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Fabrication of Mn$_2$O$_3$ nanorods: An efficient catalyst for selective transformation of alcohol to aldehyde

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A facile wet chemical approach has been devised towards preparation of self-assembled high surface area nanostructured Mn$_2$O$_3$ through an effective polymer/surfactant interaction. Its outstanding catalytic property is discovered for selective transformation of alcohols to aldehydes. The polyethylene glycol/sodium dodecyl sulphate conjugates act as soft templates for the formation of manganese oxide nanorods upon treatment of a weak base, diethanolamine to manganese acetate precursor under mild refluxing conditions. The Mn$_2$O$_3$ nanorods were found as efficient and selective catalysts for synthesis of valuable aldehydes and ketones over undesirable acid byproduct using low catalyst loading. The precursor alcohols bearing activated and unactivated aromatic rings, double and triple bonds, and chiral sugar moiety were tolerated in this direct oxidative transformation strategy developed under benign reaction conditions.

1. Introduction

Catalyst is the work-horse in synthetic chemistry.\textsuperscript{1,3} The robust reactivity and selectivity of catalyst lead to efficient transformation of raw materials into the desired pharmaceuticals, fuels, agrochemicals, pigments, polymers, commercial and natural compounds, which are essential for our highly demanding modern society. In this context, nanomaterials have tremendous potential to serve as significantly improved catalysis performance because of their active surface and interfacial atom effect, innovative new chemical property, high reactivity, low catalyst loading, environmentally benign nature, easy recovery and reusability.\textsuperscript{5-20} In recent years, size and shape-controlled synthesis of manganese oxides (MnO$_x$) nanomaterials has fascinated considerable interest from both academia and industry due to tuneable physicochemical properties,\textsuperscript{9,12} high-density magnetic storage media,\textsuperscript{13} ion-exchange,\textsuperscript{14} molecular adsorption,\textsuperscript{15} electronics,\textsuperscript{16} biosensors,\textsuperscript{17} energy storage,\textsuperscript{18} batteries\textsuperscript{19} and catalysts.\textsuperscript{20} Manganese oxides are the most attractive inorganic materials owing to their structural flexibility and availability of different oxidation states of manganese (II, III, IV) that have envisaged their structural, transport and magnetic properties\textsuperscript{21-24} in a diverse range of niche applications.\textsuperscript{25-27} Among the different oxidation states of manganese oxides, Mn$_2$O$_3$ is well known as an ideal candidate for the removal of CO and NO$_x$ from waste gas,\textsuperscript{28} decomposition of H$_2$O$_2$ into hydroxyl radicals in the catalytic peroxidation of organic effluents\textsuperscript{29} and as an oxygen storage component.\textsuperscript{30} Although, catalytic activities over transition metal oxide catalysts are lower than those over noble metal catalysts, the inherent advantages of metal oxide catalysts, such as, low cost, high thermal stability, and high mechanical strength, which make them a promising alternative for outstanding catalytic applications.\textsuperscript{3} While the catalytic activity of these materials at the nanoscale dimension depends strongly on their surface properties, the reactivity and selectivity of nanoparticles can be tuned through controlling the morphology because the exposed surfaces of the particles have distinct crystallographic planes depending on their shape.\textsuperscript{32} Therefore, synthesis of Mn$_2$O$_3$ nanoparticles with well-controlled morphology and a narrow size distribution is desirable for achieving practical applications, such as, catalysis.

Diverse synthetic approaches have been implemented in the literature for the fabrication of size and shape-selective Mn$_2$O$_3$ nanostructures and exploited their physical and chemical properties in a wide range of applications. Ganguli and co-authors prepared nanorods of anhydrous manganese oxalate as precursor to synthesize single phase nanoparticles of various manganese oxides, such as, MnO, Mn$_2$O$_3$ and Mn$_3$O$_4$ under specific reaction conditions and studied their field-dependent magnetization properties.\textsuperscript{31} Han and co-workers have reported the synthesis of Mn$_2$O$_3$ nanocrystals by the thermolysis of manganese(III) acetyl acetate on a mesoporous silica, SBA-15 and the nanocomposites showed significant catalytic activity toward CO oxidation below 523 K.\textsuperscript{34} Chen and He have described facile synthesis of mono-dispersed Mn$_2$O$_3$ nanostructures by treating a mixture of KMnO$_4$ solution and oleic acid at low temperatures (below 200 °C) and shown the application of these particles as efficient water purifiers.\textsuperscript{35} Polshettiwar and colleagues have
devised a simple strategy using aqueous solution of K₃[Mn(CN)₆] under microwave irradiation to afford the nanomaterial.¹² Gnanam and Rajendran have described the preparation of α-Mn₃O₅ nanoparticles by dropwise addition of an aqueous ammonia solution to manganese(II) chloride tetrahydrate (MnCl₂·4H₂O) in methanol under vigorous stirring and reported the optical properties of the synthesized materials.²⁶ Yang and colleagues reported the size-controlled synthesis of monodispersed Mn₃O₅ octahedra assembled from nanoparticles by a mediated N,N-dimethylformamide solvothermal route and the particles were found to exhibit catalytic activity towards CO oxidation.²⁷ Qiu et al. have described the synthesis of hierarchically structured Mn₃O₅ nanomaterials with different morphologies and pore structures from precursor containing the target materials interlaced with the polyol-based organic molecules and examined their potential as anode materials for lithium ion batteries.³⁸ Cao et al. have reported large-scale Mn₃O₅ homogeneous core/hollow-shell structures with cube-shaped and dumbbell-shaped morphologies and the particles were found to exhibit excellent performance in waste water treatment.³⁹ Najafpour and colleagues have described the synthesis of nanosized Mn₃O₅ particles by decomposition of aqueous solution of manganese nitrate at 100 °C and it was observed that the particles possessing catalytic activity towards water oxidation and epoxidation of olefins in the presence of cerium(IV) ammonium nitrate and hydrogen peroxide, respectively.⁴⁰ We envisioned fabrication of Mn₃O₅ nanorods by the soft-templated strategy which will provide roughened high surface area to offer an ideal analogue and ketones using phenyliodoacetate (PhI(OAc)₂) as a template and their catalytic activity is discovered towards generating large quantity of corresponding acid⁴³ as a by-product reaction. This approach suffers from a serious drawback of transformation of alcohols to aldehydes is a fundamental organic process (Scheme 1). In this article, we have reported an innovative fabrication approach to rod-shaped Mn₃O₅ nanostructures using polymer/surfactant assembly as soft-template and their catalytic activity is discovered towards selective oxidation of alcohols to valuable aldehydes, chiral analogue and ketones using phenyliodoacetate [PhI(OAc)₂] as an oxidizing agent.

2. Experimental

2.1 Reagents and instruments

All the reagents were used were of analytical reagent grade. Manganese(II) acetate tetrahydrate, diethanolamine (DEA), polyethylene glycol (PEG-400), sodium dodecyl sulphate (SDS) and phenyliodoacetate (PhI(OAc)₂) were purchased from Sigma Aldrich and were used without further purification. Double distilled water was used throughout the course of the experiments.

Absorption spectra were measured in a Shimadzu UV-1601 digital spectrophotometer (Shimadzu, Japan) taking the sample in 1 cm well-stoppered quartz cuvette. The surface and structural morphologies of Mn₃O₅ samples were studied by scanning electron microscopic (SEM) images were recorded by using JSM-6360 (JEOL) instrument equipped with a field emission cathode with a lateral resolution of approximately 3 nm and acceleration voltage 3 kV after sputtering the sample on silicon wafer with carbon (approx. 6 nm). Thin films were prepared by drop-coating from the aqueous-methanolic solutions of the respective samples onto silicon wafers. Transmission electron microscopy was carried out on a JEOL JEM-2100 microscope with a magnification of 200 kV. Samples were prepared by placing a drop of solution on a carbon coated copper grid and dried overnight under vacuum. High-resolution transmission electron micrographs and selected area electron diffraction (SAED) pattern were obtained using the same JEOL JEM-2010, operating at 200 kV. Energy dispersive X-ray (EDX) analysis was performed on an INCA Energy TEM 200 using an X-ray detector. Fourier transform infrared (FTIR) spectra were recorded in the form of pressed KBr pellets in the range (400-4000 cm⁻¹) with Shimadzu-FTIR Prestige-21 spectrophotometer. The powder X-ray diffraction patterns were obtained using a D8 Advanced Broker axs X-ray Diffractometer with CuKα radiation (λ = 1.540589 Å); data were collected at a scan rate of 0.5° min⁻¹ in the range of 10°-80°. Raman scattering measurements are carried out on silicon substrate in backscattering geometry using a fiber-coupled micro-Raman spectrometer equipped with 488 nm (2.55 eV) of 5 mW air cooled Ar⁺ laser as the excitation light source, a spectrometer (model TRIAX550, JY) and a CCD detector. The powder specific surface area was measured by BET analysis using a Micrometerics Tristar 3000 surface area analyzer. Thermogravimetric analysis was carried out on a Perkin-Elmer STA 6000 with the sample amount of 10 mg. The measurements were performed under nitrogen with heating from 40-800 °C (rate: 10 °C min⁻¹) and then, maintained at 800 °C for half an hour. Before TGA measurements, the samples were dried overnight in vacuum oven at 50 °C.

2.2 Synthesis of manganese oxide nanorods in polymer-surfactant conjugates

The nanostructures of manganese oxide have been synthesised using polymer-surfactant conjugates and manganese acetate tetrahydrate as the precursor salt. In a typical synthesis, an aliquot of aqueous polyethylene glycol (PEG) (0.4 mmol dm⁻³) was added to an aqueous solution of sodium dodecyl sulphate (SDS)
(2 mmol dm\(^{-3}\)) in a double-naked round-bottom flask so that the total volume of the solution is 25 mL and the mixture was stirred overnight at room temperature. Now, an amount of 0.245 g Mn(ac)\(_2\)·4H\(_2\)O was dissolved in the polymer-surfactant mixture by refluxing on a water bath at 65°C. After complete dissolution of the precursor, 100 µL diethanolamine was added and refluxing was continued for another 6 h. After about 30 min, the reaction mixture, suddenly, turned into yellowish brown from a colourless solution indicating the formation of manganese oxide nanostructures. As the refluxing was continued, the colour slowly changed into deep brown pointing out to the aggregation between the ultrasmall manganese oxide particles to rod shaped nanostructures. The water-bath was removed and the reaction mixture was stirred for 12 h at room temperature. The particles formed by this method was washed five times with slightly hot water and finally, dispersed in water. The manganese oxide nanostructures prepared by this method are stable for a month and can be stored in the vacuum desiccator without any significant agglomeration or precipitation of the particles.

2.3 General procedure for synthesis of aldehydes

The precursor alcohol (1 mmol), Mn\(_2\)O\(_3\) (1.6 mg, 0.01 mmol), PhI(OAc)\(_2\) (403 mg, 1.25 mmol) and MgSO\(_4\) (about 300 mg) were taken together in ethylenedichloride (EDC, 25 mL) and stirred magnetically at 45°C until the reaction was complete. The progress of the reaction was monitored by TLC. After completion of the reaction the post reaction mixture was filtered through a sintered funnel and the residue was washed with EDC (2×5 mL). The combined EDC was transferred to a separating funnel, washed with water (3×10 mL) and dried using activated MgSO\(_4\). The solvent was removed in a rotary evaporator at room temperature under reduced pressure. The crude product was purified by column chromatography over silica gel (60–120 mesh) using ethyl acetate-petroleum ether (1:200, v/v) as an eluent in an yield of 87% (92.5 mg, 0.87 mmol) and 4% (4.5 mg, 0.04) respectively. The structure of the desired product (2a) and byproduct (3a) were confirmed with the help of the available literature (2b-e), ketones (4a,b), acids (3a-f) and sugar aldehyde (2f) were characterized by measuring melting boiling points and also comparing the recorded NMR (\(^1\)H and \(^13\)C), FT-IR, and mass (HR-MS) spectra. Similarly other aldehydes (2b-e), ketones (4a,b), acids (3a-f) and sugar aldehyde (2f) were characterized by measuring melting boiling points, recording NMR (\(^1\)H and \(^13\)C), FT-IR, and mass (HR-MS) spectra and optical rotation, which were verified with the know literature data and spectra.

3. Results and discussion

In the present experiment, we have reported an innovative fabrication approach to rod-shaped Mn\(_2\)O\(_3\) nanostructures using polymer/surfactant assembly as soft-template and their catalytic activity is discovered towards selective oxidation of alcohols to valuable aldehydes, chiral analogue and ketones using phenyldiodiacetate [PhI(OAc)\(_2\)] as an oxidizing agent. The absorption spectral features of the as-synthesized Mn\(_2\)O\(_3\) sample in the solid state are shown in ESI 1. The estimated direct band gap of the Mn\(_2\)O\(_3\) was found to be 1.29 eV; this value is almost close to reported value of the Mn\(_2\)O\(_3\) nanostructures.\(^{48}\) The morphology, composition and crystallinity of the particles synthesized in the polymer/surfactant mixture are presented in Fig. 1. Representative scanning electron micrograph (trace a) of the Mn\(_2\)O\(_3\) particles shows bunch of elongated nanorods with length up to 1±0.3 µm and width 50±10 nm. To further examine the surface morphology of the microstructures, high magnification SEM images were recorded (trace b) and it was apparent that the surface of the particles was with roughened edge, which indicates the growth and slow transformation to rod-shaped nanostructures occur through oriented aggregation of primary nanocrystals. At the very beginning of reflux, the concentration of reactants is comparatively high; therefore, some nuclei can be formed very fast resulting in the occurrence of ultrasmall particles. The nuclei, subsequently, orient and grow fast along the (211) direction to form one dimensional nanorods.\(^{49}\) The size and shape of the nanocrystals is further
strong ring patterns due to (211), (222) and (400) planes and therefore, confirms the crystallinity of the materials. Representative energy dispersive X-ray spectrum (panel f) of Mn$_2$O$_3$ nanorods indicates that the particles are composed of Mn and O elements. The formation of manganese oxide particles in the polymer-surfactant conjugates has been studied through FTIR spectroscopy (ESI 2). It is seen that the Mn–O bond stretching frequencies appears in the range of 450–680 cm$^{-1}$ along with two strong peaks at 630 and 525 cm$^{-1}$ that arise due to the stretching vibration of Mn–O and Mn–O–Mn bonds, indicating the formation of Mn$_2$O$_3$ in the polymer/surfactant conjugates. The X-ray diffraction pattern of the representative hybrid rod-shaped assemblies is shown in ESI 3; all diffraction peaks implying a crystalline structure are consistent with the standard values of bulk Mn$_2$O$_3$ [JCPDS No -41-1442].

Fig. 2 shows the Raman spectrum of the as-prepared nanorods under ambient condition. The structure of Mn$_2$O$_3$ belongs to I$_{a}$$_{3}$ symmetry group with $\alpha = 9.41$ and possess cubic bixbyite structures. The bands at 310, 366 and 655 cm$^{-1}$ could be ascribed to the out of plane bending modes of Mn$_2$O$_3$, the asymmetric stretch of bridge oxygen species (Mn–O–Mn) and the symmetric stretch of Mn$_2$O$_3$ respectively in correspondence to that obtained for bulk MnOx particles.

Fig. 2. Raman spectrum of the manganese oxide/polymer-surfactant hybrid assemblies dried in air.

Thermogravimetric analysis (ESI 4) of the as-dried powder sample shows two weight loss steps in the curve: 8.9 wt% loss corresponding to the water desorption (up to 200 °C), and a weight loss of 32.1 wt% over 200-800 °C as a result of the decomposition of polymer/surfactant assemblies, verifying that the polymer/surfactant conjugates are, indeed, incorporated into the nanostructures. The textural properties of the Mn$_2$O$_3$ microrods were investigated by Brunauer–Emmett–Teller (BET) gas-sorption measurements performed at 77 °K of the as-dried powder sample under vacuum as shown in ESI 5. The specific surface area and Langmuir surface area of the microrods have been measured to be ca. 13.60 m$^2$ g$^{-1}$ and 22.27 m$^2$ g$^{-1}$, respectively from which it is evident that Mn$_2$O$_3$ nanorods, synthesised in the present experiment, manifest high BET surface area to provide a platform for the catalytic organic transformation.

In the initial experiments, we have decided not to apply high temperature for the desired catalytic oxidation (Scheme 1) of our model substrate benzylalcohol (1a, $R=\text{Ph}$, shown in ESI 6) to benzaldehyde (2a) using $\lambda^{3}$-hypervalent iodane, so that the possibility of forming byproduct benzoic acid (3a, entry 1, Table 1) could be avoided. After several experiments using as-synthesised Mn$_2$O$_3$ nanorods (1 mol%) we discovered its catalytic property for the oxidative dehydrogenation reaction using PhI(OAc)$_2$ (1.25 mmol), which revealed about 60% conversion at 50 °C to afford benzaldehyde (2a, yield: 45%) with high selectivity (2a:3a = 9:1). The yield (68%) was improved on use of PhICl$_2$ (entry 2). Gratifyingly utilizing commercially available PhI(OAc)$_2$ the conversion (100%), reaction rate (2 h), yield (96%) and selectivity (2a:3a = 47:3) were significantly improved under the similar reaction conditions (entry 3). The optimized oxidation process was found utilizing as low as 0.01 mol% of the nanorods as described in the entry 7, which was obtained (entries 5-8) by changing the reaction temperature (50-40 °C) and catalyst loading (1-0.005). The reaction rate (70% in 12 h), yield (48%) and selectivity (2a:3a = 2:3) were drastically reduced in absence of the Mn$_2$O$_3$-NPs (entry 9). Ethylene dichloride was found as the suitable solvent because the other polar aprotic solvents such as dichloromethane (CH$_2$Cl$_2$), tetrahydrofuran (THF) and acetonitrile (entries 10-12), nonpolar toluene (entry 13) and protic methanol or water (entries 14,15) were not effective for the unprecedented catalytic process.

The diverse catalytic activity of the Mn$_2$O$_3$-nanorods was evaluated utilizing various types of alcohols under the optimized reaction conditions (entry 1, Table 2 as shown in ESI 6). The benzyl alcohols bearing activated (1b) and deactivated (1c) aromatic moiety (entries 2,3, Table 2) were tolerated in this reaction to afford corresponding aldehyde with excellent yield and selectivity (entries 2,3). Interestingly in presence strongly electron withdrawing -NO$_2$ group the reaction rate was enhanced (from 4.5 to 3 h) with respect to activated aromatic nucleus (1b), which simultaneously reduced the selectivity from 19:1 to 23:2 (entries 2,3).

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Scheme 1. Direct synthesis of aldehydes using Mn$_2$O$_3$-nanorods catalyst
corresponding aldehydes with 90-92% yield and outstanding selectivity (19:1). We turned our attention applying the benign strategy for oxidation of sugar-based chiral alcohol (1f, entry 6) and under the similar reaction conditions it afforded corresponding optically pure aliphatic aldehyde (2f) with high yield (76%) and selectivity (91:9). The diverse catalytic activity of the Mn₂O₃-nanorods was also successfully exploited on functionalized secondary alcohols (1g, 1h) to obtain corresponding ketones (4a, 4b, entries 8,9) without formation of the byproduct benzoic acid (3a). The catalytic reaction was tested with bulk Mn₂O₃ and it was seen that the particles could not selectively transform the alcohols to aldehydes. A comparative account highlighting utility of Mn₂O₃ nanorods and some other catalysts towards the oxidation of alcohols is presented in ESI 7. This unprecedented property of Mn₂O₃-nanorods under very low catalyst loading (0.01 mol%) provides new prospects and perspectives in catalysis towards discovery of new materials, innovative catalytic activity and novel organic transformation to afford functional molecules for our highly demanding modern society.

### 4. Conclusion

In conclusion, hydrolysis of manganese precursor in the presence of polymer/surfactant soft template has been found to be an effective strategy for the fabrication of Mn₂O₃ nanorods. The nanorods are crystalline and offer roughen surface and large surface area that installs new and innovative catalytic activity such as direct synthesis of valuable aldehydes through oxidation of alcohols in a highly chemoselective fashion. This new synthetic strategy for low dimensional manganese oxide material could be exploited for fabrication of novel inorganic materials with controlled superstructures and unusual functionalities. This unprecedented catalytic activity of Mn₂O₃ nanorods provides new prospects and perspectives in catalysis for the pursuance of novel organic transformations to afford functional molecules for our highly demanding modern society.

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### Supporting Information

Characterization details of synthesized materials, reaction schemes, catalysis details with tables. This material is available free of charge at http://www.rsc.org.

### References