

Supporting Information for

DNA mediated fast Synthesis of Shape-selective ZnO Nanostructures and their Potential Applications in Catalysis and Dye Sensitized Solar Cells (DSSCs)

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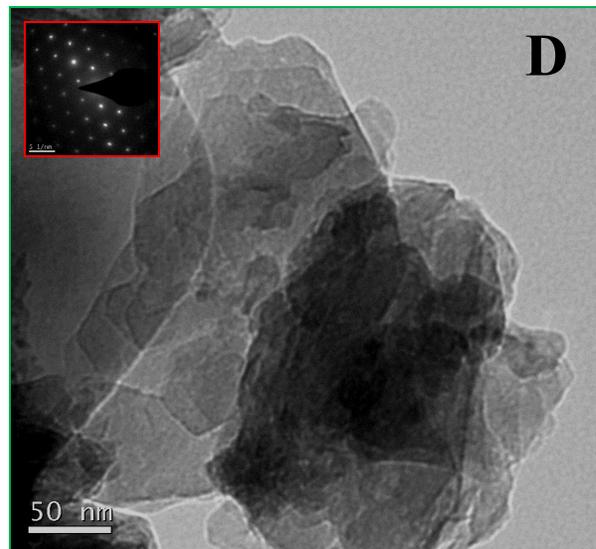
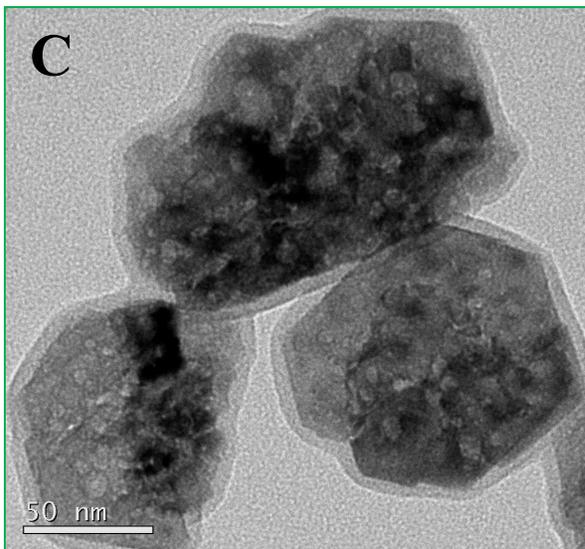
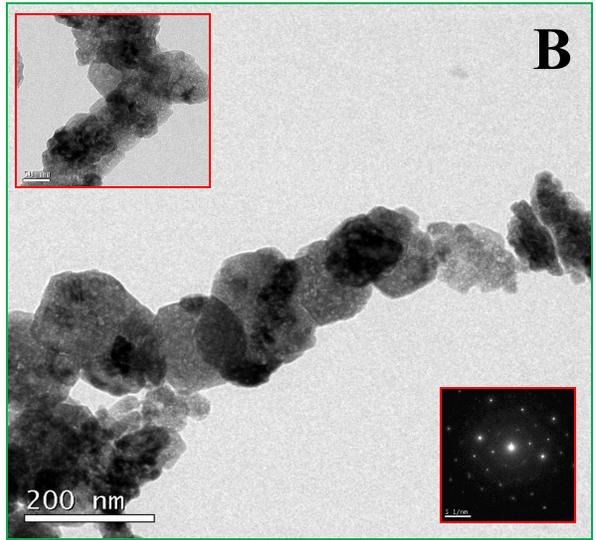
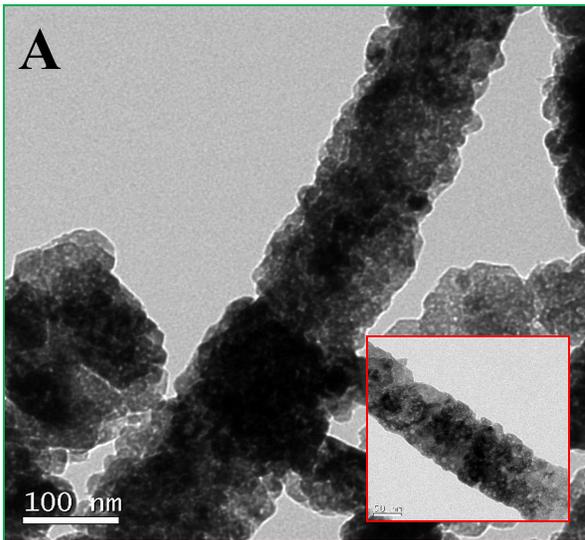
Instruments.

The synthesized shape-selective DNA-ZnO nanomaterials were characterized using several spectroscopic techniques. The UV-Visible (UV-Vis) absorption spectra were recorded in a Hitachi (model U-4100) UV-Vis-NIR spectrophotometer equipped with a 1 cm quartz cuvette holder for liquid samples. A part of the samples also characterized with another double beam spectrophotometer purchased from Unico (model 4802 UV-Vis spectrophotometer). The transmission electron microscopy (TEM) analysis was done with a Tecnai model TEM instrument (TecnaiTM G2 F20, FEI) with an accelerating voltage of 200 KV. The Field Emission Scanning Electron Microscopy (FE-SEM) analysis was recorded with Zeiss ultra FE-SEM instruments. The Energy Dispersive X-ray Spectroscopy (EDS) analysis was done with the FE-SEM instrument where a separate EDS detector (INCA) was connected to that instrument. The LASER Raman measurements were carried out with Renishaw inVia Raman Microscope using an excitation wavelength of 632.8 nm (He-Ne laser). The excitation light intensity in front of the objective was ~10 mW with a spectral collection time of 1 sec for Raman experiment. The integration time for our measurement was set to 10 sec. The X-ray diffraction (XRD) analysis was done using a PAN analytical Advanced Bragg-Brentano X-ray powder diffractometer (XRD) with Cu K_α radiation ($\lambda = 0.154178$ nm) with a scanning rate of 0.020 s⁻¹ in the 2θ range 10-90°. The Fourier Transform Infrared (FT-IR) spectroscopy analysis was done with the model Nexus 670 (FTIR), Centaurms 10X (Microscope) having spectral Range 4,000 to 400 cm⁻¹ with a MCT-B detector. The photoluminescence (PL) study was done with Varian (Cary Eclipse Winflr) fluorescence spectrophotometer (serial number el02045776) both in excitation and emission mode using xenon lamps. The thermal analysis study was recorded with a thermal analyser-simultaneous TGA/DTA instrument with model name SDT Q600 and the analysis was performed in air. A hot air oven (temperature up to 1000 °C) was used to anneal the samples at specific temperature. A domestic microwave (MW) oven (Samsung Company, DE68-03714B) was used for the MW heating during the entire synthesis. The output power was 1000 W and the operating frequency was 2450 MHz. For DSSC sample preparation, the thickness of working electrode was measured by SJ-301 surface roughness tester. The photovoltaic (current-voltage, I-V) measurement was performed by using a solar simulator having model number SS80AAA under the light illumination of 1000 W/m². A spin coater

was used for coating the ZnO samples over glass substrate and purchased from Spektron Company, Chennai. The rotating speed was 1000 rpm and the samples were coated for totally 180 seconds (three times with 60 second each) over glass substrate for the catalysis study and 100 second over FTO plate for DSSC study.

Preparation of sample for other various characterizations.

The shape-selective DNA-ZnO nanostructures were characterized using UV-Vis, TEM, FE-SEM, photoluminescence (PL), EDS, XRD, Raman, FT-IR, and thermal analysis studies. The DNA-ZnO nanostructures solution after successive centrifugation and annealing was used for the measurement in UV-Vis spectrophotometer. For UV-Vis study a liquid solution was made by sonicating the solid ZnO powder for 30 min with DI water. The same liquid solution of ZnO was used for TEM sample preparation and other thin films preparation. The samples for TEM was prepared by placing a drop of the corresponding DNA-ZnO NPs solution over carbon coated Cu grid followed by slow evaporation of solvent at ambient conditions. The dispersed aqueous DNA-ZnO nanostructures were used for the PL measurement. For EDS, XRD, Laser Raman, and FT-IR analysis, glass slides were used as substrates for thin film preparation. The slides were cleaned thoroughly in acetone and sonicated for about 30 min. The cleaned substrates were covered with the DNA-ZnO nanostructures solution and then dried in air. After the first layer was deposited, subsequent layers were deposited by repeatedly adding more ZnO nanostructures solution and drying. Final samples were obtained after 5-6 depositions and then analyzed using the above techniques. For FE-SEM analysis, the samples were prepared in a similar way as discussed before on glass slides but only a single deposition was done. For TGA/DTA analysis, the ZnO dry nano powders are directly used for the measurement. For catalysis study, DNA-ZnO thin film was prepared using a spin coater over glass substrate and dried in oven under 60 °C for 30 min in hot air oven.



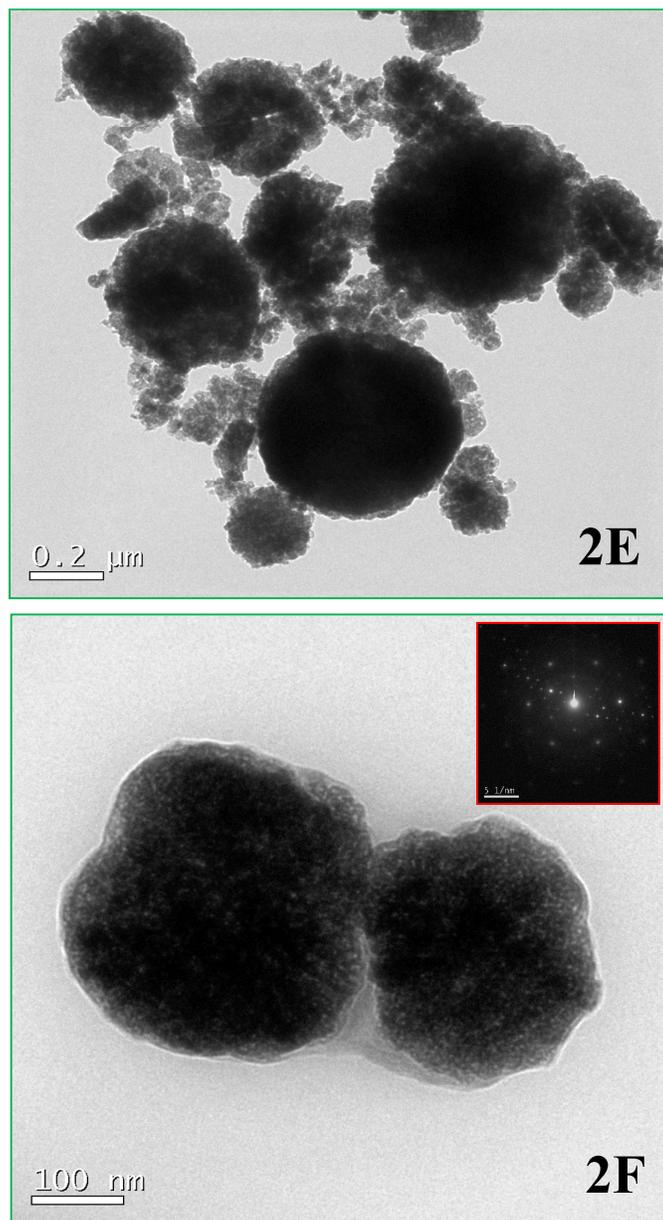


Figure S-1: The transmission electron microscopy (TEM) images of shape-selective DNA-ZnO nanostructures. (A) and (B) show the low magnified TEM images of DNA-ZnO NPs having wire-like shape from the different parts of the sample where the inset of both shows their corresponding higher magnified image. The inset of (B) also shows the selected area electron diffraction (SAED) pattern. (C) and (D) shows the low and high magnified DNA-ZnO NPs having flake-like shapes. The inset of (D) shows the corresponding SAED pattern. (E) show the low magnified TEM image of ZnO NPs having flower-like structure where (F) shows the image of a single nano-flower. The inset of (F) shows the corresponding SAED pattern.

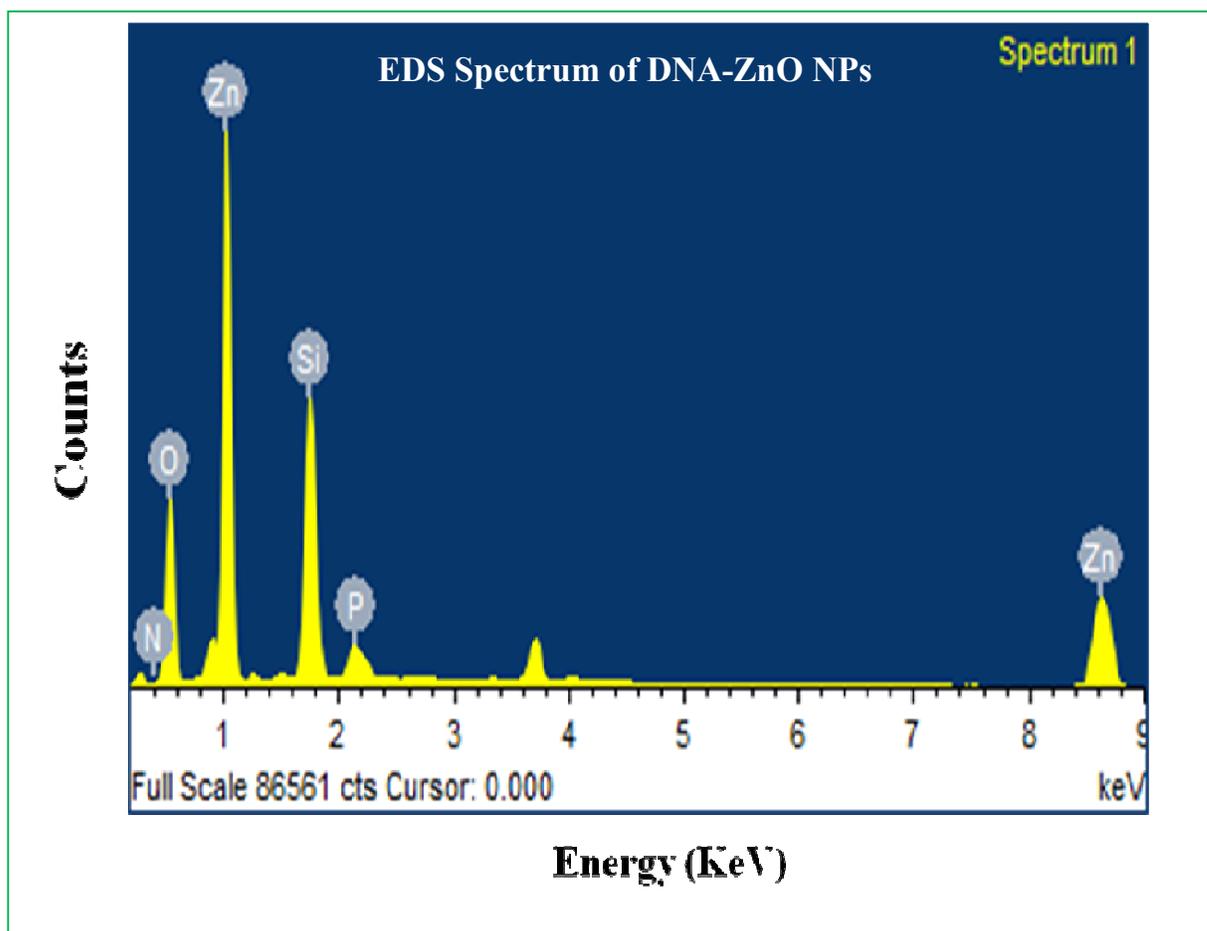


Figure S-2: The energy dispersive X-ray spectroscopic (EDS) analysis of DNA-ZnO nanostructures which consists of the peaks for Zn, O, Si and P.

Thermal analysis of as-synthesized ZnO NPs on DNA scaffold.

In order to characterize the thermal stability and crystalline condition of ZnO NPs on DNA, a thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) were examined. The as-synthesized ZnO samples were heated from RT to 1000 °C with an increment of 10 °C/min in air. Figure S-3 shows the combined TGA and DTA curve of ZnO NPs having wire-like shapes. As an example we describe the detailed analysis taking wire-like ZnO although we did the analysis for other shape also (result not shown here). Curve A, Figure S-3 shows the TGA curve of ZnO NPs with wire-like shape and from the curve we can see that first weight loss takes place at a temperature 100 to 280 °C which is due to evaporation of crystallized water molecule. The second weight loss takes place above 400 °C is due to removal of excess DNA molecules with the ZnO particles. A broad peak started from 450 °C to 820 °C is due to crystallization of ZnO. From the TGA curve we can see that initially we started analysis with 4.08 mg and after heating up to 1000 °C, the amounts of sample remain is 3.80 mg. So the % of weight loss is 6.86%. Curve B, Figure S-3 shows the DTA curve of the same sample which shows an endothermic peak at ~ 308.83 °C.

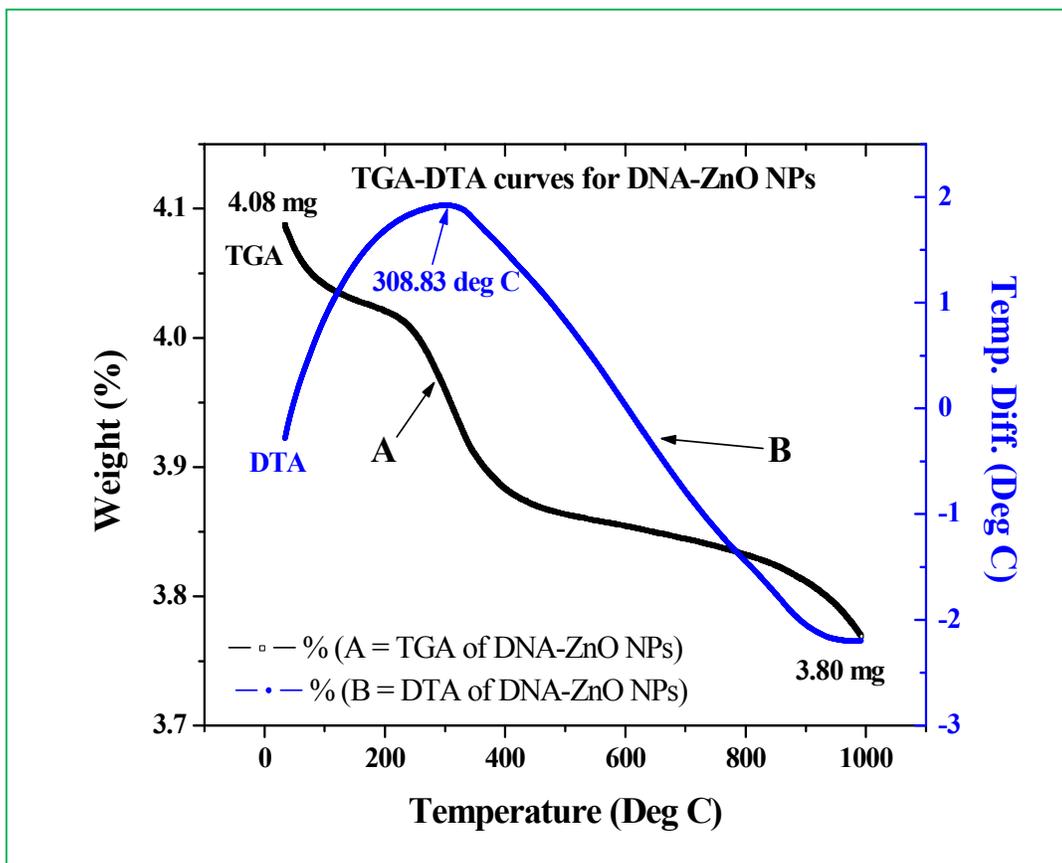


Figure S-3: Combined thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) plots of the DNA-ZnO nanostructures. Curve (A) shows the TGA curve and curve (B) shows the DTA curve.

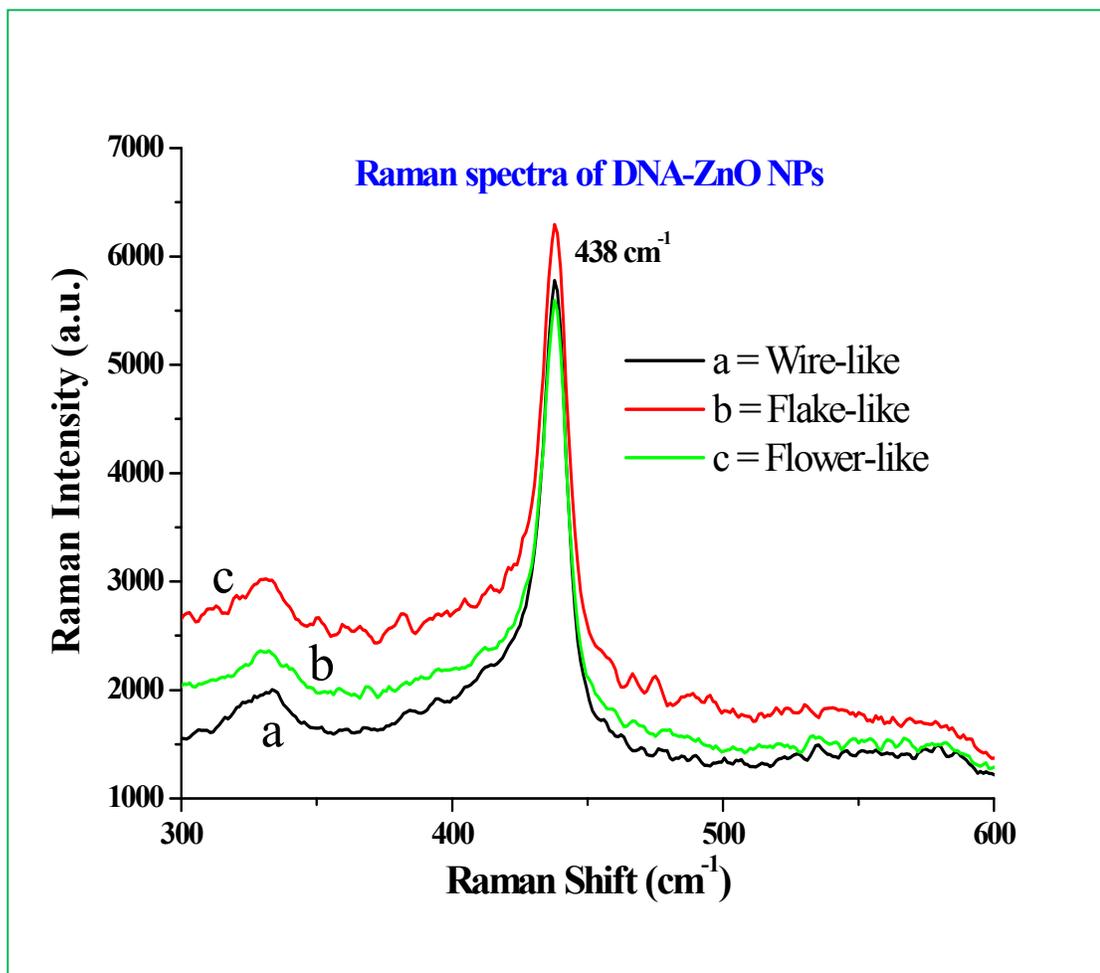


Figure S-4: The Laser Raman spectra of the shape-selective ZnO NPs on DNA. Curve a, b and c denotes the Raman spectra for wire-like, flake-like and flower-like DNA-ZnO NPs respectively.

Study of other reaction parameters.

To get the particles with uniform and definite shape we have conducted few control experiments for the formation of shape-controlled ZnO NPs on DNA. We have varied the concentration of Zn(II) salt, DNA, NaOH and microwave heating time. The shape controlled ZnO NPs, on DNA are formed at a specific concentration that are given in details in Table 1 (in main text). From the Table 1, we can see that wire-like ZnO NPs are formed when DNA concentration was high compared to other sets. Once the DNA concentration reduced they formed flake-like and flower-like shape. It is observed that comparatively higher conc. of Zn(II) ion, flower-like or flake-like shape are formed whereas at a low concentration of Zn(II) ion, generates wire-like shapes. We have checked that at high DNA concentration (final concentration $\sim 2.5 \times 10^{-3}$ M), the ZnO particles formed but they results agglomerated structure as seen in Figure S-5A. At low concentration of DNA (final concentration $\sim 10^{-6}$ M or less), the ZnO NPs formed mostly spherical shapes. We have seen that Zn(II) ions concentration also affect the formation of shape-selective ZnO NPs. When Zn(II) ion concentration is very high (~ 1 M), the reaction generates a mixture of different shapes as seen in Figure S-5B. On the other hand while Zn(II) ion concentration is less ($\sim 10^{-4}$ M), the reaction takes long time to generate the ZnO particles and the yield of the product is also less due to the low concentration of Zn(II) ions in solution. While we used NaOH concentration is very high ($\sim 2-3$ M), the ZnO particles are formed immediately but results agglomerated structure as seen in Figure S-5C. Again, when NaOH concentration is low ($\sim 10^{-4}$ M or less), the reaction takes less time to form ZnO particles. Moreover, we have also checked that 2 min microwave heating is sufficient to generate the shape-selective ZnO particles. Less time (~ 30 sec or 1 min) generate ZnO NPs but particles are not grown fully as observed from TEM analysis (not shown here). Microwave heating for longer period $\sim 3-10$ min does not change much about the particles morphology. Although microwave heating for 20-30 min, generates agglomerated flake-like structures (Figure S-5D). We have checked the pH of the solution mixture and the pH value was below 7 in all the cases. So from the above control experiments it is confirmed that the shape-selective ZnO NPs are formed at a specific concentration while in other concentrations generate un-uniform, agglomerated or mixture of different shaped ZnO nanostructures.

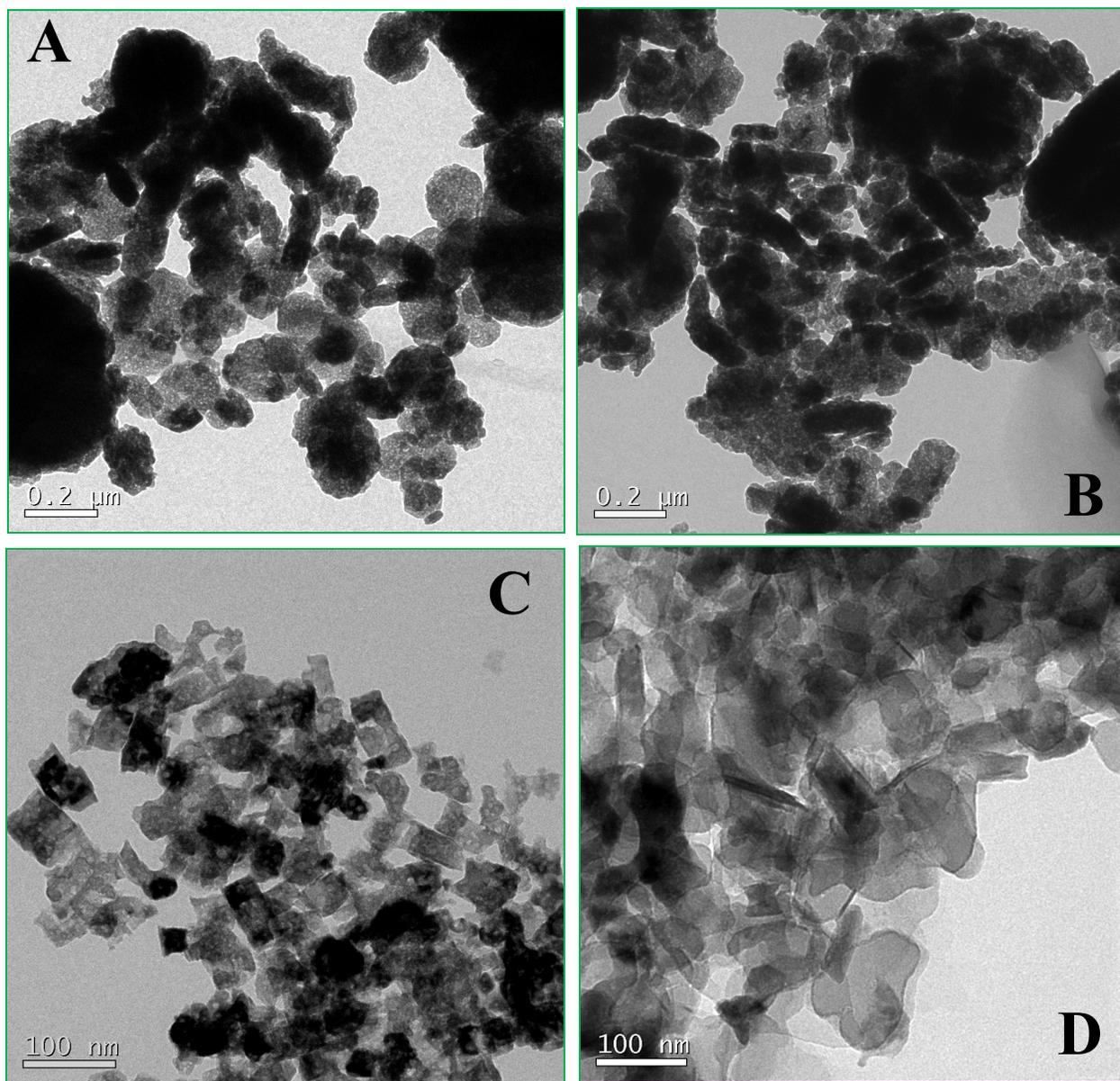
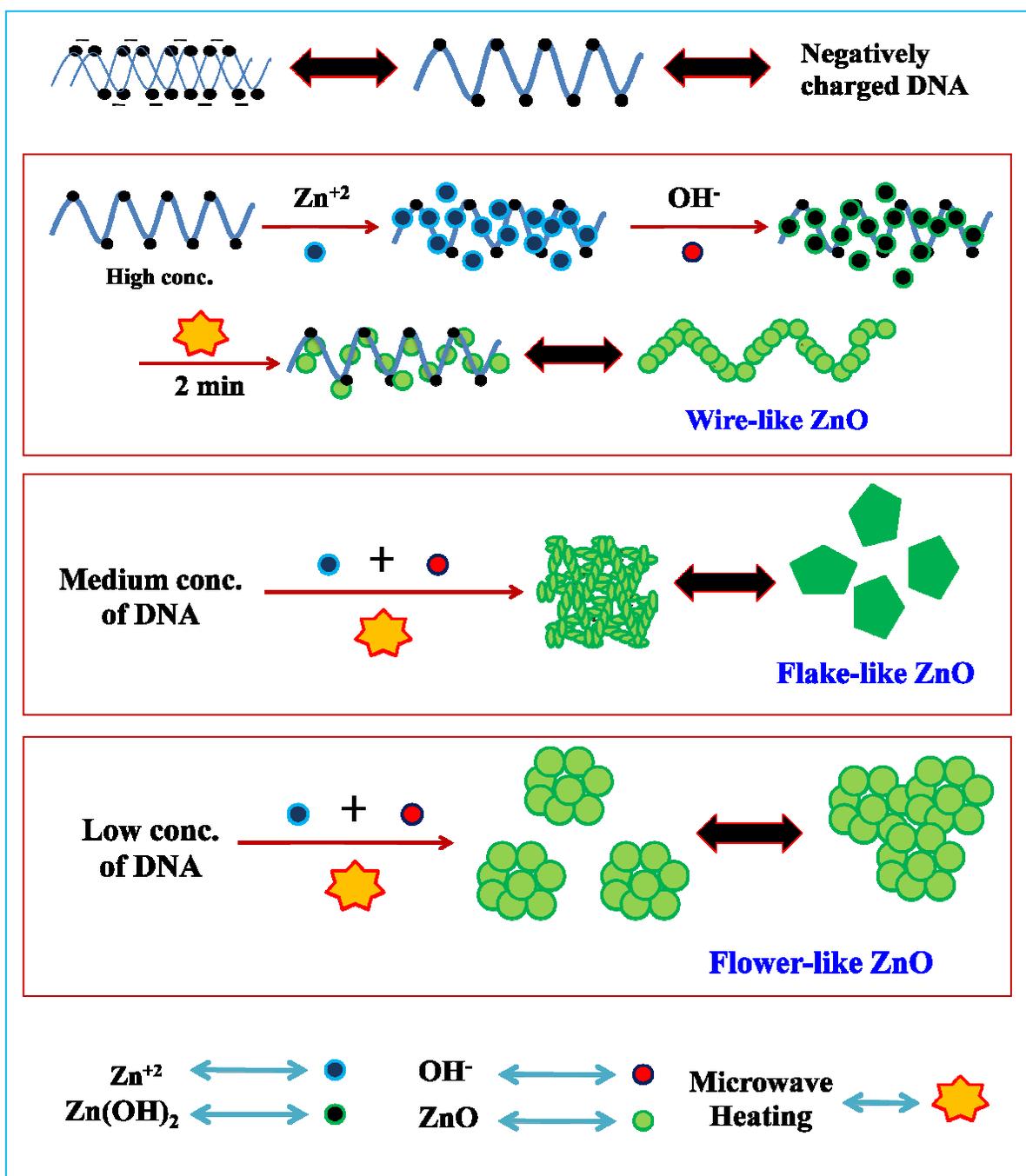


Figure S-5, A-D: The transmission electron microscopy (TEM) images of shape-selective DNA-ZnO nanostructures at different controlled condition. (A) at very high DNA concentration; (B) at high Zn(II) ion concentration; (C) at high NaOH concentration; (D) at excess microwave heating for 20-30 min.



Scheme S-1: The schematic formation and growth of shape-selective ZnO NPs on DNA having wire-like, flake-like and flower-like shapes.