Supplementary Information

for

Chemical Synthesis of Blue-emitting Metallic Zinc Nano-hexagons

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1. Additional TEM images of zinc nano-hexagons.

The relative size and thickness of the zinc nano-hexagons can be manipulated by varying the reaction temperature and/or feeding ratio of zinc precursor and capping ligand (oleylamine, OAM). The following TEM images demonstrate the particle size and shape variability achieved under different reaction conditions.

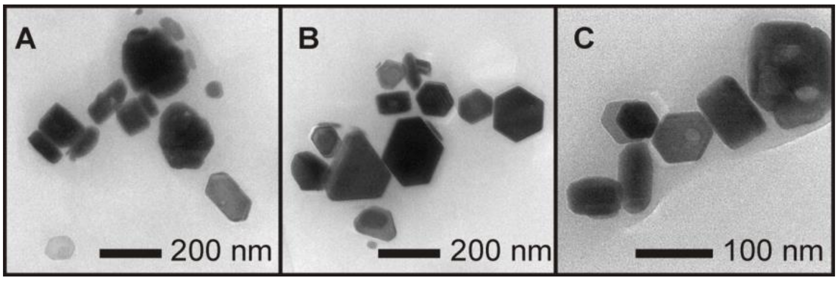

Fig. S1 TEM images of zinc nano-hexagons (thickness of 60 nm and diameter of ~60-180 nm) synthesized with feeding ratio of Zn:OAM = 1:4 at 200 °C.

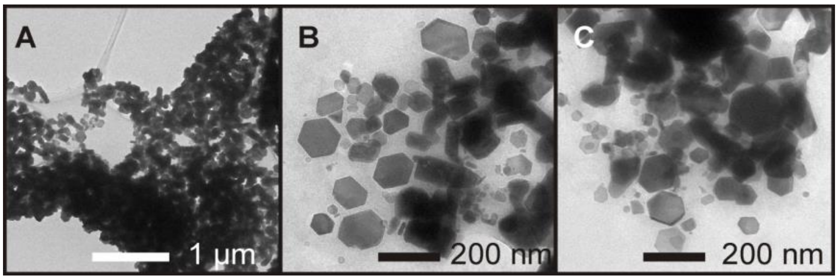

Fig. S2 TEM images of zinc nano-hexagons (diameter of ~150-200 nm) synthesized with feeding ratio of Zn:OAM = 1:2 at 200 °C.

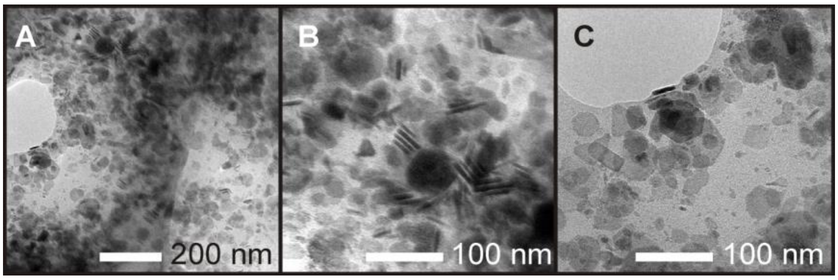

Fig. S3 TEM images of zinc nano-hexagons (thickness of ~6 nm and diameter of ~60 nm) synthesized with feeding ratio of Zn:OAM = 1:20 at 150 °C.

2. Crystalline size calculated from Scherrer Equation

Scherrer equation relating the crystalline size and the broadening of the XRD peak:

$$d = K\lambda/(\beta\cos\theta) \qquad \text{(Equation S1)}$$

where d [nm] is the mean size of the crystalline domain (crystalline size) of the nanoparticles, K is the shape factor (dimensionless) which has the typical value of 0.9 (but depends on the shape of nanoparticles), λ [nm] is the X-ray wavelength, β [rad] is the peak width at half the maximum intensity (FWHM) and θ [rad] is the peak position (Bragg angle). K=0.9, and λ=0.15418 nm were used to calculate the mean crystalline size (d) of zinc nano-hexagons.

3. UV-Vis spectrum of Zn NHexs

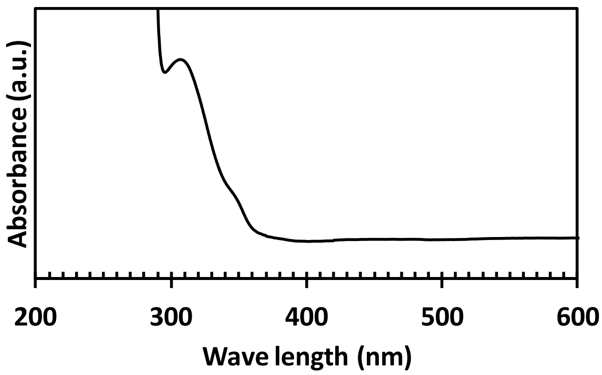

Fig. S4 UV-Vis spectrum of Zn NHexs.

4. Partial oxidation of zinc nano-hexagons when exposed to the air

The zinc nano-hexagons were exposed to open air for 2 weeks. In the resulting TEM images (Figure S5) some small particles were found on the surface of the nano-hexagons. The partial surface oxidation can be clearly observed in XPS spectra (Figure S6) for Zn2p area even though in the XRD pattern, no oxide peaks can be detected (Figure S7). These results indicate that the zinc oxides may have an amorphous structure or they have a very small crystal size which can cause significant peak broadening and could not be observed in XRD. The partial oxidation of zinc nano-hexagons may result in suppressed photoluminescence emission as mentioned in the main text.

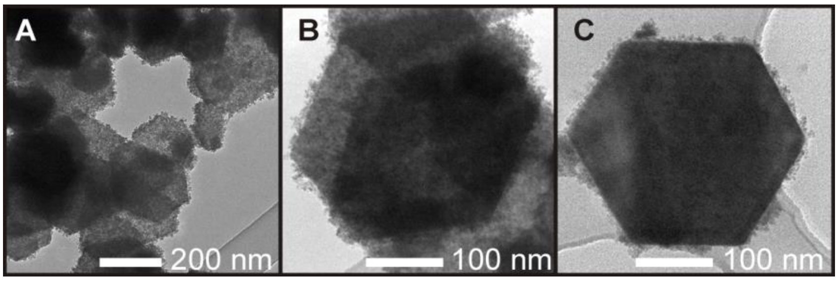

Fig. S5 TEM images of partially oxidized zinc nano-hexagons after exposure to the air for an extended period of time.

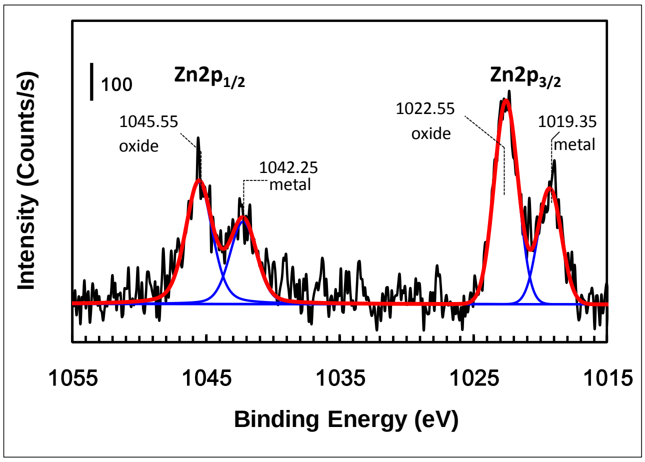

Fig. S6 XPS spectrum of partially oxidized zinc nano-hexagons after exposure to the air in the Zn2p area. The peaks at 1019.35 and 1042.25 eV belong to zinc metal and the two peaks at higher binding energy (1022.55 and 1045.55 eV) arise from zinc oxide.

Table S1. Peak parameters of partially oxidized zinc nano-hexagons.

	$Zn2p_{3/2}$ (metal)	$Zn2p_{1/2}$ (metal)	$Zn2p_{3/2}$ (oxide)	$Zn2p_{1/2}$ (oxide)
Peak position (eV)	1019.35	1042.25	1022.55	1045.55
FWHM (eV)	2	2.3	2.1	2.3
Peak separation (eV)	22.9		23.0	
Spin-orbit intensity ratio	1.4		1.67	

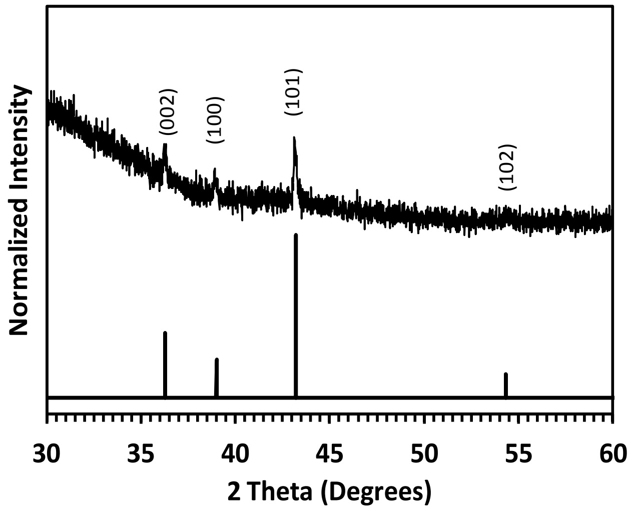

Fig. S7 XRD pattern of zinc nano-hexagons exposed to the air for two weeks. The peaks were indexed to hexagonal phase zinc (JCPDS No. 03-065-5973).

5. Zn NHexs synthesized using feeding ratio of Zn:OAM = 1:2

The Zn NHexs are found to have very low intensity PL (Fig. S8) which may be associated with the oxidation of the Zn NHexs. The oxidation can be explained based on the fact that the Zn NHexs synthesized using less OAM (feeding ratio Zn:OAM = 1:2, Supporting Information Fig. S2) is not well stabilized (compared to the Zn NHexs synthesized using feeding ratio of Zn:OAM = 1:30) by the capping molecules, resulting in oxidation. As a result, we observe the surface oxides in the XPS spectra (Fig. S9).

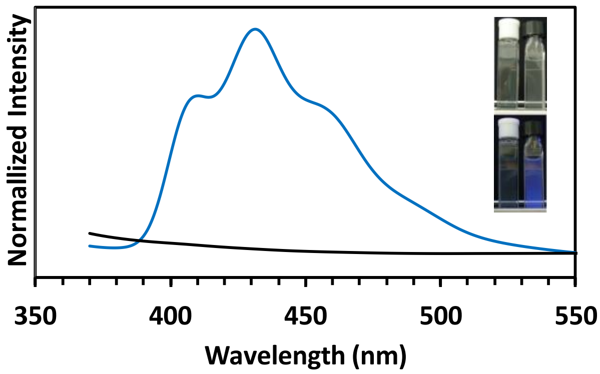

Fig. S8 Photoluminescence emission spectra of the Zn NHexs synthesized using feeding ratio of Zn:OAM = 1:2 (black curve, Supporting Information Fig. S2) and Zn NHexs with feeding ratio of Zn:OAM = 1:30 (blue curve, Fig. 1 in main text). Excitation wavelength used for the emission spectra was 310 nm. The inset shows photographs of the hexane/toluene 1:1 (vol/vol) dispersion of the zinc NHexs synthesized using a feeding ratio of Zn:OAM = 1:2 (left), and hexane/toluene 1:1 (vol/vol) zinc NHexs synthesized using feeding ratio of Zn:OAM = 1:30 (right) taken without (top) and with (bottom) UV illumination.

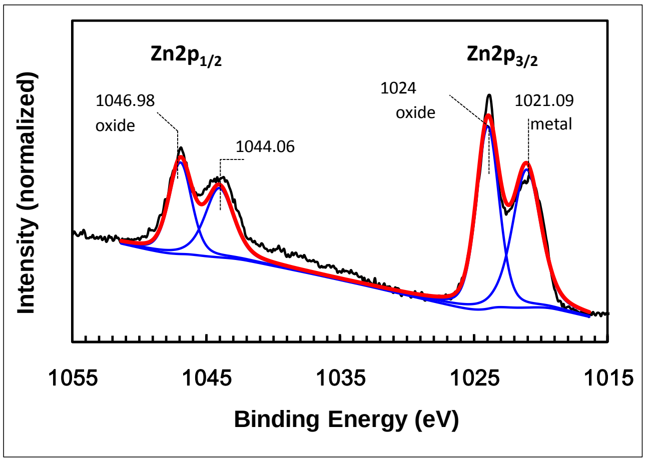

Fig. S9 XPS spectrum of zinc nano-hexagons synthesized using feeding ratio of Zn:OAM = 1:2 in the Zn2p area. The peaks at 1021.09 and 1044.06 eV belong to zinc metal and the two peaks at higher binding energy (1024 and 1046.98 eV) arise from zinc oxide.