

Supplementary Materials

Strongly coupled Mn₃O₄-Porous Organic Polymer Hybrid: A Robust, Durable and Potential Nanocatalyst for Alcohol Oxidation Reactions

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Characterization Techniques:

Powder X-ray diffraction (PXRD) patterns of different samples were recorded with a Bruker D8 Advance X-ray diffractometer operated at a voltage of 40 kV and a current of 40 mA using Ni-filtered Cu K α ($\lambda=0.15406$ nm) radiation. Ultra High Resolution Transmission electron microscopy (UHR-TEM) images were recorded in a JEOL JEM 2010 transmission electron microscope with operating voltage 200 kV equipped with a FEG. Field emission scanning electron microscopic images of samples were obtained using a JEOL JEM 6700 field emission scanning electron microscope (FE-SEM). Nitrogen sorption isotherms were obtained using a Quantachrome Autosorb 1C surface area analyzer at 77 K. Prior to the measurement, the samples were degassed at 357 K for approximately 8 h in high vacuum. Solid-state CP-MAS NMR studies were performed using a Bruker Avance III HD 400 MHz NMR spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on an Omicron nanotech operated at 15 kV and 20 mA with a monochromatic Al K α X-ray source. Chemical analysis was performed by using Optima 2100 DV (Perkin-Elmer) inductively coupled plasma atomic emission spectroscopy (ICP-AES). Raman spectra on cleaned silicon substrate were measured with a Raman microscope (LabRAM HR, Horiba Yvon). The excitation wavelength of the irradiating light was 632.8 nm (He-Ne Laser, Melles Griot, laser excitation 0.1mW) and signals were collected by using $\times 50$ objective lens. Quadrupole ion trap Mass Spectrometer equipped with Thermo Accela LC and Agilent 6890 GC system equipped with a flame ionization detector were used for analysis of catalytic reactions.

Experimental Section:

Synthesis of Porous organic polymer (POP):

In a typical synthesis procedure, divinylbenzene (5.99 mmol, 781 mg) and 2,4,6-triallyoxy-1,3,5-triazine (1.49 mmol, 373 mg) were mixed together in acetone (15 mL). Azobisisobutyronitrile AIBN (0.152 mmol, 25 mg) was subsequently added into the previous mixture and the resulting mixture was stirred at room temperature under nitrogen atmosphere for 6 h. We have hydrothermally treated the final reaction mixture in an autoclave at 120°C under static condition for 24 h and then cooled down to room temperature. The as-synthesized POP material was isolated as a white solid material which was dried in air at room temperature and used for further reactions.

Synthesis of $\text{Mn}_3\text{O}_4@\text{POP}$ hybrid material:

A suspension of 100 mg as-synthesized POP material in Ethanol (40 mL) was placed in a round bottom flask (100 mL). Subsequently, aqueous solution of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (4 mL 0.2 (M)) was added into the dissolved mixture in a round bottom flask. The mixture was allowed to stir at room temperature for 2 h to obtain a light brown color homogeneous solution. Then NH_4OH (28 wt%, 1 mL) was added dropwise with constant stirring at room temperature and the solution color changed into deep brown. After 1 h the resulting mixture was kept at 80 °C for 10 h under refluxing condition and then loaded into a Teflon-lined stainless steel autoclave under hydrothermal treatment at 160°C for 3 h. Brown colored solid was isolated after the filtration washed with methanol and acetone. Further drying was carried out by leaving the sample in air at room temperature. The resultant deep brown colored material was denoted as $\text{Mn}_3\text{O}_4@\text{POP}$ for further studies.

Synthesis of $\text{Mn}_3\text{O}_4@\text{SiO}_2$ hybrid material:

-NH₂ functionalized SiO₂ material was synthesized according to the previous reported procedure. A suspension of 100 mg SiO₂-NH₂ in Ethanol (40 mL) was placed in a round bottom flask (100 mL). Subsequently, aqueous solution of Mn(OAc)₂.4H₂O (4 mL 0.2 (M)) was added into the dissolved mixture in a round bottom flask. The mixture was allowed to stir at room temperature for 2 h to obtain a light brown color homogeneous solution. Then NH₄OH (28 wt%, 1 mL) was added dropwise with constant stirring at room temperature and the solution color changed into deep brown. After 1 h the resulting mixture was kept at 80 °C for 10 h under refluxing condition and then loaded into a Teflon-lined stainless steel autoclave under hydrothermal treatment at 160°C for 3 h. Brown colored solid was isolated after the filtration washed with methanol and acetone. Further drying was carried out by leaving the sample in air at room temperature. The resultant deep brown colored material was denoted as Mn₃O₄@SiO₂ for further studies. Mn loading in Mn₃O₄@SiO₂ is 0.436 mmol/g as determined by ICP-AES analysis.

Synthesis of $\text{Mn}_3\text{O}_4@\text{TiO}_2$ hybrid material:

TiO₂ material was synthesized according to the previous reported procedure. A suspension of 100 mg TiO₂ in Ethanol (40 mL) was placed in a round bottom flask (100 mL). Subsequently, aqueous solution of Mn(OAc)₂.4H₂O (4 mL 0.2 (M)) was added into the dissolved mixture in a round bottom flask. The mixture was allowed to stir at room temperature for 2 h to obtain a light brown color homogeneous solution. Then NH₄OH (28 wt%, 1 mL) was added dropwise with constant stirring at room temperature and the solution color changed into deep brown. After 1 h the resulting mixture was kept at 80 °C for 10 h under refluxing condition and then loaded into a Teflon-lined stainless steel autoclave under hydrothermal treatment at 160°C for 3 h. Brown colored solid was isolated after the filtration washed with methanol and acetone.

Further drying was carried out by leaving the sample in air at room temperature. The resultant deep brown colored material was denoted as $\text{Mn}_3\text{O}_4@\text{TiO}_2$ for further studies. Mn loading in $\text{Mn}_3\text{O}_4@\text{TiO}_2$ is 0.429 mmol/g as determined by ICP-AES analysis.

Synthesis of $\text{Mn}_3\text{O}_4@\text{Al}_2\text{O}_3$ hybrid material:

Al_2O_3 material was purchased commercially from Sigma Aldrich. A suspension of 100 mg Al_2O_3 in Ethanol (40 mL) was placed in a round bottom flask (100 mL). Subsequently, aqueous solution of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (4 mL 0.2 (M)) was added into the dissolved mixture in a round bottom flask. The mixture was allowed to stir at room temperature for 2 h to obtain a light brown color homogeneous solution. Then NH_4OH (28 wt%, 1 mL) was added dropwise with constant stirring at room temperature and the solution color changed into deep brown. After 1 h the resulting mixture was kept at 80 °C for 10 h under refluxing condition and then loaded into a Teflon-lined stainless steel autoclave under hydrothermal treatment at 160°C for 3 h. Brown colored solid was isolated after the filtration washed with methanol and acetone. Further drying was carried out by leaving the sample in air at room temperature. The resultant deep brown colored material was denoted as $\text{Mn}_3\text{O}_4@\text{Al}_2\text{O}_3$ for further studies. Mn loading in $\text{Mn}_3\text{O}_4@\text{Al}_2\text{O}_3$ is 0.439 mmol/g as determined by ICP-AES analysis.

Synthesis of $\text{Mn}_3\text{O}_4@\text{C}$ hybrid material:

A suspension of 100 mg carbon/activated charcoal in Ethanol (40 mL) was placed in a round bottom flask (100 mL). Subsequently, aqueous solution of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (4 mL 0.2 (M)) was added into the dissolved mixture in a round bottom flask. The mixture was allowed to stir at room temperature for 2 h to obtain a light brown color homogeneous solution. Then NH_4OH (28 wt%, 1 mL) was added dropwise with constant stirring at room temperature and the solution color changed into deep brown. After 1 h the resulting mixture was kept at 80 °C for 10 h under refluxing condition and then loaded into a Teflon-lined stainless steel

autoclave under hydrothermal treatment at 160°C for 3 h. Brown colored solid was isolated after the filtration washed with methanol and acetone. Further drying was carried out by leaving the sample in air at room temperature. The resultant deep brown colored material was denoted as Mn₃O₄@C for further studies. Mn loading in Mn₃O₄@C is 0.405 mmol/g as determined by ICP-AES analysis.

Catalytic Evaluation of Mn₃O₄@POP nanocatalyst:

The catalytic tests were carried out in a two-necked round bottom flask. In a typical experiment, Mn₃O₄@POP catalyst (20 mg) was added to an acetonitrile solution (10 mL) and sonicated for 15 minutes to disperse thoroughly. 1-phenyl ethanol (1.5 mmol, 0.18 mL, 180 mg) was added and stirred at room temperature. Aqueous solution of TBHP (0.38 mL, 3 mmol, 70 wt% in H₂O, 1:2 ratio with alcohol) was added slowly to the mixture solution with constant stirring at room temperature. The resulting mixture was kept at 80 °C under refluxing condition for 12 h. After cooling at room temperature catalyst was separated by centrifugation and the reaction mixture was first analyzed by Quadrupole ion trap Mass Spectrometer equipped with Thermo Accela LC for identification of the reactants and products. The products were then quantified using an Agilent 6890 GC system equipped with a flame ionization detector.

Reusability of Mn₃O₄@POP nanocatalyst for catalytic alcohol oxidation reaction:

The efficacy of Mn₃O₄@POP nanocatalyst was evaluated by conducting oxidation reaction under optimized reaction conditions considering 1-phenylethanol as a model substrate. In this test, a mixture of Mn₃O₄@POP (100 mg), 1-phenylethanol (7.5 mmol, 0.900 g), aqueous TBHP (70wt% in H₂O, 15 mmol) was kept under refluxing condition at 80 °C for 12 h in CH₃CN (50 mL). After the reaction was finished the catalyst was separated from the reaction mixture by centrifugation technique and then washed with acetone, oven dried (80 °C

temperature) and then directly used for the next catalytic run without further purification or activation. High temperature calcination technique, addition of acid or base or reducing agents are not needed for the reactivation of our catalyst. Our catalyst can be successively recycled and reused for at least 15 catalytic cycles without significant loss in catalytic activity and deactivation. A slight drop in the conversion but with the preservation of selectivity of desired product (%) from the 15th to 16th cycle is observed. In every case our recovery of catalyst from the reaction mixture is almost 100%.

Hot filtration test: We have performed the hot filtration test to examine heterogeneous nature of Mn₃O₄@POP nanocatalyst in alcohol oxidation reaction considering 1-phenylethanol as model substrate under optimized reaction condition. In this test, a mixture of Mn₃O₄@POP (20 mg), 1-phenylethanol (1.5 mmol, 0.180 g, 0.18 mL), aqueous TBHP (70wt% in H₂O, 3 mmol) was kept under refluxing condition at 80 °C for 9 h in CH₃CN (10 mL). After 9 h the Mn₃O₄@POP catalyst was separated from the hot reaction mixture and 55% conversion of 1-phenylethanol to acetophenone was achieved as determined by GC analysis. Then the reaction was continued at the same reaction temperature but no further progress of conversion was observed beyond 57%. Our investigation obviously signifies that no leaching of catalytic active species took place in the reaction mixture during catalytic reaction. After 20 hr of the reaction trace amount Mn was detected in the reaction mixture (light brown solution) by Atomic Absorption Spectroscopy (AAS) analytical technique. At the end of reaction the catalyst was removed and excess 1-phenylethanol was poured into the filtrate. We have further carried out this reaction with leached homogenously Mn species for another 24 h at 80 °C. But only 2-3% product conversion was provided after 24 h. This experimental result also demonstrated us that leached manganese species contributed to the catalytic oxidation of alcohol but didn't catalyze this reaction up to full conversion.

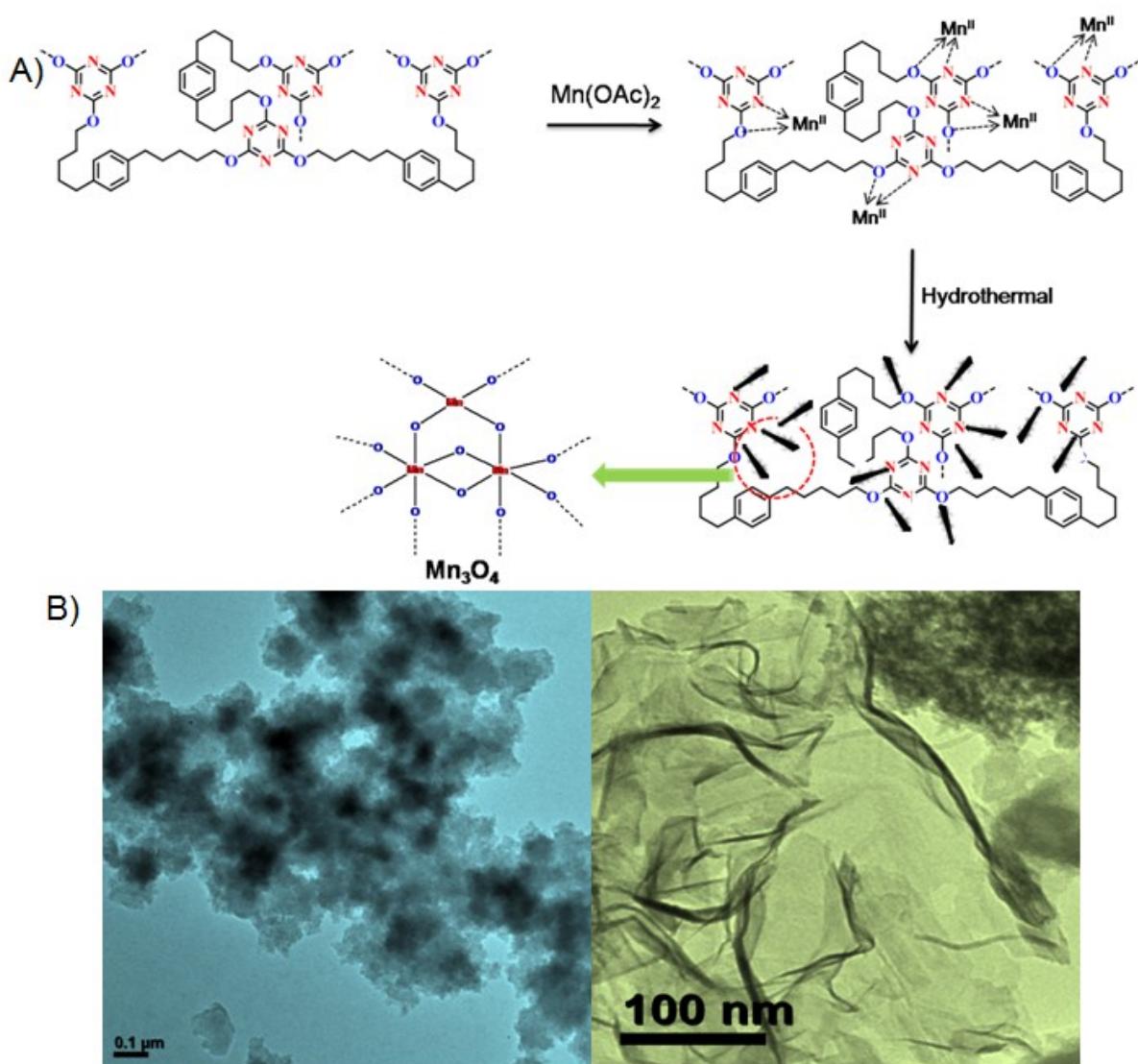


Figure S1: A) Proposed structure of the $\text{Mn}_3\text{O}_4@\text{POP}$ catalyst and B) TEM images of as-synthesized porous organic polymer (POP).

Table S1: C, H, N analysis of the respective materials

Materials	Carbon (%)	Hydrogen (%)	Nitrogen (%)
As-synthesized POP	78.230	7.091	5.189
$\text{Mn}_3\text{O}_4@\text{POP}$	75.242	5.634	3.287

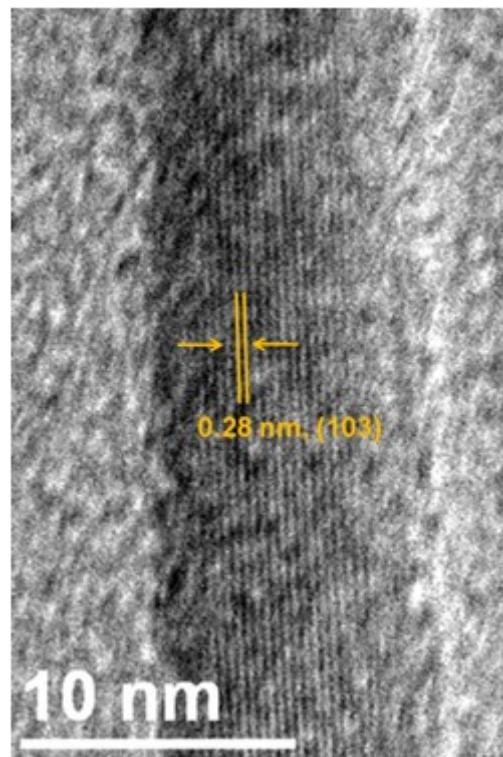


Figure S2: HR-TEM image of Mn₃O₄@POP nanocatalyst.

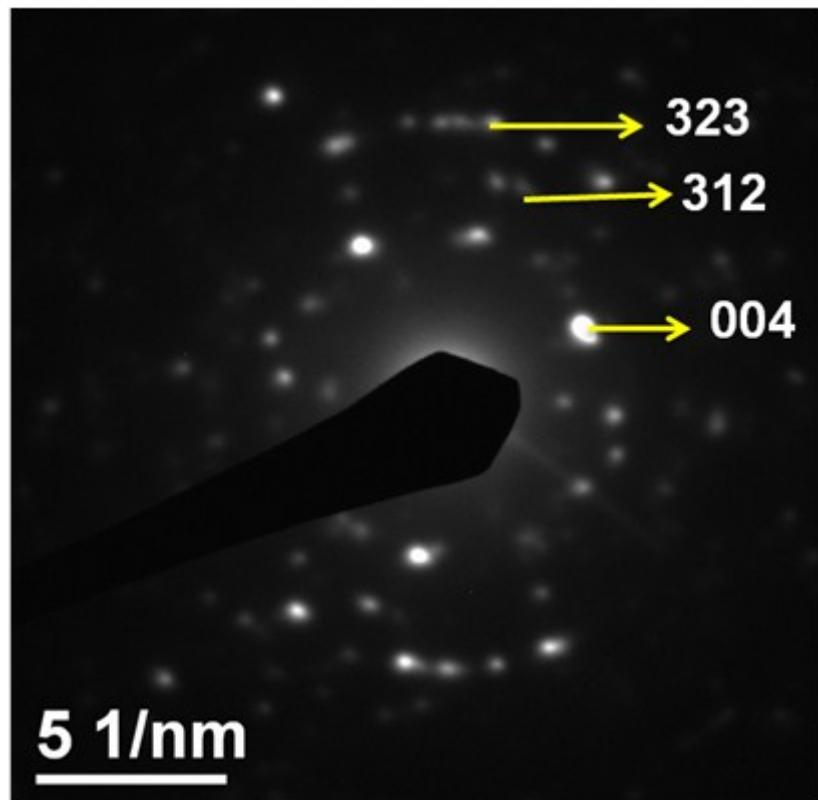


Figure S3: Selected Area Electron Diffraction (SAED) pattern TEM image of Mn₃O₄@POP-hybrid.

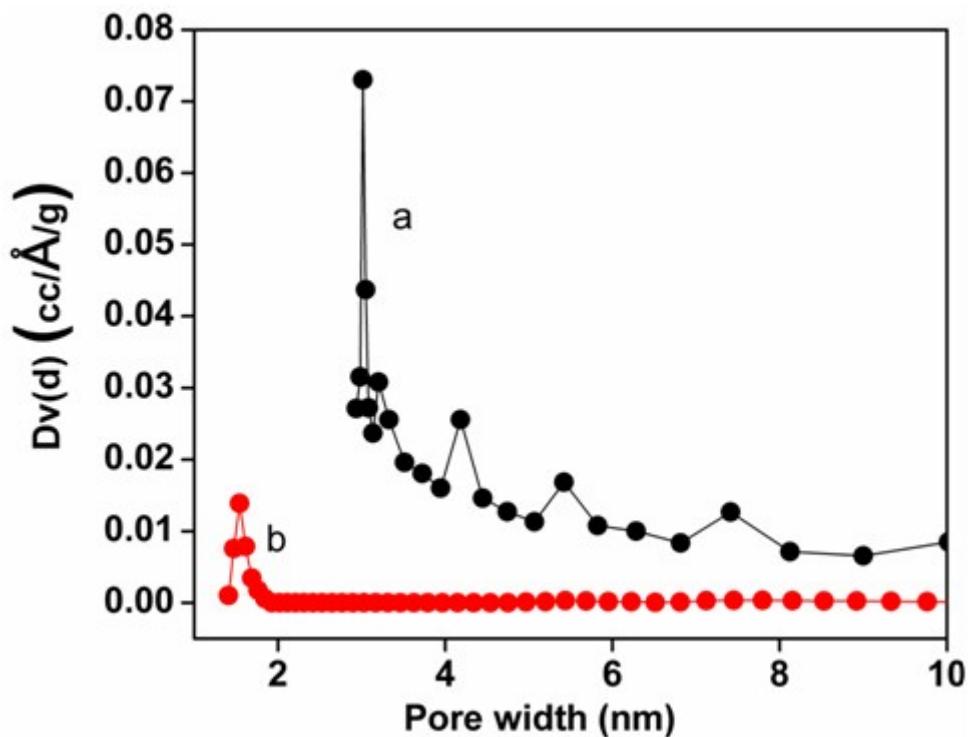


Figure S4: Pore-size distributions of a) as-synthesized porous organic polymer (POP) and b) Mn₃O₄@POP nanocatalyst.

Pore size distributions of the as-synthesized POP and Mn₃O₄@POP-hybrid materials have been calculated from N₂-adsorption/desorption isotherms by employing NLDFT (Non-Local-Density-Functional-Theory) methods (Figure S4). The peak centred at 3.01 nm (Figure S4a) with a narrow pore size distribution for as-synthesized POP material can be assumed for the presence of mesoporous structure. Shrinkage in the pore dimension for Mn₃O₄@POP-hybrid material (pore dimension 1.52 nm, Figure S4b) signified accumulation of manganese ions into the interior cavity of porous organic polymer.

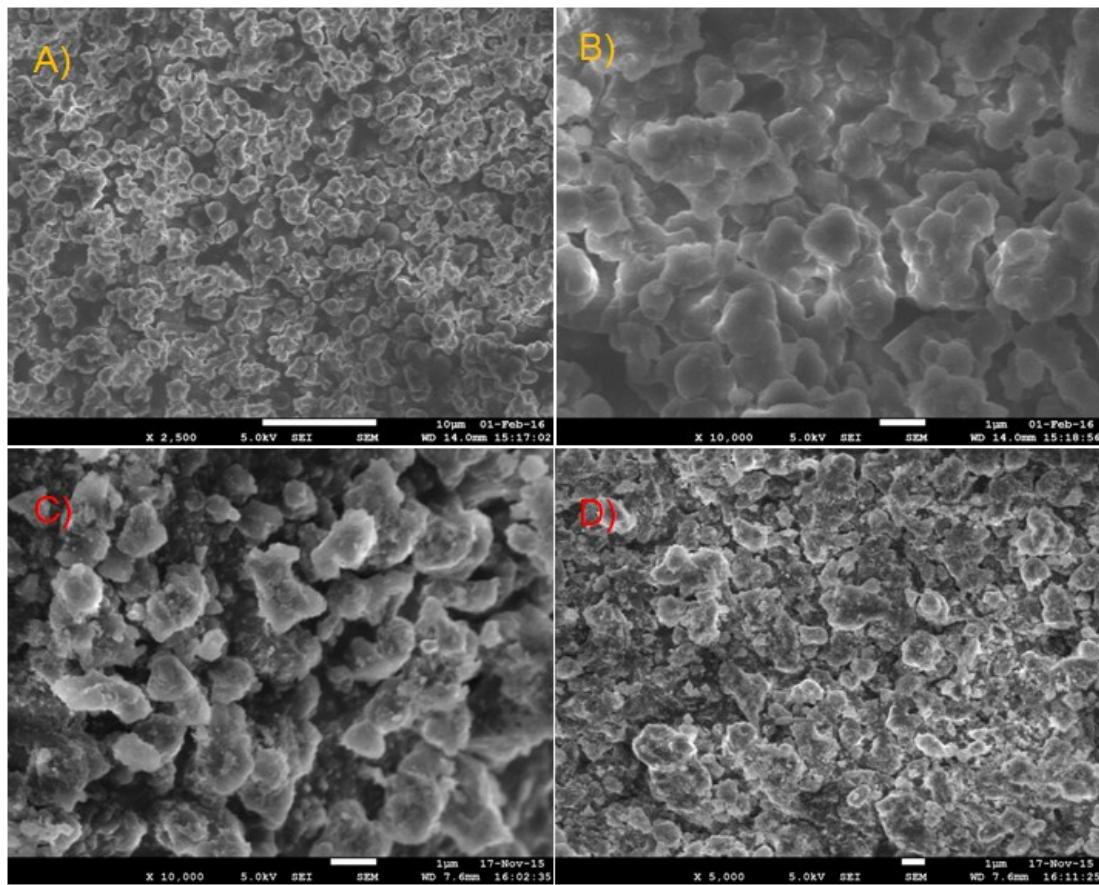


Figure S5: FE-SEM images of as-synthesized POP (A & B) and Mn_3O_4 @POP-hybrid (C & D) materials, respectively.

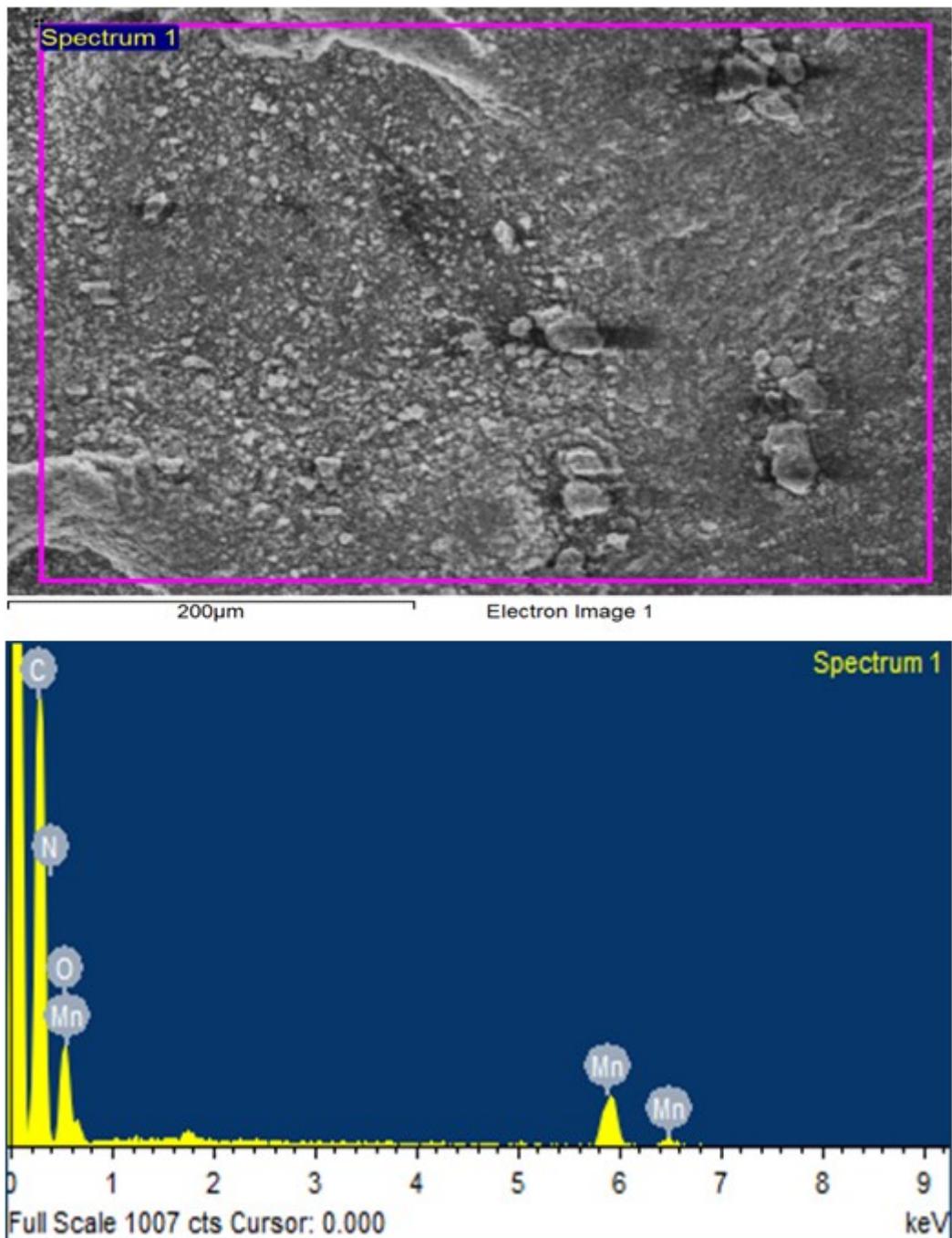


Figure S6: Selected FE-SEM image and the corresponding Energy-dispersive X-ray spectrum of $\text{Mn}_3\text{O}_4@\text{POP}$ -hybrid material.

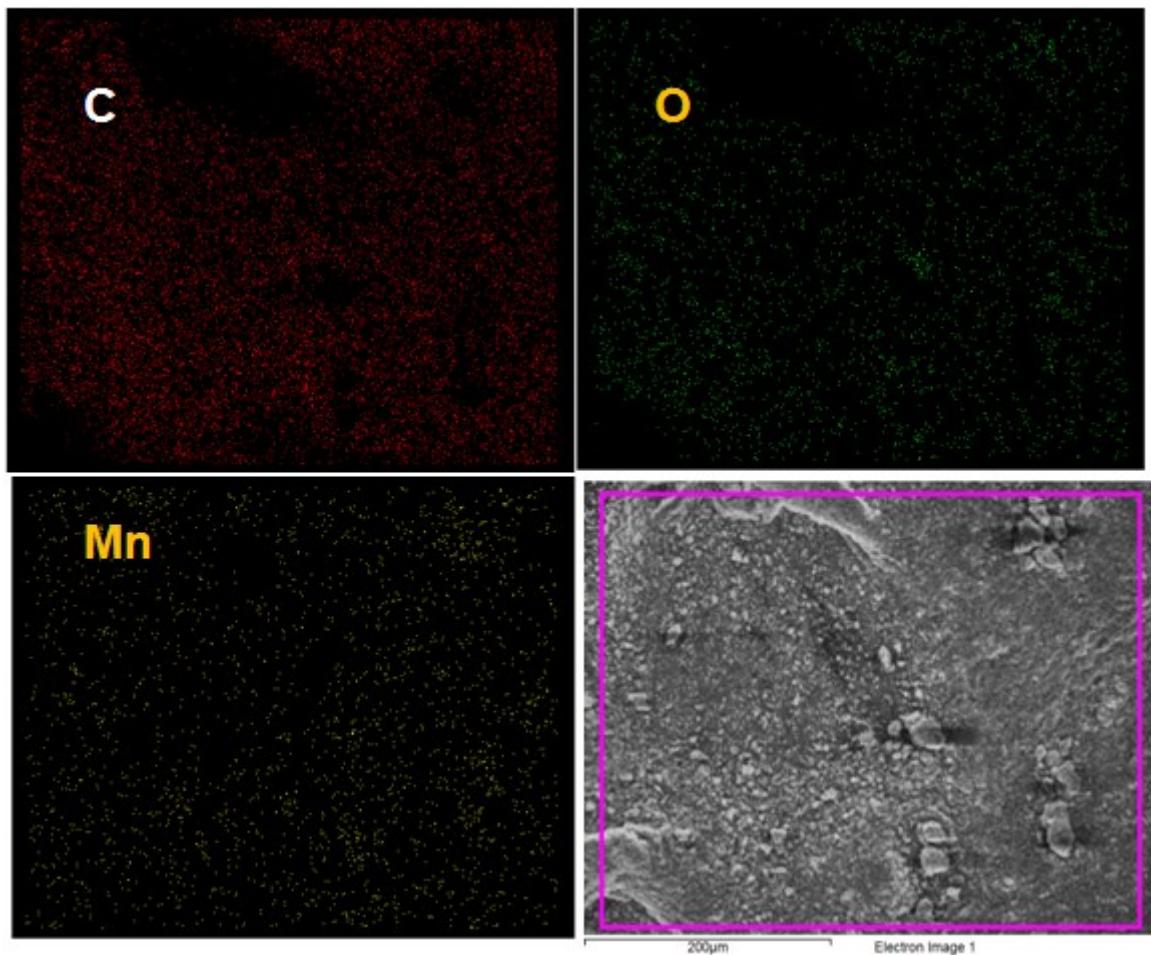


Figure S7: Elemental mapping of C, O and Mn for $\text{Mn}_3\text{O}_4@\text{POP}$ -hybrid material.

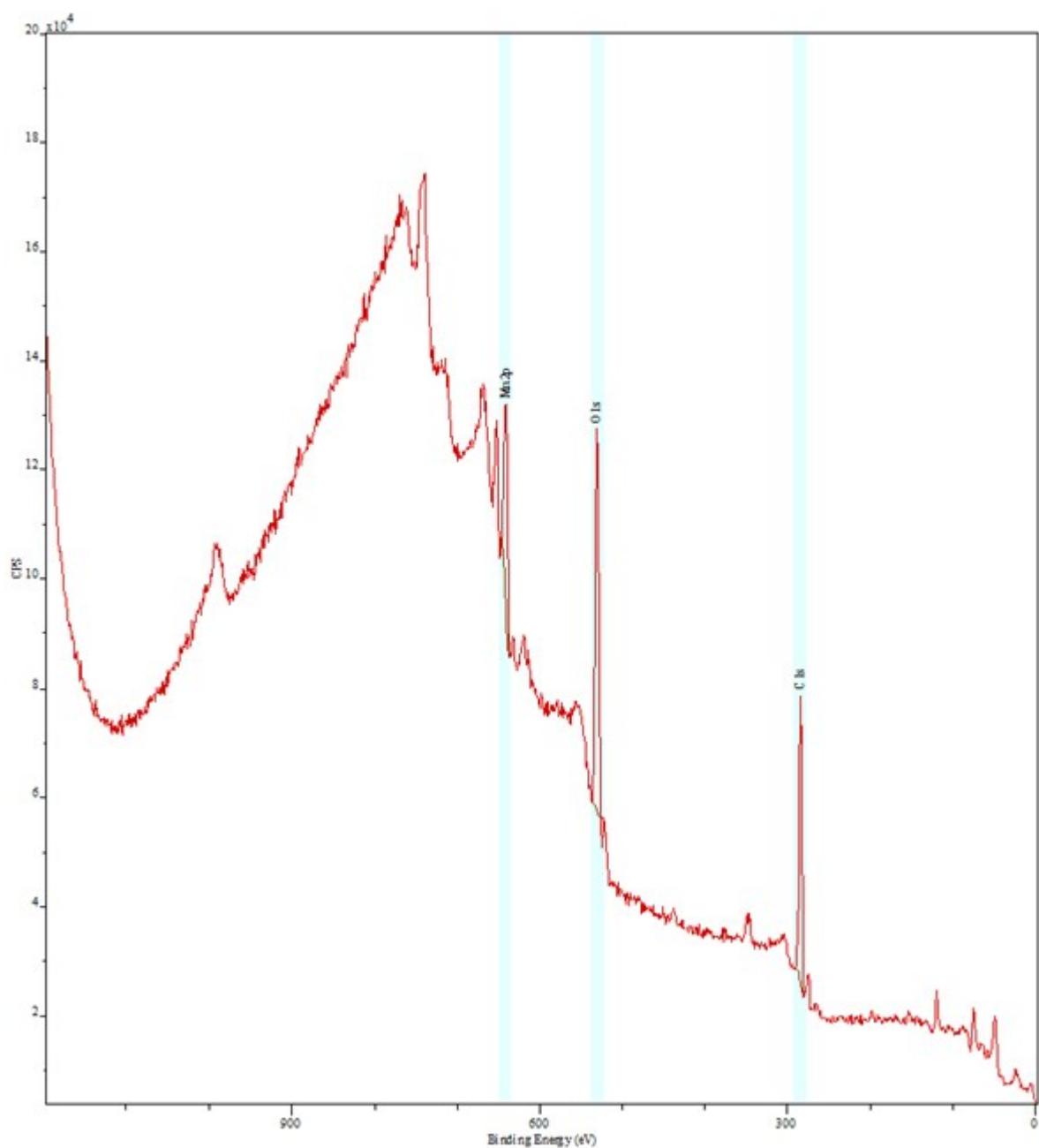


Figure S8: XPS (X-ray photoelectron spectroscopy) survey spectrum of $\text{Mn}_3\text{O}_4@\text{POP}$ -hybrid material.

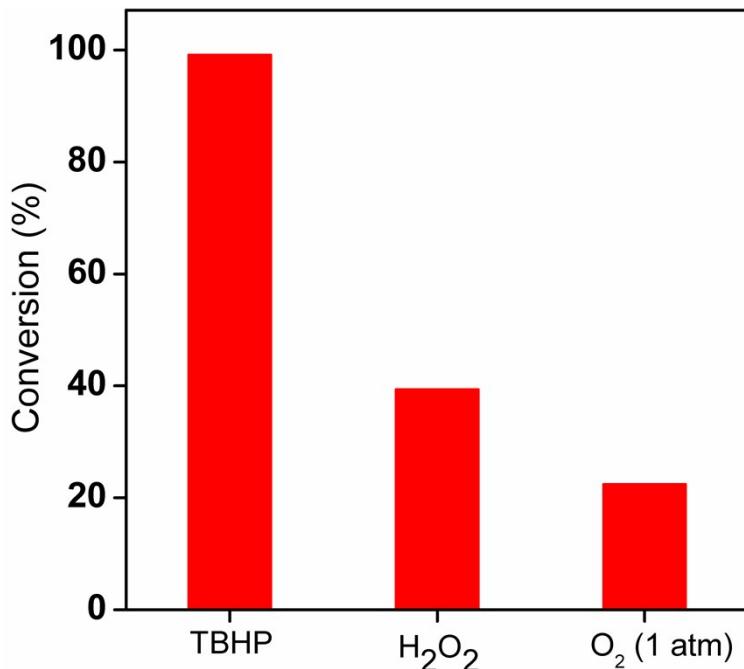


Figure S9: Use of different oxidising agents for 1-phenylethanol oxidation with $\text{Mn}_3\text{O}_4@\text{POP}$ -hybrid material. Reaction conditions: 1-phenylethanol (1.5 mmol, 180 mg), CH_3CN (10 mL), TBHP (70 wt% in H_2O , 3 mmol, 0.38 mL), H_2O_2 (30 wt% in H_2O , 6 mmol) 80°C , O_2 (1 atmosphere pressure), $\text{Mn}_3\text{O}_4@\text{POP}$ Catalyst (20 mg).

We have examined the effect of different oxygen source for the catalytic oxidation of 1-phenylethanol in the presence of $\text{Mn}_3\text{O}_4@\text{POP}$ nanocatalyst at 80°C in CH_3CN (Figure S9). In this optimization study we have employed Aqueous solution of TBHP (70 wt% in H_2O , 3 mmol, 0.38 mL), H_2O_2 (30 wt% in H_2O , 6 mmol) and O_2 (1 atmosphere pressure). All the reactions have been carried out for 12 h. Aqueous solution of TBHP (70 wt% in H_2O) has been considered as the best oxygen source for this oxidation reaction while 39.4% and 22.5% conversions have been achieved using aqueous solution of H_2O_2 (30 wt% in H_2O) and O_2 (1 atmosphere pressure).

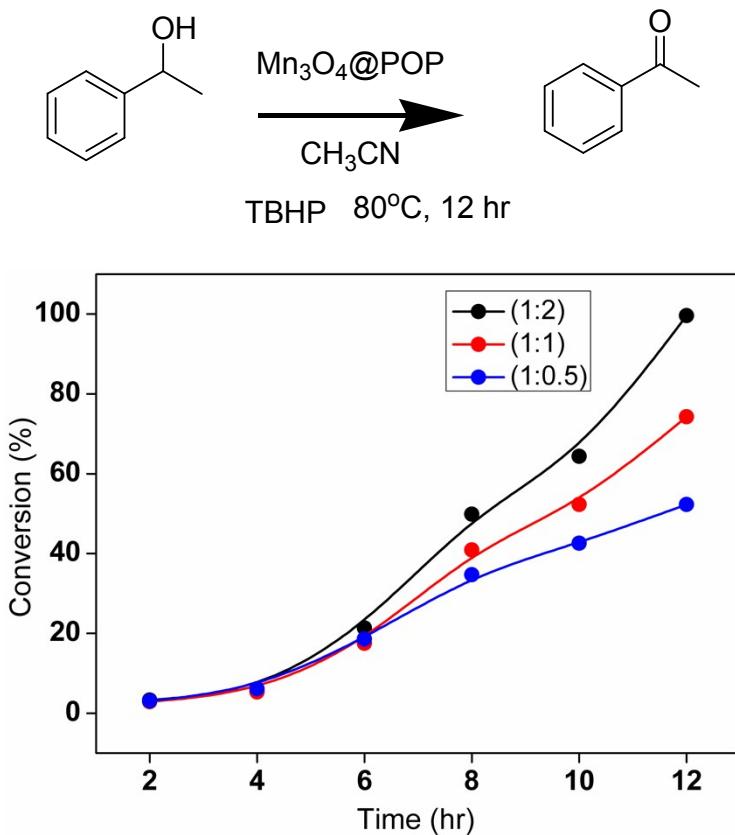
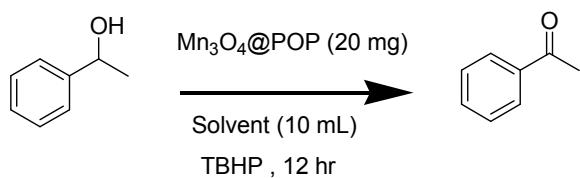


Figure S10: Catalytic activity of Mn₃O₄@POP-hybrid material for 1-phenylethanol oxidation as a function of 1-phenylethanol/TBHP molar ratio. **Reaction conditions:** 1-phenylethanol (1.5 mmol, 180 mg), CH₃CN (10 mL), TBHP (70 wt% in H₂O), Mn₃O₄@POP Catalyst (20 mg).

Study on the variation of the catalytic activity with respect to the 1-phenylethanol: TBHP (70 Wt% in H₂O) mole ratio at 80°C employing our Mn₃O₄@POP catalyst designates an enhancement in the catalytic conversion of 1-phenylethanol to acetophenone is observed with the increase of mole ratio from (1:0.5) to (1:2). This gradual enhancement in catalytic performance with the increase of mole ratio can be attributed to the high availability liquid oxygen source thereby promoting the activation of O-O bond in the presence of Mn₃O₄ nanocatalyst. 1-phenylethanol: TBHP (70 Wt% in H₂O) mole ratio value is 1:2 has been considered as the optimum for this reaction at 80°C temperature in CH₃CN.

Table S2: Screening of various solvents for 1-phenylethanol oxidation catalyzed by $\text{Mn}_3\text{O}_4@\text{POP}$ catalyst



Solvent	Temperature (°C)	Con (%)	TON	TOF (h ⁻¹)
CH ₃ CN	80	99.2	163.15	13.5
MeOH	65	8.7	14.3	1.19
EtOH	80	9.7	15.95	1.32
THF	65	7.9	12.99	1.08
PhCH ₃	110	23.2	38.15	3.17
H ₂ O	100	33.0	54.27	4.52

Reaction conditions: 1-phenylethanol (1.5 mmol, 180 mg), Solvent (10 mL), TBHP (70 wt% in H₂O, 3 mmol, 0.38 ml), Time (12 h), $\text{Mn}_3\text{O}_4@\text{POP}$ Catalyst (20 mg). TOF (Turn Over frequency)= Moles of substrate converted per mole of active site per hour.

Table S3: Effect of reaction temperature for 1-phenylethanol oxidation catalyzed by $\text{Mn}_3\text{O}_4@\text{POP}$ catalyst



Temperature($^{\circ}\text{C}$)	Conversion (%)	TON	TOF (h^{-1})
25	17.4	28.61	2.38
40	23.2	38.15	3.17
60	86.2	141.77	11.8
80	99.6	163.81	13.6

Reaction conditions: 1-phenylethanol (1.5 mmol, 180 mg), Solvent CH_3CN (10 mL), TBHP (70 wt% in H_2O , 3 mmol, 0.38 ml), Time (12 h), $\text{Mn}_3\text{O}_4@\text{POP}$ Catalyst (20 mg). TOF (Turn Over frequency)= Moles of substrate converted per mole of active site per hour.

We have investigated effect of reaction temperature for catalytic oxidation of 1-phenylethanol employing $\text{Mn}_3\text{O}_4@\text{POP}$ catalyst in CH_3CN by varying the temperature from 25°C to 80°C . It is quite obvious from the above Table S3 that an enhancement in TOF value from 2.38 h^{-1} to 13.6 h^{-1} has been achieved with the increase of temperature from 25°C to 80°C . This result clearly suggested that the high temperature (80°C) is necessary for the activation of C-H, O-H and O-O bonds by interacting with alkanols/TBHP followed by cleavage of O-O bond to liberate oxygen source.

Table S4: Effect of catalyst dose for 1-phenylethanol oxidation catalyzed by $\text{Mn}_3\text{O}_4@\text{POP}$ catalyst

Catalyst Loading (mmol)	Conversion (%)	TON	TOF (h^{-1})
2 mg (0.000912)	21	345.39	17.2
5 mg (0.00228)	46	302.63	15.1
10 mg (0.00456)	65	213.8	13.3
15 mg (0.00684)	78	171.05	10.6
20 mg (0.00912)	99	162.82	13.5

Reaction conditions: 1-phenylethanol (1.5 mmol, 180 mg), Solvent CH_3CN (10 mL), TBHP (70 wt% in H_2O , 3 mmol, 0.38 ml), Time (12 h), $\text{Mn}_3\text{O}_4@\text{POP}$ Catalyst. TOF (Turn Over frequency)= Moles of substrate converted per mole of active site per hour.

Effect of catalyst dose study considering our $\text{Mn}_3\text{O}_4@\text{POP}$ catalyst for 1-phenylethanol oxidation has been conducted under optimized reaction condition by varying mol% loading of manganese. Only 21% conversion in 12 h was obtained when 0.000912 mmol Mn incorporated catalyst has been used. Interestingly, with the increase of Mn loading an increase in catalytic conversion of 1-phenylethanol to acetophenone is observed (Table S4) due to direct proximity of manganese to the POP support. The activation of O-H in alcohol and O-O bond in Oxygen-donors are likely to get involved an intimate contact with catalytically active Mn species. Activation of the O-H bond is triggered with coordination of the oxo functionality owing to the oxophilic nature of Mn_3O_4 .

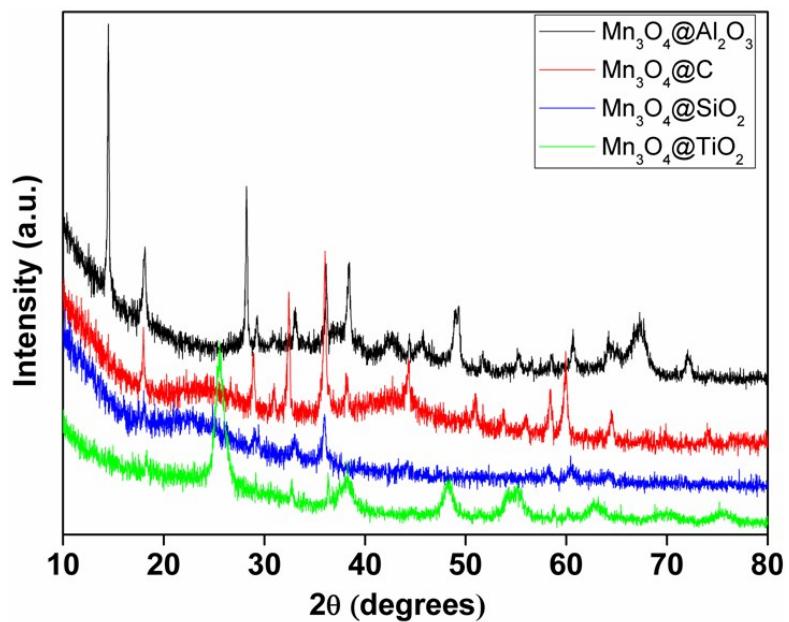


Figure S11: Wide angle powder X-ray diffraction patterns of all prepared conventional Mn₃O₄ based catalysts.

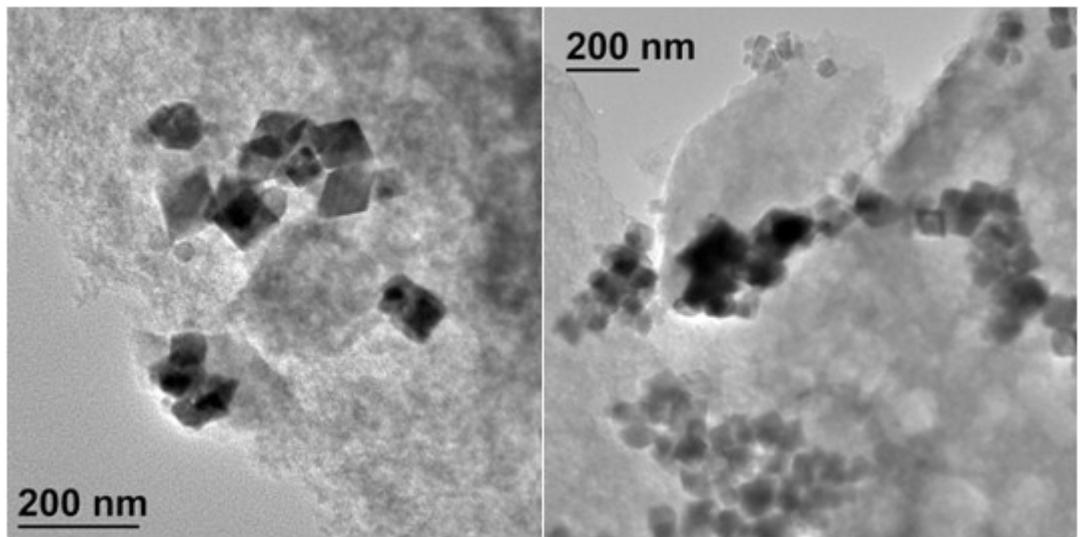


Figure S12: HR-TEM images of Mn₃O₄@C material.

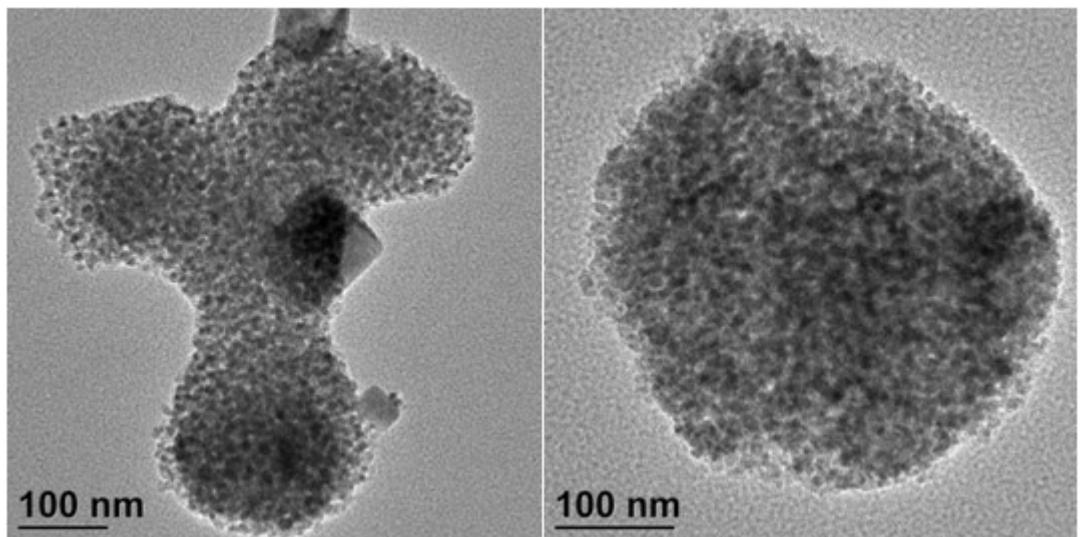


Figure S13: HR-TEM images of Mn₃O₄@TiO₂.

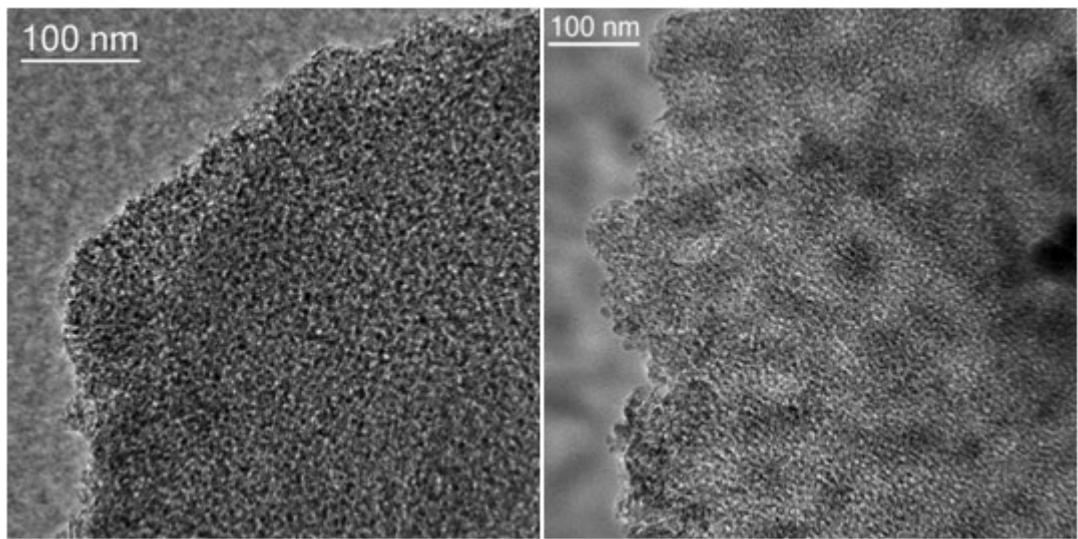


Figure S14: HR-TEM images of Mn₃O₄@Al₂O₃.

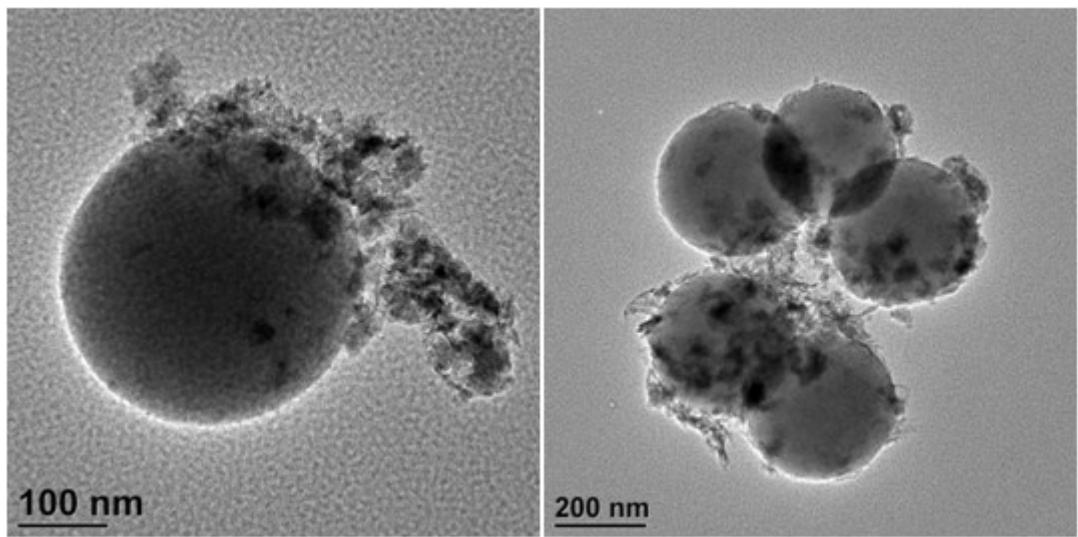


Figure S15: HR-TEM images of Mn₃O₄@SiO₂.

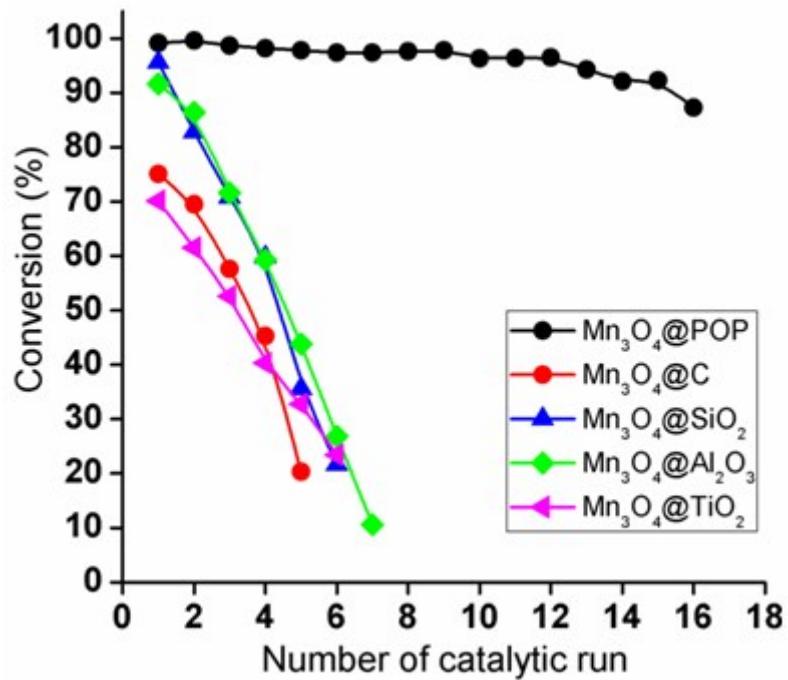


Figure S16: Conversion for the oxidation of 1-phenyl ethanol to acetophenone in the presence of $\text{Mn}_3\text{O}_4@\text{POP}$, $\text{Mn}_3\text{O}_4@\text{C}$, $\text{Mn}_3\text{O}_4@\text{SiO}_2$, $\text{Mn}_3\text{O}_4@\text{Al}_2\text{O}_3$ and $\text{Mn}_3\text{O}_4@\text{TiO}_2$ catalysts, respectively.

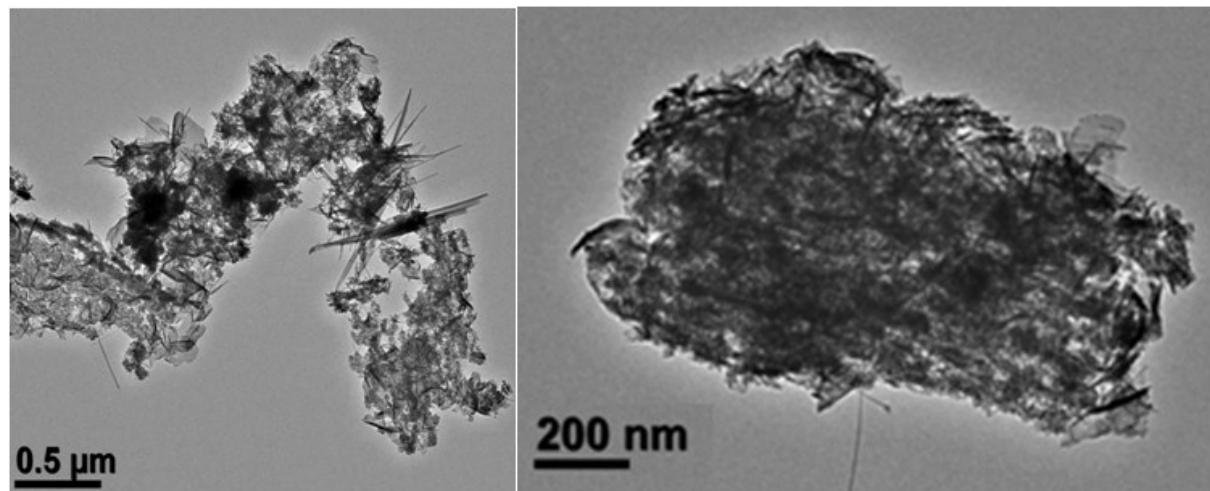


Figure S17: TEM images of Reused $\text{Mn}_3\text{O}_4@\text{POP}$ catalyst after 15th catalytic cycle.

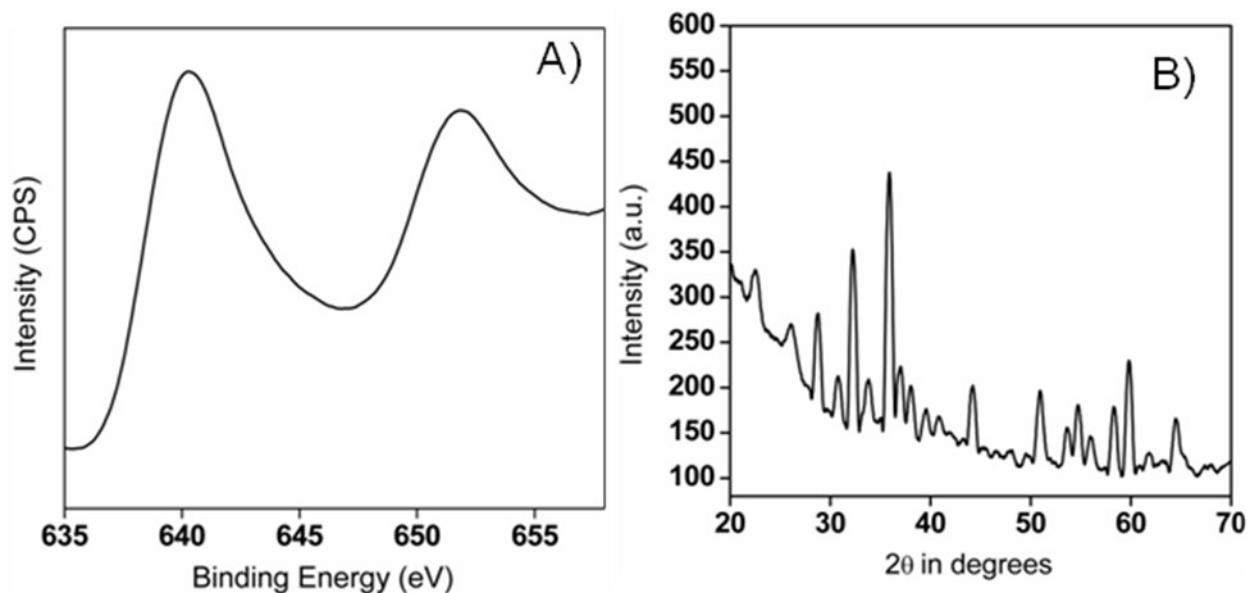


Figure S18: XPS spectrum of Mn in 2p region (A) and wide angle powder XRD pattern of Reused $\text{Mn}_3\text{O}_4@\text{POP}$ catalyst after 15th catalytic cycle.

Characterization of Reused $\text{Mn}_3\text{O}_4@\text{POP}$ nanocatalyst for Catalytic Alcohol Oxidation Reaction:

Our newly designed $\text{Mn}_3\text{O}_4@\text{POP}$ nanocatalyst was characterized after the catalysis employing TEM, XRD, and XPS analytic tools in order to guarantee thermal and mechanical stability of the catalyst. TEM images (Figure S17) after 15th catalytic run predict us that Mn_3O_4 nanoneedles are strongly anchored and well dispersed on the external surface of TRIA-POP. XPS spectrum of reused $\text{Mn}_3\text{O}_4@\text{POP}$ nanocatalyst in Mn-2p region (Figure S18A) signifies that the electronic state of Mn_3O_4 NP remains unaffected after the catalytic reactions. Wide angle Powder XRD pattern of reused $\text{Mn}_3\text{O}_4@\text{POP}$ catalyst after 15th catalytic cycles is provided in the Figure S18B suggesting nicely preservation of characteristic reflection patterns after the catalytic cycles.

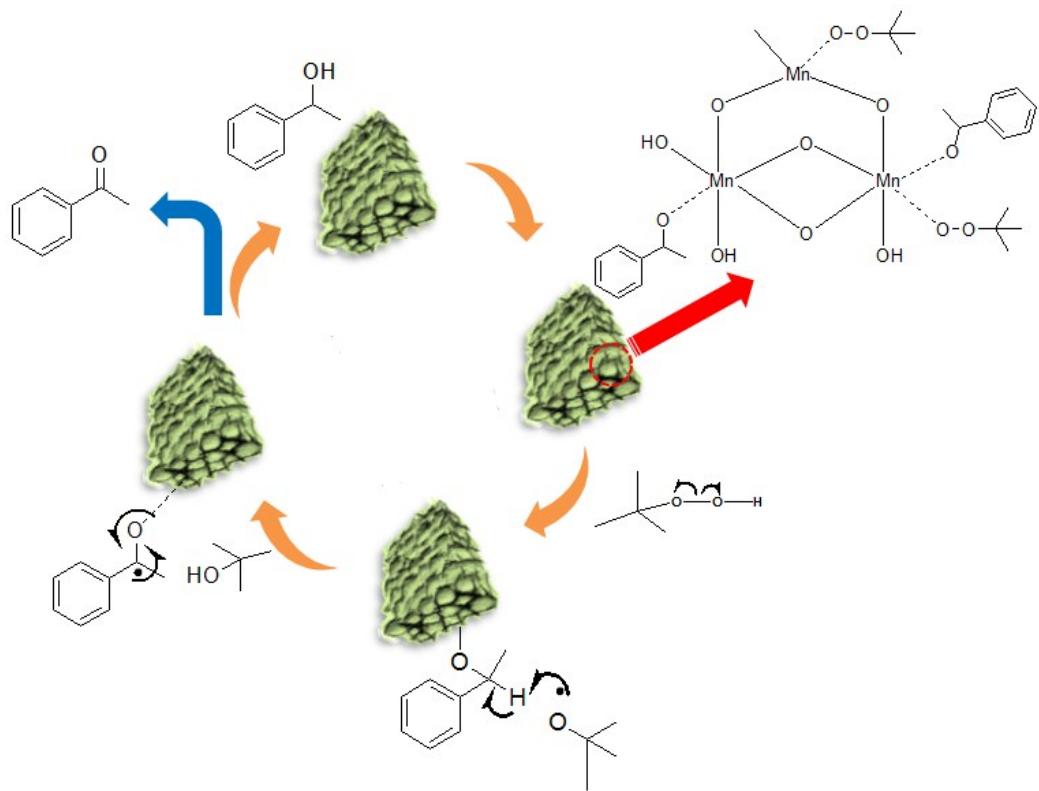


Figure S19: Plausible Reaction Pathway for oxidation reaction over $\text{Mn}_3\text{O}_4@\text{POP}$ catalyst.