Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Efficient and Selective Oxidation of Toluene to Benzaldehyde on Manganese Tungstate Nanobars: A Noble Metal-Free Approach

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Table S1. Comparative literature survey on direct oxidation of toluene to benzaldehyde with different heterogeneous catalysts.

Entry	Catalyst	Temp.	Oxidant	Condition	C_T[a](%)	S_{BAD}[b] (%)	Ref.
1	$[Cu(CNMP)_2.H_2O]$	70	H_2O_2	Heated under atmospheric pressure	65.5	35	1
2	V_2O_5 Bulk Material	360	O_2	Tubular quartz fixed-bed micro-reactor	58.3	58.9	2
3	V_2O_5Nanobelts	340	O_2	Tubular quartz fixed-bed micro-reactor	33.6	49.1	2
4	Co_4Al oxide	70	TBHP	Heated under atmospheric pressure	8.2	77.6	3
5	Cu/Al_2O_3	190	O_2	Heated in pressurised autoclave	2.5	85.7	4
6	$Cu/SnCl_2$	120	air	Heated in pressurised autoclave	18.5	49.2	5
7	V_2O_5-ZrO_2	57	air	Heated in a U-tube fixed-bed micro-reactor	24	33	6
8	V_2O_5/Ag_2O	400	O_2	Tubular quartz fixed-bed micro-reactor	30.4	9.5	7
9	V-Ag-Ni-O	400	air	Heated in a U-tube fixed-bed micro-reactor	21	76	8
10	Cu/ZSM-5	180	H_2O_2	Heated in pressurised autoclave	96.4	3.4	9
11	Au-Pd/TiO_2	80	TBHP	Heated under atmospheric pressure	5.3	32	10
12	Cs-PMA	R.T.	TBHP	Heated under atmospheric pressure	1.1	97	11
13	Ag–Cu–BTC	160	O_2	Heated in pressurised autoclave	20.1	90.6	12
14	V-Mo-Fe-O	80	H_2O_2	Heated under atmospheric pressure	40.3	84.5	13
15	Ag-WO_3	80	H_2O_2	Heated under atmospheric pressure	42	93	14
16	$MnWO_4$ NB	80	H_2O_2	Heated under atmospheric pressure	59.5	90	This Work

[a]C_T = Conversion rate of toluene, [b]S_{BAD} = Selectivity of benzaldehyde

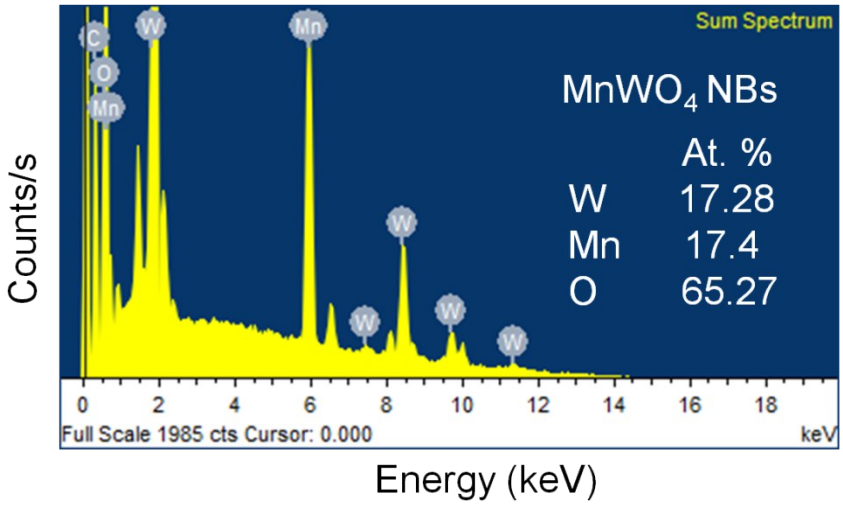

Figure S1. EDAX spectrum of $MnWO_4$ NBs and its elemental composition (atomic %)

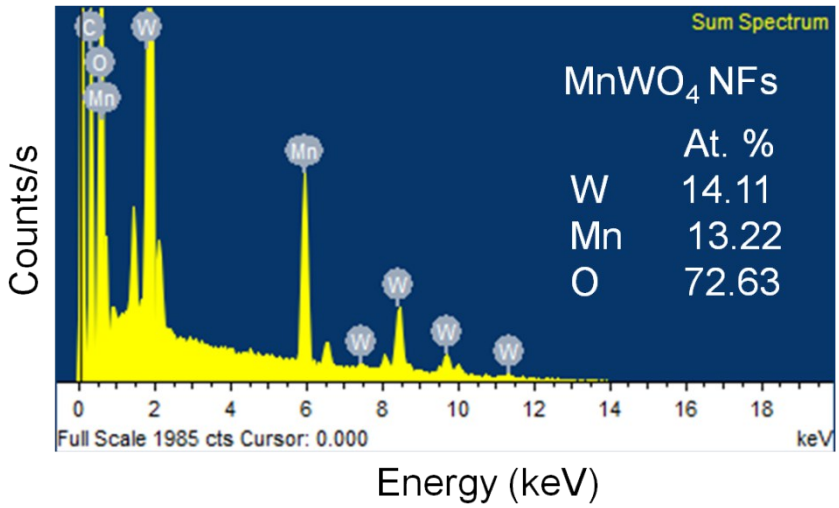

Figure S2. EDAX spectrum of $MnWO_4$ NFs and its elemental composition (atomic %)

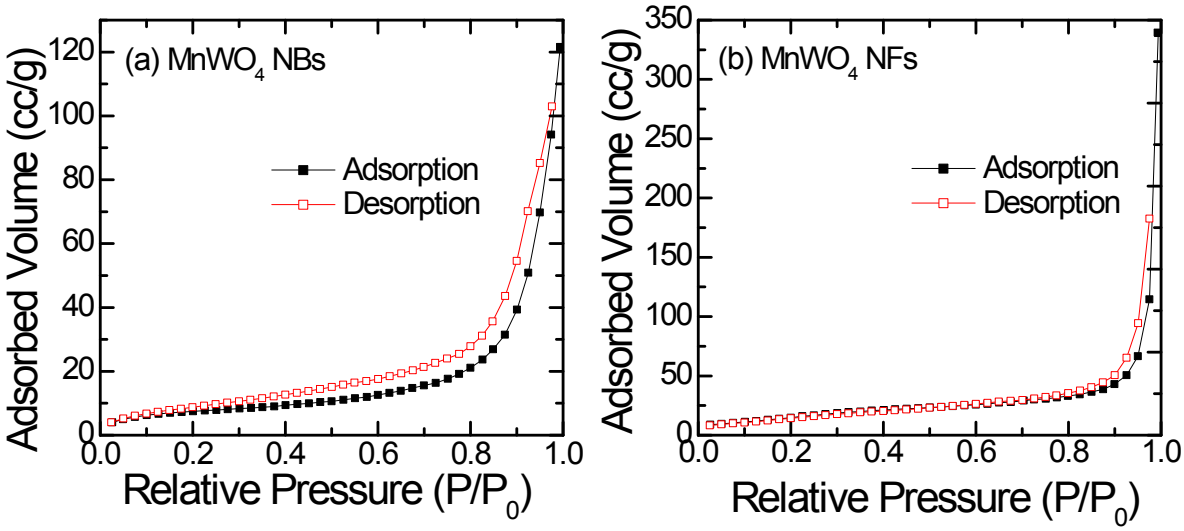

Figure S3. N_2 adsorption/desorption isotherms of (a) $MnWO_4$ NBs and (b) $MnWO_4$ NFs at 77K

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-18.2	Peak 1:	-14.1	52.7	8.95
Zeta Deviation (mV):	23.2	Peak 2:	-45.2	28.6	12.4
Conductivity (mS/cm):	0.00951	Peak 3:	13.6	18.4	9.69
Result quality :	See result quality report				

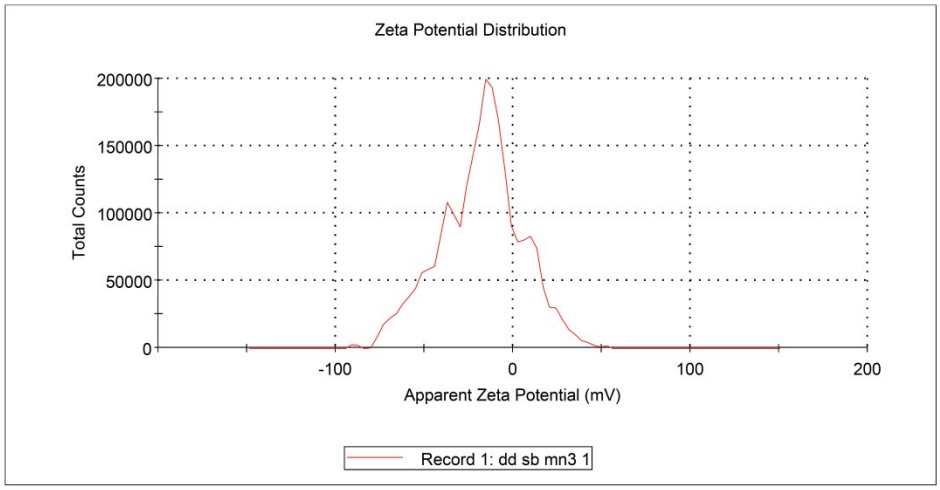

Figure S4. Zeta potential measurement of $MnWO_4$ NBs via DLS method

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-0.0594	Peak 1:	-0.0594	100.0	2.47
Zeta Deviation (mV):	2.47	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm):	2.65e-4	Peak 3:	0.00	0.0	0.00
Result quality :	See result quality report				

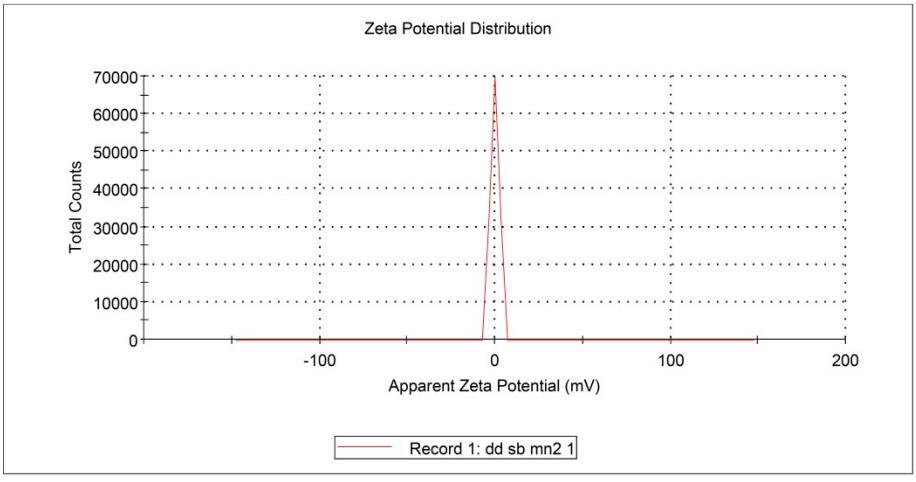

Figure S5. Zeta potential measurement of $MnWO_4$ NFs via DLS method

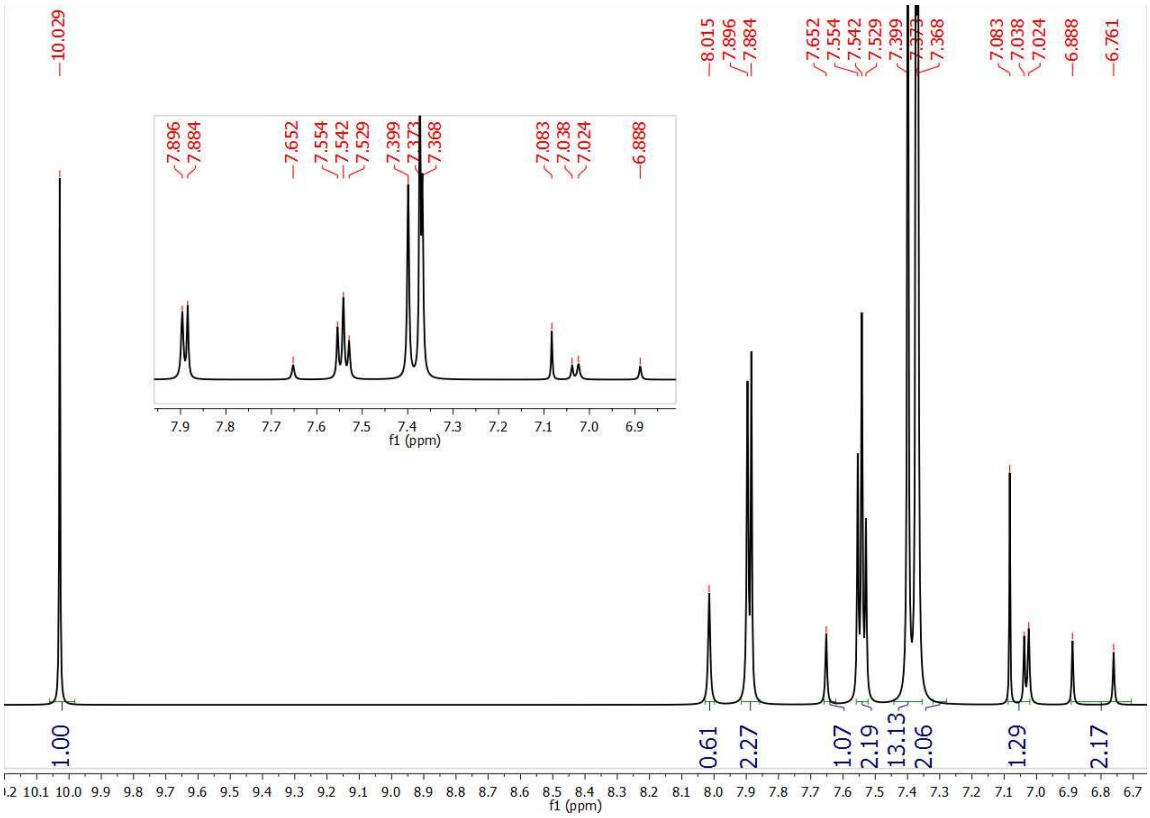

Figure S6. NMR analysis of crude reaction mixture showing aldehyde peak at 10.02 ppm

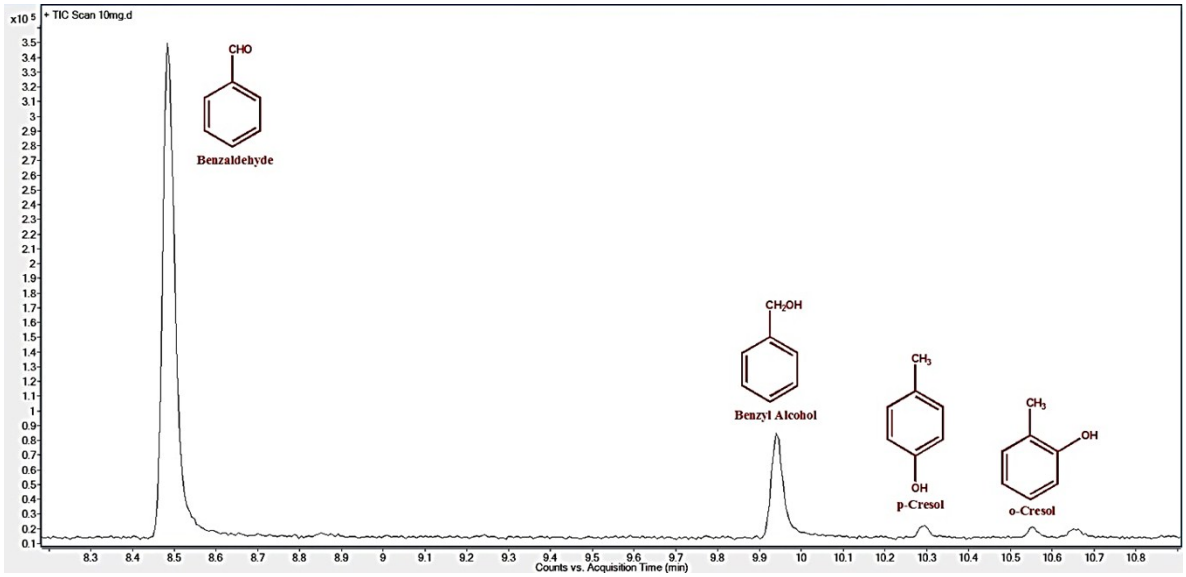

Figure S7. Product profile obtained from oxidation of toluene in terms of GC response time

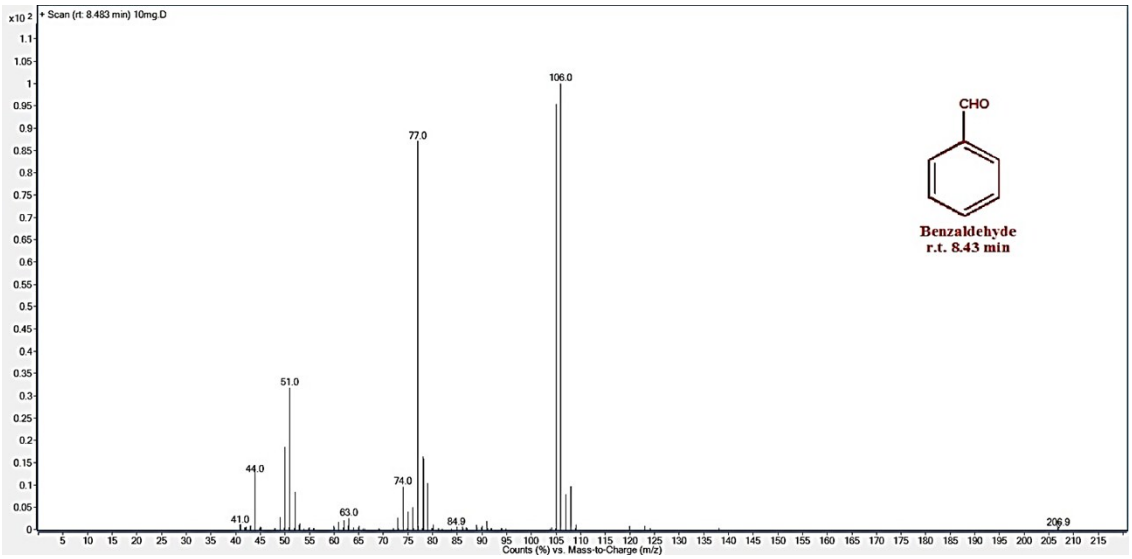

Figure S8. Mass spectra of benzaldehyde obtained from GC-MS analysis at retention time of 8.43 min

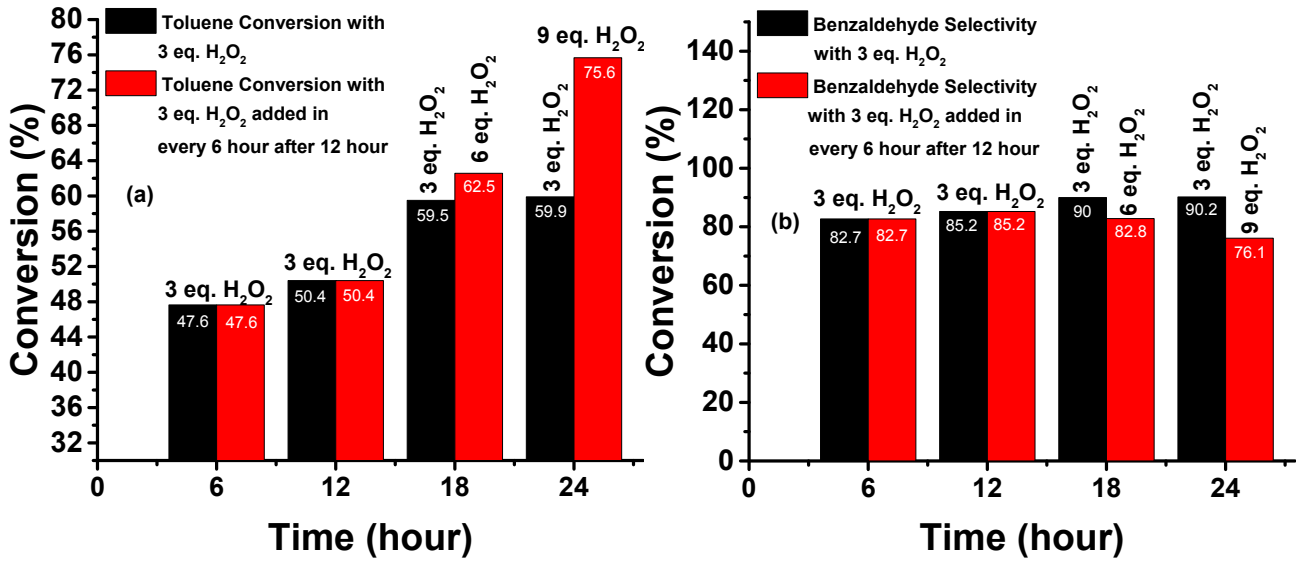

Figure S9. (a) Toluene conversion (b) Benzaldehyde selectivity for a typical reaction under optimal condition (■) with 3 eq. H_2O_2, (■) with 3 eq. H_2O_2 added in every 6 h after 12 h.

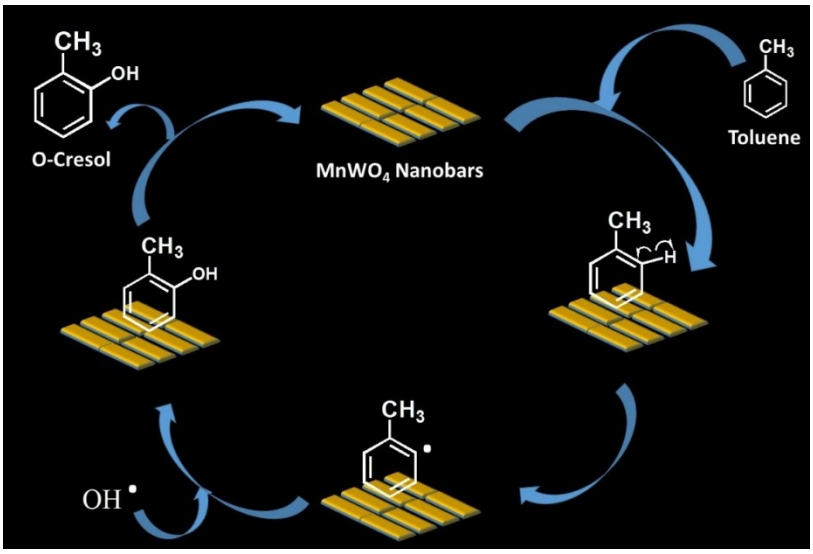

Figure S10. Plausible reaction pathway for the generation of additional by-product,i.e., o-cresol.

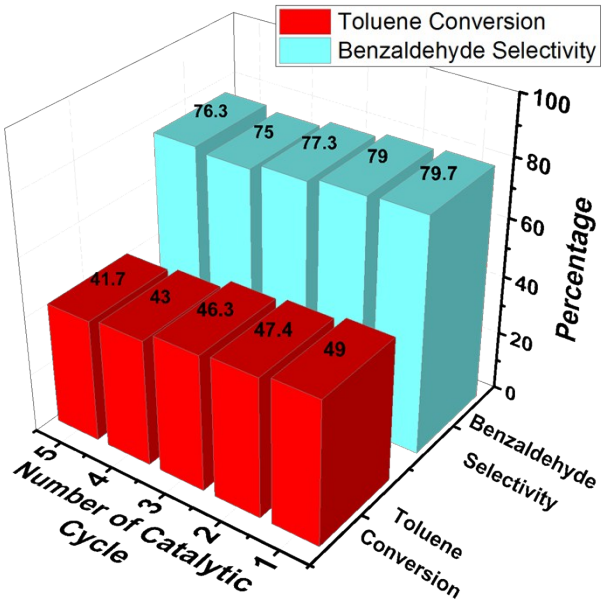

Figure S11. Recyclability test of oxidation of toluene to benzaldehyde by $MnWO_4$ NBs catalyst up to 5 catalytic cycle (■) Toluene conversion and (■) Selectivity towards benzaldehyde; Reaction Parameters: Toluene = 0.2 g, H_2O_2 conc. = 3eq., Catalyst Loading = 0.01 g, Solvent = 8 mL CH_3CN, Temperature = 60°C, Time = 18 h.

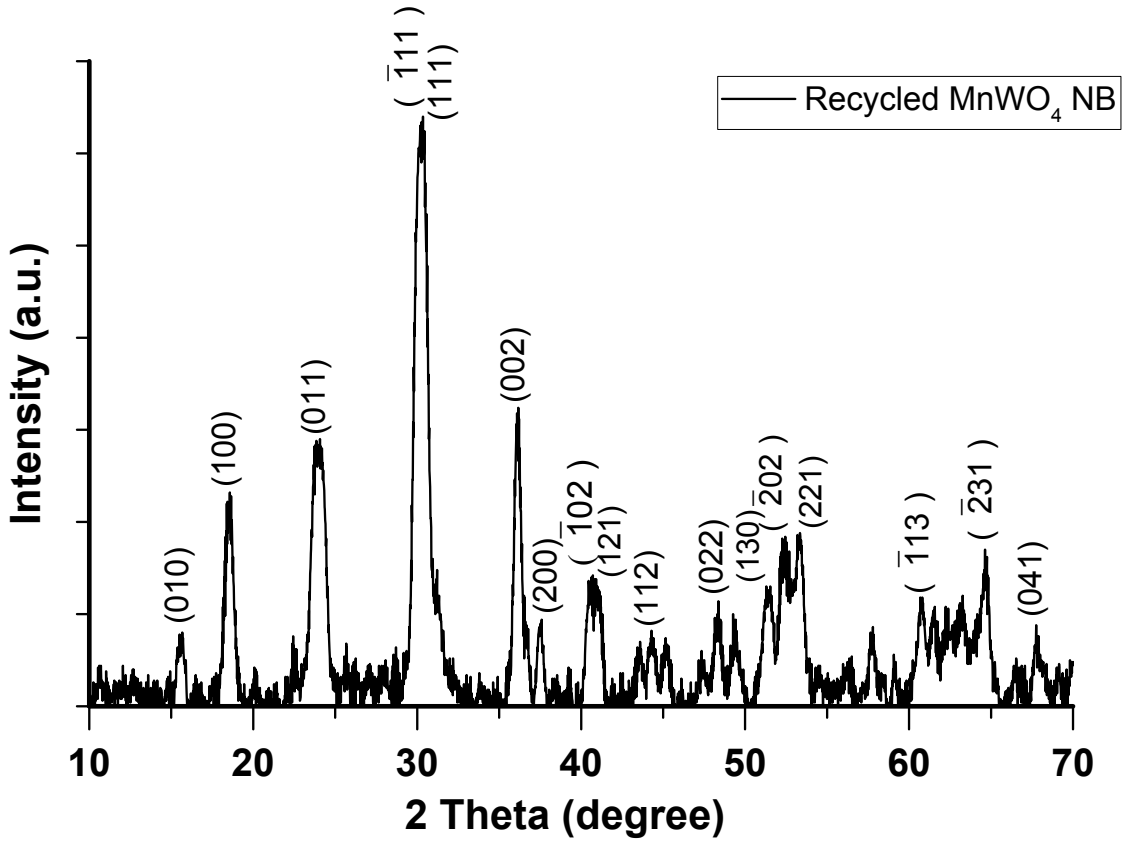

Figure S12. XRD pattern of recovered $MnWO_4$ NBs catalyst after 5 catalytic cycles

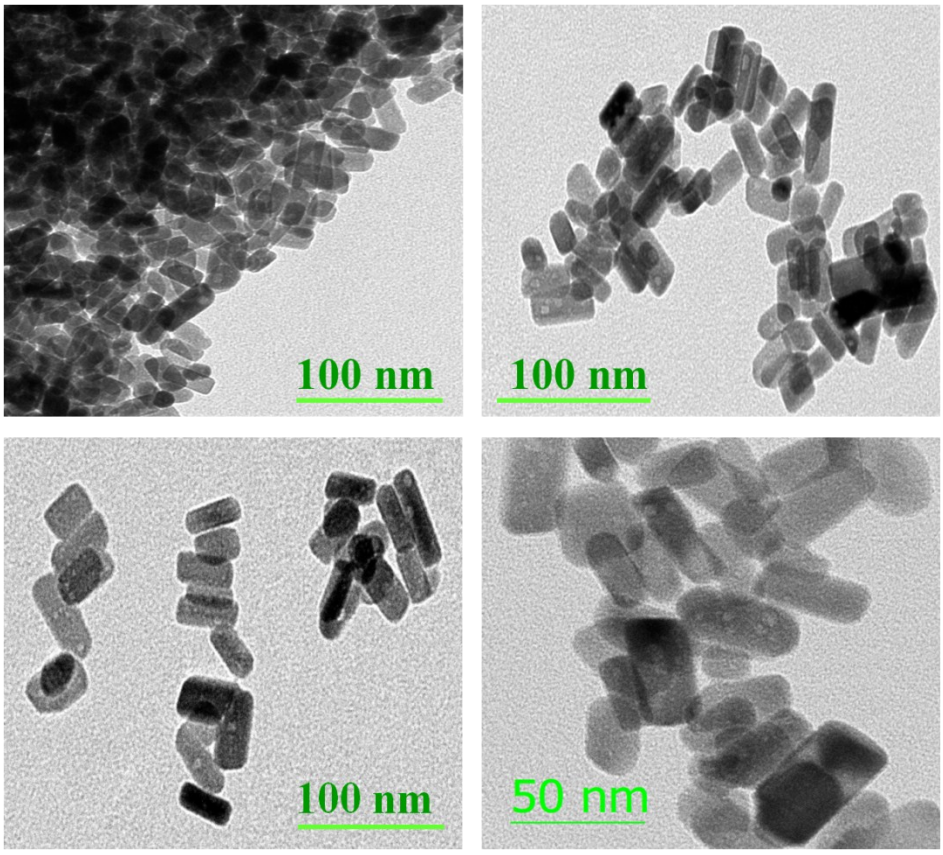

Figure S13. TEM analysis of recovered $MnWO_4$ NBs catalyst after 5 catalytic cycles

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