Supporting Information:

Dopant Induced Shape Evolution of Colloidal Nanocrystals:

The Case of Zinc Oxide

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Figure S1. Additional HRTEM images of pure ZnO nanocrystals and the corresponding EDX spectrum. (A) Paired ZnO nanopyramids, which were often found in the HRTEM observations, possibly due to attachment of two differently charged basal planes of the nanopyramids. (B) An enlarged image of the nanocrystal displayed in (A) (the top left one). The (0002) lattice fringes are observed which show that the nanocrystals grow along the *c*-axis of the WZ lattice. (C) EDX spectrum, which shows that the constitution elements are Zn and O.

Figure S2. A typical TEM image of the nanocrystals from the 90% $\text{Mg}(\text{St})_2$ reaction.

Figure S3. TEM analyses of the tetrapods from the 5% Mg(St)_2 reaction. (A) A typical TEM image of the resulting nanocrystals, illustrating that the sample consists of quality tetrapods with uniform dimensions. (B) Histogram showing the distribution of diameters of 200 randomly selected tetrapod arms. (C) and (D) Additional HRTEM images of two tetrapod arms with WZ structure. (E) EDX spectrum of the product from the 5% Mg(St)_2 reaction, which suggests existence of Zn, Mg and O elements. The silicon signal arises from the EDX detector.

Figure S4. HRTEM images by direct imaging core regions of two tetrapods from the 5% $\text{Mg}(\text{St})_2$ reaction. (B) and (D) are higher magnification images of (A) and (C), respectively. Although the images are taken on tilted tetrapods and some features related to the polytypism model of WZ arms growing from ZB cores can be identified, direct imaging on the tetrapods is difficult to get atomic resolution images that fully uncover the crystalline features of the whole core area.

Figure S5. Additional TEM images of the nanocrystals from the 5% $\text{Mg}(\text{St})_2$ reaction. (A) A TEM image showing a tetrapod with a bipod close to it. Note that tetrapods dominate in the product from the 5% $\text{Mg}(\text{St})_2$ reaction and bipods or tripods are occasionally observed. (B) A HRTEM image of the tetrapod arm which points upward. (C) A HRTEM image of the central region of the bipod, suggesting a polytypism model of WZ arms growing from a ZB core.

Figure S6. TEM analyses of the ultrathin nanowires from the 50% Mg(St)₂ reaction. (A) A typical TEM image of the quality ultrathin nanowires. (B) and (C) Histograms showing the respective distributions of lengths and diameters of 200 randomly selected ultrathin nanowires. (D) EDX spectrum of the ultrathin nanowires from the 50% Mg(St)₂ reaction, suggesting the presence of Zn, Mg and O elements.

Figure S7. Additional HRTEM images of the ultrathin nanowires from the 50% $\text{Mg}(\text{St})_2$ reaction.

Scale bars: 5 nm.

Figure S8. Additional HRTEM images of the ultrathin nanowires from the 50% $\text{Mg}(\text{St})_2$ reaction.

(A) and (C) Two tadpole-like ultrathin nanowires. (B) and (D) The corresponding head regions of the two wires in (A) and (C) at higher magnification, respectively.

Table S1. ICP-AAS analyses of the nanocrystals from the reactions with different molar ratios of Mg(St)₂ in the reagents.

Initial [Mg] (at.%)	[Mg] in NCs (at.%)	[Zn] in NCs (at.%)
2	1.9	98.1
5	3.0	97.0
10	5.5	94.5
20	8.7	91.3
30	11.6	88.4
40	16.8	83.2
50	22.6	77.4
60	52.4	47.6
70	73.0	27.0
80	74.4	25.6
90	87.9	12.1

Figure S9. XPS analyses on selected samples. XPS spectra of the nanocrystals from (A) the 5% Mg(St)₂ reaction, (B) the 10% Mg(St)₂ reaction, and (C) the 50% Mg(St)₂ reaction. The XPS binding energies were calibrated by referring the C 1s to 284.6 eV. The occurrence of Mg 1s core level centered at *ca.* 1304 eV, together with the XRD and HRTEM results, suggests the incorporation of Mg ions into the ZnO lattice with the divalence oxidation state.

Figure S10. STEM and line-scan EDX results. (A) and (B) A typical HAADF-STEM image of the tetrapods from the 5% Mg(St)₂ reaction and a corresponding line-scan EDX spectrum. (C) and (D) A typical HAADF-STEM image of the ultrathin nanowires from the 50% Mg(St)₂ reaction and a corresponding line-scan EDX spectrum.

Figure S11. Detailed experimental description for the quantitative etching experiments. The purified nanocrystals from the 5% $\text{Mg}(\text{St})_2$ reaction was dissolved in hexane, leading to a solution with a concentration of *ca.* 0.6 mg/ml. Trifluoroacetic acid was used as etchant. A series of etchant solutions with different concentrations but the same volume (Table S2) was prepared. The etchant solutions (1.9 ml) were added into the nanocrystal solutions (0.7 ml) within 5 min under stirring. The reactions were lasted for 1 h to make sure that the etching processes were completed. TEM and UV-Vis measurements were conducted for each solution. For the elemental analysis of the etched nanocrystals, the samples were purified by extensive methanol extraction to remove species containing the ions etched away from the oxide nanocrystals and the residuals of the etchant.

Table S2. Etchant solutions for the corresponding etching experiments.

Experiment No.	Etchant diluted in hexane (total volume 1.9 ml)
Etching Ref.	0 mmol
Etching 1	5×10^{-6} mmol
Etching 2	1×10^{-5} mmol
Etching 3	1.5×10^{-5} mmol
Etching 4	2×10^{-5} mmol

Figure S12. TEM analyses of the nanocrystals from the 20% $\text{Mg}(\text{St})_2$ reaction. (A) A TEM image of the product from the 20% $\text{Mg}(\text{St})_2$ reaction, illustrating co-existence of branched nanocrystals (tetrapods, tripods, and bipods) and tadpole-like nanowires. (B) A HRTEM image of a tetrapod with one WZ arm pointing upward. Inset is the corresponding FFT pattern. (C) and (E) HRTEM images of a tadpole-like nanowire and the head area of the nanowire (with higher magnification), suggesting that the single crystalline nanowire with WZ structure is grown from the WZ head by sharing c -axis direction. (D) and (F) A HRTEM image of core region of a bipod and the corresponding two-dimensional atomic simulation, indicating the polytypism model of WZ arms growing from a ZB core. (G) EDX spectrum of the product from the 20% $\text{Mg}(\text{St})_2$ reaction, indicating the presence of Zn, Mg and O elements.

Figure S13. TEM analyses of the nanocrystals from the 80% $\text{Mg}(\text{St})_2$ reaction. (A) A HRTEM image of a particle with cubic structure from the 80% $\text{Mg}(\text{St})_2$ reaction, viewed along the zone axis of [001]. Inset is the corresponding FFT pattern. (B) EDX spectrum of the irregular particles from the 80% $\text{Mg}(\text{St})_2$ reaction, suggesting constitution elements of the particles: Mg, Zn and O.

Figure S14. (A) Optical bandgap and emission energy plotted as a function of Mg content in the nanocrystals determined by ICP-AAS. A common approach assuming a parabolic dependence of absorption coefficient (α) on photon energy ($h\nu$), i.e., $\alpha \propto \sqrt{h\nu - E_g}$, has been used to determine the optical bandgap. (B) Photoluminescence spectra (excited at 300 nm) of the nanocrystals from the 0%, 2%, 5%, 10%, 20%, 30%, 40% and 50% Mg(St)₂ reactions. The intensity ratio of near-band-edge (NBE) emission to deep level emission is conversed when the molar ratio of Mg(St)₂ in the reagents exceeds 10%. Therefore, the intensity is normalized to the NBE emission and the green emission, for the former and latter 4 spectra, respectively.

Figure S15. Temporal evolution of UV-Vis spectra of purified nanocrystals from (A) the 5% $\text{Mg}(\text{St})_2$ reaction and (B) the 50% $\text{Mg}(\text{St})_2$ reaction, respectively.

Figure S16. (A)-(C) Typical TEM images of the nanocrystals from the 5% Mg(St)₂ reaction at different reaction times: (A) 3 min; (B) 4 min; (C) 8 min. (D)-(F) Typical TEM images of the nanocrystals from the 50% Mg(St)₂ reaction at different reaction times: (D) 3 min 30 sec; (E) 5 min; (F) 8 min.

Figure S17. TEM images of tetrapods from a set of reactions, in which the total quantity of metal precursors, with fixed $\text{Mg}(\text{St})_2\text{:Zn}(\text{St})_2$ ratio of 5:95 mol.%, is varied from 0.75 mmol to 1.5 mmol. (A) 0.7125 mmol of $\text{Zn}(\text{St})_2$ and 0.0375 mmol of $\text{Mg}(\text{St})_2$ were used as starting materials. (B) 0.95 mmol of $\text{Zn}(\text{St})_2$ and 0.05 mmol of $\text{Mg}(\text{St})_2$ were used as starting materials. (C) 1.425 mmol of $\text{Zn}(\text{St})_2$ and 0.075 mmol of $\text{Mg}(\text{St})_2$ were used as starting materials. The scale bar of the TEM images is 50 nm.

Figure S18. Schematic illustration of the seeded growth experiment. Aliquots were taken out at 4 intervals during the process so that the growth of the nanocrystals can be monitored by UV-Vis and TEM.

Figure S19. TEM images of small ZnO particles taken from the reaction mixture of the seeded growth experiment at 4 min, before the injection of the Mg precursor, demonstrating WZ structure of the seeds. (A) and (B) Typical TEM images of the ZnO particles. (C) and (D) HRTEM images of ZnO particles imaged along two different zone axes. Insets are the corresponding indexed FFT patterns. Note that in order to get atomic resolution images with high contrast we imaged two particles with large diameters. The majority of the particles in the TEM observations have diameters less than 3 nm. (E) and (F) HRTEM images of ZnO particles with well-resolved (0002) lattice planes.

Figure S20. TEM analyses of the tetrapods from the seeded growth experiment. (A) A TEM image of the resulting branched nanocrystals (4 min after the injection of the Mg precursor). (B) and (C) Additional HRTEM image of a bipod and the corresponding two-dimensional atomic simulation, confirming the formation of crystalline domains with ZB structure.

Figure S21. FTIR spectra of the surface ligands on oxide nanocrystals from the 0%, 5%, and 50% Mg(St)₂ reactions, respectively.

Figure S22. (A)-(C) Control experiments for the 5% $\text{Mg}(\text{St})_2$ reaction, in which certain amounts of additional HSt were introduced. (A) UV-Vis spectra. (B) A typical TEM image of the nanocrystals from the reaction starting with 0.95 mmol of $\text{Zn}(\text{St})_2$, 0.05 mmol of $\text{Mg}(\text{St})_2$, and 0.1 mmol of HSt. (C) A typical TEM image of the nanocrystals from the reaction starting with 0.95 mmol of $\text{Zn}(\text{St})_2$, 0.05 mmol of $\text{Mg}(\text{St})_2$, and 0.5 mmol of HSt. (D)-(F) Control experiments for the 50% $\text{Mg}(\text{St})_2$ reaction, in which certain amounts of additional HSt were introduced. (D) UV-Vis spectra. (E) A typical TEM image of the nanocrystals from the reaction starting with 0.5 mmol of $\text{Zn}(\text{St})_2$, 0.5 mmol of $\text{Mg}(\text{St})_2$, and 0.1 mmol of HSt. (F) A typical TEM image of the nanocrystals from the reaction starting with 0.5 mmol of $\text{Zn}(\text{St})_2$, 0.5 mmol of $\text{Mg}(\text{St})_2$, and 0.5 mmol of HSt.

Figure S23. (A) Typical UV-Vis spectra and (B)-(D) TEM images of the nanocrystals from the control experiments for the 0%, 5%, and 50% Mg(St)₂ reactions, respectively, in which ODE, the reaction solvent was replaced by n-octadecane.

Figure S24. Three-dimensional structural models for MgO, CdO, MnO, and NiO, revealing the rock-salt structure (same space group Fm-3m) of these oxides.

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