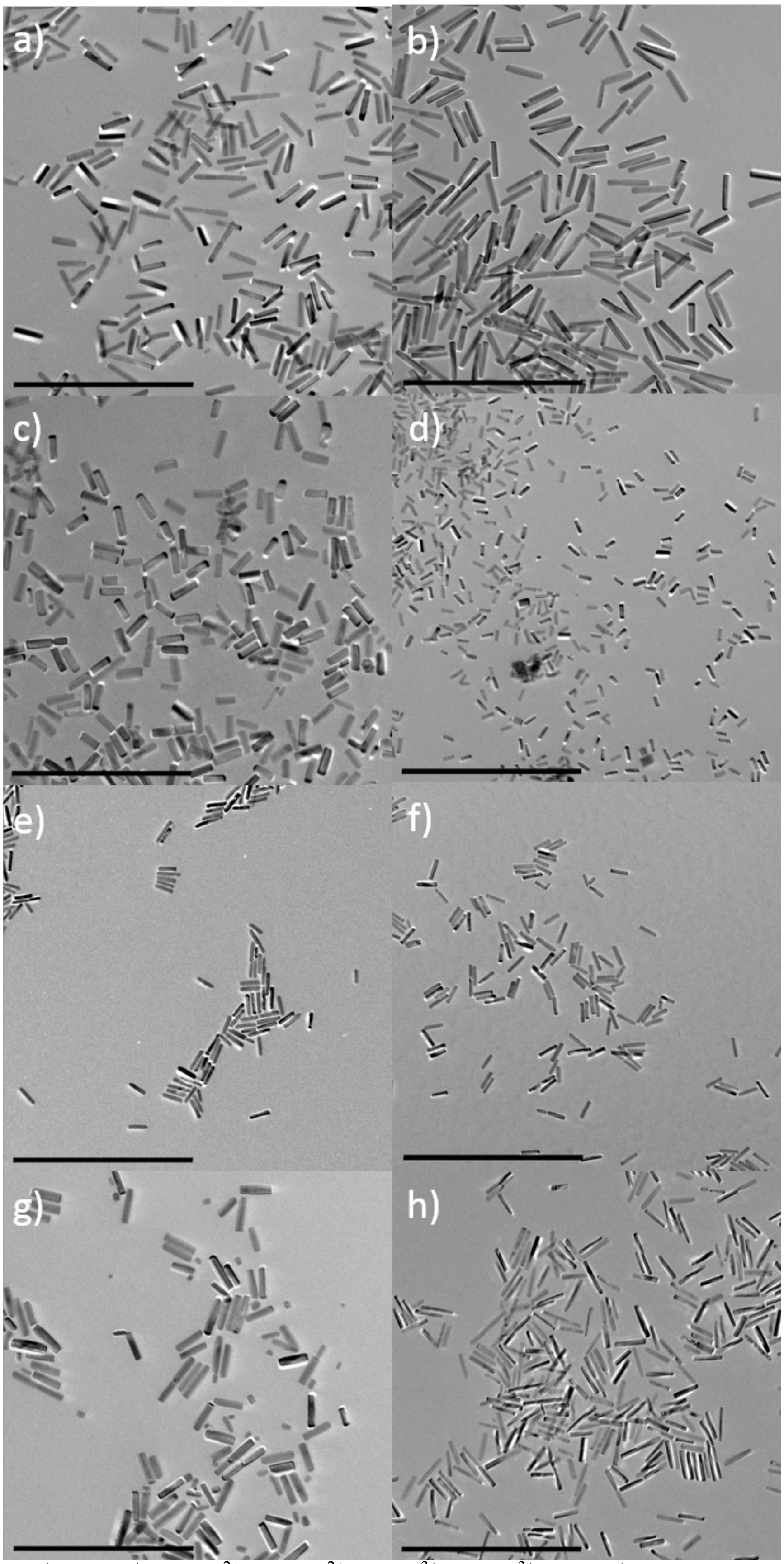
ESI-1: Pure ZnO nanorods prepared via the emulsion-based method.

TEM micrographs of ZnO at different magnifications (a) 30kx magnification inset of a) shows electron diffraction pattern. (b) 400kx magnification and (c) is the FFT pattern of b) showing the crystalline character.



ESI-2: Additional analytical data for different M@ZnO particles grown for χM = 0.03%.

TEM micrographs (magnified images):

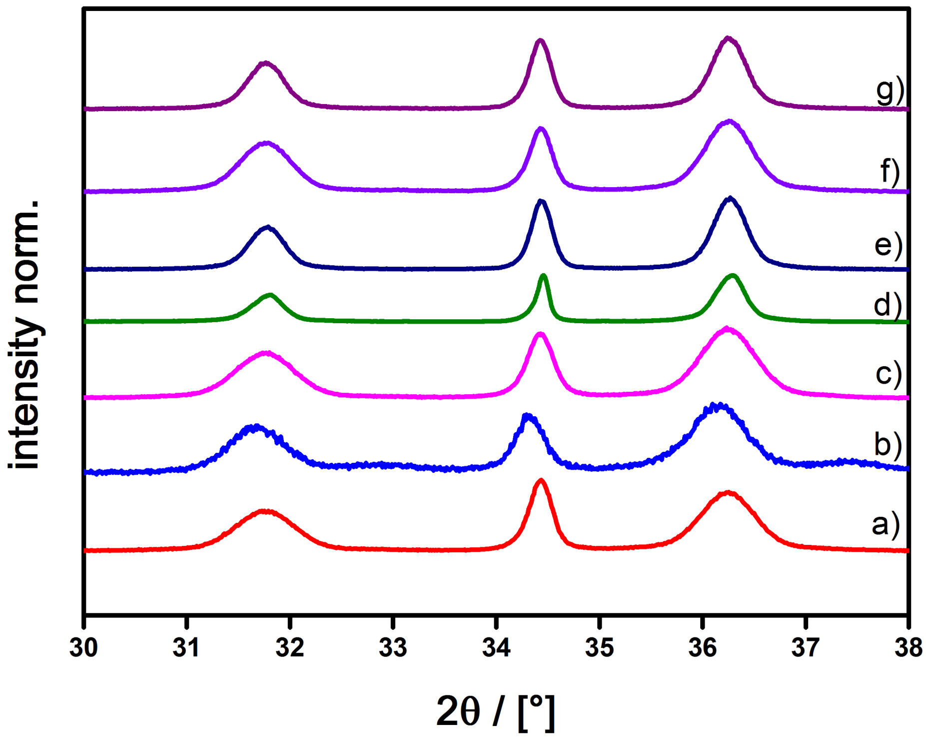


(a) Al^{3+}, (b) Li^{+}, (c) Cu^{+}, (d) Zn^{2+}, (e) Mn^{2+}, (f) Eu^{3+}, (g) La^{3+}, (h) Na^{+}. Scale bar = 500 nm.

Length D*c* and width D*ab* of doped ZnO nanoparticles with $\chi = 0.03\%$.

	Dopant	Dab in nm	Dc in nm
a)	Al^{3+}	19	77
b)	Li^{+}	21	90
c)	Cu^{+}	13	65
d)	Zn^{2+}	12	36
e)	Mn^{2+}	14	70
f)	Eu^{3+}	12	88
g)	La^{3+}	23	72
h)	Na^{+}	16	81

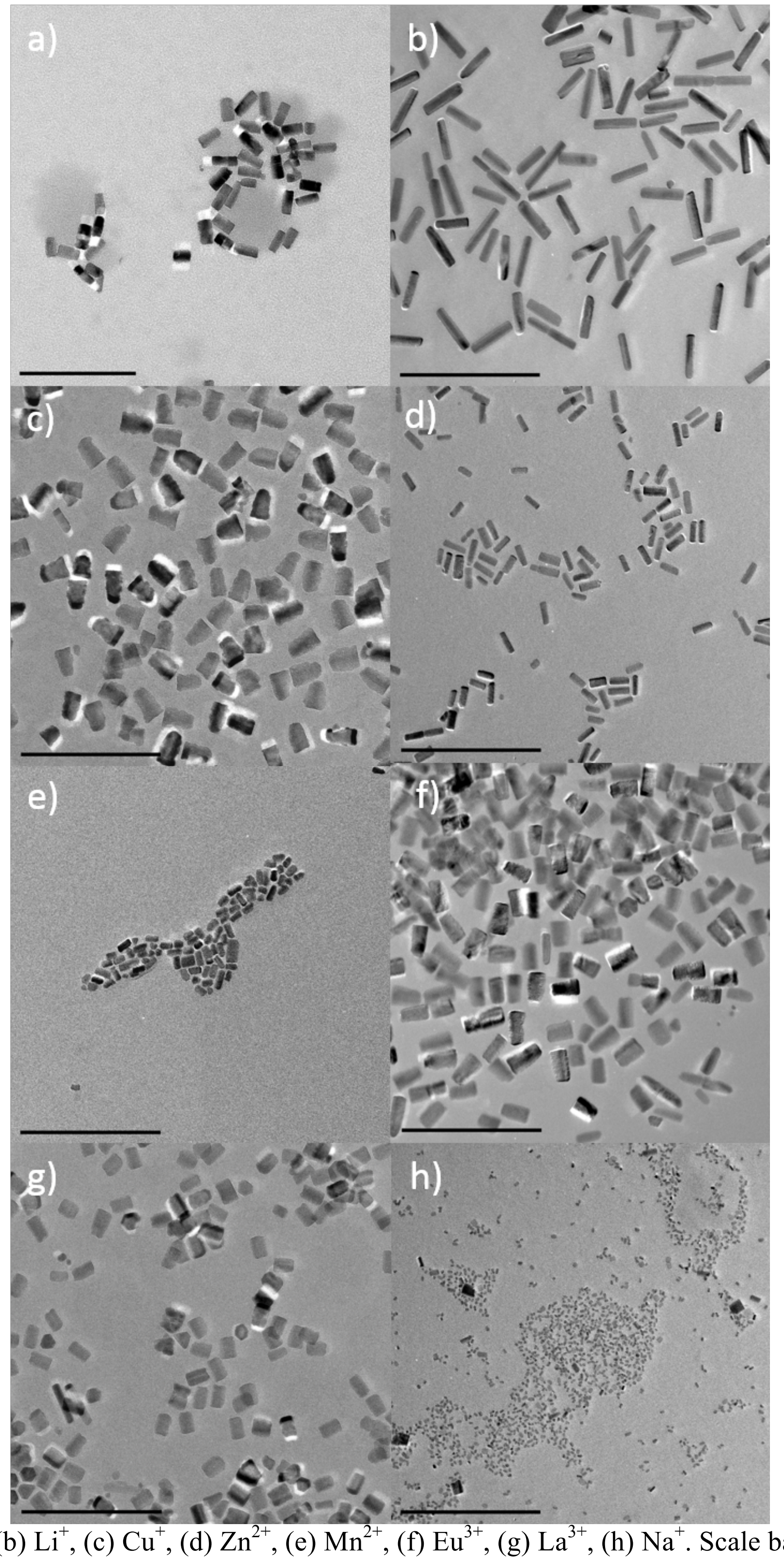
X- ray diffraction



(a) Li^{+}, (b) Cu^{+}, (c) Zn^{2+}, (d) Mn^{2+}, (e) Eu^{3+}, (f) La^{3+}, (g) Na^{+}. XRD pattern show the region of [100], [002] and [101] diffraction. For all patterns the particles length is represented by the change in the ratio of the [002] and [101] reflexes, indicating that the nanoparticles vary with the dopant.

(b) Additional analytical data for the different M@ZnO nanorod particles grown for $\chi M = 0.7\%$.

TEM micrographs (magnified images):

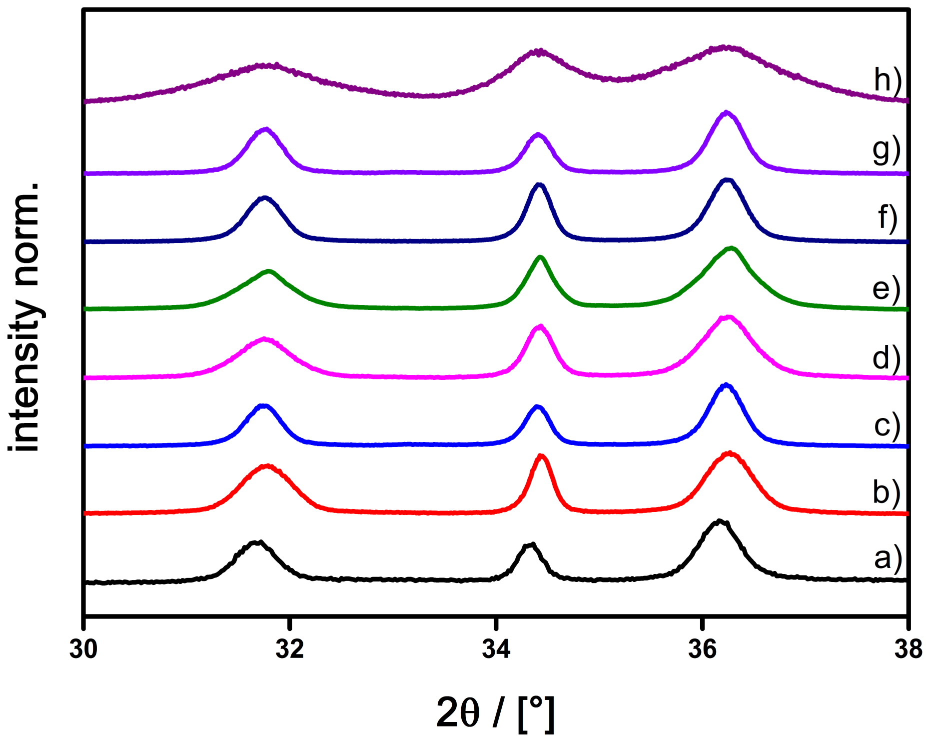


(a) Al^{3+}, (b) Li^{+}, (c) Cu^{+}, (d) Zn^{2+}, (e) Mn^{2+}, (f) Eu^{3+}, (g) La^{3+}, (h) Na^{+}. Scale bar = 200 nm.

Length D*c* and width D*ab* of doped ZnO nanoparticles with $\chi = 0.7\%$.

	Dopant	Dab in nm	Dc in nm
a)	Al^{3+}	21	43
b)	Li^{+}	15	63
c)	Cu^{+}	29	49
d)	Zn^{2+}	12	29
e)	Mn^{2+}	11	22
f)	Eu^{3+}	22	40
g)	La^{3+}	18	34
h)	Na^{+}	5	10

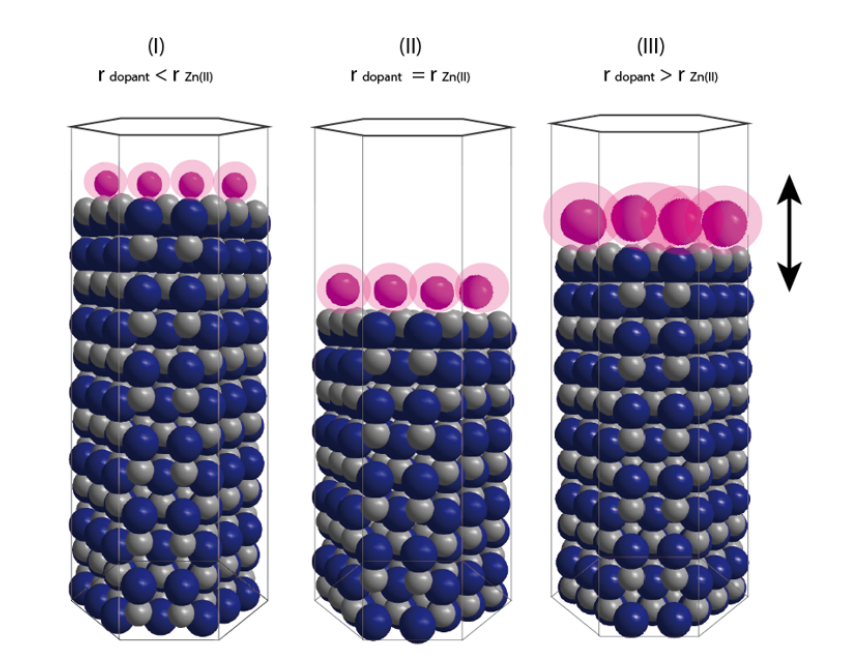
X- ray diffraction:



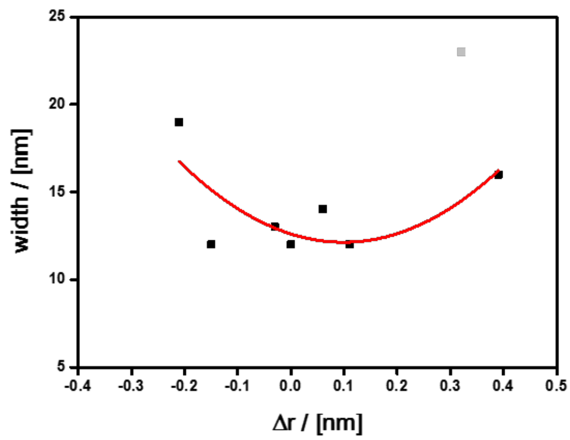
(a) Al^{3+}, (b) Li^{+}, (c) Cu^{+}, (d) Zn^{2+}, (e) Mn^{2+}, (f) Eu^{3+}, (g) La^{3+}, (h) Na^{+}. XRD pattern show the region of [100], [002] and [101] diffraction. For all patterns the particles length is represented by the the change in the ratio of the [002] and [101] reflexes, indicating that the nanoparticles vary with the dopant as also shown in TEM micrographs.

ESI-3: Proposed effect of cations on the growth of ZnO nanorods.

a)



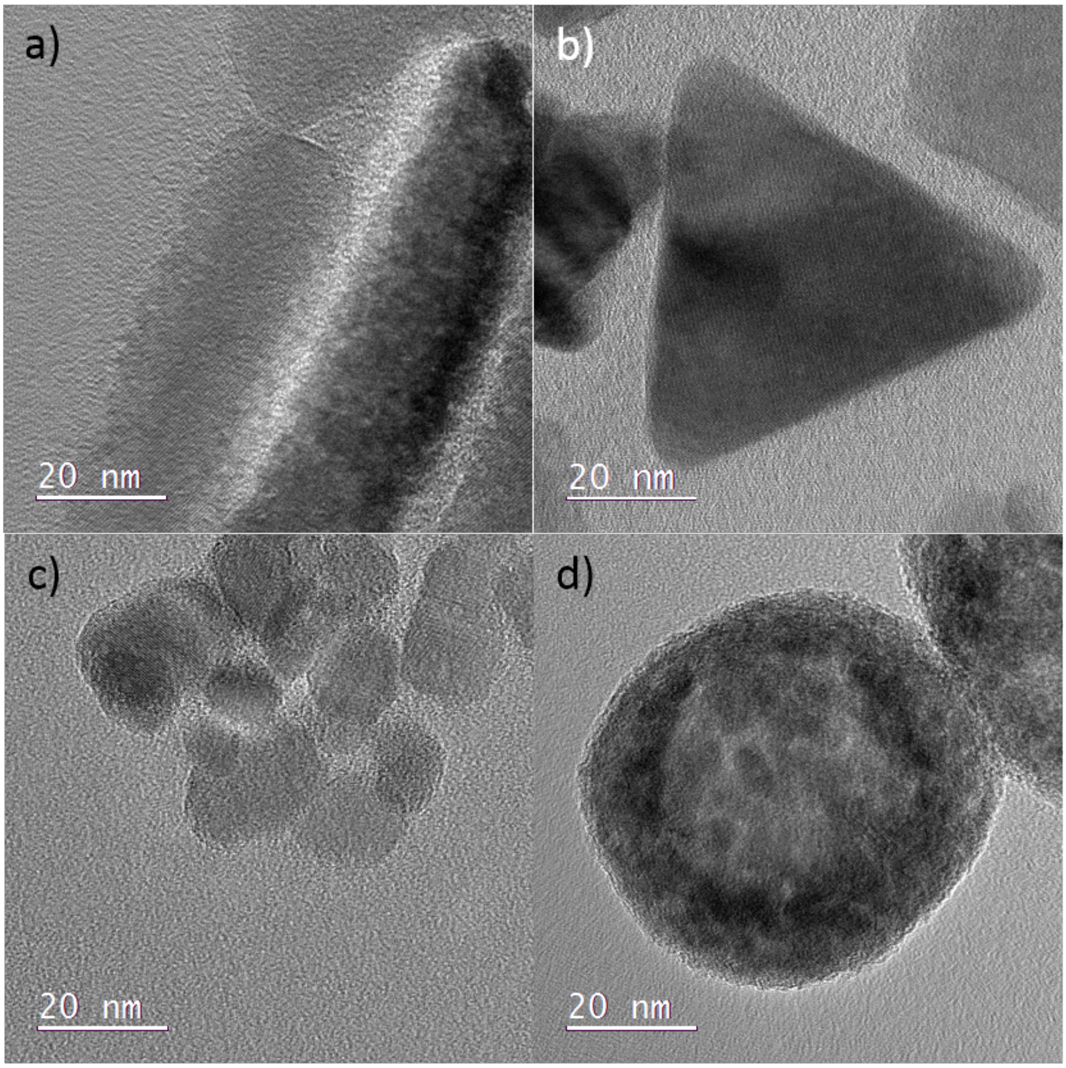
b)



Schematic illustration of the interaction between ionic size of the element to be incorporated into ZnO lattice and resulting particle length. a) ZnO nanorods with hexagonal shape interacting with ions (I) smaller than the ionic size of Zn^{2+} ($r(Zn^{2+})$) (II) about the same size as $r(Zn^{2+})$ and (III) larger than $r(Zn^{2+})$ resulting in different length. b) Correlation between the particle width and difference of ionic size compared to Zn^{2+}. Data for particle width was extracted from TEM micrographs.

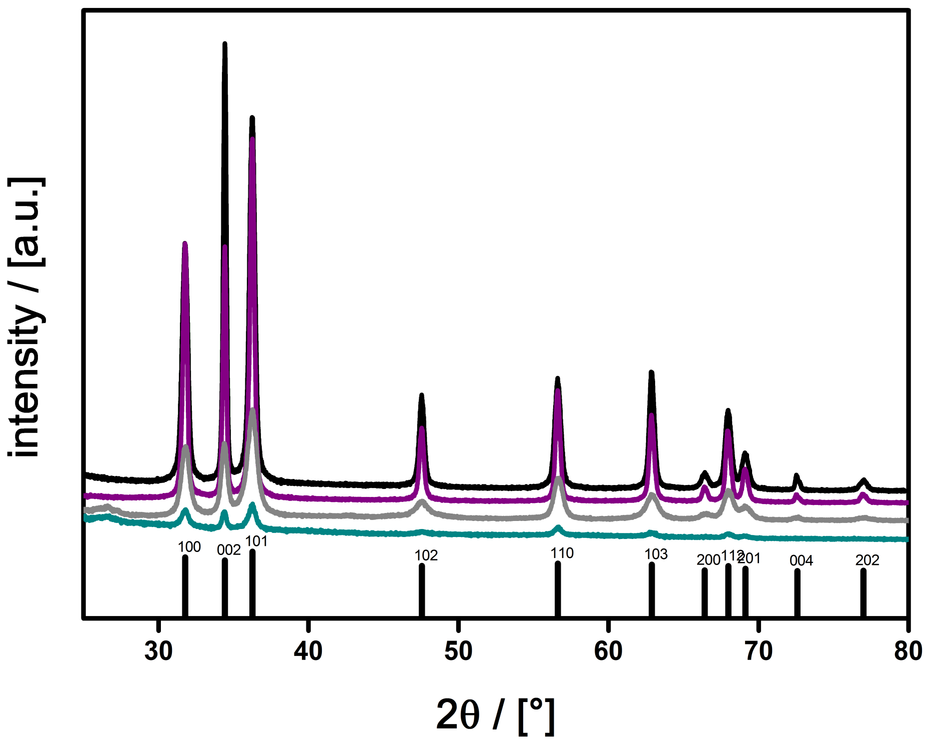
ESI-4: Additional data for differently shaped particles.

(i) TEM micrographs of pure ZnO nanoparticles (reference sample) prepared using the emulsion-based method:



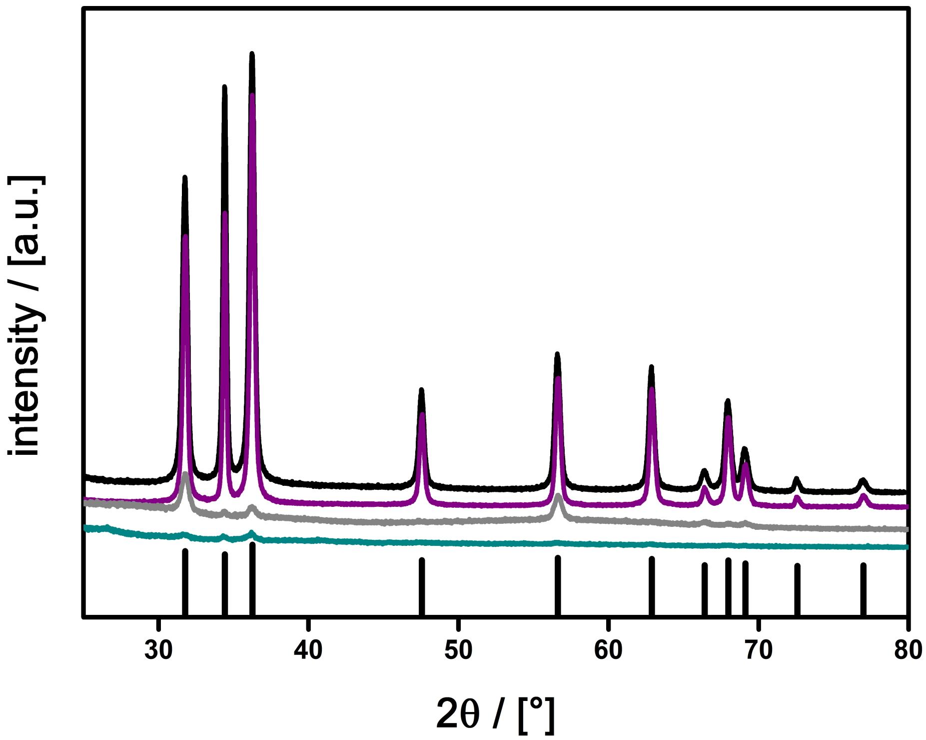
a) Nanorods b) Nanoprisms c) Nanoplates and d) hollow nanospheres.

(ii) PXRD patterns of ZnO:



Different ZnO materials: nanorods (black), nanoprisms (purple), nanoplates (light grey) and hollow nanospheres (green). In black ZnO reference pattern and indices. From nanorods, nanoprism to nanoplates and nanospheres reflexes decrease in intensity and sharpness confirming decreasing crystal quality.

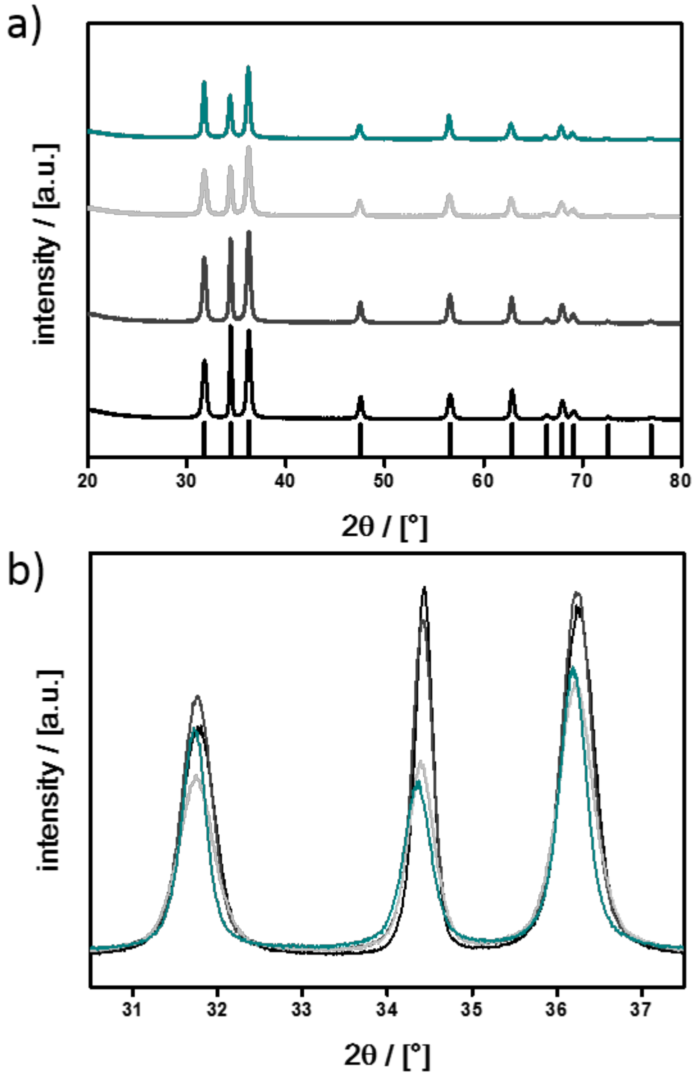
(iii) PXRD of Eu@ZnO for different morphologies:



Different Eu@ZnO materials: nanorods (black), nanoprisms (purple), nanoplates (light grey) and hollow nanospheres (green). In black ZnO reference pattern. From nanorods, nanoprism to nanoplates and nanospheres reflexes decrease in intensity and sharpness confirming decreasing crystal quality

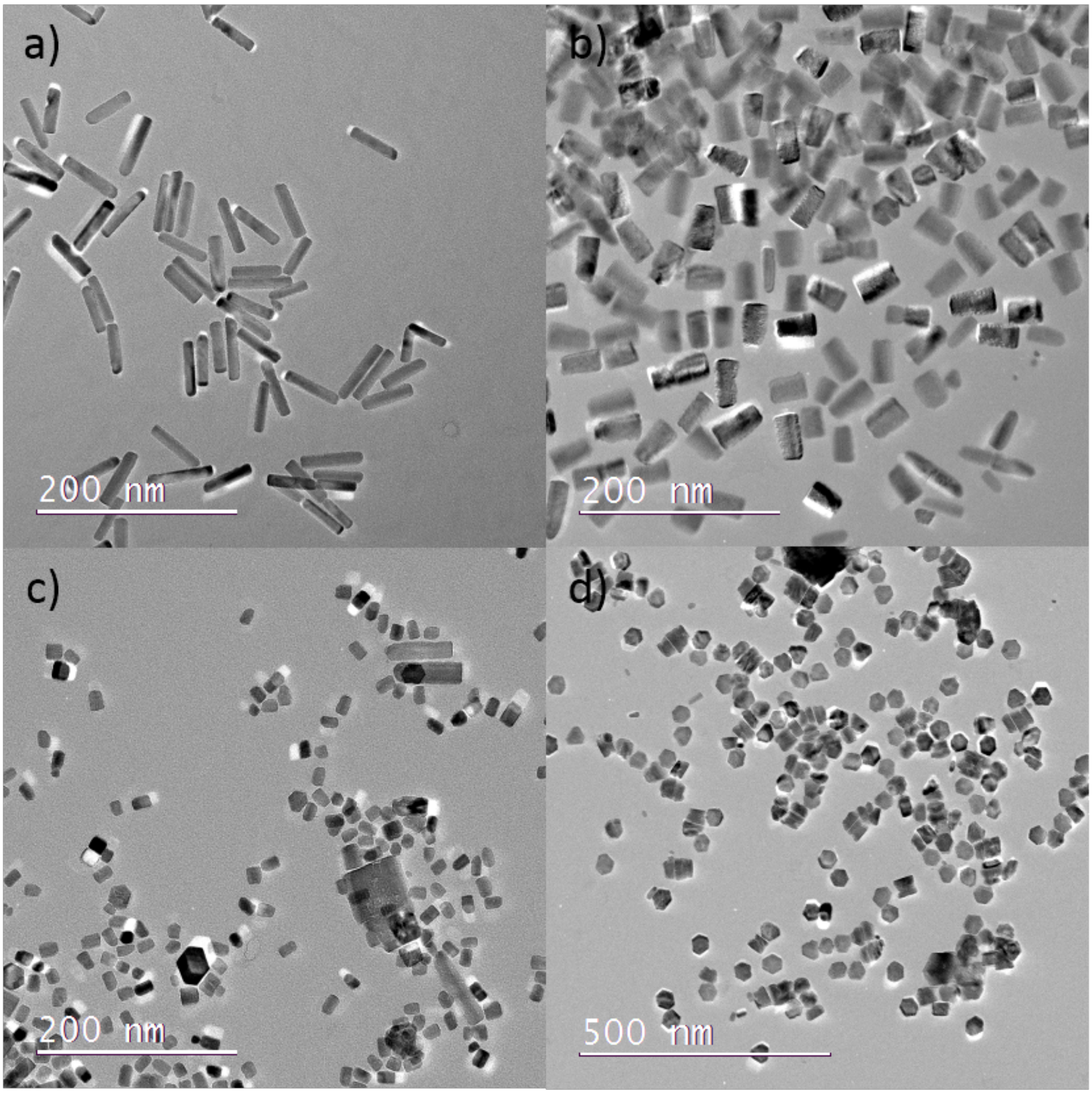
ESI-5: Additional analytical data for the different Eu@ZnO particles grown for different Eu^{3+} concentration.

(i) PXRD patterns of Eu@ZnO (a) overview pattern and (b) pattern in the region of [100], [002] and [101] diffraction.



a) χ_{Eu} = 0.03% (black), χ_{Eu} = 0.7 % (dark grey), χ_{Eu} = 1.0 % (light grey), χ_{Eu} = 2 % (green) and in black ZnO reference. b) inset of a) at the angle 2Θ 30°-37°. At all shown concentration there are no additional reflexes in comparison to ZnO reference pattern. For increasing doping concentration a decrease in signal intensity and change in the ratio for the [002] and [101] reflexes are observed, indicating that the particle experience a change in their elongated form.

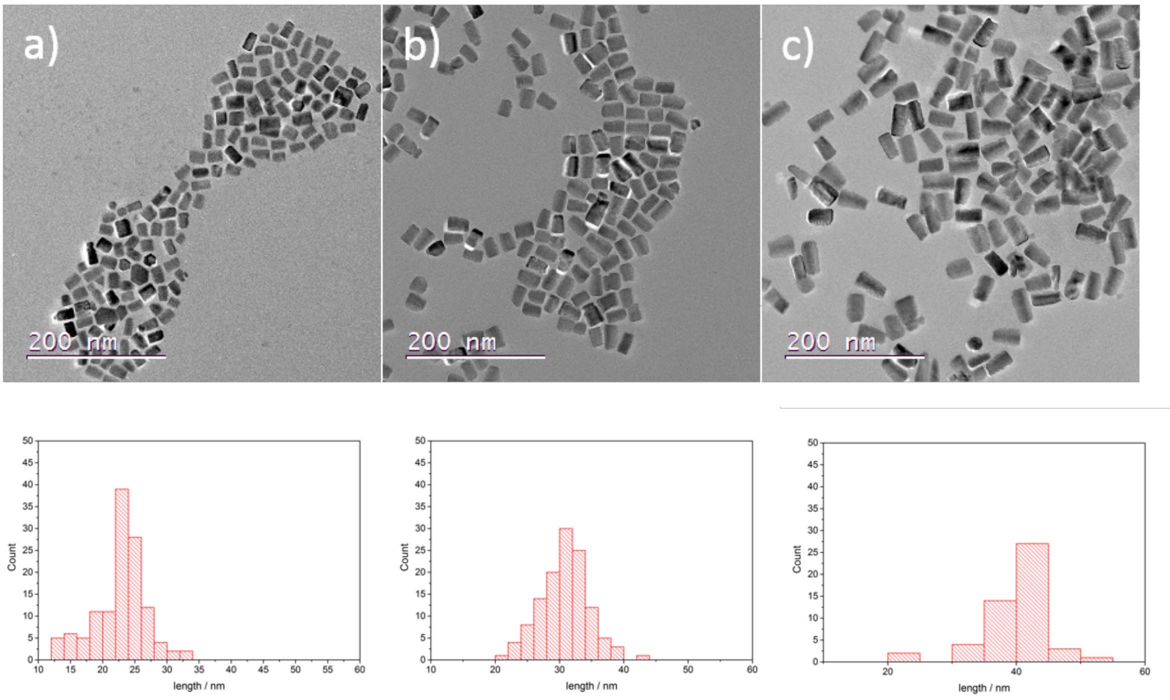
(ii) TEM micrographs of Eu@ZnO (magnified images):



a) χ_{Eu} = 0.03%, b) χ_{Eu} = 0.7 %, c) χ_{Eu} = 1.0 %, d) χ_{Eu} = 2 %.

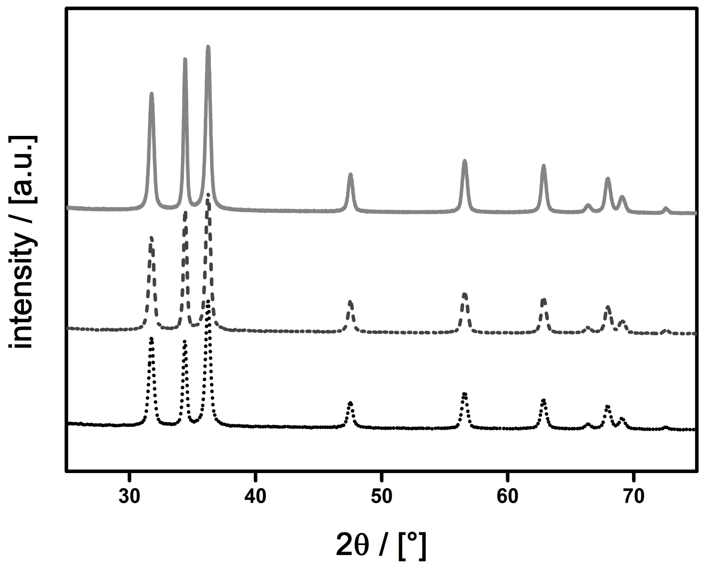
ESI-6: Eu@ZnO nanorods with different length.

Statistical evaluation of TEM micrographs:



(a) sample with D_c = 20 nm; (b) sample with D_c =30; (c) sample with D_c = 40 nm

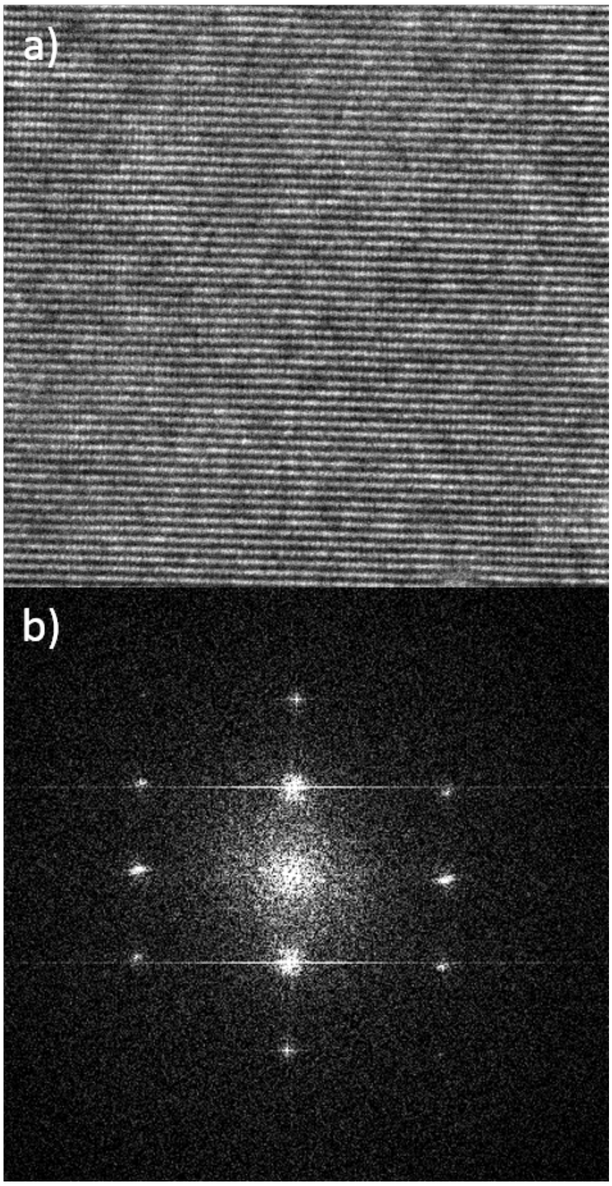
X- ray diffraction:



Eu@ZnO nanorods with length of 20 nm (dotted), Dc = 30 nm (dashed) and Dc = 40 nm (line). Half width of reflex increases with smaller angles.

ESI-7: HRTEM analysis of Eu@ZnO.

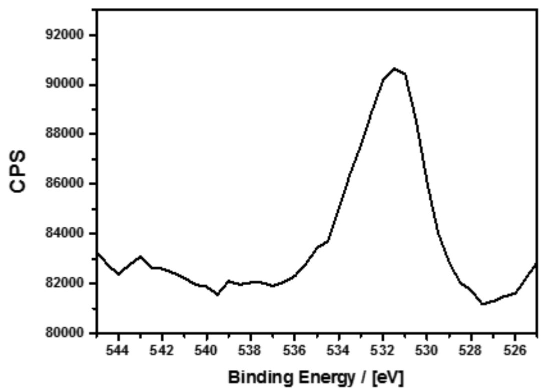
a) **HRTEM area of an analysed Eu@ZnO nanorod and b) FFT pattern of shown area. Indicating high quality crystalline character.**



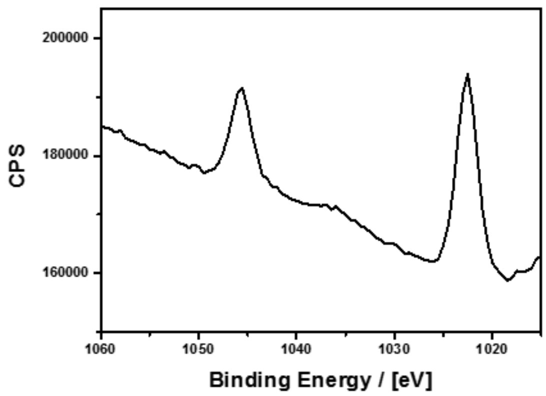
ESI-8: XPS and EPR spectroscopy performed on Eu@ZnO nanorods.

i) a) XPS signal of oxygen s1 region and b) zinc 2p region c) europium 3d region.

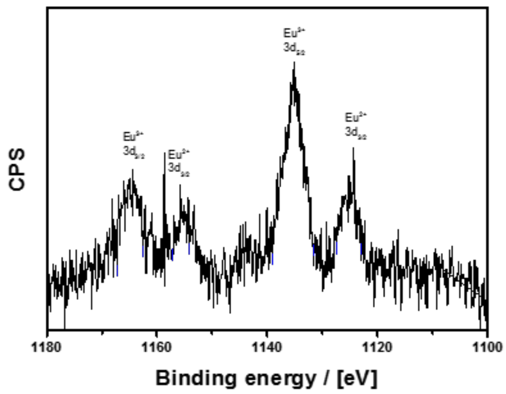
a)



b)

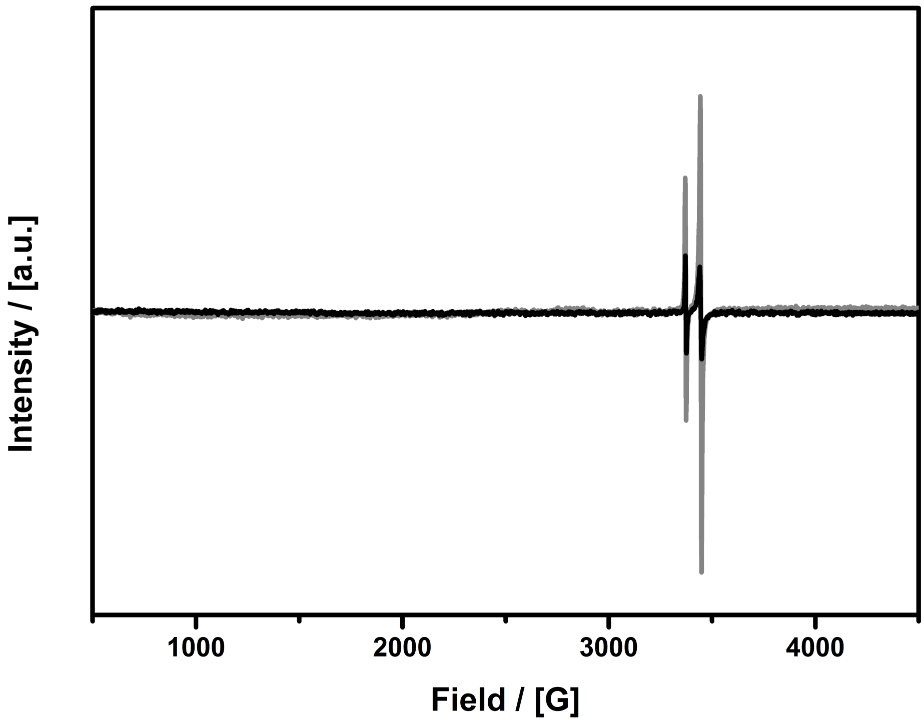


c)



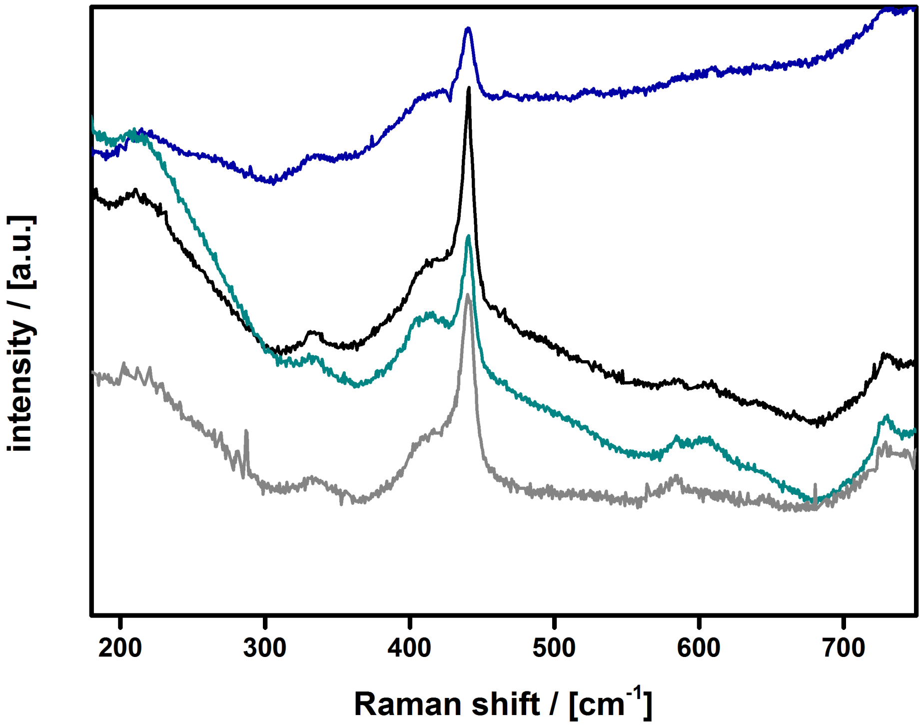
a) Signal at 531 eV is contributed by the oxygen species O 1s in the crystal lattice of ZnO. b) Zn 2p region with signals at 1045.5 eV and 1022.4 eV for ZnO. c) Both oxidation states are observable in Eu-$3d_{3/2}$ and Eu-$3d_{5/2}$ levels for Eu^{2+} = 1155 eV, 1124 eV and Eu^{3+} = 1164 and 1135 eV. Vercaemst et al. has observed mixed valence behavior of Eu containing compounds due to interconfiguration fluctuation.

(ii) EPR spectroscopy of Eu@ZnO and ZnO rods.



Eu@ZnO (black) and ZnO (grey). No signal was found at g = 4.195 for the Eu^{2+} species.

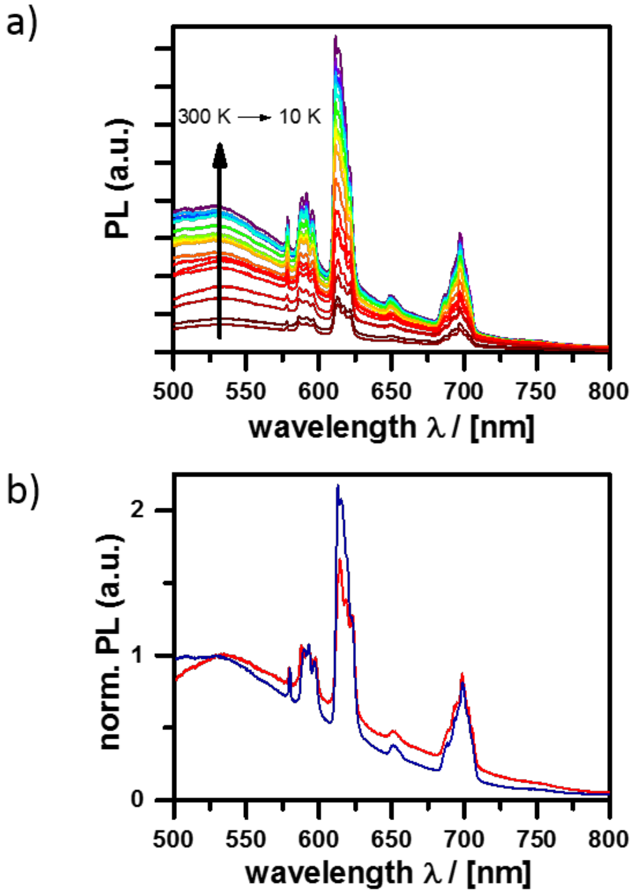
ESI-9: Micro-Raman comparison between ZnO and Eu@ZnO nanorods.



Room temperature Raman spectra of ZnO (blue) and Eu@ZnO with different europium content 0.7 at% (black), 1 at% (green) and 2 at% (grey) excited at 487 nm. The Raman mode at 439 cm^{-1} can be assigned to E_2(high) and shifts to lower wavenumbers with increasing doping concentrations confirming the europium incorporation into ZnO. The Raman mode becomes broader from 0 at% to 2 at% indicating that the high crystallinity of the nanoparticles decreases.

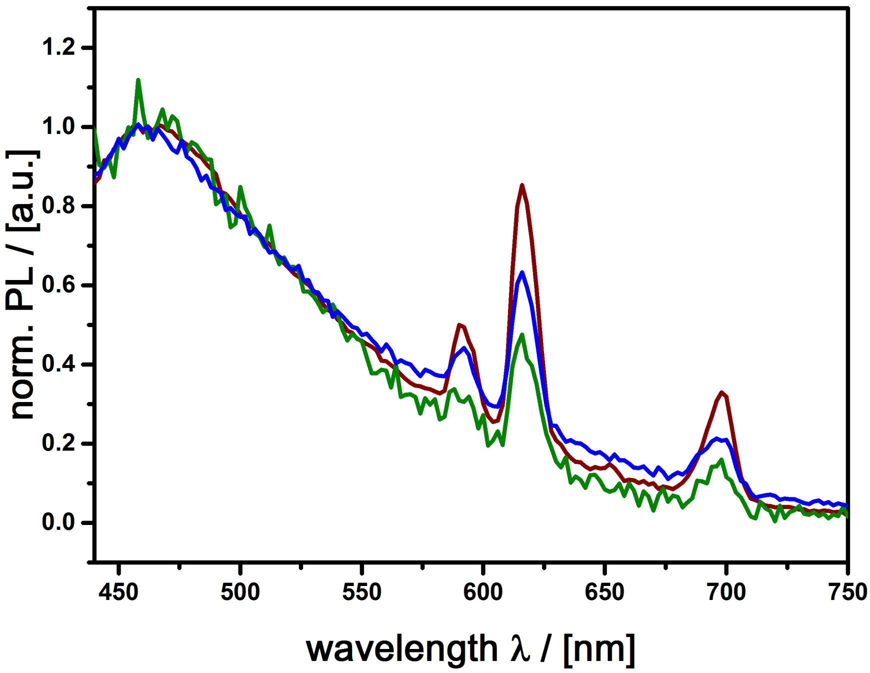
ESI-10: Additional information on photoluminescent properties of Eu@ZnO materials.

(i) Temperature-dependent spectra determined for (λ_{ex} = 407 nm).



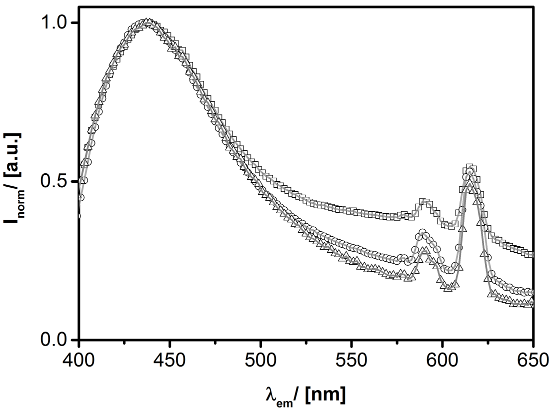
Temperature dependent photoluminescence spectra of Eu@ZnO nanorods with 0.7 at% Eu^{3+} concentration. (a) PL spectra for decreasing temperature from 300 K (red) to 10 K (blue). (b) Comparison between 10 K (blue) and 300 K (red).

<u>(ii) PL spectra (λ_{ex} = 405 nm) of Eu@ZnO nanorods containing different amount of Eu^{3+}.</u>



Normalized spectra obtained for different Eu^{3+} concentrations (red ≅ 2%; blue ≅ 1%; green ≅ 0.7%).

(iii) PL spectra ((λex = 380 nm) of Eu@ZnO nanorods with different aspect ratio.



Nanorods with different aspect ratio: Rc/ab = 1 (squares), 1.5 (circles), 2 (triangles).