

Electronic Supplementary Information

“A new insight into the adsorption-dissolution growth mechanism of zinc oxide hollow hexagonal nanotowers”

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Experimental methods:

Synthesis of ZnO Nanostructures.

5 g of (*N*-Cetyl-*N,N,N*-trimethyl ammonium bromide) CTAB (HPLC Lab Reagents) was weighed and added slowly into 120 mL double de-ionized water (Thermo-Scientific, 18.2 MΩ) while stirring at room temperature. The mixture was stirred for 10 minutes and further sonicated in ultra sonic bath for 20 minutes. After that 10 g of zinc acetyl acetonate monohydrate ($\text{Zn}(\text{acac})_2 \cdot \text{H}_2\text{O}$) or zinc 2,4-pentenedionate monohydrate (Alfa Aesar) was added slowly while stirring the reaction mixture and kept for sonication for about 30 minutes to dissolve the ($\text{Zn}(\text{acac})_2 \cdot \text{H}_2\text{O}$). 5 ml of 28% ammonium hydroxide (NH_4OH) solution (Alfa Aesar) was slowly added to the reaction mixture of ($\text{Zn}(\text{acac})_2 \cdot \text{H}_2\text{O}$) and CTAB, and sonicated for 30 minutes. The solution suspension was transferred into Teflon-lined stainless steel autoclave which was kept in oven for 5 hours at 200°C. Later the autoclave was cooled down naturally. A white precipitate suspended in yellow solution was formed. The precipitate was centrifuged (Kubota 4200) at 4500 rpm at room temperature and washed with distilled water several times and finally dried at 60°C on hot plate. This was termed as as-synthesized sample. As-synthesized sample was calcined at 550°C in muffle furnace for 5 hrs and used for further characterization.

Control reaction was carried out to monitor the growth of the ZnO hollow hexagonal nanotowers. All the parameters were kept constant except reaction temperature which was 80°C. Sample was collected from reaction solution after certain time intervals while continuing the reaction.

Instrumentation:

XRD spectroscopy: The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer (wavelength 0.154 nm, $\text{Cu}_{K-\alpha}$).

Scanning electron microscopy (SEM): SEM measurements were carried out using Sigma Carl Zeiss Field Emission Scanning Electron Microscope. For preparing specimen, a small amount of sample powder was dispersed in ethanol solvent and sonicated using Digital Ultrasonic Cleaner LMUC Series for 10 minutes. Then a small drop of suspension was placed on flat surface of the silicon wafers which were then put in sample holder of FE-SEM machine.

TEM: Transmission electron microscopy imaging was performed using Technai G2 200kV TEM (FEI) instrument. For these experiments, nanopowder was subjected to ultrasonication in ethanol for a few minutes and then the solution was placed on the copper grids using microcapillary tubes.

UV-Vis spectroscopy: UV-vis absorption spectra of samples of ZnO were measured using Analytik Jena UV-spectrophotometer. The sample was then prepared by dispersing 1.0 mg of sample powder in 4 mL ethanol. The dispersion was sonicated for 10 minutes and then absorbance of the sample was measured. Before taking the absorbance of the specimen, the UV-Vis spectrometer was calibrated by taking solvent, ethanol in this case, in both the sample cuvette and reference cuvette.

Photoluminescence spectroscopy: Photoluminescence characterization was done with ISS P110 spectrophotometer (Detector: Ocean optics HR2000+)

FT-IR: FT-IR spectra of these samples were measured using Bruker IFS48 Infrared spectrometer. The sample in powder form was placed on sample holder.

Raman spectroscopy: Raman spectra were taken on LAB RAM HR 800 HORIBA JobinYvon.

Spectroscopic Characterization of Nanostructures:

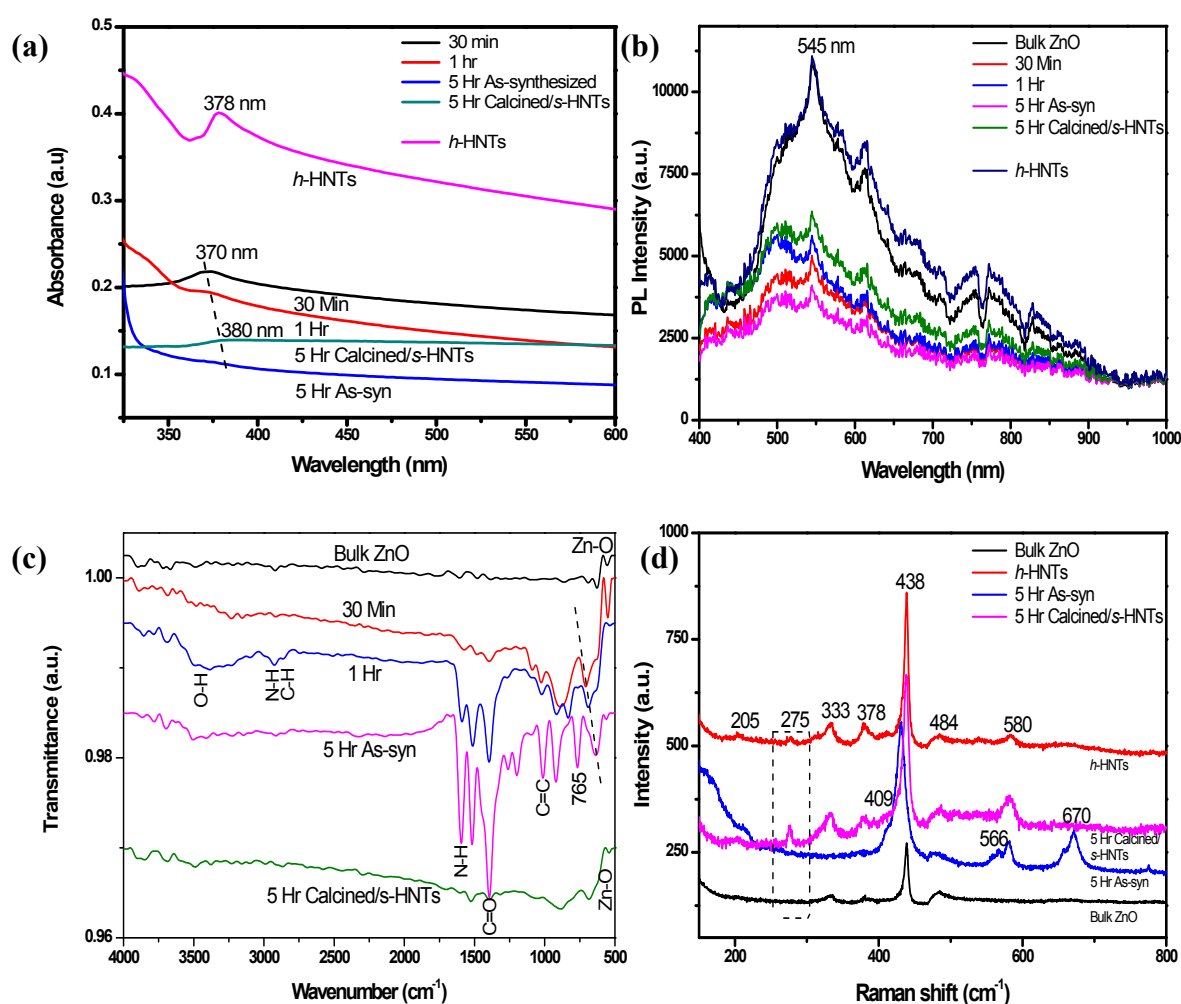


Fig. S1 Spectroscopic characterization of ZnO samples. Characterization of ZnO samples obtained from hydrothermal reactions carried out at 80°C and 200°C, and having diverse morphologies, *viz.*, hierarchical structures, *s*-HNTs and *h*-HNTs as indicated. (a) UV-Visible absorption spectra, (b) Photoluminescence spectra. (c) FTIR spectra (d) Raman spectra. Bulk ZnO powder was taken as standard for comparison.

UV-Vis absorption spectra of ZnO nanostructures were recorded as shown in Fig. S1-a. The main absorption peaks were found to be located around 378 nm for the calcined samples of ZnO (both solid and hollow HNTs); red-shifted from other uncalcined samples by about 8 nm. The bathochromic shift observed may be attributed due to hierarchical hexagonal morphology of the nanotowers. Prominent absorption peak at 378 nm for the calcined sample from the solvothermal reaction carried out at 200°C indicates well-evolved highly crystalline morphology of ZnO hollow nanotowers which can be corroborated with scanning electron microscopy images. Room temperature photoluminescence spectra with an excitation wavelength (370 nm) were measured to further characterize the ZnO nanostructures.

All these samples showed a weak emission at around 545 nm, which was designated green emission (see Fig. S1-b). This green emission originates from the radiative recombination of photogenerated holes with electrons occupying oxygen vacancies.^{1, 2} The visible emission of ZnO nanostructures has a much broader band ranging from 400 to 900 nm which is usually attributed to deep-level emission caused by defects of oxygen vacancies.³ Considering the large surface area-volume ratio in nanostructures, the broadening observed in the visible emission can be ascribed to abundant surface defects. The hollow nanotowers, which show smooth outer and inner surfaces, exhibit comparatively increased PL intensity.

FTIR spectra recorded at room temperature within the range of 500 cm^{-1} to 4000 cm^{-1} for ZnO samples collected at various stages of the hydrothermal reaction (Fig. S1-c). Spectrum of bulk ZnO standard was also recorded for comparison. Metal oxides generally exhibit absorption bands below 1000 cm^{-1} (fingerprint region), which arises from inter-atomic vibrations. It was found that the peculiar zinc oxide absorption band with stretching mode of Zn-O was around 550 cm^{-1} , which corresponds to E2 form of hexagonal ZnO wurtzite crystal (lattice) structure.⁴ The bands observed between 1150 cm^{-1} to 650 cm^{-1} showed gradual shift in their respective band positions during the nanostructures evolution. In particular, significant change in band position observed from 711 cm^{-1} to 693 cm^{-1} to 636 cm^{-1} during evolution of nanomorphology. These noteworthy featured bands in this region are attributed to the C=C bending vibrations present in zinc acetylacetonate. Gradual band-shift is indicative of the reaction of the zinc precursor to form $\text{Zn}(\text{OH})_2$ and subsequently ZnO. The band at around 1400 cm^{-1} is because of C=O stretching mode and is from precursor material zinc acetyl acetonate. The IR bands around and 2900 cm^{-1} might be due to and C-H stretching, respectively and are probably aroused from precursor CTAB. The band at around 1580 cm^{-1} might be due N-H bending from CTAB. It is to be noted that a new band emerged at 765 cm^{-1} was observed for as-synthesized ZnO which has hierarchical morphology along with some sheet-like structures. This band is indicative of the C-H bending mode and could be from intermediate unknown compound. The IR band at \sim 1606 cm^{-1} corresponds to bending vibration due to adsorbed H_2O (moisture) on ZnO particles.⁵ The strong absorption around 3400 cm^{-1} corresponds to the asymmetric and symmetric stretching H-O-H vibration from $\text{Zn}(\text{OH})_2$.⁴

Raman spectroscopy is one of the most common investigation techniques which provide information on the structural and chemical properties such as orientation, crystallinity and existence of defects and impurities. Figure S1-d shows the room temperature Raman spectra of ZnO nanostructures obtained. ZnO is a wurtzite crystal with C_{6v} ⁴ symmetry having uniaxial crystallinity. In an ideal backscattering configuration, $A_1(\text{TO})$, $A_1(\text{LO})$, $E_1(\text{TO})$, and E_2 modes are allowed in first-order Raman scattering, when the incidence direction with respect to crystal axis is not defined.¹ Although each ZnO nanotower is c -axis oriented, the whole nanotowers are randomly arrayed. Therefore, the three aforementioned modes i.e. $A_1(\text{TO})$ at 378 cm^{-1} , $E_1(\text{TO})$ at 409 cm^{-1} , and $E_2(\text{high})$ at 438 cm^{-1} , appear as

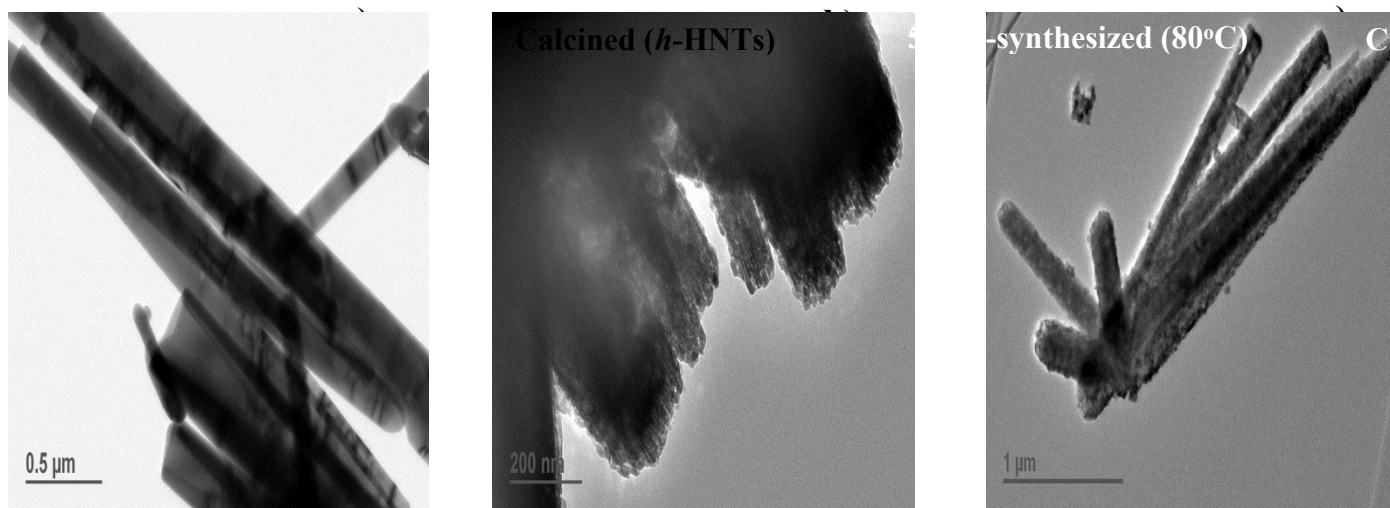
shown. The peak at 333 cm^{-1} is assigned as $E_2(\text{high})$ - $E_2(\text{low})$ mode and $A_1(\text{LO})$ mode is observed at 536 cm^{-1} . The peak at 580 cm^{-1} is attributed to the $E_1(\text{LO})$ mode. The large surface area, high surface roughness, and hierarchical structure (see Fig. 2 in the manuscript for SEM images of the ZnO nanostructures synthesized) imply the pronounced enhancement of surface activity compared with that of bulk crystal and this may activate normally forbidden $E_1(\text{LO})$ mode. This is the reason why we observe $E_1(\text{LO})$ mode at 580 cm^{-1} for all ZnO nanostructures shown except bulk ZnO. In addition, the peak observed at 670 cm^{-1} is due to multiple phonon scattering process.¹ It is worth noting that there observed a shift in band position from 438 to 432 cm^{-1} for hierarchical nanostructure (5 h as-synthesized). The E_2 (high) mode not only broadened, but also shows an asymmetric broadening towards the low frequency side. FTIR spectra also denoted emergence of new band at 765 cm^{-1} (Fig. S1-c) for these hierarchical structures.

Energy dispersive X-ray (EDX) spectroscopy and transmission electron microscopy

Supplementary Table 1: Weight% and atomic% of ZnO samples* by Energy dispersive X-ray (EDX) spectroscopy at various stages of hydrothermal reactions

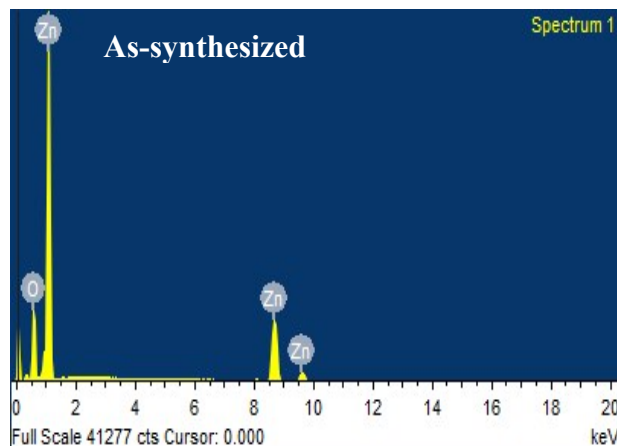
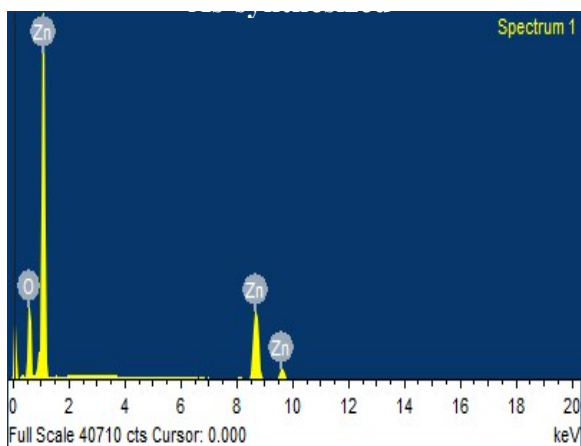
	Sample Description	Weight %		Atomic %	
		Oxygen	Zinc	Oxygen	Zinc
Hydrothermal reaction at 200°C	As-synthesized	23.14	76.86	55.15	44.85
	Calcined (<i>h</i> -HNTs)	24.75	75.25	57.34	42.66
Hydrothermal reaction at 80°C	30 min	23.96	76.04	56.29	43.71
	1 hr	30.56	69.44	64.26	35.74
	5 hr as-synthesized	37.61	62.39	71.12	28.88
	5 hr calcined (<i>s</i> -HNTs)	18.49	81.51	48.11	51.89

* Amount of carbon present in the sample materials is not considered as carbon tape was used as substrate for SEM-EDX measurements.

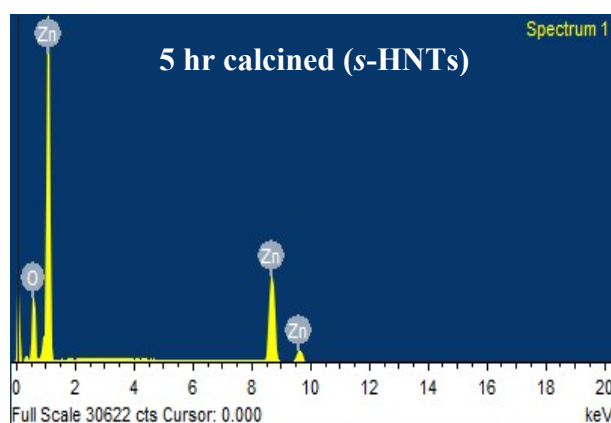
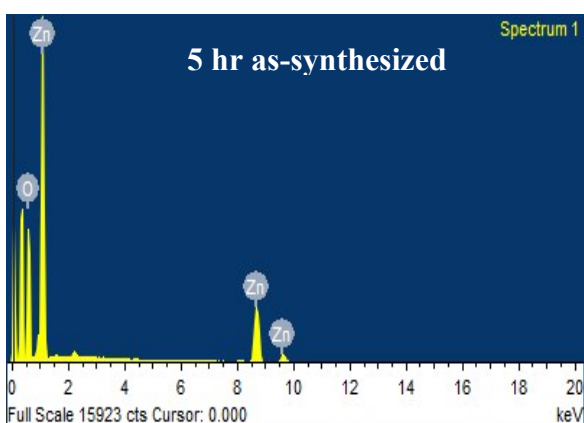
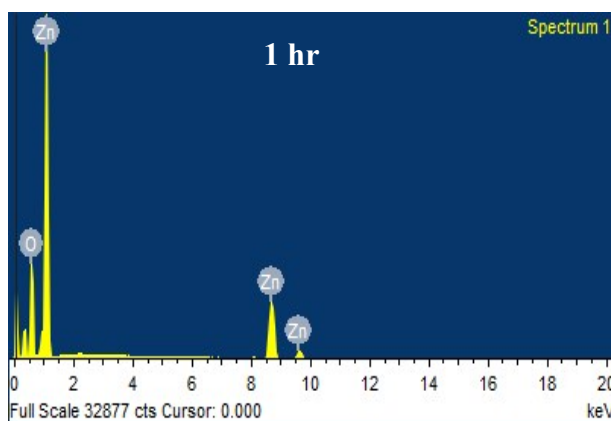
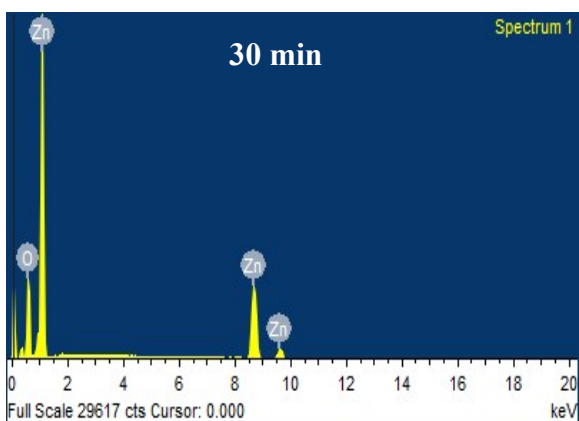


Supplementary Figure S2: Transmission electron microscopy images of **a**, calcined ZnO sample obtained from the hydrothermal reaction carried out at 200°C. ZnO samples obtained from hydrothermal reaction at 80°C, **b**, as-synthesized sample (5 h), **c**, solid nanotowers obtained by calcination at 550°C.

(a) Hydrothermal reaction at 200°C



(b) Hydrothermal reaction at 80°C (Control)



Supplementary Figure S3: Energy dispersive X-ray (EDX) spectra of ZnO samples at various stages of hydrothermal reactions

References:

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