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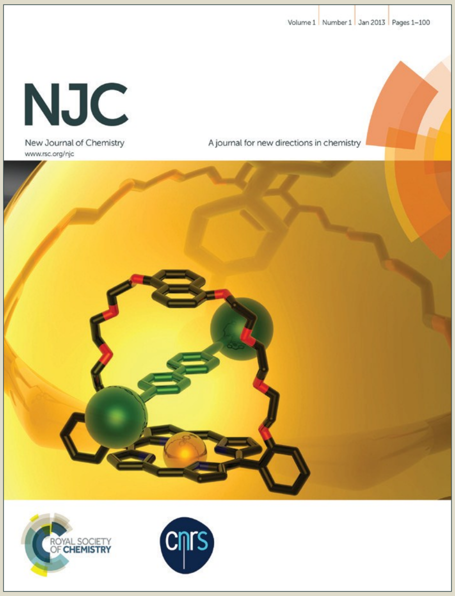

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Synthesis, Characterization and Application of γ-MnO_2/Graphene Oxide for Selective Aerobic Oxidation of Benzyl Alcohols to Corresponding Carbonyl Compounds

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Abstract

Facile low temperature approach was used to synthesize γ-MnO_2 on the surface of graphene oxide (GO) through simple wet precipitation method using $MnSO_4$ as precursor. X-ray diffraction analysis and Raman spectroscopy confirmed the formation of γ-phase MnO_2 in MnO_2/GO nanocomposites. Transmission electron microscopy studies showed γ-MnO_2 exists as flower and needle structures in GO with an average size of approximately 15 nm. Inductive coupled plasma atomic emission spectroscopy studies confirm a 62.5 wt. % loading of γ-MnO_2 in GO nanocomposites. γ-MnO_2/GO catalyst shows good activity for the selective aerobic oxidation of benzyl alcohols to corresponding carbonyl compounds even when present in sub-stoichiometric amounts giving 91% yield over 3 h under mild reaction conditions. The catalyst showed high activity even after three cycles indicating good recyclability.

Keywords : heterogeneous catalyst, GO, γ-MnO_2/GO, flower shaped, benzyl alcohol, benzaldehyde

Introduction

Manganese dioxide (MnO_2) is reported to be one of the most stable oxides with high catalytic activity and low cost. MnO_2 exists in α, β, and γ forms depending on the arrangement of the basic [MnO_6] octahedral unit.[1,3] Polymorphism had opened broad range of applications in catalysis, biosensors, energy storage.[1-3] Several efforts have been directed towards the synthesis of polymorphs of MnO_2 with different morphology.[3-6] However, only few reports have focused on the synthesis of MnO_2 hierarchical architecture.[7,8] Among MnO_2 phases, γ-phase MnO_2 is more active catalytically in comparison to α and β-phases.

MnO_2 is commonly used as catalyst for selective oxidation of aromatic alcohols to carbonyl compounds. However, it is used in in greater than stoichiometric amounts, thereby generating large amount of waste. Owing to its high activity, γ-MnO_2 when used in greater than stoichiometric amounts for catalyzing the oxidation gives large amount of undesirable over-oxidation products such acids and esters. Therefore, α-MnO_2 is commonly employed for industrial oxidations. Several noble metal and nano-catalysts have been reported for this industrially important oxidation. Over 98 % conversion has been reported using metallic and bimetallic catalysts such as gold-copper on silica,[10] palladium nanoclusters.[11] Gold nanoparticles in presence of trace amount of metal carbonates,[12] Ru supported on Al_2O_3[13] have showed almost 99% selectivity. Kamimura and co-workers reported use of sub-stoichiometric amount (28 % mol) of Co activated birnessite MnO_2 for oxidation of benzyl alcohols to corresponding carbonyl compounds at 110 °C and oxygen atmosphere obtaining 84 % yield in 24 h.[9] However, performance of the catalyst under aerobic conditions was much lower. Use of pure oxygen for oxidations is typically not feasible, and loss of noble metal-based catalysts during processing is also a concern.

Performance of inorganic nanostructures can be enhanced by tethering it with carbonaceous materials like highly ordered pyrolytic graphite, graphene, graphene oxide (GO), etc. GO, in particular, has been shown to enhance catalytic activity by synergistic charge delocalization, oxidizing properties, etc. Additionally, GO due to its large surface area and good thermal stability is ideal as catalytic support.[14,15] Oxygenated functional groups such as epoxy, carboxyl and hydroxyl, attached on GO sheet act as anchor sites for growth of inorganic nanostructures, complexation of ions, etc.[16] Recently, transition metal free oxidation pathway using graphene oxide (GO) as ‘carbocatalyst’ has been reported for oxidation of benzyl alcohols.[17,18] However, the methodology involved long reaction times even under sonicating conditions as well as the large catalytic loading. During oxidation of benzyl alcohols to carbonyl compounds, the elimination of hydrogen from the hydroxyl groups is considered to be the rate determining step, and an alkali is added to accelerate the rate of elimination. GO can complex with ions such as potassium, and the acceleration of elimination can be achieved using a mild base such as K_2CO_3. Further tethering MnO_2 on GO, we can exploit the synergistic charge transfer effects stabilizing carbanion formed during the reaction, thereby enhancing the catalytic activity of MnO_2. Thus, γ-MnO_2/GO composite is expected to be an excellent catalyst, and when used in sub-stoichiometric amounts, formation of most over-oxidation products could also be prevented.

Here, we report methodology for low temperature synthesis of 3D nanostructures of γ-MnO_2 supported on GO nanocomposites combining high catalytic ability of γ-MnO_2 with high surface area and thermal stability of GO. γ-MnO_2/GO nanocomposites were characterized using X-ray diffraction, Raman spectroscopy, inductively coupled plasma-atomic emission spectroscopy, thermogravimetric analysis and high resolution transmission electron microscopy. Catalytic activity of γ-MnO_2/GO nanocomposites was studied for selective aerobic oxidation of benzyl alcohols to benzaldehyde. α-MnO_2 nanorods supported on GO have been previously reported as an active catalyst for amide synthesis in aqueous media.[19] However, the significance of crystal phase and precursor for MnO_2 synthesis was not explicated. Further, the reaction was carried out under 3 MPa pure oxygen pressure while our methodology pursues oxidation of benzyl alcohol under aerobic conditions at atmospheric pressure, and at much lower catalyst loading. The effect of temperature, loading of base and recycle of catalyst on yield was also studied.

Experimental

Materials

Manganese sulfate ($MnSO_4$), potassium permanganate ($KMnO_4$), 2-propanol (AR grade) were purchased from S. D. Fine Chemicals Ltd., Mumbai. De-ionized water was used for the all the experiments.

Synthesis of γ-MnO_2/GO nanocomposites

Graphene oxide (GO) was prepared from natural graphite powder by modified Hummer method.[20] γ-MnO_2/GO nanocomposites were synthesized by simple chemical precipitation method. Graphene oxide (0.60 g) was dispersed in de-ionized water (50 cm^3) by sonicating for 30 min, followed by addition of $MnSO_4$ (1.80 g) and 2-propanol (50 cm^3) under continuous stirring. Reaction mixture was heated to 80 °C for 15 min under vigorous stirring. Aqueous solution of $KMnO_4$ (0.6 g/5 cm^3) was added drop-wise to the above refluxing solution. After 30 min, the reaction mixture was cooled and centrifuged. The residue obtained was further washed with DI water, followed by 2- propanol for removal of any inorganic salts formed in reaction and was then dried at 30 °C for 24 h.[1]

Characterization of γ-MnO_2/GO nanocomposites

Crystal structure of the γ-MnO_2/GO nanocomposites was studied using X-ray diffraction (2θ = 5° to 80°, Bruker X- ray Diffractometer, D8-Advance) with a data scanning rate of 0.016 sec/step, using monochromatized Cu Kα radiation (1.5406 Å). Raman spectra were analyzed by HR-800 (Horiba Scientific) by using an excitation at 632 nm. Size of γ-MnO_2/GO nanocomposites was determined using high resolution transmission microscopy (HR-TEM, JEOL, 2100). Images were collected with an operating voltage of 200 kV. Fourier transform infrared spectra (FTIR) were recorded on Bruker-VERTEX 80V instrument aligned with Ultra-Scan interferometer with a resolution of 1 cm^{-1} wave number. MnO_2 loading on GO surface was calculated by using inductive coupled plasma (ICP-AES, Element XR, Thermo Fisher Scientific, Germany). This was further supported by Thermogravimetric analysis (TGA) carried out from 30 to 700 °C with Thermax 700 TGA at a heating rate of 20 °C min^{-1} in air flow.

Catalytic oxidation of benzyl alcohols

Alcohol (1.0 mmol), γ-MnO_2/GO (0-10% mole basis), K_2CO_3 (0-1.0 mmol) and 3 cm^3 toluene were stirred for appropriate time in a 10 cm^3 reactor at 80°C under aerobic conditions. Reaction was monitored using thin-layer chromatography (TLC). After completion of reaction, the reaction mass was cooled to 30 °C, followed by filtration to recover the catalyst. Reaction mass was washed with DI water (2 × 5 cm^3). The organic layer was concentrated under vacuum and further purified by column chromatography (silica gel 100-200 mesh, hexane/ethyl acetate) to obtain corresponding products.

Catalyst recycle

Catalyst was recovered by filtering it from reaction mixture cooled to 30 °C. Filtered catalyst was washed with DI water until neutral pH was obtained. It was then washed with 2-

propanol. The residue was further dried at 30 °C for 12 h followed by 4 h drying at 50 °C and was then used for the oxidation of alcohol.

Results and Discussion

γ-MnO_2/GO nanocomposites were synthesized by wet impregnation by oxidation $MnSO_4$ precursor. The nanocomposites were characterized and evaluated for selectively catalyzing aerobic oxidation of benzyl alcohols to benzaldehyde. γ-phase of the MnO_2 was confirmed by X-ray diffraction and Raman analysis. MnO_2 loading was confirmed by inductive coupled plasma (ICP-AES) and thermal stability was studied using thermogravimetric analysis (TGA) analysis. High resolution transmission microscopy (HR-TEM) was used to determine the morphology of MnO_2 nanoparticles.

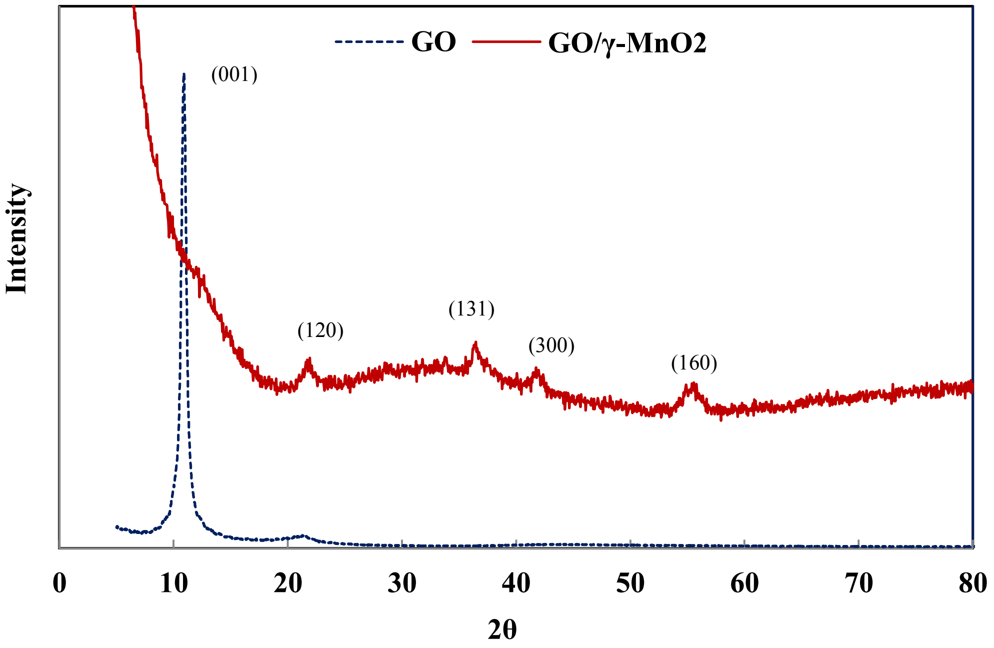


Figure 1. XRD pattern of GO and γ-MnO_2/GO nanocomposites.

Powder XRD pattern of GO shows an intense and sharp diffraction peak of GO at *2θ* = 10.34° corresponds to (001) reflection giving an interlayer d-spacing of 0.85 nm (Figure 1). This value of d-spacing is higher than in pristine graphite (0.34 nm) due to the localization of several oxygenated functional groups on the graphite sheet.[20] In γ-MnO_2/GO nanocomposites, (001) diffraction peak of GO disappeared. Diffraction peaks of γ-MnO_2/GO nanocomposites at *2θ* values of 22.11°, 37.76°, 43.07° and 55.84° correspond to (120), (131), (300) and (160) lattice planes respectively, indicating formation of closely packed hexagonal crystal structure of γ-

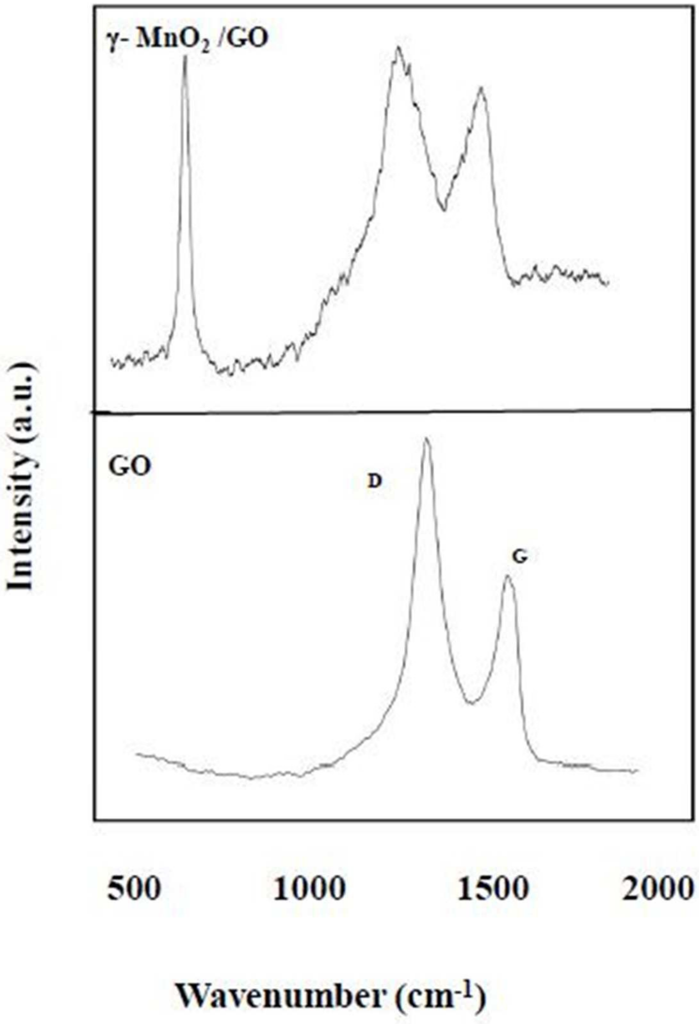


Figure 2. Raman spectra of GO and γ-MnO_2/GO nanocomposites

MnO_2 (ICDD-JCPDS No. 14-0644).[21] Average size of γ-MnO_2 nanocrystals estimated using Scherrer equation is 19.5 nm. On the other hand, the (001) diffraction peak of layered GO in the γ-MnO_2/GO nanocomposite disappeared (Figure 1). This is due to the incorporation of MnO_2 nanocrystals within the GO sheets, resulting in exfoliation and disturbance of regular stacking of GO sheets.

Structural and electronic changes due to the growth of MnO_2 crystals on GO sheets were studied by Raman spectroscopy. Figure 2. shows a sharp peak at 648 cm^{-1} in γ-MnO_2/GO nanocomposites spectrum, which can be attributed to γ-phase of MnO_2.[21] Raman spectra of γ-MnO_2/GO nanocomposites show red shift of characteristic G (1583 cm^{-1} to 1603 cm^{-1}) and D (1331 cm^{-1} to 1356 cm^{-1}) peaks as compared to GO which is an important evidence of the strong coupling and charge transfer between the γ-MnO_2 and GO sheet.[22] Interaction of γ-MnO_2 with GO was also investigated using FTIR spectroscopy (Figure 3). In GO, the stretching frequencies of carbonyl group ($\upsilon_{C=O}$) and alkoxy group ($\upsilon_{C\text{-}O}$) are observed at 1742 cm^{-1} and 1050 cm^{-1}

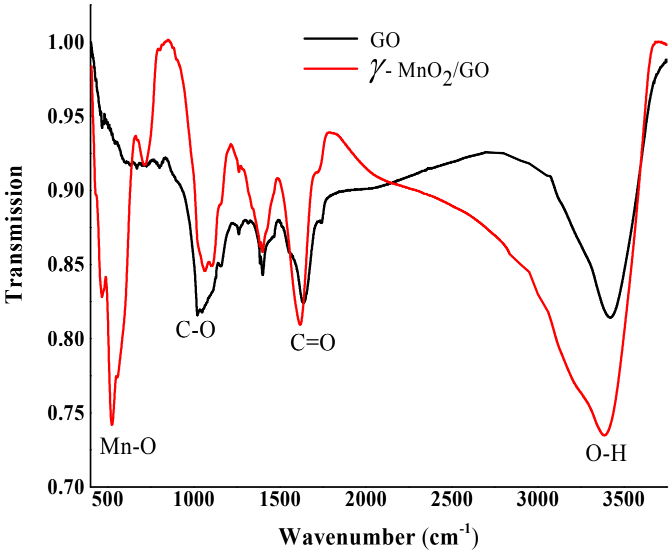


Figure 3. FTIR spectra of GO oxide and γ-MnO_2/GO

respectively. Broad peak at 3418 cm^{-1} is due to stretching of hydroxyl groups ($\upsilon_{O\text{-}H}$) present on surface of GO. Peak at 1638 cm^{-1} indicates skeletal vibrations from unoxidized graphitic carbon ($\upsilon_{C=C}$).[23,24] In γ-MnO_2/GO nanocomposites, bands located at 466 cm^{-1} and 524 cm^{-1} can be ascribed to Mn-O vibrations in MnO_2.[25,26] Frequencies of vibration of carbonyl ($\upsilon_{C=O}$) group significantly shift towards lower wavenumber viz. 1729 cm^{-1}, which indicate interaction of γ-MnO_2 with GO sheets.

Morphology of γ-MnO_2 and manganese loading was determined by HR-TEM and ICP-AES analyses, respectively. Figure. 4 (a) displays TEM image of pure GO which possesses a thin sheet like silky transparent morphology, whereas γ-MnO_2/GO nanocomposites (Figure. 4 (b) and 4 (c)) exhibit a dispersion of flower and needle shaped MnO_2 nanocrystals on the surface as well

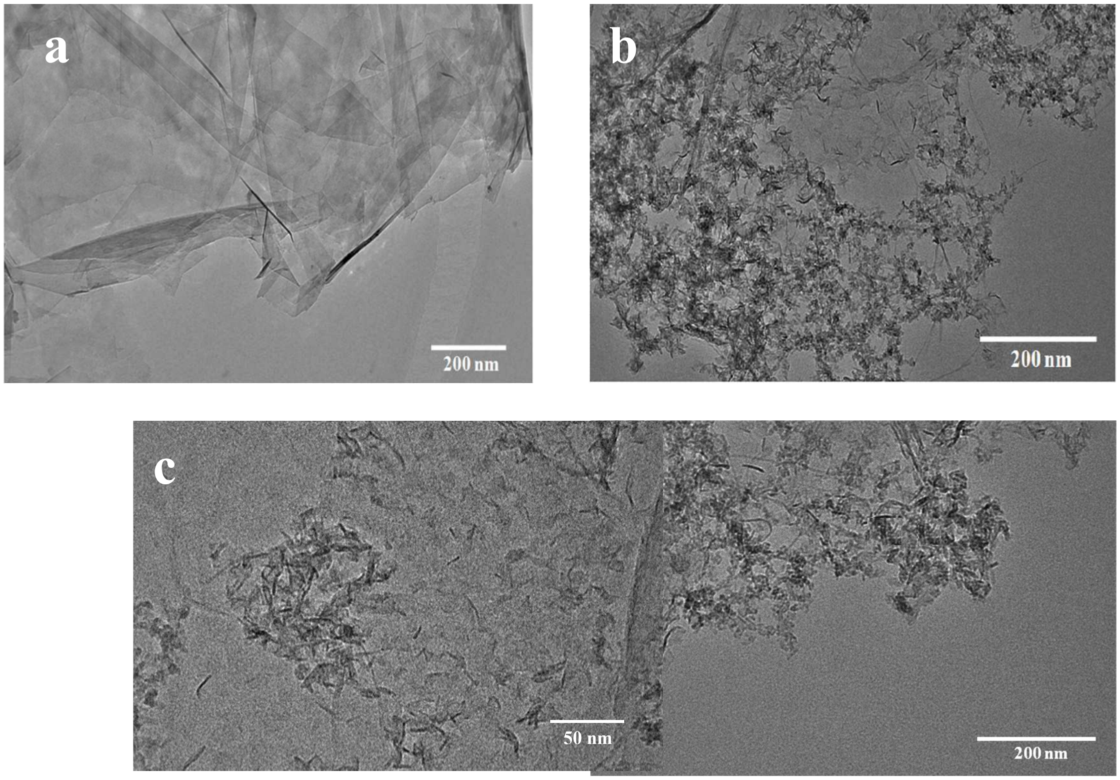


Figure 4. HR-TEM images of (a) GO, (b) γ-MnO_2/GO, (c) γ-MnO_2/GO at higher magnification and (d) γ-MnO_2/GO after 2 recycles

as on the edge of GO sheets. GO sheets in γ-MnO_2/GO appear slightly crumpled due to attachment of γ-MnO_2 with oxygenated functional groups on the GO surface, as compared to pure GO sheets. The few nanocrystals appears dark while others appear bright, which indicates that MnO_2 nanocrystals are attached to both sides of GO sheets. The size of the synthesized MnO_2 nanocrystals, were found to be range of 15-30 nm. TEM image of catalyst obtained after two recycles is shown in Figure 4 (d), shows slight aggregation of MnO_2 crystal. *In-situ* bonding of divalent Mn^{2+} (formed by the dissociation of $MnSO_4.2H_2O$ in aqueous 2-propanol) to the negatively charged oxygenated functional groups present on plane and on edges of GO sheets. On addition of $KMnO_4$ solution at 80 °C, several nuclei are generated in a short duration from the redox reaction occurring between Mn^{2+} and Mn^{7+}, which further leads to formation of MnO_2.[1] MnO_2 crystalline pattern and morphologies is related to arrangement of basic MnO_6 octahedron units.[27] Mn atoms of the MnO_6 octahedron may link with O atoms of GO functional groups *via* an intermolecular hydrogen bond or a covalent coordination bond. These O atoms on GO act as anchor sites for the growth of MnO_2 crystals and hence the regular layer stacking of GO sheets gets disturbed. The flower and needle shaped MnO_2 nanocrystals in the γ-MnO_2/GO nanocomposites were formed in H_2O/2-propanol mixture. Further, confinement for growth of crystals between GO sheets probably leads to formation of flower and needle shaped structures on the planes of GO sheets.

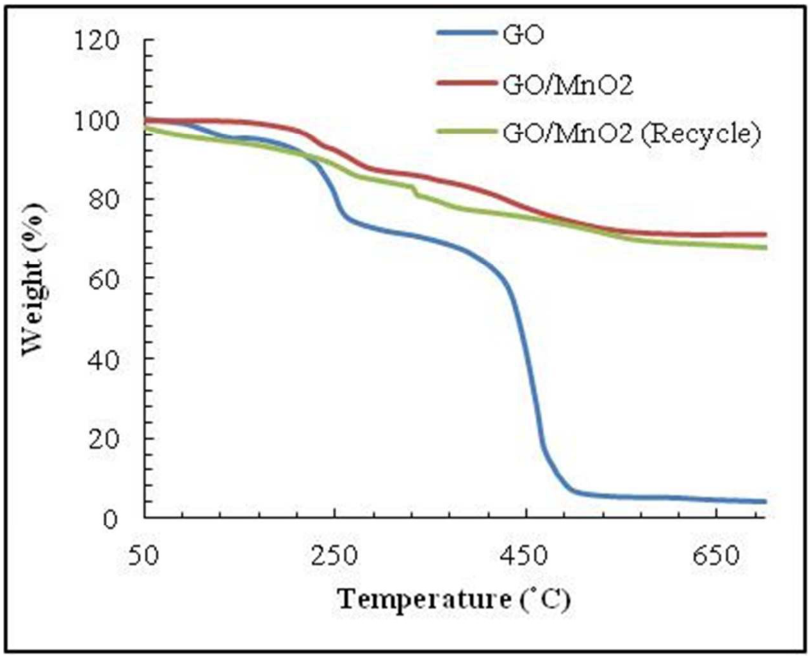
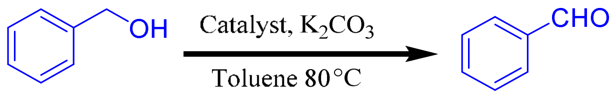


Figure 5. Thermogravimetric analysis of pure γ-MnO_2 and γ-MnO_2/GO after 2nd recycle.

ICP-AES analysis indicates 39.5% (w/w) of Mn present in the γ-MnO_2/GO nanocomposites, giving about 62.5 wt.% of MnO_2 in nanocomposites. Thermogravimetric analyses (TGA) was carried out to determine the stability of γ-MnO_2/GO (Figure 5). Due to heating in air, GO sheets get oxidized while MnO_2 gets converted into Mn_2O_3.[1,29,30] GO showed 22% weight loss between 100 to 200 °C, which is attributed to the loss of free and bound moisture. Further, significant weight loss, observed between 200-700 °C, can be attributed to the loss of chemical functionality and oxidation of GO sheets. Total weight loss of γ-MnO_2/GO nanocomposites was found to be 38.5%, this may be due to degradation of GO and loss of oxygen during conversion of MnO_2 to Mn_2O_3.

Catalytic activity of γ-MnO_2/GO nanocomposite was studied for selective oxidation of benzyl alcohol to benzaldehyde with air as the oxidant at different temperatures, 50 °C and 80 °C; catalyst loading, 5-20 % mol; and in presence and absence of base, K_2CO_3 (Table 1). The yield of benzaldehyde obtained after 5 h was found to be only 3 % and 6 % in the presence of

Table 1 Reaction for oxidation of benzyl alcohol to benzaldehyde[a]



Entry	Catalyst	Base (K_2CO_3) (mmol)	Catalyst (% mol)	Temp. (°C)	Yield (%)
1	GO	-	10	50	3
2	GO	-	10	80	6
3	γ-MnO_2/GO	-	10	80	35
4	GO	1.0	10	50	10
5	GO	1.0	10	80	15
6	γ-MnO_2/GO	1.0	10	50	**91**
7	γ-MnO_2/GO	1.0	5	50	42
8	γ-MnO_2/GO	1.0	15	50	75
9	γ-MnO_2/GO	1.0	20	50	72
10	γ-MnO_2/GO	0.5	10	80	**91**[b]

[a] Reaction conditions: Substrate: benzyl alcohol (1 mmol), catalyst (5, 10, 15 and 20% mmol), solvent (3 mL), base (1.0 mmol), time 5 h

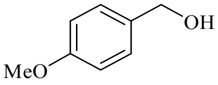
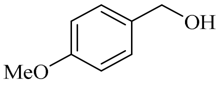
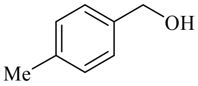
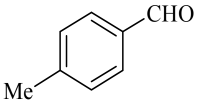
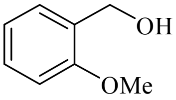
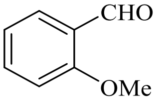
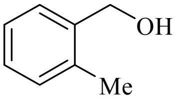
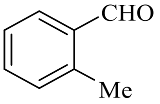
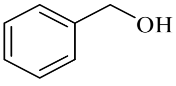
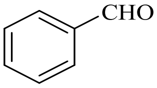
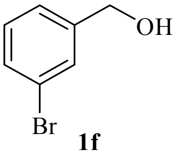
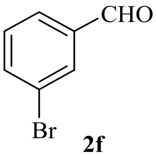
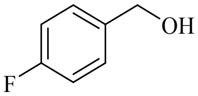
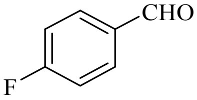
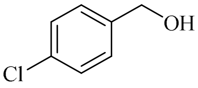
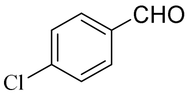
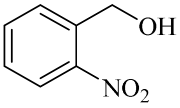
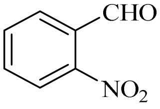
[b] time: 3 h

GO without K_2CO_3 at 50 °C and 80 °C respectively. Addition of 1 mmol of K_2CO_3 with GO showed an increase in the yield, however overall yield being only 10% and 15% at 50 °C and 80 °C respectively. Use of γ-MnO_2/GO nanocomposites led to almost 9 fold increment in reaction yield as compared to pure GO both in presence and in absence of base at 50 °C. As the catalyst loading decreased from 10 to 5 % mol, yield was found to be decrease from 91% to 42%, respectively. However, an increase in catalyst loading to 20 % mol also decreased the yield due to over-oxidation to benzoic acid and benzyl benzoate. Also, yield obtained in absence of base was low. Yield obtained for optimum reaction parameters at 50 °C was compared to that obtained at 80 °C. At higher temperature, the same yield was obtained in only 3h and in presence of lower amount of base.

The effect of electron withdrawing and electron donating functional groups of the reactant on the catalytic activity was studied and is discussed (Table 2). Aromatic alcohols bearing electron donating groups at *para*-position (1a, 1b) showed slightly better yield than those with the electron donating group (1c, 1d) at *ortho*-position possibly due presence of steric hindrance in the latter. Presence of halogen (F, Cl or Br) substituent results in lowered yield (79-84%). However, the yield of the aldehyde is not significantly affected by the position of the halogen substituent. The substitution of electron withdrawing –NO_2 group (1i) at *ortho* position retards the reaction, resulting in longer reaction time with only 62% aldehyde formation.

The recovery efficiency and reuse potential of γ-MnO_2/GO nanocomposites (catalyst) was studied for 4-methoxy benzyl alcohol as the model substrate (1a). The catalytic activity of the recycled catalyst resulted in slightly lower yield (91% after 1st recycle and 88% after 2nd recycle) with negligible loss after as compared to the freshly prepared catalyst (Table 3). Recycled γ-MnO_2/GO was further characterized by ICP-AES, TGA and TEM analysis. ICP-AES analysis of recycled catalyst confirmed presence of 59 wt. % of MnO_2. Further, Mn was not detected during ICP-AES analysis of the reaction mass and therefore, leaching of γ-MnO_2 was in reaction mass was negligible. TGA analysis of recycled catalyst showed weight-loss trends similar to the pristine catalyst. TEM images of γ-MnO_2/GO nanocomposites (catalyst) after second recycle showed slight aggregation and wrinkling of GO sheets (Figure 4d). This agglomeration may be the cause of marginal decrease in the catalytic activity of recycled catalyst.

Table 2. γ-MnO_2/GO catalyzed oxidation of alcohols to carbonyl compounds.[a]

Entry	Substrate	Product	Yield (%)
1	 **1a**	 **2a**	93
2	 **1b**	 **2b**	90
3	 **1c**	 **2c**	85
4	 **1d**	 **2d**	82
5	 **1e**	 **2e**	91[c]
6	 **1f**	 **2f**	84
7	 **1g**	 **2g**	79
8	 **1h**	 **2h**	81
9	 **1i**	 **2i**	62

[a] Reaction conditions: Substrate (1 mmol), solvent: toluene (3 mL), catalyst (10 % mol), K_2CO_3 (0.5 mmol), temperature: 80 ℃, time: 5 h

Table 3. Catalyst activity upon reuse of the catalyst

Catalyst	**Fresh**	**First**	**Second**
Yield (%)	93	91	88

[a] Reaction conditions: Substrate: 4-methoxy benzyl alcohol (1 mmol), solvent: toluene (3 mL), catalyst (10 % mol), K_2CO_3 (0.5 mmol), temperature: 80 ℃, time: 5 h

We propose that γ-MnO_2/GO catalyzes the oxidation synergistically (Figure 6). Oxygen atoms in benzyl alcohol initially adsorb on MnO_2. K_2CO_3 undergoes dissociation in presence of GO. K^+ ions formed are coordinated to GO leaving free CO_3^{2-} ions,[31] which increase the rate hydrogen elimination, the rate determining step, from the transition complex formed between MnO_2 and benzyl alcohol, producing carbanion. This carbanion undergoes charge transfer giving benzaldehyde. During the reaction, Mn (IV) undergoes reduction to Mn (II), which gets converted back to Mn (IV) by oxygen. Increased reactivity of the catalyst can be attributed to the complexation of potassium ions with functional groups in GO, which ultimately accelerates the rates of oxidation. In this reaction, GO acts both as a catalyst support and as a surface initiator for the base dissociation, while MnO_2 mediates the oxidation.

Conclusion

We have developed methodology for the synthesis of γ-MnO_2/GO nanocomposites by a simple non-hydrothermal, wet precipitation method without the use of any external stabilizer or surfactant. We used a mixture 2- propanol/water as solvent which restricts the structure and orientation of crystals during MnO_2 growth on GO sheets. This γ-MnO_2/GO nanocomposite acts as an efficient and easily recyclable heterogeneous catalyst for the selective aerobic oxidation of benzyl alcohols into corresponding aldehydes in presence of a mild base. The resulting process is

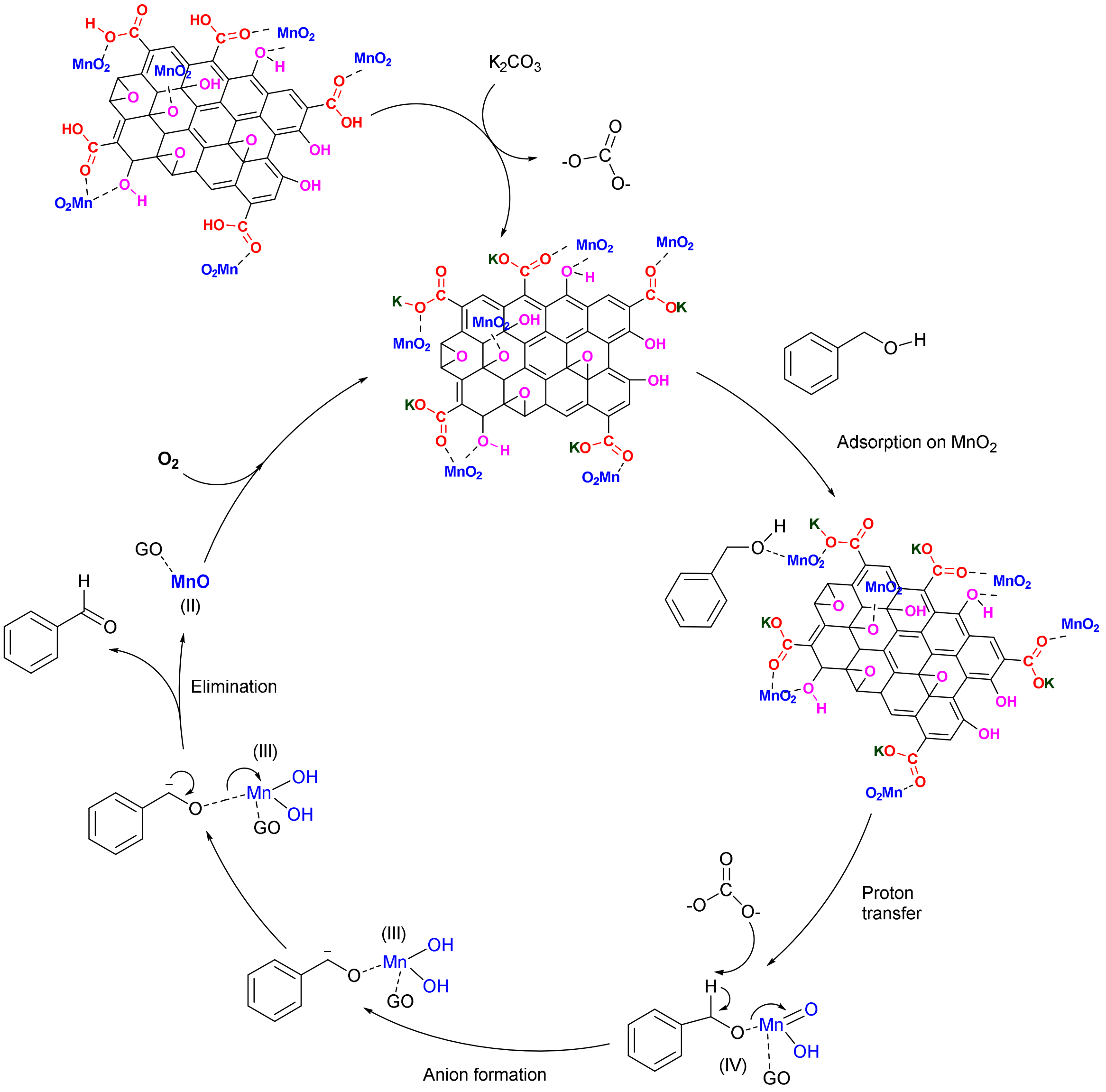


Figure 6. Proposed mechanism for oxidation of benzyl alcohol by using γ-MnO$_2$/GO as catalyst

very selective giving only benzaldehyde using lower amount of base and atmospheric oxygen as oxidant.

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Graphical Abstract

Synthesis, Characterization and Application of γ-MnO_2/Graphene Oxide for Selective Aerobic Oxidation of Benzyl Alcohols to Corresponding Carbonyl Compounds

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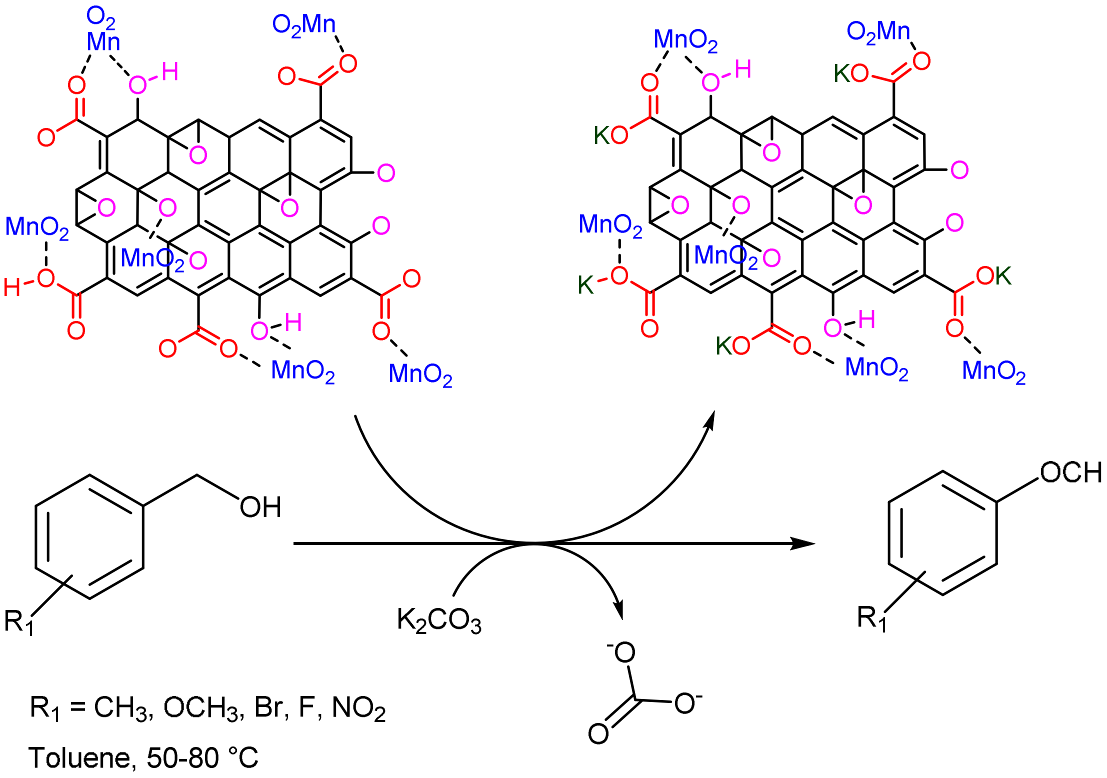
Graphic



R_1 = CH_3, OCH_3, Br, F, NO_2

Toluene, 50-80 °C

Text

Selective aerobic oxidation of benzyl alcohols to corresponding aldehydes catalyzed by sub-stoichiometric amount of novel γ-MnO_2/GO nanocomposites giving over 90 % yield.