Supporting Information

Morphological evolution of 2D MnO_2 nanosheets and their shape transformation to 1D ultra long MnO_2 nanowires for robust catalytic activity

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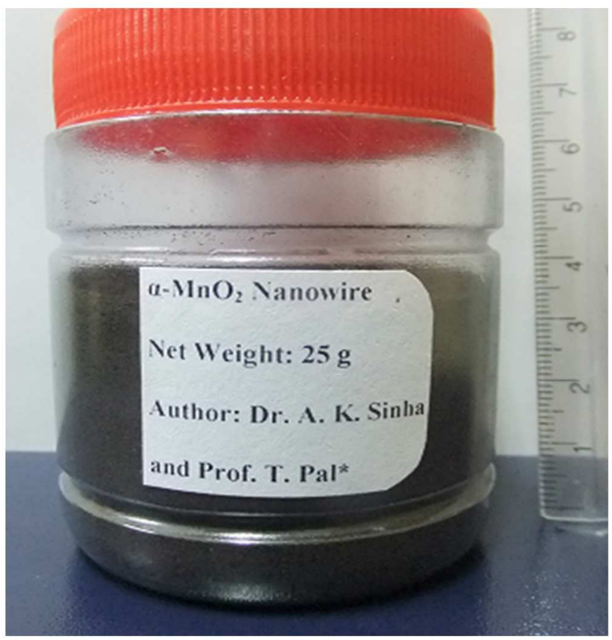
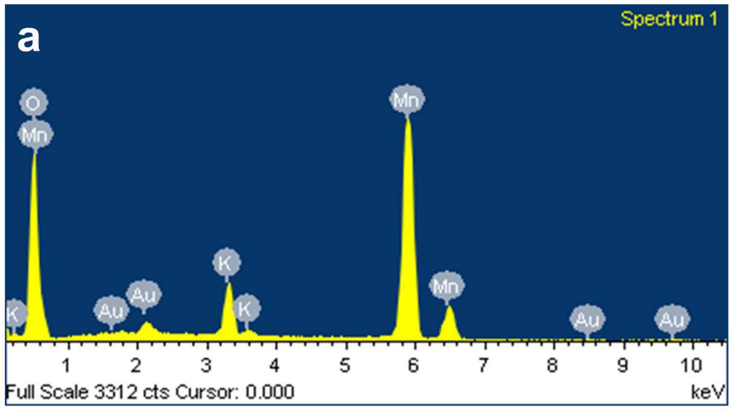
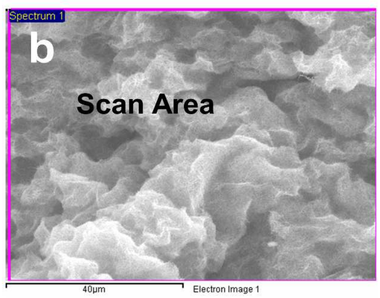
Supporting Information Figure S1. Digital Picture of Gram level α-MnO_2 Nanowires synthesis by Wet Chemical Route and Images a and b represents 25 g of α-MnO_2 nanowires.



Supporting Information Figure S2. EDS pattern of α-MnO_2 nanowires (a), scan area and elemental composition (b)

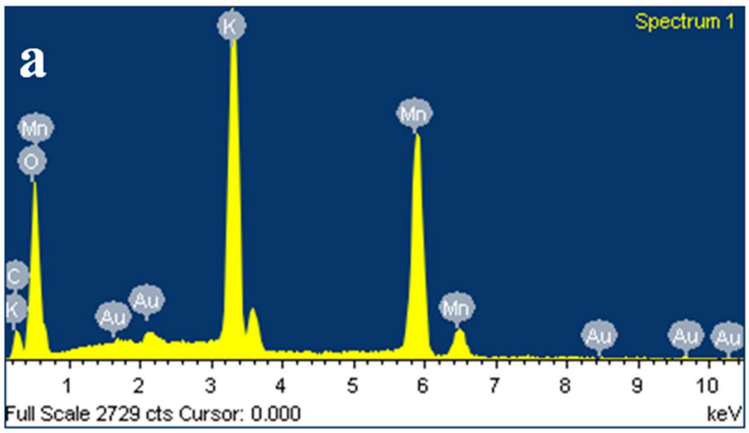


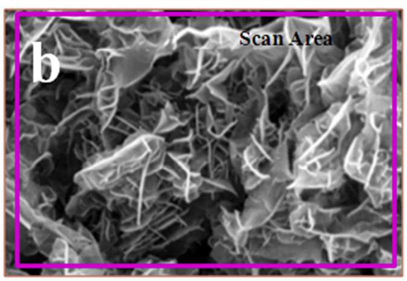


Element	Weight%	Atomic%
O K	35.13	65.02
K K	5.29	4.01
Mn K	56.64	30.53
Au M	2.94	0.44
Totals	100.00	

The EDS pattern shows the presence of Mn, O and K elements in α-MnO_2 nanowires. The element Au comes from conductive gold coating.

Supporting Information Figure S3. EDS pattern of δ-MnO_2 nanosheets (a), scan area and elemental composition (b).

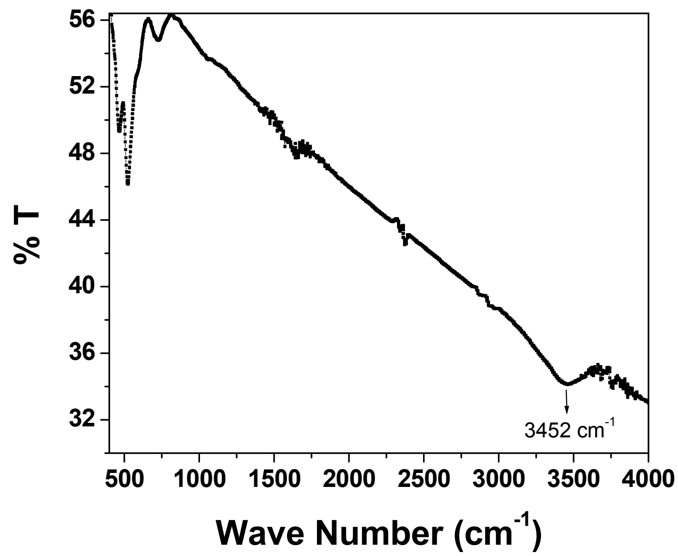




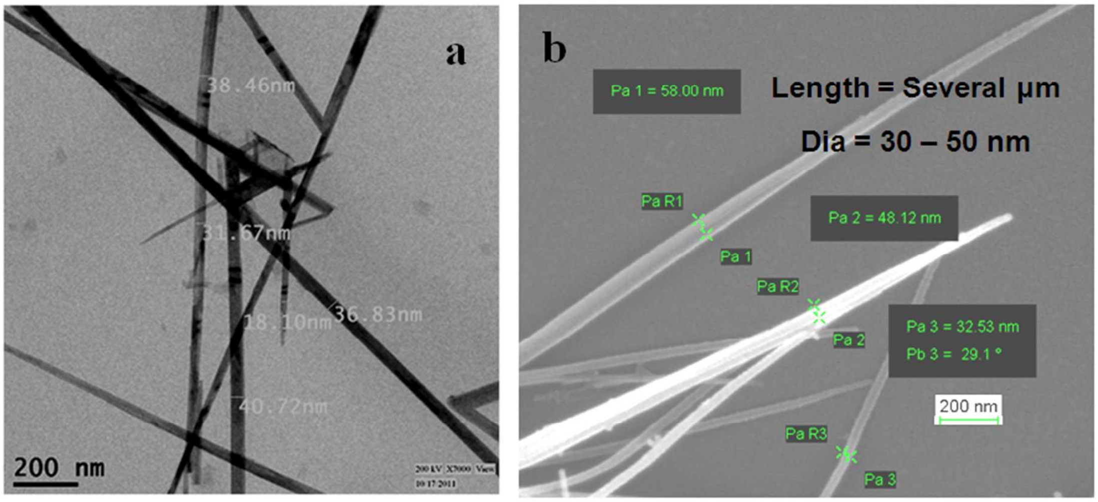
Element	Weight%	Atomic%
C K	12.00	23.38
O K	34.90	51.04
K K	19.70	11.79
Mn K	32.02	13.63
Au M	1.38	0.16

The EDS pattern shows the presence of Mn, O and K elements in δ-MnO_2 nanosheets. The element Au comes from conductive gold coating and Carbon comes from capping CH_3COO^- ion.

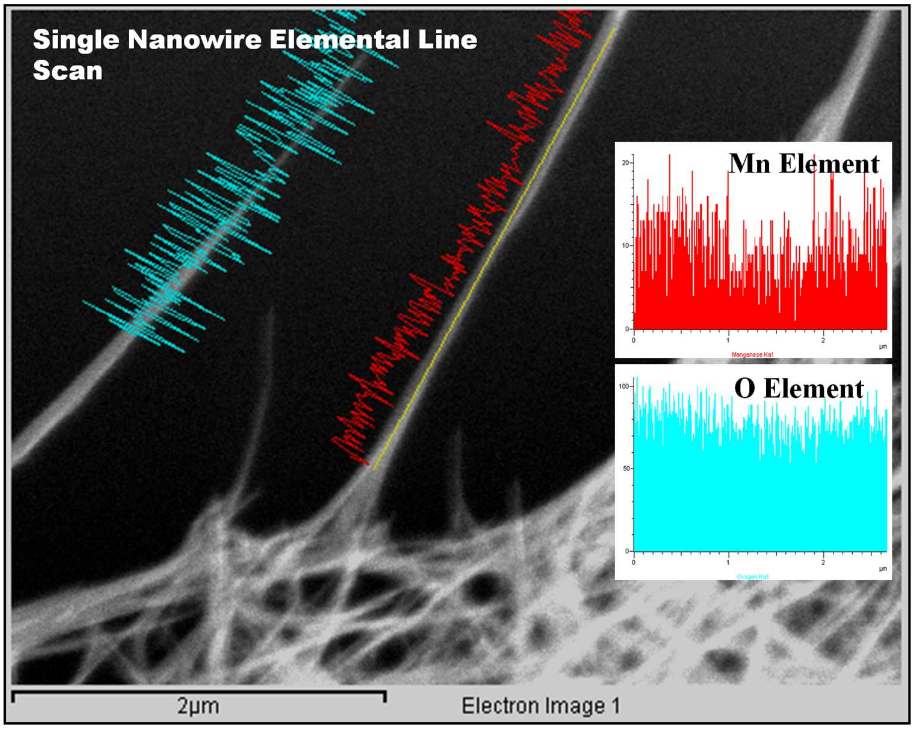
Supporting Information Figure S4. FTIR spectra of α-MnO_2 nanowires.



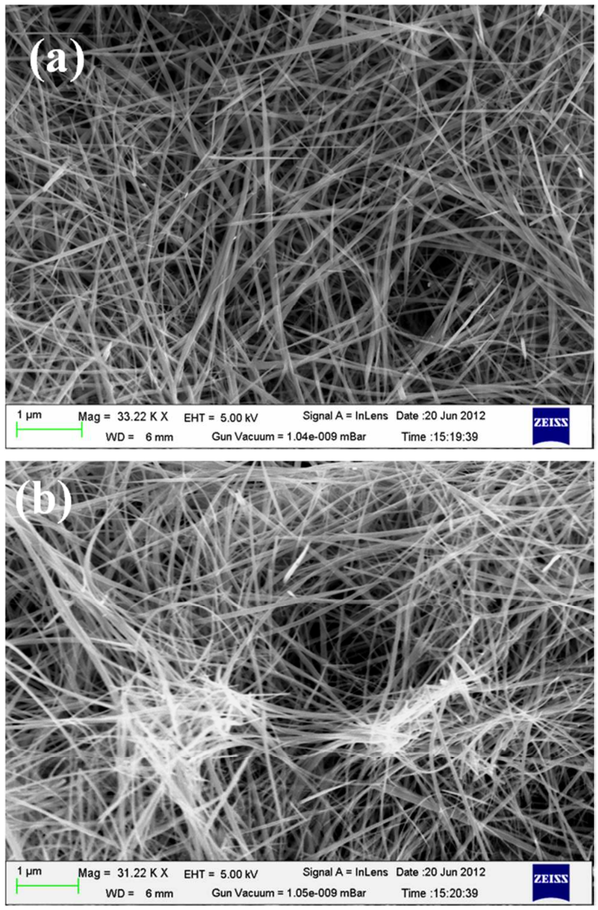
Supporting Information Figure S5. Diameter and length of the α-MnO_2 nanowires from TEM (a) and FESEM analysis (b).



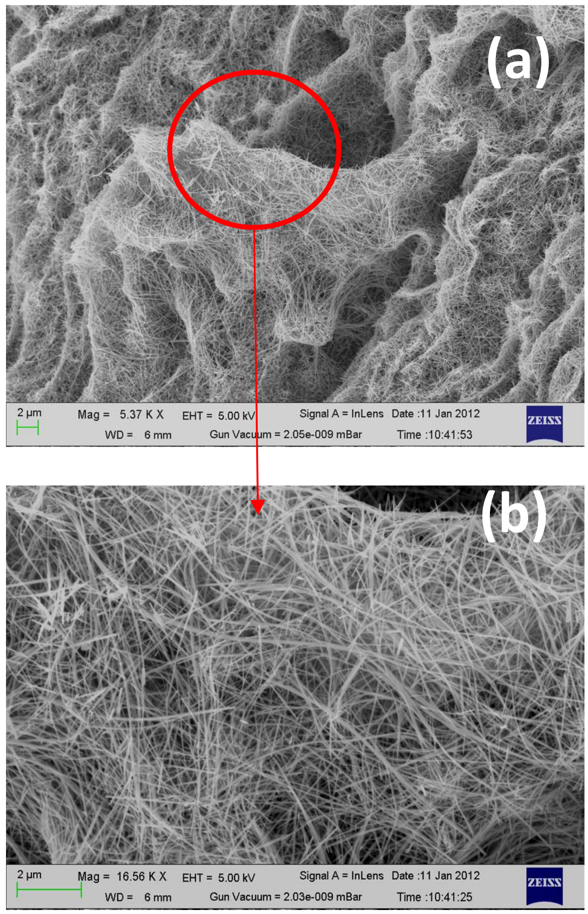
Supporting Information Figure S6. Elemental mapping on the surface of single α-MnO_2 nanowire.



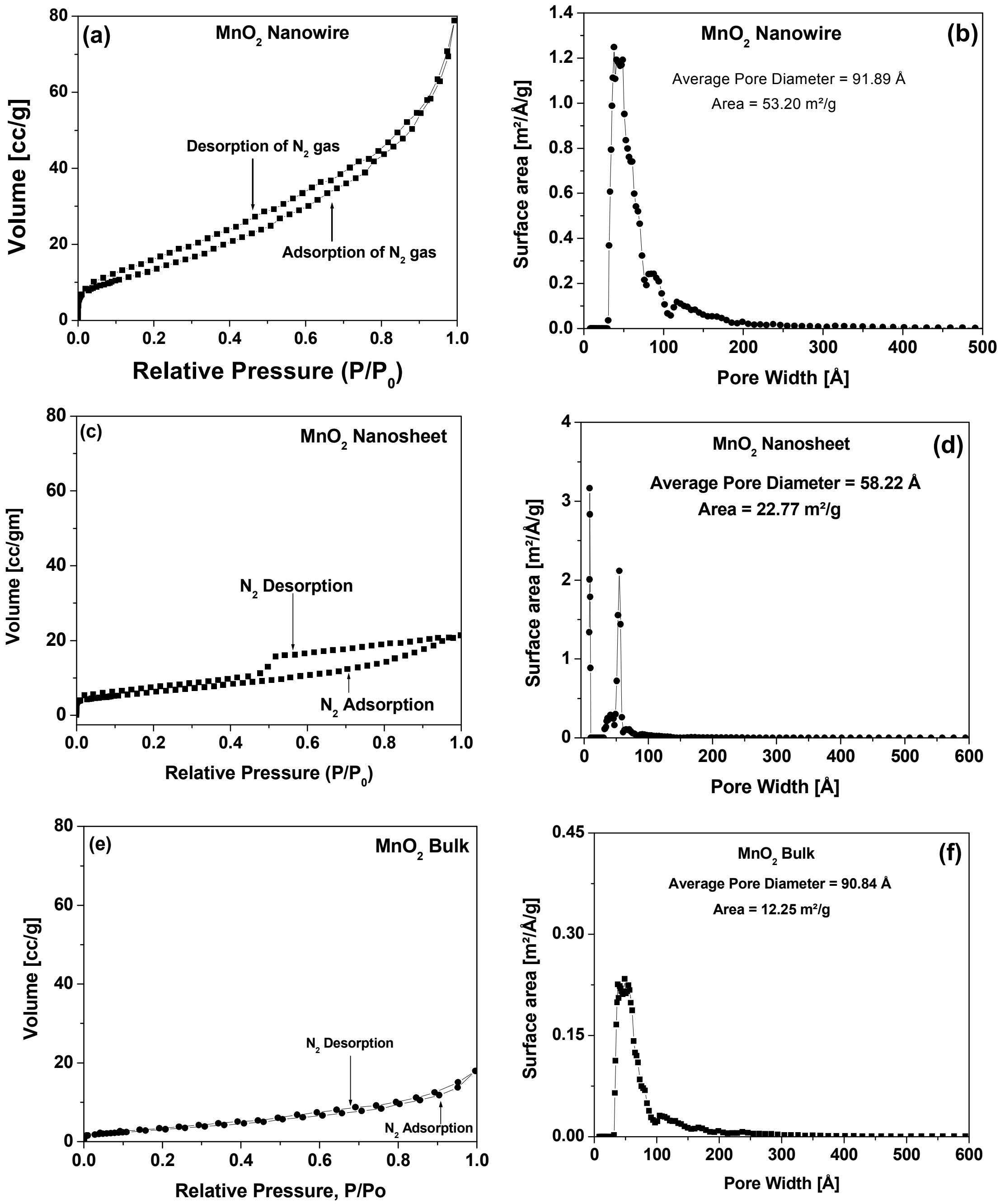
Supporting Information Figure S7. Dry heat treatment or annealing of as prepared α-MnO_2 nanowires at 200°C (a) and 400°C (b) in presence O_2 atmosphere for 4 hrs.



Supporting Information Figure S8. Surface morphology of α-MnO_2 nanowires sheet of membrane formation which is appeared as pallet after dring on water bath at 70-90°C.



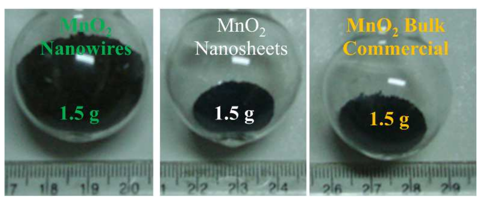
Supporting Information Figure S9. Comparison *of* Nitrogen adsorption–desorption isotherm *(a, c and e)* and the BJH pore size distribution *(b, d and f)* between MnO_2 nanowire, nanosheet and commercial bulk MnO_2.



The sumerized results of total surface area and average pore diameter of different type of MnO_2 are given bellow.

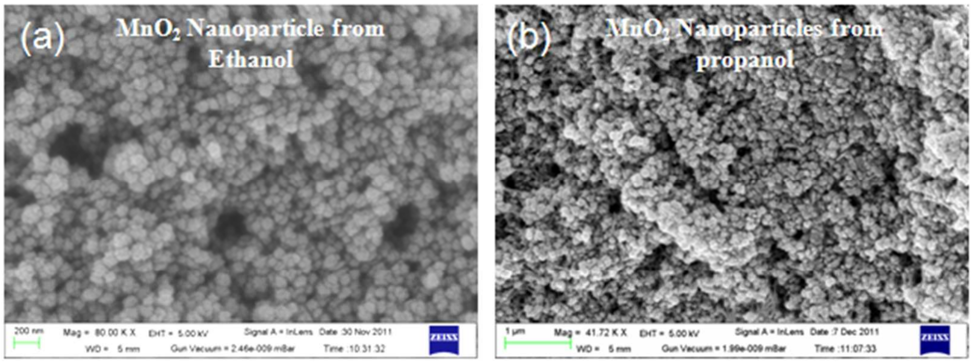
Type of MnO_2	***Total Surface Area (m^2/g)***	***Average Pore Diameter (Å)***
Nanowire	*53.20*	*91.89*
Nanosheet	*22.77*	*58.22*
Commercial Bulk MnO_2	*12.25*	*90.84*

The three type MnO_2 materials with fixed weight (1.5 g) have different volume which is given in bellow by digital images.

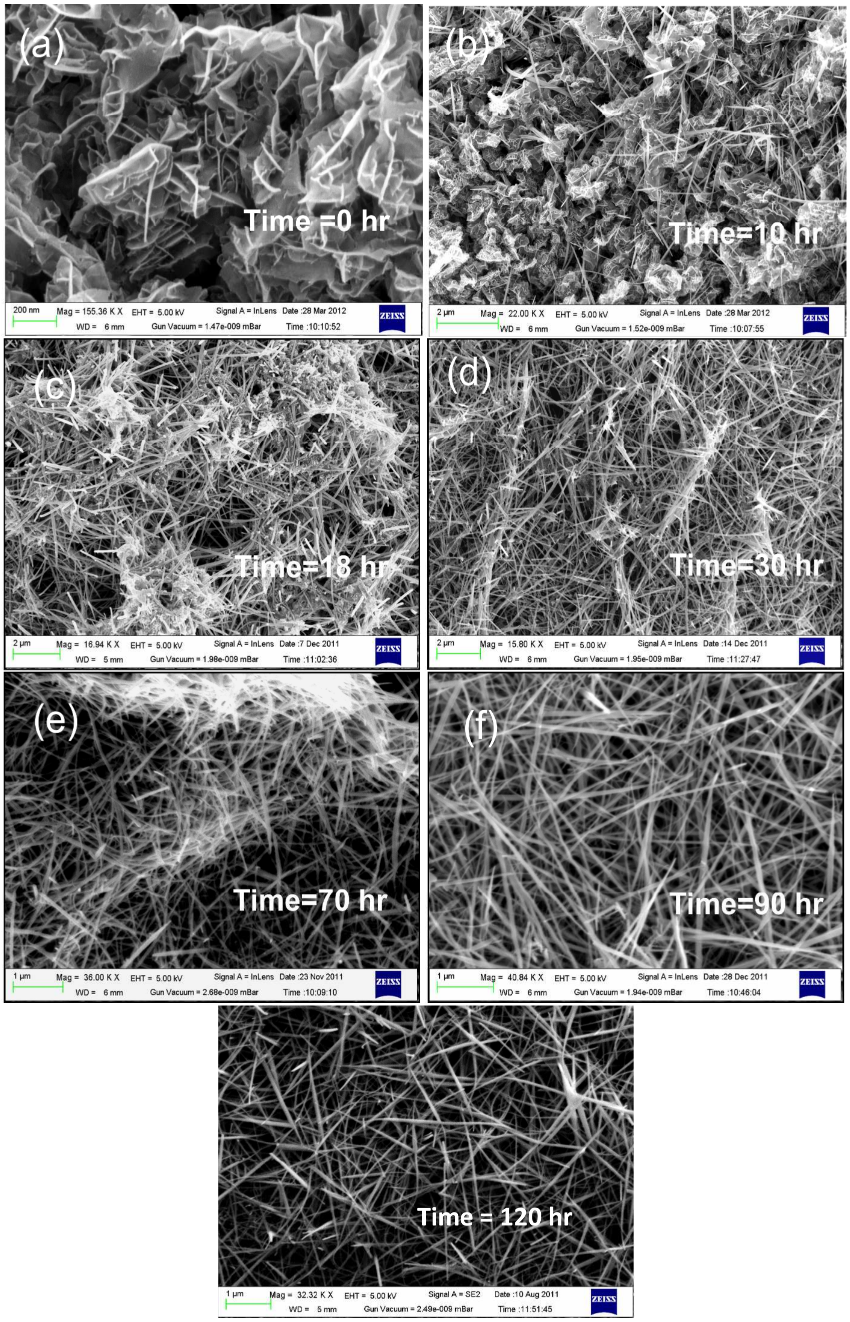


The image indicates that MnO_2 nanowire have a high surface area than other two.

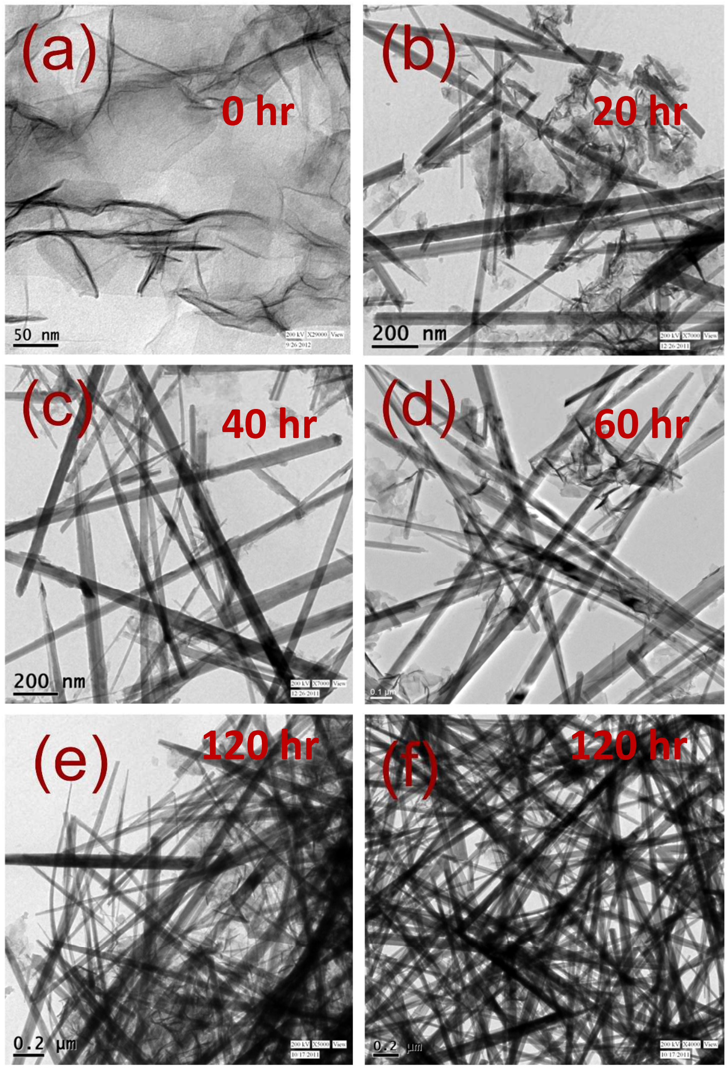
Supporting Information Figure S10. Spherical MnO_2 nanoparticle formation from the reaction between $KMnO_4$ and ethanol (a) or propanol (b).



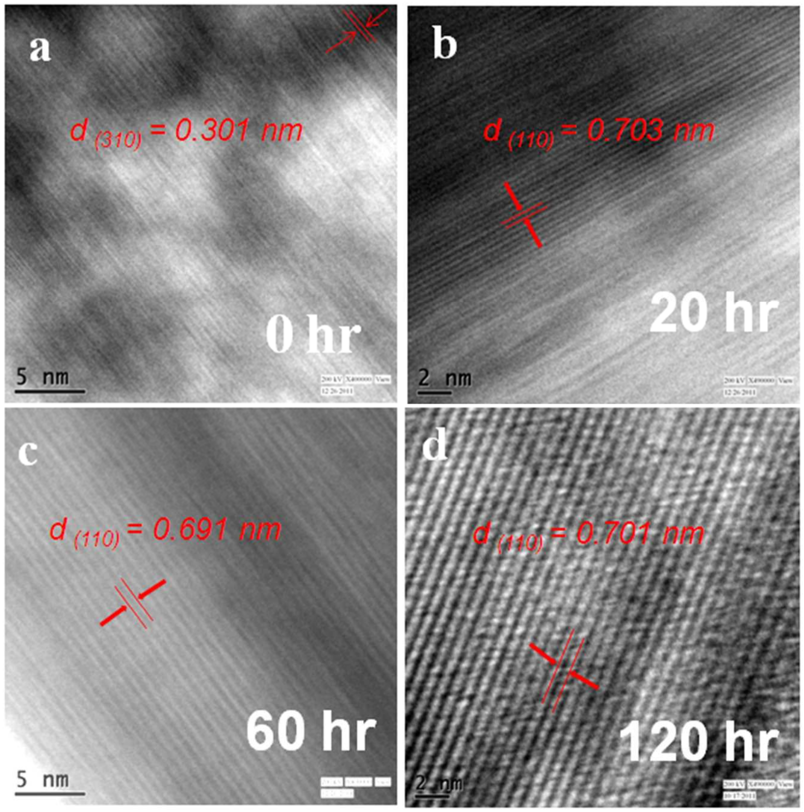
Supporting Information Figure S11. Step wise growth mechanism of α-MnO_2 nanowires formation from δ-MnO_2 nanosheets at different time gaps.



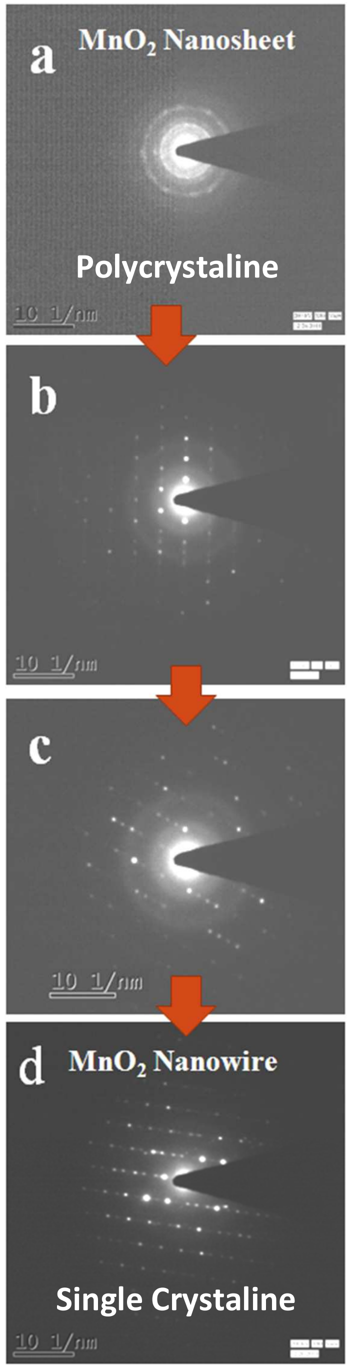
Supporting Information Figure S12. Step wise growth mechanism of α-MnO_2 nanowires from δ-MnO_2 nanosheets at different times.



Supporting Information Figure S13. Development of lattice gap during shape transformation from δ-MnO_2 nanosheets (a) to α-MnO_2 nanowires (d) via intermediates (b and c).



Supporting Information Figure S14. Development of SAED pattern of MnO_2 nanosheet (a), intermediates (b and c) and nanowire (d).



Supporting Information Figure S15. Details procedure of MnO_2 catalyst bed preparation

We have prepared MnO_2 membrane and wheel under suction using porcelain buchner funnel and vacuum pump set up. The set up is shown in below in figure S14a.

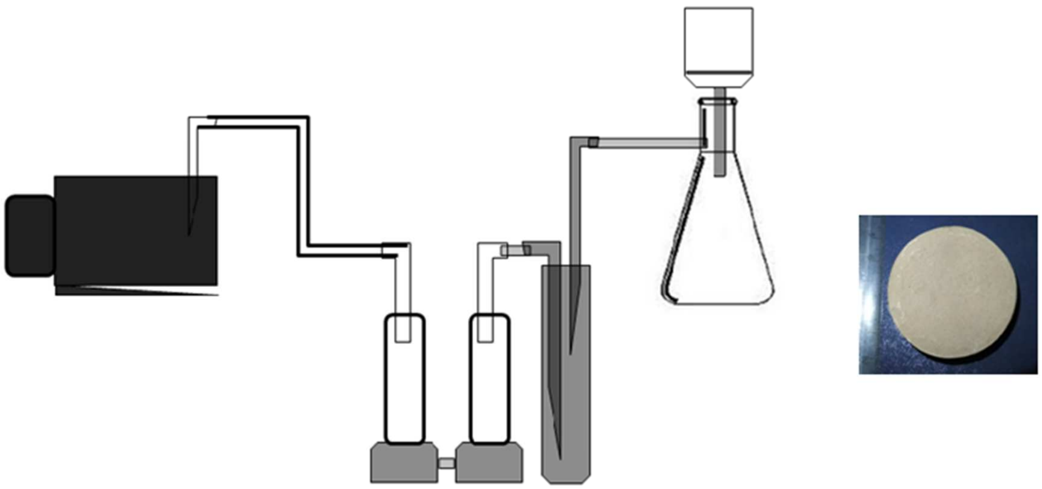


Figure S14a. Instrumental set up for the fabrication of MnO_2 wheel and membrane.

The water suspension of α-MnO_2 nanowire as colloidal solution was poured into a porcelain buchner funnel with a whatmann whatman no. 1 filter paper. By using a vacuum pump, the filtration was carried out and α-MnO_2 nanowires are deposited as an interlaced membrane on the filter bed. The deposited α-MnO_2 nanowires look like a membrane or wheel. Then it was heated at 180°-200°C and the dried membrane or wheel was used as catalysis bed for hydrolysis reaction.

α-MnO_2 nanowires have high surface area and the individual nanowires have length several micrometers and diameter in few nanometer regions. When the as-obtained nanowires suspension is filtered by using vacuum filtration technique through a Whatman filter paper (NO. 1), a sheet of membrane like cake is formed. The nanowires are interlaced, closely packed on the filter paper during vacuum filtration and dried at room temperature (26°-30 °C) and then at 200 °C in dry oven. We have also prepared a porous cylindrical wheel that also composed of α-MnO_2 nanowires which is shown in figure S14b. The cylindrical wheel has a diameter in the range of centimeters (the height is 0.6 cm and diameter is 5 cm). The total volume and weight of the cylindrical wheel are 58.92 cm^3 and 6.605 gm respectively.

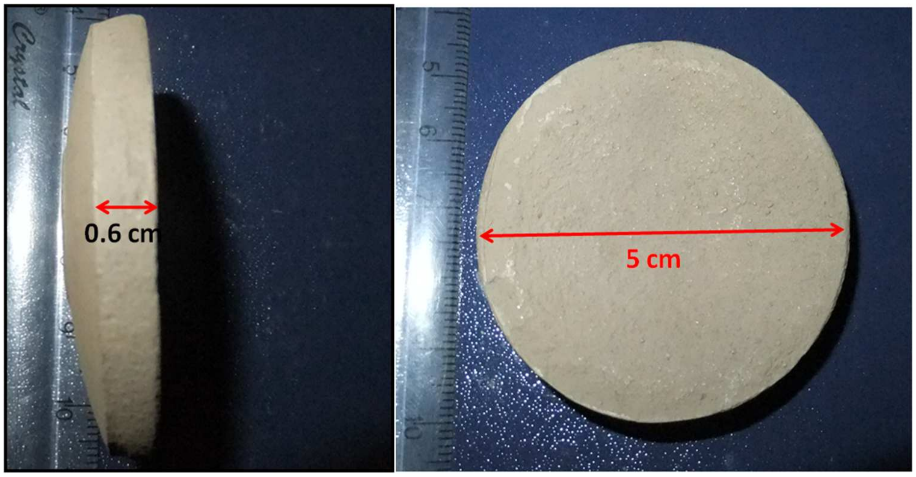


Figure S14b. Digital image of MnO_2 wheel with dimension.

Weight of the cylindrical wheel is 6.605 gm.

The density of MnO_2 material is reported and it's value 5.026 gm/cm^3.

So according to literature value of density, the net volume of the cylindrical wheel is (6.605/5.026 cm^3) i.e. 1.31 cm^3 (if there are no nanogap in the cylindrical wheel)

But the total volume of the cylindrical wheel is 58.92 cm^3.

Therefore total nanogap volume in the cylindrical wheel is (58.92-1.31) cm^3 i.e. 57.61 cm^3. So the cylindrical wheel is with highly porous architecture.

We have used this MnO_2 cake like bed as a reusable catalyst for hydrolysis reaction. If we used MnO_2 spherical particle or MnO_2 nanosheet for the preparation of membrane or wheel, it is impossible to make a cake like assembly by vacuum filtration. Only nanowire morphology is responsible for the fabrication of membrane/wheel with interlaced but long nanowires.

Supporting Information Figure S16. ^{1}H NMR spectra of benzamide compound.