Modular Synthetic Design Enables Precise Control of Shape and Doping in Colloidal Zinc Oxide Nanorods

*Saahil Mehra §, Emory M. Chan ||, Alberto Salleo §**

§ Department of Materials Science and Engineering, Stanford University, Stanford, California, 94305
|| The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, 94720
*Corresponding Author: *asalleo@stanford.edu*

Supporting Information:
Table of Contents:

1. Experimental Details
   a. Stock Solution Preparation
   b. Synthesis of Undoped Zinc Oxide Nanorods
   c. Synthesis of Al-doped Zinc Oxide Nanorods
   d. Washing Nanoparticles
   e. Characterization Details
   f. Structural Formulas of Synthetic Precursors

2. Size Distributions
   a. Diameter Statistics for Syntheses in Figure 1
   b. Diameter Statistics for Syntheses in Figure 2 A-C
   c. Length Statistics for Syntheses in Figure 2 D-E

3. Synthetic Optimization
   a. Comparison of Oleyl Alcohol vs. 1,12-Dodecanediol as Nucleophiles
   b. Effect of Adding Oleyl Alcohol Throughout Synthesis
   c. Effect of Multiple Injection Sets with no Phosphonic Acid
   d. Effect of Different Phosphonic Acid Alkyl Chain Lengths/Concentrations
   e. Effect of Using Different Zinc Precursors
   f. Nanorod diameter distributions as a function of TDPA concentration
   g. Further Characterization of Al-doped ZnO Nanorods
   h. Further Characterization of ZnO Nanorods

4. Table: Synthetic Details

1. Experimental Details:

b. Stock Solution Preparation:

These mixtures were prepared prior to performing a nanorod synthesis and added to the reaction bath individually by WANDA at specified times throughout a synthesis. Stock solutions were intentionally designed to contain only one key reactant (zinc precursor, dopant, activator, surfactant) to enable modular synthetic design – the presence of each reactant could be intentionally tuned throughout a synthesis. Further, they were designed to be stable solutions to prevent precipitation during the synthesis and enhance synthetic reproducibility.

ZnAc Stock Solution
1:3:3 ZnAc:TOPO:DOE

Typically, 50 mmol Zinc acetate dihydrate, 150 mmol TOPO, and 150 mmol DOE were mixed in a 500 mL 3-neck flask and heated while stirring to 150 °C under vacuum. The initially turbid solution bubbled significantly under vacuum (indicating the dehydration of the zinc acetate) and eventually turned into a clear yellow solution. After 2 hours under vacuum, the solution was transferred to the WANDA nitrogen glove box. This stock solution typically enabled 20-25 syntheses until it needed to be replenished. After 24 hours of sitting at room temperature, the solution would become turbid but could easily be re-dissolved by stirring on a hotplate at 100 °C for 10 minutes. TOPO was used to facilitate the dissolution of ZnAc in the solution mixture and prevent precipitation.

TDPA Stock Solution
1:1:8 TDPA:TOPO:DOE

Typically, 25 mmol TDPA, 25 mmol TOPO, and 200 mmol DOE were mixed in a 500 ml 3-neck flask and heated while stirring to 150 °C under vacuum. The initially turbid solution eventually turned completely clear as the TDPA dissolved. After 2 hours under vacuum, the solution was transferred to the WANDA nitrogen glove box. This stock solution typically enabled 20-25 syntheses until it needed to be replenished. This stock solution was typically stable for up to one month at room temperature and could easily be re-dissolved by stirring on a hotplate at 100 °C for 10 minutes. TOPO was used to facilitate the dissolution of TDPA into the stock solution and prevent it from crystallizing at low temperatures.

AlAcac Stock Solution
1:60 AlAcac:DPE

Typically, 5 mmol AlAcac and 300 mmol DPE were added to a 3-neck flask and heated while stirring to 50 °C under nitrogen flow to melt the DPE. The mixture was subsequently heated under vacuum up to 150 °C while stirring, becoming a clear solution after 10-15 minutes. After two hours, the stock solution was transferred to the WANDA nitrogen glove box. The stock solution was stable for 24 hours at room temperature and was easily re-dissolved by stirring on a hotplate at 100 °C for 10 minutes.

c. Synthesis of Undoped Zinc Oxide Nanorods

All undoped nanocrystal syntheses were performed using WANDA, which is housed in a nitrogen glove box. Typically, 518 mg 1:3:3 ZnAc:TOPO:DOE, 586 mg 1:1:8 TDPA:TOPO:DOE, and 5.820 g of DOE were added to a 40 mL disposable glass vial (See Table S4). The required stock solutions and pure chemicals (OlAlc, DOE) were placed on the WANDA reaction deck and kept stirring at 100 °C to ensure they remained dissolved throughout the course of the synthesis. The reaction mixture was heated to the injection temperature (255-285 °C), T_{inj}, at a ramp rate of 25 °C/min. After incubating at T_{inj} for 20 minutes, 402 mg OlAlc was rapidly injected (300 μL/s) into the reaction bath at T_{inj} and the temperature was decreased to the growth temperature (235-270 °C), T_{growth}.[1] The growth temperature was typically 15-20 °C below the injection temperature. It is important to note that the TOPO:Zn molar ratio was kept approximately constant (3:1 TOPO:Zn) for every synthesis reported in this manuscript.

Ten minutes after the initial hot injection of OlAlc, the first injection set was performed. Each injection set was a sequence of stock solution/precursor injections into the reaction bath. The stock solutions were injected slowly (17 μL/s) to minimally perturb the reaction temperature. A typical synthesis involved 20 injection sets spaced 5 minutes apart of 107 mg 1:1:8 TDPA:TOPO:DOE, 155 mg 1:3:3 ZnAc:TOPO:DOE, and 121 mg OlAlc. This corresponds to 30% (mol) of Zn injected in each injection set compared to the initial amount of zinc precursor present. After the final injection set was complete, the reaction temperature was maintained at T_{growth} for 10 minutes until it was cooled to room temperature by nitrogen flow. Table S4 provides the details of each synthesis presented in this manuscript.

d. Synthesis of Al-doped Zinc Oxide Nanorods:

All doped nanocrystal syntheses were performed using WANDA in an air-free environment. In a typical doped synthesis, the exact same procedure for undoped zinc oxide nanorods was used with the following changes. First, a specified amount (corresponding to a molar % of Al relative to Zn) of 1:60 AlAcac:DPE was added initially to the 40 mL vial prior to heating to T_{inj}. In addition, throughout the synthesis, each injection set sequence was modified to add the specified amount of 1:60 AlAcac:DPE in between the injections of 1:3:3 ZnAc:TOPO:DOE and OlAlc.

For example, in a 15% (mol) Al-doped zinc oxide nanorod synthesis, 395 mg of the 1:60 AlAcac:DPE stock solution was added to the 40 mL disposable glass vial prior to the start of the reaction. For each of the injection sets, 119 mg of 1:60 AlAcac:DPE was added in between the injections of 1:3:3 ZnAc:TOPO:DOE and OlAlc. Table S4 contains the molar equivalents of each reactant used throughout the synthesis.

e. Washing:

The reaction mixture was washed at least twice prior to any characterization. In the first washing step, the thick, white reaction mixture (~10-15 mL) was removed from

[1] For a slow heating synthesis performed with 1,12-Dodecanediol, the alcohol was placed in the reaction mixture and heated to temperature and the ZnAc:TOPO:DOE stock solution was rapidly injected at T_{inj} instead.

WANDA, transferred to a 50 mL centrifuge tube, and diluted with 10 mL chloroform. Subsequently, 25 mL of 2-propanol were added to induce flocculation. The resulting mixture was centrifuged for 10 minutes at 9000 RPM. The supernatant was discarded, and the precipitate from the first washing step was a thick, white, diamond-shaped pellet that was dispersed in 10 mL chloroform. The dispersed precipitate/ chloroform mixture was a thick, white liquid. Subsequently, 5-7 mL each of OctAm and NonAc were rapidly added to the mixture, which caused the mixture to become translucent/clear and notably warmer after 20-30 seconds. The use of OctAm and NonAc has been recently used in isolating cadmium chalcogenide nanocrystals from unreacted precursors[2,3] and was adapted for this synthesis. It was observed that NonAc etches zinc oxide over a course of hours, so care was taken to minimize the time that NonAc was present in the washing mixtures. Finally, 3-5 mL of 2-propanol was added to the mixture until it became slightly cloudier. The mixture was then centrifuged at 9000RPM for 15 minutes, yielding a dense pellet as the final precipitate. Any further purification steps were performed only with chloroform and 2-propanol.

f. Characterization Details:

Transmission Electron Microscopy (TEM):

Images of purified nanoparticles were acquired using a Zeiss Libra 120 TEM and 120 kV acceleration. Samples for TEM analysis were prepared by drop-casting a drop of $CHCl_3$ solution containing zinc oxide nanorods onto holey carbon grids. High-resolution TEM images were obtained using a JEOL-2100 microscope with a LaB_6 filament equipped with a Gatan camera.

Size statistics were tabulated using ImageJ software. For nanorods with tapered shapes, diameter measurements were made at the widest and thinnest areas on each nanocrystal. About 200 measurements were used for each diameter and length histogram.

X-ray Diffraction:

Diffraction patterns were acquired using a Bruker Discovery D8 X-ray diffractometer with Cu Kα1 radiation (λ = 1.5406 Å). The diffractometer was equipped with a General Area Detector Diffraction System (GADDS). All samples were fabricated by drop-casting a solution of nanocrystals in $CHCl_3$ onto a silicon substrate.

Absorbance Spectroscopy:

Spectra were obtained using ASD, Inc. QualitySpec Pro spectrophotometer of nanocrystals dispersed in tetrachloroethylene. Absorption spectra shown in Figure 3 of the manuscript were all normalized to the zinc oxide band edge absorption at 375 nm.

ICP-AES:

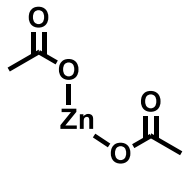
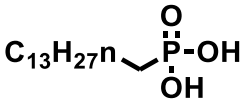
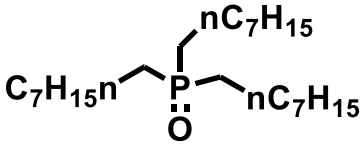
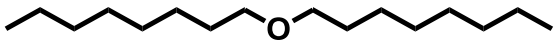
Elemental analysis of Al and Zn was performed using a Varian 720/730 Series spectrometer. Undoped and Al-doped zinc oxide nanorod samples were digested in concentrated HNO_3.

---

[2] Owen et al., *J. Am. Chem. Soc.*, **2008**, *130* (37), pp 12279–12281

[3] Sadtler et al, *J. Am. Chem. Soc.*, **2009**, *131* (14), pp 5285–5293

Table S1F. Structural formulas of synthetic precursors
The role of each precursor in the reaction is also indicated

Metal Precursor	Zinc Acetate [ZnAc]	
Nucleophile	Oleyl Alcohol [OlAlc]	
Surfactant	Tetradecyl-phosphonic Acid [TDPA]	
Surfactant	Trioctylphosphine Oxide [TOPO]	
Solvent	Dioctyl Ether [DOE]	

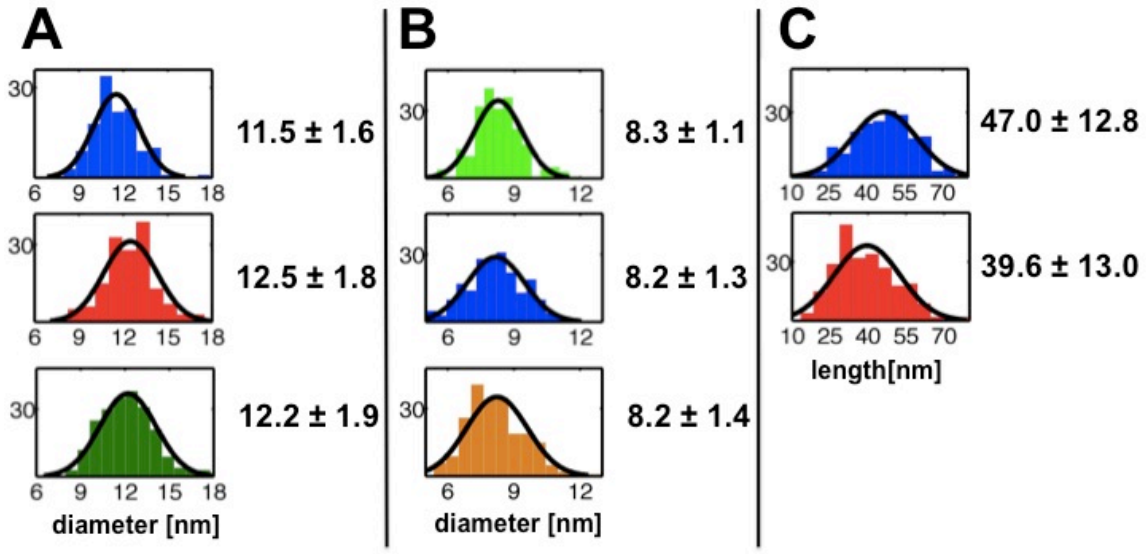


Figure S2. Size statistics of colloidal ZnO nanorods. (A) Diameter statistics for nanorods shown in Fig. 1A, (B) diameter statistics for nanorods shown in Fig. 2A-C, and (C) length statistics for nanorods shown in Fig. 2D-E. Colors correspond to the TEM images in Figs. 1 and 2.

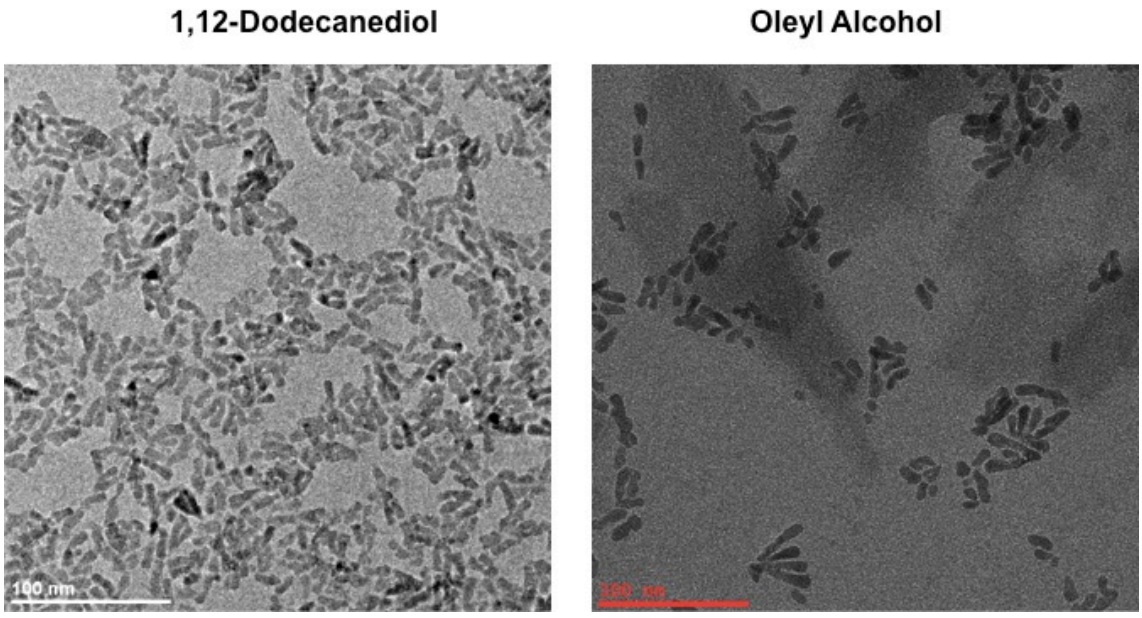


Figure S3A. TEMs of zinc oxide nanocrystals obtained using 1,12-Dodecanediol or Oleyl Alcohol as a nucleophile with no injection sets[4]. All scale bars 100 nm.

[4] Oleyl Alcohol was chosen because it is a liquid at room temperature and is this easily compatible with any syringe pump apparatus. Since 1,12-Dodecanediol is solid at room temperature, additives are required to create a homogeneous liquid solution capable of being injected. The relative molar amounts of oleyl alcohol used were twice as much as the amount of 1,12-Dodecanediol, which was chosen in order to keep the molar amounts of –OH groups constant.

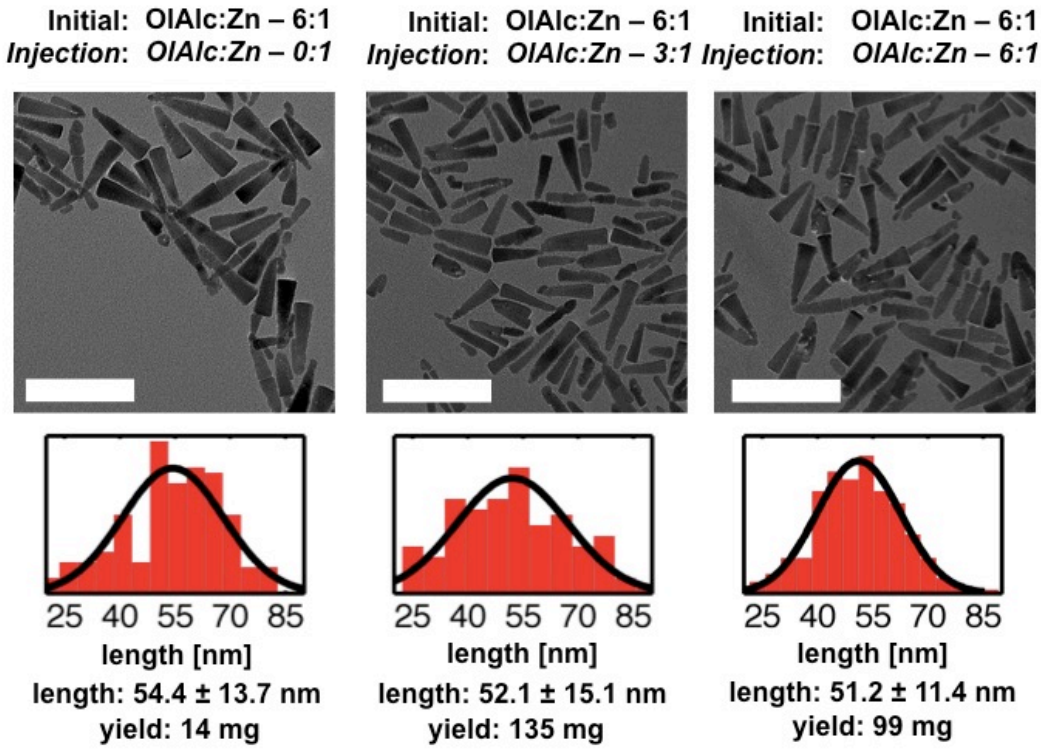


Figure S3B. Comparison of nanorod syntheses performed with increasing (from left to right) oleyl alcohol amounts in each injection set[5]. Size distribution histograms indicate similar nanorod dimensions. The yield significantly increases with addition of oleyl alcohol throughout the course of the synthesis. All scale bars are 100 nm.

[5] No size selection was intentionally performed in the yield calculations. Yields were estimated by weighing the isolated precipitate after leaving the precipitate under vacuum for 15 minutes.

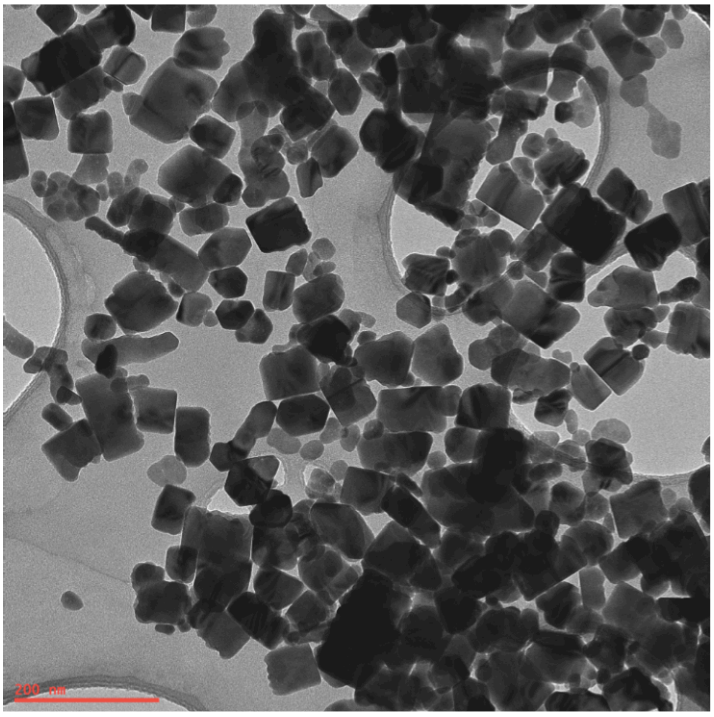


Figure S3C. Effect of phosphonic acid on synthesis. TEM image of nanocrystal synthesis performed with **no** phosphonic acid surfactant used (initially and during each addition set). Scale bar is 200 nm.

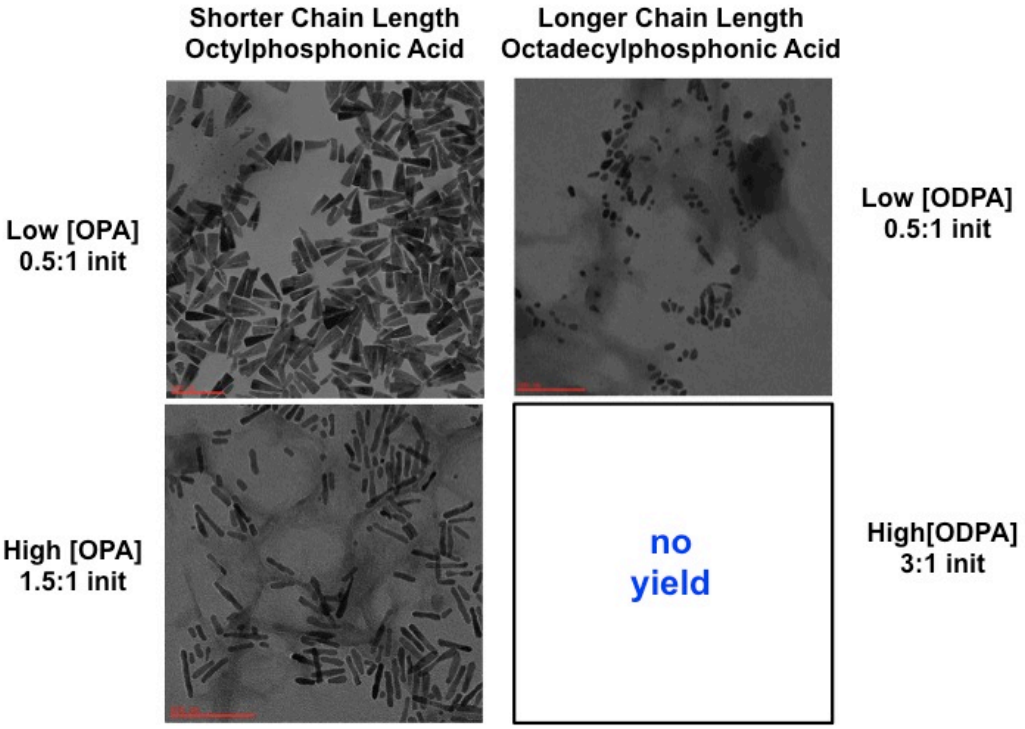


Figure S3D. Effects of different alkylphosphonic acid chain lengths and concentration on nanorod morphology and yield. All scale bars are 100 nm.

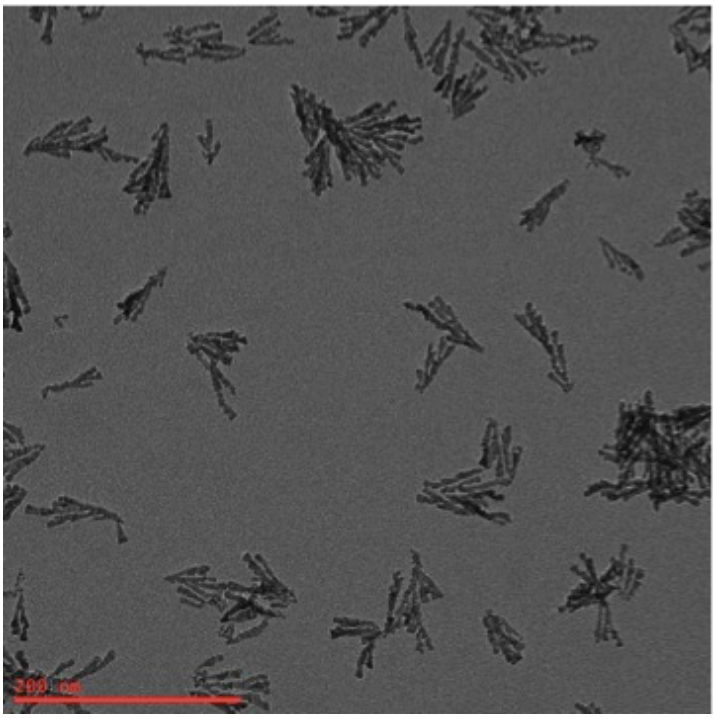


Figure S3E. Effect of a longer alkyl chain zinc carboxylate precursor, zinc undecylnate, on the nanorod morphology.[6] Scale bar is 200 nm.

[6] A shorter alkyl chain zinc carboxylate precursor, zinc formate, was tested and no yield was obtained. This is likely due to precipitation of zinc formate from the reaction mixture prior to the alcoholysis reaction.

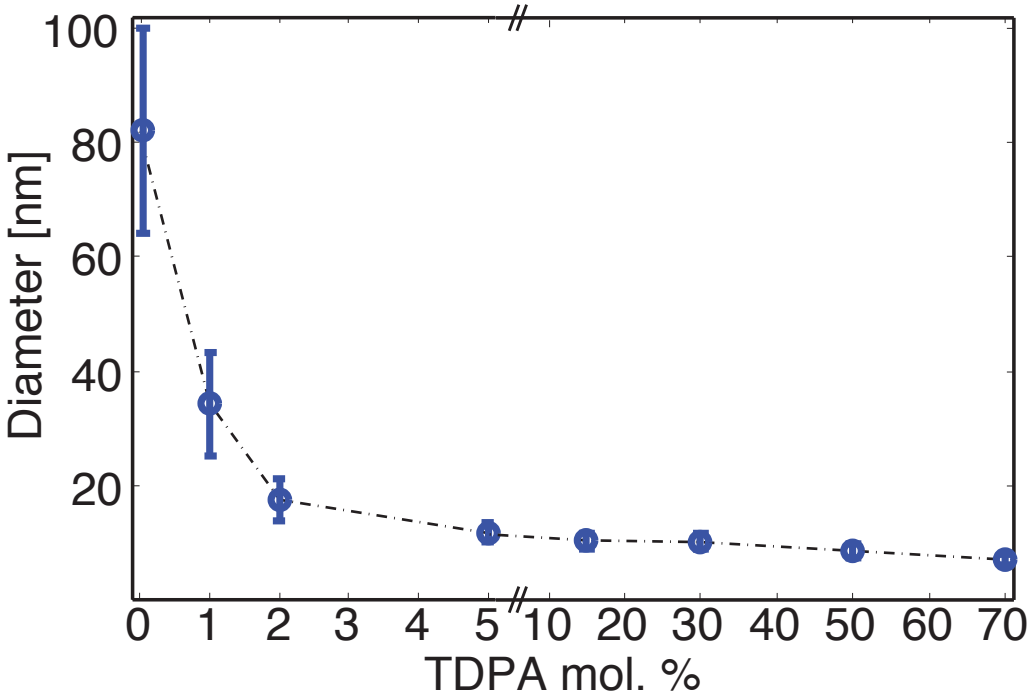
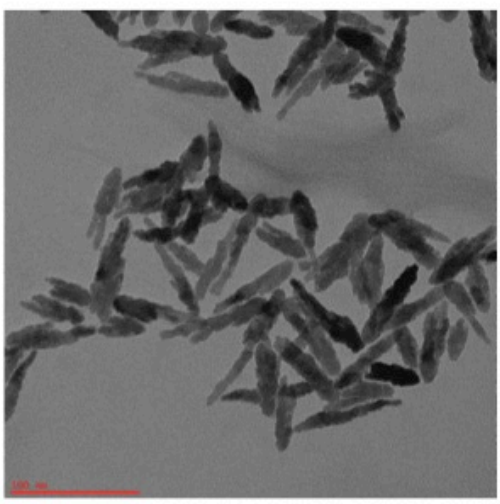
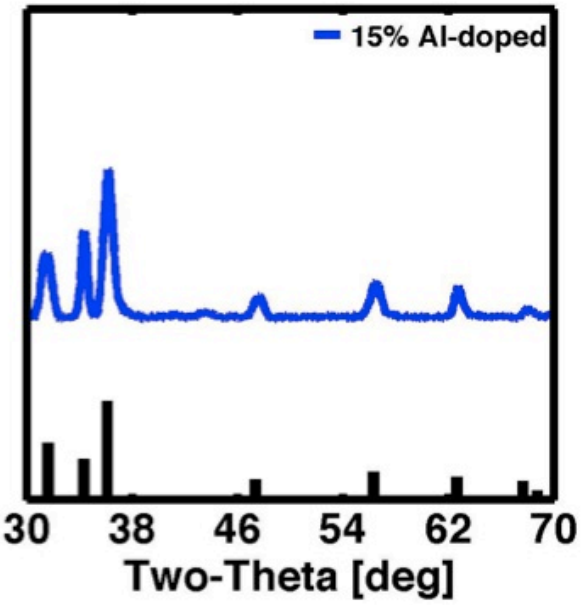


Figure S3F. Nanorod diameter distributions as a function of TDPA concentration. Nanorods were synthesized with varying TDPA:Zn molar ratios – see Figure 4 in the manuscript. The TDPA:Zn molar ratio is described as the mol. % of TDPA in the synthesis. Dashed line serves as a guide to the eye.





Initial dopant present (mol % Al)	*9*	*15*
Dopant concentration by ICP-AES (at % Al)	*0.96*	*1.59*

Figure S3G. TEM of 15% (mol) Al doped ZnO nanorods (top left), XRD patterns of 15% Al-doped ZnO nanorods (top right), and dopant incorporation efficiency as determined by ICP-AES[7] (bottom). Scale bar is 100 nm.

[7] Doping levels estimated from Zn (206 nm) and Al (308 nm) peaks.

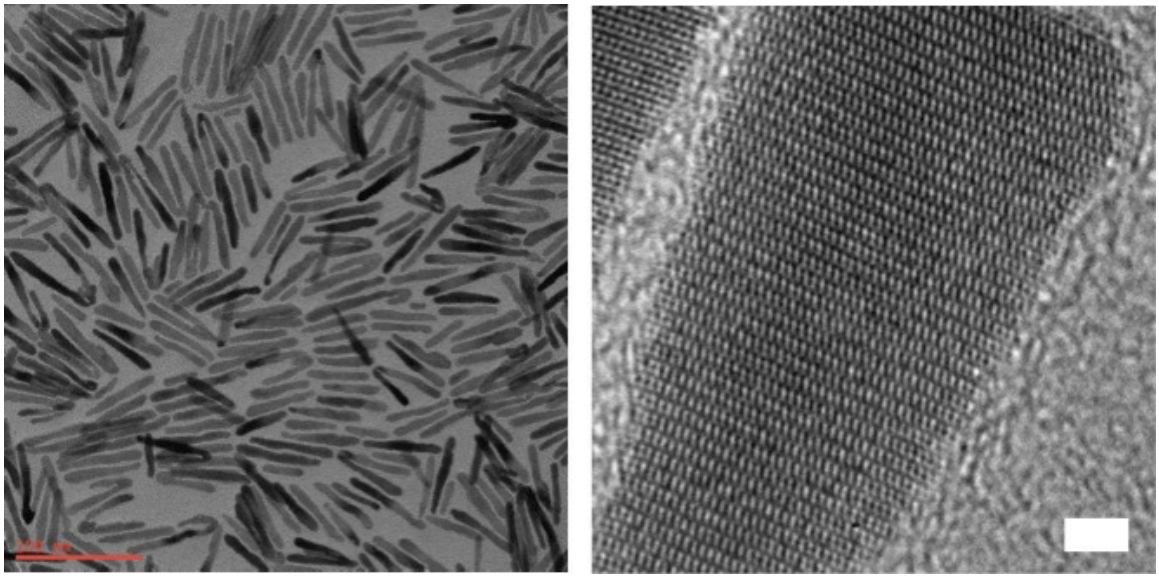


Figure S3H. Low resolution TEM of undoped ZnO nanorods (left) and high resolution TEM of undoped ZnO nanorods (right). Scale bar for left image is 100 nm, and the scale bar for right image is 2 nm.

Table S4. Synthetic Details. Addition rates and molar amounts for nanorod syntheses

Reaction Variables		Synthesis (Figure References)							
		Fig. 1A-C	**Fig. 3A**	**Fig. 3B**	**Fig. 3C**	**Fig. 3D**	**Fig. 3E**	**Fig. 4A-H[4]**	**Fig. 5A**
Injection T [°C]		*270*	*270*	*270*	*270*	*255*	*285*	*270*	*270*
Growth T [°C]		*250*	*250*	*250*	*255*	*235*	*265*	*250*	*255*
Initial ZnAc [mmol]		*0.5*	*0.25*	*0.25*	*0.25*	*0.25*	*0.25*	*0.25*	*0.25*
Type of Alcohol: (Alc)		1,12-Dodeca-nediol	Oleyl Alcohol	Oleyl Alcohol	Oleyl Alcohol	Oleyl Alcohol	Oleyl Alcohol	Oleyl Alcohol	Oleyl Alcohol
Initial Reactant molar ratios[8]	Alc: ZnAc	*3.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*
	TDPA: ZnAc	*0.50 : 1*	*0.75 : 1*	*0.90 : 1*	*0.85 : 1*	*0.90 : 1*	*0.90 : 1*	***X**: 1*	*0.90 : 1*
	AlAcac: ZnAc	-	-	-	-	-	*0.15 : 1*	-	*0.15 : 1*
Injection sets		*20*	*10*	*25*	*30*	*20*	*20*	*30*	*20*
Number of injections per injection set		*1*	*3*	*3*	*3*	*3*	*3*	*3*	*4*
Injection set Spacing [min]		*30*	*5*	*5*	*10*	*5*	*5*	*7*	*5*
Total number of injections[9]		*20*	*31*	*76*	*91*	*61*	*61*	*91*	*81*
Molar ratio of ZnAc in each injection set to initial ZnAc		*0.26 : 1*	*0.30 : 1*	*0.30 : 1*	*0.20 : 1*	*0.30 : 1*	*0.30 : 1*	*0.20 : 1*	*0.30 : 1*
Reactant molar ratios during Injection Sets	Alc: ZnAc	-	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*
	TDPA: ZnAc	-	*0.50:1*	*0.55:1*	*0.50:1*	*0.55:1*	*0.55:1*	***X**:1*	*0.55:1*
	AlAcac: ZnAc	-	-	-	-	-	*0.15 : 1*	-	*0.15 : 1*
Effective addition rate [µmol/min]	Alc	-	*90*	*90*	*30*	*90*	*90*	*42.9*	*90*
	TDPA	-	*7.49*	*8.25*	*2.5*	*8.25*	*8.25*	*3.93*	*8.25*
	ZnAc2	*4.3*	*15*	*15*	*5*	*15*	*15*	*7.15*	*15*
	AlAcac	-	-	-	-	-	*2.25*	-	*2.25*
Final molar ratios of reactants[10]	Alc: ZnAc	*0.45 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*	*6.00 : 1*
	TDPA: ZnAc	*0.08 : 1*	*0.56 : 1*	*0.59 : 1*	*0.55 : 1*	*0.60 : 1*	*0.60 : 1*	*X : 1*	*0.60 : 1*
	AlAcac: ZnAc	-	-	-	-	-	*0.15 : 1*	-	*0.15 : 1*
Reaction total amounts [mmol]	Alc	*1.5*	*6.00*	*12.75*	*10.50*	*10.50*	*10.50*	*10.50*	*10.50*
	ZnAc	*3.29*	*1.00*	*2.13*	*1.75*	*1.75*	*1.75*	*1.75*	*1.75*
	TDPA	*0.25*	*0.56*	*1.26*	*0.96*	*1.05*	*1.05*	*1.75**X***	*1.05*
	AlAcac	-	-	-	-	-	*0.26*	-	*0.26*

[8] After the initial hot injection of oleyl alcohol and prior to injection sets
[9] Total injections performed during synthesis, including the initial hot injection
[10] After the completed synthesis
[4] Molar ratios of TDPA:Zn are expressed in the form of X:1, where X is the TDPA mol. % of ZnAc maintained throughout the entire synthesis (X varies from 0-0.7, or 0 to 70% of ZnAc)