

## Online Supporting Information's for

### **A new Route for the Shape-selective formation of Magnetic MnWO<sub>4</sub> Nanomaterials on DNA Scaffold: Catalytic and Supercapacitor Applications**

**U. Nithiyantham,<sup>†</sup> Sivasankara Rao Ede,<sup>†</sup> T. Kesavan,<sup>#</sup> P. Ragupathy,<sup>#</sup> M. D. Mukadam,<sup>§</sup> S.  
M. Yusuf<sup>§</sup> and Subrata Kundu<sup>†\*</sup>**

<sup>†</sup>Electrochemical Materials Science (ECMS) Division, <sup>#</sup>Fuel Cell Division, CSIR-Central Electrochemical Research Institute (CECRI), Karaikudi-630006, Tamil Nadu, INDIA.

<sup>§</sup>Solid State Physics Division, Bhabha Atomic Research Centre (BARC), Trombay, Mumbai 400085, INDIA.

#### **Instruments**

The shape-selective MnWO<sub>4</sub> nanomaterials on DNA scaffold were characterized using several spectroscopic techniques. The UV-Visible (UV-Vis) absorption spectra were recorded in double beam spectrophotometer purchased from Unico (model 4802 UV-Vis spectrophotometer) equipped with a 1 cm quartz cuvette holder for liquid samples. A part of the samples also characterized with another. The transmission electron microscopy (TEM) analysis was done with a Tecnai model TEM instrument (Tecnai™ G2 F20, FEI) with an accelerating voltage of 200 KV. The Brunauer-Emmett-Teller (BET) analysis was performed with Quantachrome® ASiQwin™ © 1994-2012, Quantachrome Instruments v2.02 and nitrogen (N<sub>2</sub>) gas is used as an adsorptive for the determination of the surface area. The Energy Dispersive X-ray Spectroscopy (EDS) analysis was done using the Field Emission Scanning Electron Microscopy (FE-SEM) instrument where a separate EDS detector (INCA) was connected to that instrument. The X-ray diffraction (XRD) analysis was done using a PAN analytical Advanced Bragg-Brentano X-ray powder diffractometer (XRD) with Cu K $\alpha$  radiation ( $\lambda = 0.154178$  nm) with a scanning rate of 0.020 s<sup>-1</sup> in the 2 $\theta$  range 10-90°. 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  $\sim 10$  mW with a spectral collection time of 1 sec for Raman experiment. The integration time for our measurement was set to 10 sec. The Fourier Transform Infrared (FT-IR) spectroscopy analysis was done with the model Nexus 670 (FT-IR), Centaurms 10X (Microscope) having spectral Range 4,000 to 400  $\text{cm}^{-1}$  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 a xenon pump 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  $^{\circ}\text{C}$ ) was used to anneal the samples at specific temperature. The DC magnetization measurements were carried out, using a vibrating sample magnetometer (Cryogenic, UK make) and the electrochemical studies were carried out using an electrochemical work station (Princeton Applied Research, PARSTAT 4000) and further details are given below. 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.

#### **UV-Visible and Energy Dispersive X-ray Spectroscopy (EDS) analysis**

Figure S-1 shows the diffuse reflectance spectra of solid  $\text{MnWO}_4$  nanomaterials for three different morphologies. The spectra for the aqueous dispersion are given in main document as Figure 1. Figure S-3 shows the energy dispersive X-ray spectroscopic (EDS) analysis of the rice-like  $\text{MnWO}_4$  nanomaterials on DNA scaffold. Here, we showing the analysis taking rice-like  $\text{MnWO}_4$  nanomaterials although other morphology also expected to generate similar types of spectra feature as all are prepared by using the DNA molecule. An EDS analysis is used to identify the probable elements present in the product and the spectrum is consists of the different peaks corresponding to Mn, O, W, P and Na. The large and high intense peak for W, Mn and O came from the  $\text{MnWO}_4$  nanomaterials. The small intense P peak came from the DNA which is used as a stabilizing or capping agent for the formation and growth of the  $\text{MnWO}_4$  nanomaterials. A very low intense Na peak is also appeared probably from the DNA or from the  $\text{Na}_2\text{WO}_4$  as used during our synthesis.

#### **LASER Raman study**

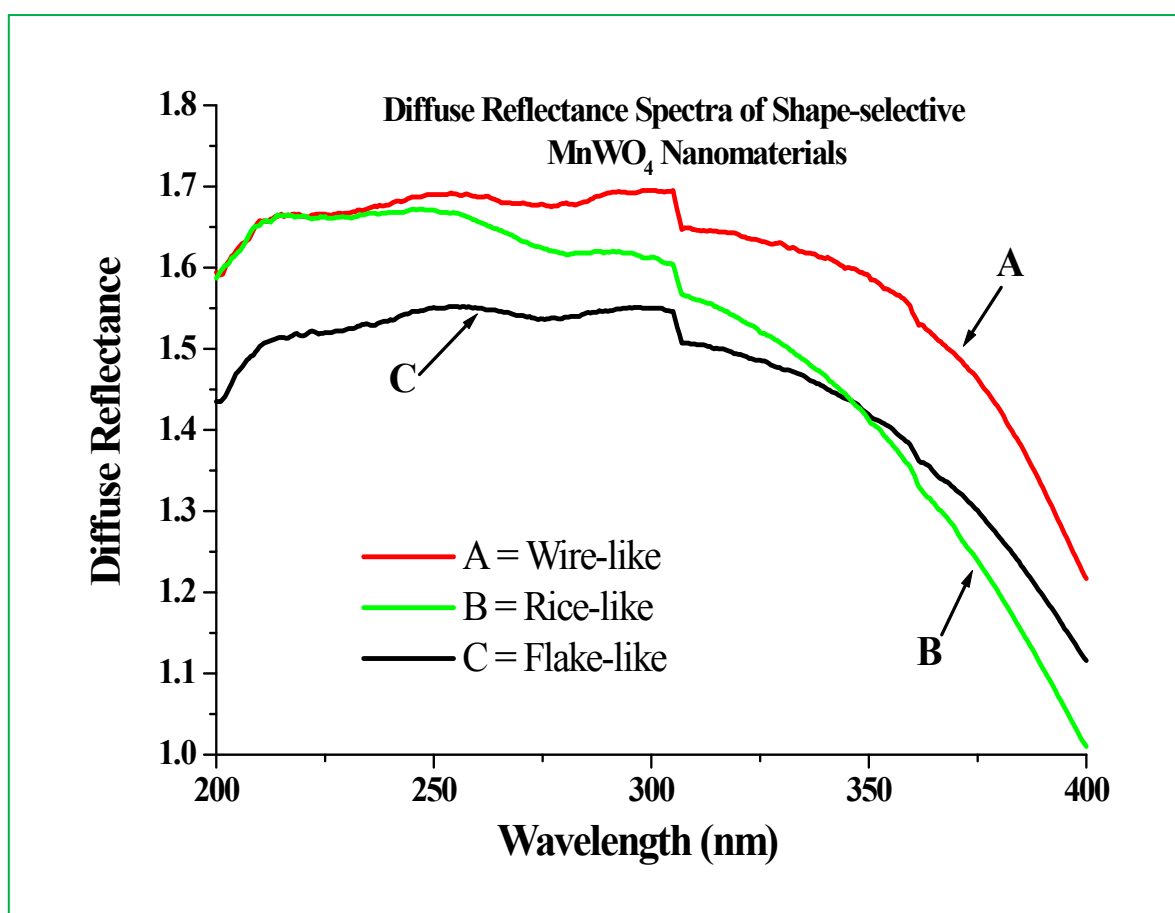
Figure S-4 shows the LASER Raman spectra of the shape-selective  $\text{MnWO}_4$  nanomaterials on DNA. In Figure S-4, curve A, B and C indicates the spectra for wire-like, flake-like and rice-like morphology respectively. The Raman spectra is very similar to those

of huebnerite structured  $\text{MnWO}_4$ .<sup>40</sup> Two very strong bands at  $917\text{ cm}^{-1}$  and  $889\text{ cm}^{-1}$  is belongs to symmetric  $A_g$  mode and a weak  $775\text{ cm}^{-1}$  band belongs to anti-symmetric  $B_g$  mode of terminal  $\text{WO}_2$  group. The  $701$  and  $672\text{ cm}^{-1}$  band corresponds to asymmetric  $A_g$  and  $B_g$  modes of  $(\text{W}_2\text{O}_4)_n$  chain. The  $547\text{ cm}^{-1}$  and  $513\text{ cm}^{-1}$  band corresponds to asymmetric  $A_g$  and  $B_g$  mode. The  $403\text{ cm}^{-1}$  and  $331\text{ cm}^{-1}$  band corresponds to the deformation mode of terminal  $\text{WO}_2$  group.<sup>41</sup> The  $257\text{ cm}^{-1}$  and  $206\text{ cm}^{-1}$  bands corresponds to the deformation mode of the  $A_g$  due to cationic sub-lattices. It was found that at lower wave-number the vibration frequency is small and the structure is more regular. Whereas at higher wave number, the vibration frequency is much higher and the structure is more distorted which found similarity by others.<sup>42</sup> Our result found similarity with earlier reports by Thongtem et al. for their study on  $\text{MnWO}_4$  nanomaterials.<sup>42</sup>

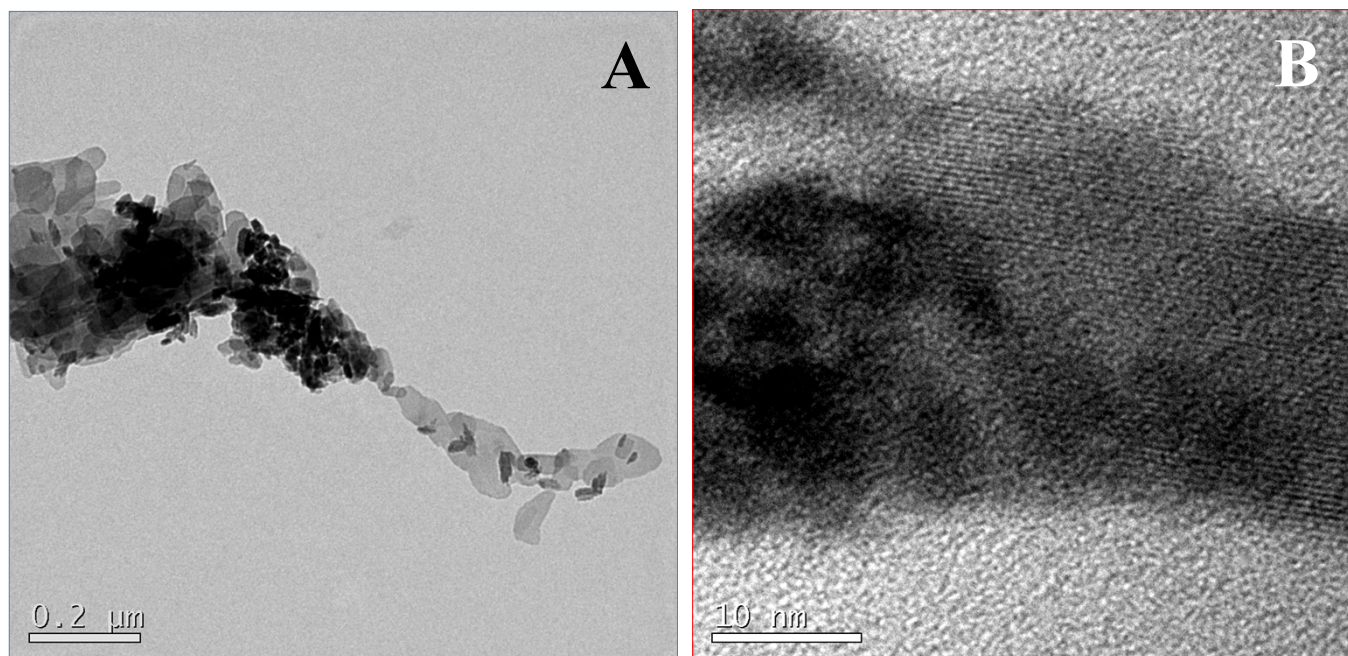
### **Study of other reaction parameters**

We did some control experiments and checked the effect of different reaction parameters on the formation of shape-selective  $\text{MnWO}_4$  nanomaterials on DNA. The specific morphology of rice-like, flake-like and wire-like shapes are formed at a particular concentration those are given details in Table 1 (in main text). From Table 1 we can see that at low DNA concentration, rice-like shapes are formed whereas at high DNA concentration the wire-like shapes are formed, while at intermediate concentration, flake-like shapes are formed. We did few control experiments keeping other reagents concentration fixed to check the specific role of DNA or other reaction parameters. We have observed that when we use DNA concentration very high like  $\sim 1.27 \times 10^{-1}$  (M) or more, the  $\text{MnWO}_4$  particles formed aggregated structure as seen in Figure S-5A. Similarly, when we used DNA concentration very low  $\sim 1.3 \times 10^{-5}$  (M), the  $\text{MnWO}_4$  particles formed agglomerated structure due to presence of very less amounts of stabilizer as seen in Figure S-5B. Similar types of results (aggregated structure) obtained in absence of DNA also. In the synthesis, if we used Mn(II) salt concentration very high ( $\geq 5 \times 10^{-1}$  M), the solution immediate resulted white color precipitate just after addition of  $\text{Na}_2\text{WO}_4$  and from the TEM analysis it was shown that the solution contains mixture of different shapes with no specific morphology (Figure S-5C). On the other hand when Mn(II) salt concentration very less ( $\leq 10^{-4}$  M), the reaction takes long time for the generation of particles and amounts of product is also very less. Similar types of observation was also noticed for  $\text{Na}_2\text{WO}_4$  where at high concentration of tungstate ions results the formation of particles very fast while low concentration take longer time with lower yield of the particles. We also observed that the microwave heating time is important

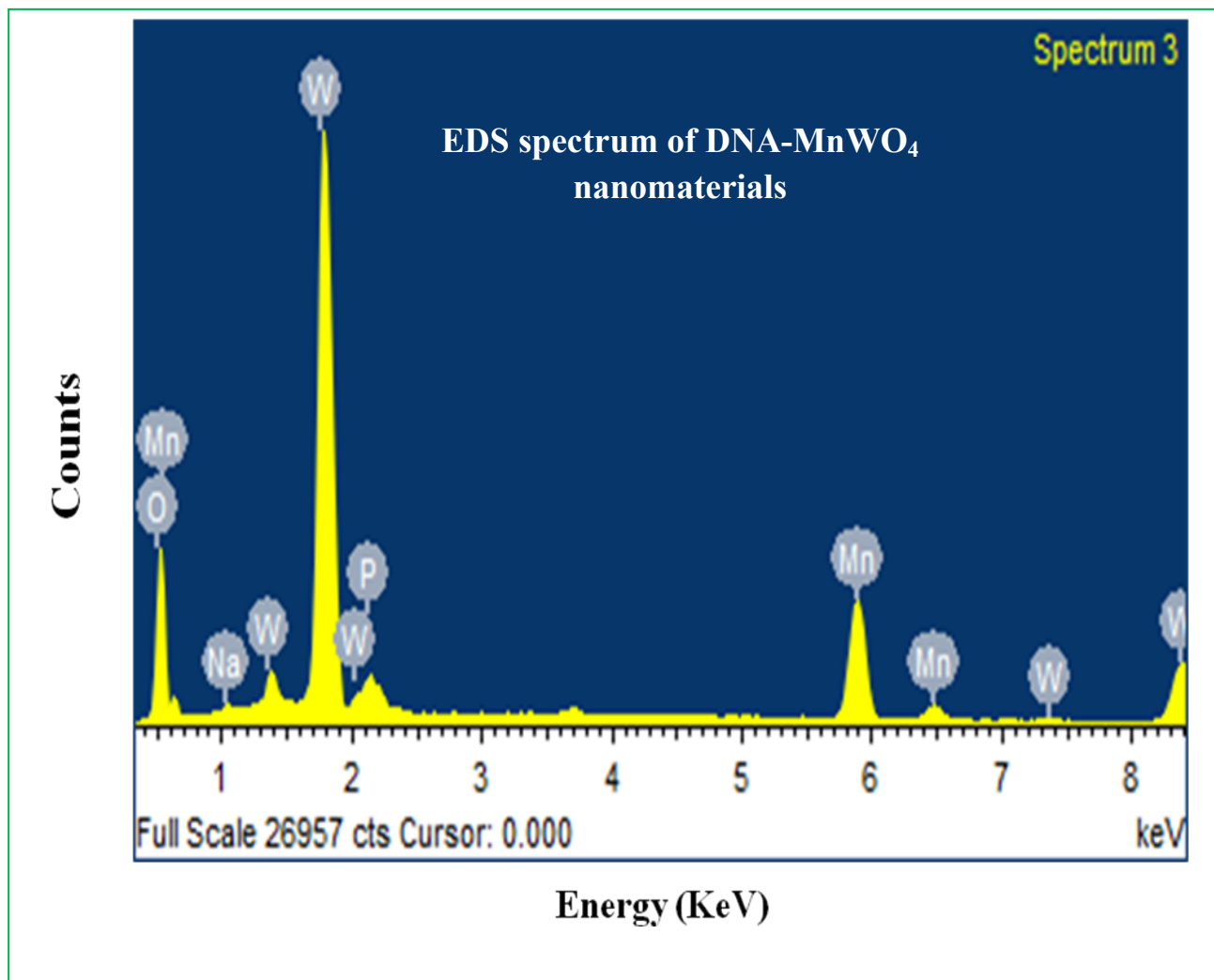
parameter for the formation of shape-selective  $\text{MnWO}_4$  nanomaterials. We have seen that five minute heating time is sufficient to the generation of  $\text{MnWO}_4$  particles with specific morphology as given in Table 1. While we heat the reaction mixture for longer period ( $> 10$  minute) there is no significant change of particles morphology was observed whereas, heating the solution mixture for lesser time (40-60 seconds), results spherical particles as observed from the TEM image at Figure S-5D. So from all the above control experiments it is confirmed that the  $\text{MnWO}_4$  nanomaterials at specific morphology are formed only at a certain concentrations.



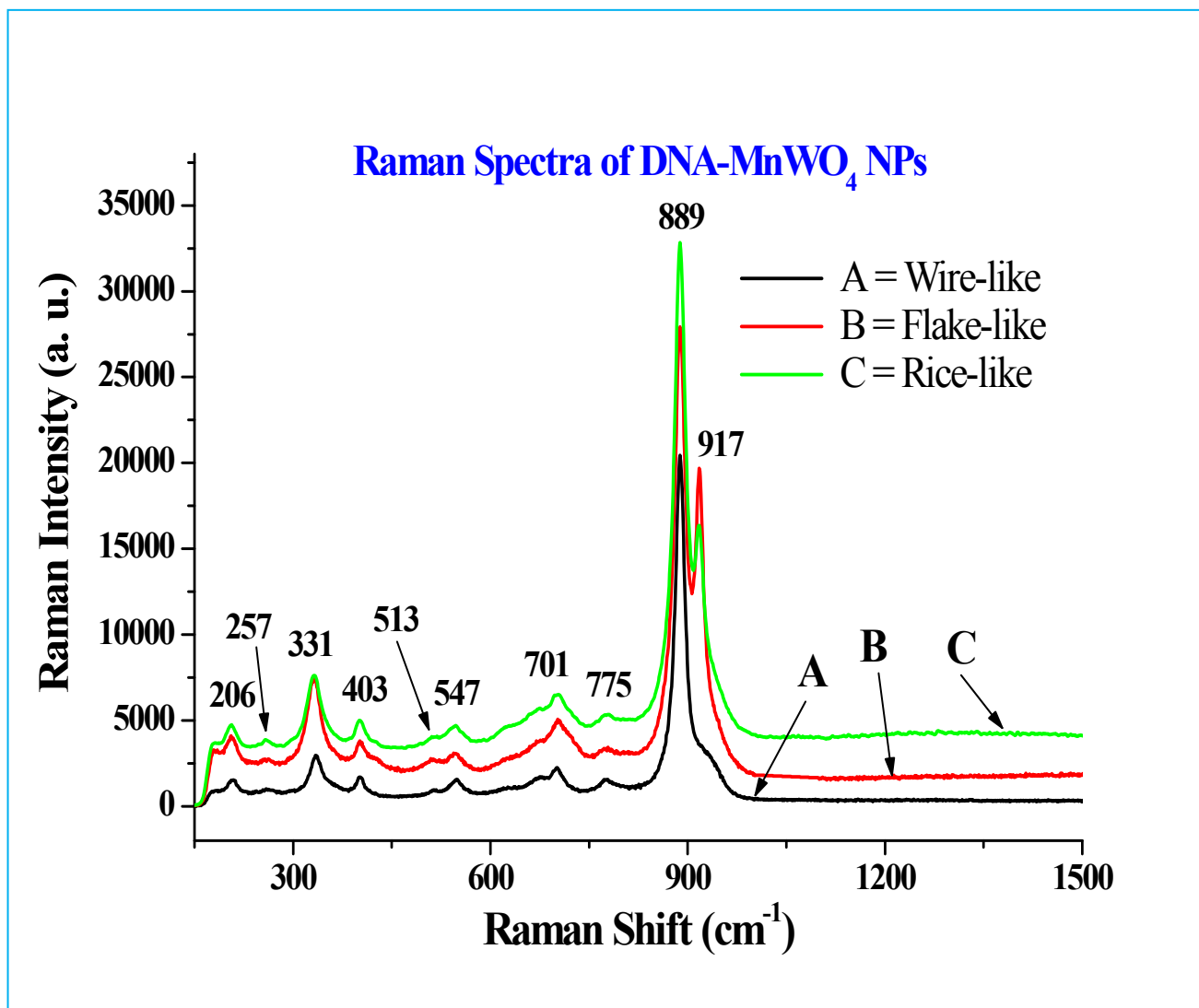
**Figure S-1:** UV-Vis diffuse reflectance spectra of solid  $\text{MnWO}_4$  nanomaterials. Curve A, B and C denotes the spectra for wire-like, rice-like and flake-like morphologies respectively.



**Figure S-2, A-B:** The transmission electron microscopy (TEM) images of the wire-like DNA-MnWO<sub>4</sub> nanomaterials. (A) at very low magnification; (B) at very high magnification.

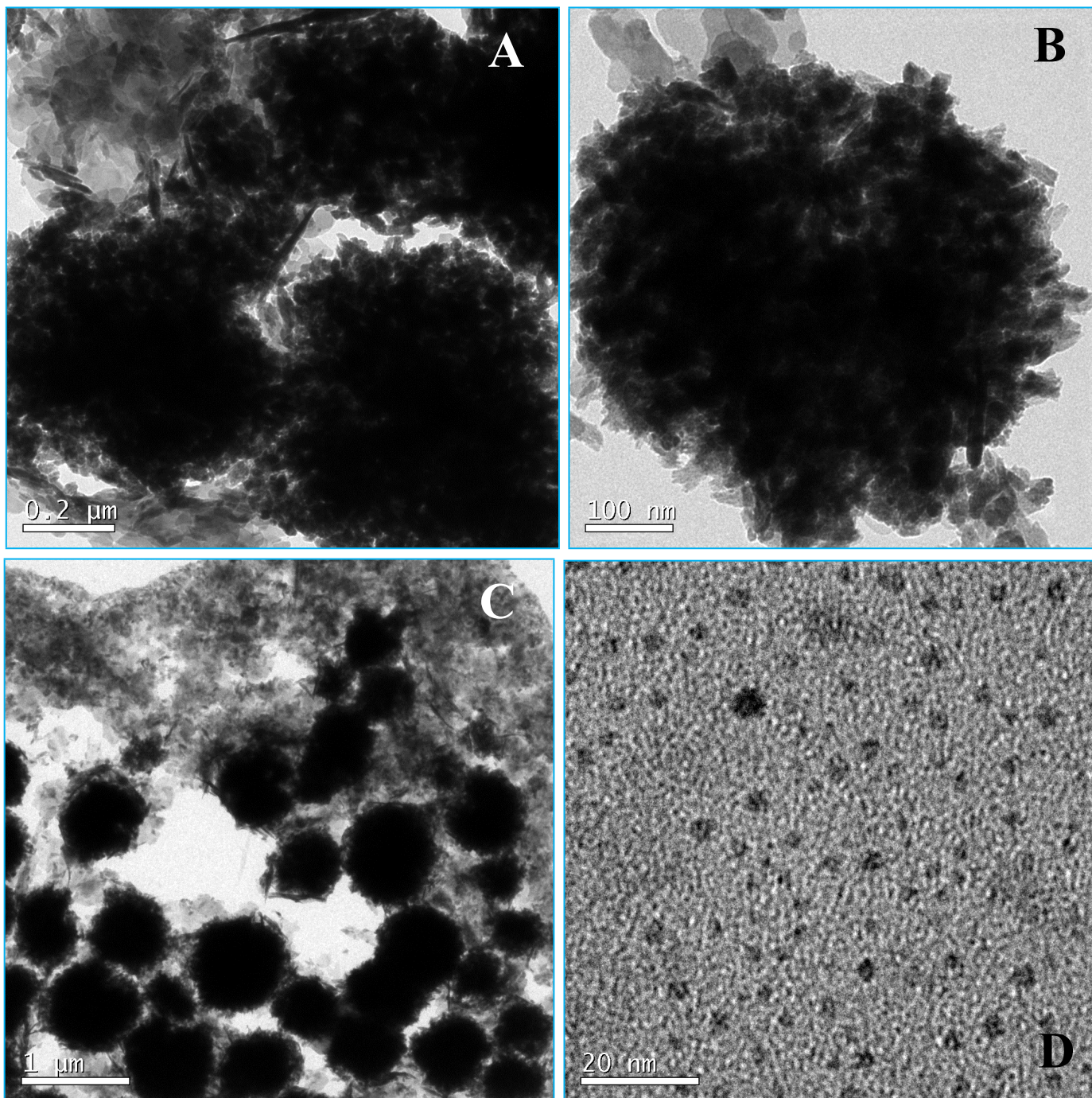


**Figure S-3:** The energy dispersive X-ray spectroscopic (EDS) analysis of DNA-MnWO<sub>4</sub> nanomaterials which consists of the peaks for Mn, O, W, P and Na.



**Figure S-4:** The LASER Raman spectra of the shape-selective MnWO<sub>4</sub> nanomaterials on DNA. Curve A, B and C indicates the spectra for wire-like, flake-like and rice-like morphology respectively.





**Figure S-5, A-D:** The transmission electron microscopy (TEM) images of shape-selective DNA-MnWO<sub>4</sub> nanomaterials at different controlled condition. (A) at very high DNA concentration; (B) at very low DNA concentration; (C) at high Mn(II) ion concentration; (D) at less microwave heating time for 40-60 second.



<b>FT-IR bands - de-oxyribo nucleic acid (DNA)-Experimental and Reported values<sup>43</sup></b>		
<b>FT-IR bands (cm<sup>-1</sup>) (experimentally observed)</b>	<b>FT-IR frequency range (cm<sup>-1</sup>) (reported value)<sup>43</sup></b>	<b>Absorbing bonds/vibration types</b>
3435 and 3734	3100-3750	v (OH group in DNA/water)
2921	2800-2950	Symmetric stretching vibration (C-H bonds in -CH <sub>2</sub> group)
1635	1732-1595	C=O, C-N, N-H <sup>43</sup>
-	1492-1480	Bending ( $\delta$ ) of C-H bond in CH <sub>2</sub>
1236	1170-1300	Asymmetric stretching of PO <sub>2</sub> - group
1084	1140-990	v (C-O-C, C-C) <sup>43</sup>
961	800-1000	De-oxyribose region

**Table T-1:** The details about the different FT-IR bands reported for DNA, the experimentally bands we observed and the corresponding bond assignments.

References 40-43 in the above text are given in the main document.