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ORIGINAL PAPER

Graphene oxide nanosheets supported manganese(III) porphyrin: a highly efficient and reusable biomimetic catalyst for epoxidation of alkenes with sodium periodate

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Abstract Efficient epoxidation of alkenes catalyzed by *tetrakis*(*p*-aminophenyl)porphyrinatomanganese(III) chloride, [Mn(TNH_2PP)Cl], supported on graphene oxide nanosheets, is reported. The catalyst, [Mn(TNH_2PP)Cl]@GO, was prepared by covalent attachment of amino groups of porphyrin to carboxylic acid groups of GO. This new heterogenized catalyst was characterized by ICP, FT-IR and diffuse reflectance UV–vis spectroscopies, scanning electron microscopy and transmission electron microscopy. This catalyst was applied as an efficient and reusable catalyst in the epoxidation of alkenes with $NaIO_4$ at room temperature, in the presence of imidazole as axial ligand. The most noteworthy advantage of [Mn(TNH_2PP)Cl]@GO is its high reusability in the oxidation reactions, in which the catalyst was reused several times without significant loss of its catalytic activity.

Keywords Graphene oxide · Manganese porphyrin · Supported catalyst · Epoxidation · Sodium periodate

Introduction

Catalytic epoxidation of alkenes in the liquid phase is an important area in synthetic organic chemistry because epoxides are very useful and essential precursors in the synthesis of various important substances like plasticizers, perfumes and epoxy resins [1]. Transition metal complexes of porphyrin and Schiff base ligands have been extensively used as models for the heme-containing cytochrome P-450 [2]. Cytochorome P-450 catalyzes a wide variety of reactions including oxygen transfer to heteroatoms, epoxidation of olefins, hydroxylation of aromatic hydrocarbons and oxidative degradation of chemically inert xenobiotics such as drugs and environmental contaminants [3]. To mimic the action of cytochrome P-450 monooxygenation enzyme, simple oxygen atom donors such as PhIO, ClO^-, H_2O_2, ROOH and IO_4^- have been used in the oxidation reactions catalyzed by metalloporphyrins [4–9]. One of the most important disadvantageous of homogeneous metalloporphyrin and Schiff base complexes is the catalyst deactivation by formation of μ-oxo dimer complex. Therefore, heterogenization of these catalysts is of great importance from industrial point of view; this could combines the advantages of homogeneous catalysts (high activity, selectivity, etc.) with the benefits of heterogeneous catalysts (easy catalyst separation, long catalytic life, thermal stability and recyclability) [10]. Up to now, several homogeneous and heterogenized metalloporphyrin catalysts have been developed for the oxidation of organic compounds [11–45].

Graphene, a two-dimensional material composed of several planar sheets of sp^2-bonded carbon atoms, has attracted tremendous attention due to its unique thermal, chemical, physical, mechanical and electrical properties [46–50]. Since 2004, it has been as a promising candidate for generating novel hybrid materials with excellent properties for a wide variety of potential applications in catalyst support [51, 52], electronic components [53, 54], chemical sensors [55, 56], and Li ion batteries [57–59]. However, the graphene is chemically inert and has no surface functionalization and therefore, it is difficult to support the catalytic active species on its surface [60, 61]. The carbonyl, carboxyl and hydroxyl

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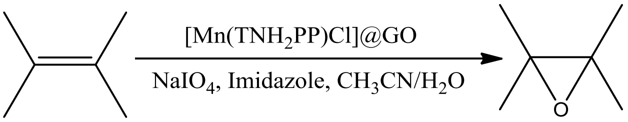


Scheme 1 Epoxidation of alkenes with NaIO$_4$ in the presence of [Mn(TNH$_2$PP)Cl]@GO]

functional groups can be introduced on the surface of graphene nanosheets by its oxidation with strong oxidants [62, 63]. The produced GO is insoluble in most solvents and can be used as catalyst support. In continuation of our interest on the oxidation of organic compounds catalyzed by supported manganese(III) porphyrins, and by combining the advantages of GO as catalyst support and high catalytic activity of Mn(III) porphyrins in the alkene epoxidation, here, we report highly efficient epoxidation of alkenes with sodium periodate catalyzed by *tetrakis*(*p*-aminophenyl) porphyrinatomanganese(III) chloride, Mn(TNH$_2$PP)Cl, supported on functionalized grapheme oxide, GO (Scheme 1).

Experimental

Materials and methods

The alkenes were obtained from Merck chemical company and passed through a column containing active alumina to remove peroxide impurities. *Tetra*(*p*-aminophenyl)porphyrin was prepared and metallated according to the literature [64, 65]. FT-IR spectra were obtained with potassium bromide pellets in the range 400–4000 cm^{-1} on a JASCO 6300 spectrophotometer. The diffuse reflectance UV–vis spectra, (DR UV–vis), were recorded by a JASCO V-670 UV–vis spectrophotometer. A field emission scanning electron micrograph of [Mn(TNH$_2$PP)Cl]@GO was taken on a Philips Sigma FE-SEM instrument. Transmission electron micrograph of the catalyst was recorded by a EM10C-100 kV instrument. The ICP analyses were carried out by a Perkin-Elmer Optima 7300 DV spectrometer. Gas chromatography experiments (GC) were performed by a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 M. In the GC experiments, *n*-decane was used as an internal standard.

Preparation of graphene oxide nanosheets supported manganese porphyrin, [Mn(TNH$_2$PP)Cl]@GO

Preparation of graphene oxide nanosheets

GO was prepared via a modified Hummer's method where graphite powder was vigorously stirred with H$_2$SO$_4$ and KMnO$_4$ at 35 °C for 4 h to yield GO [66, 67]. The oxidized product was treated with H$_2$O$_2$ to remove residual permanganate ions before copious washing with a dilute acid solution (1 M HCl). After filtration, the GO product was dried under air before further use.

Chlorination of GO-COOH

In a 100-ml round-bottomed flask equipped with a condenser and a magnetic stirrer bar, GO-COOH (1 g), and SOCl$_2$ (50 ml) were mixed and refluxed for 12 h. After this, the reaction mixture was cooled and the SOCl$_2$ was evaporated. The resulting precipitate was chlorinated graphene oxide, GO-COCl.

Supporting of [Mn(TNH$_2$PP)Cl] on GO-COCl

To a solution of Mn(TNH$_2$PP)Cl (0.1 g) in DMF (100 ml), GO-COCl (1 g) and triethylamine (5 ml) were added and the reaction mixture was vigorously stirred at 100 °C for 72 h. After cooling the mixture, the black solids were collected by filtration, washed thoroughly with dichloromethane, methanol and diethyl ether, successively, and dried in vacuum for several hours.

General procedure for alkene epoxidation with NaIO$_4$ catalyzed by [Mn(TNH$_2$PP)Cl]@GO

To a mixture of alkene (1 mmol), [Mn(TNH$_2$PP)Cl]@GO (0.032 mmol) and imidazole (0.2 mmol) in CH$_3$CN (10 ml), a solution of NaIO$_4$ (2 mmol) in H$_2$O (10 ml) was added and the reaction mixture was stirred magnetically at room temperature. The progress of the reaction was monitored by GC. At the end of the reaction, the reaction mixture was diluted with Et$_2$O (20 ml) and filtered. The catalyst was thoroughly washed with Et$_2$O and combined washings and filtrates were purified on a silica gel plate or a silica gel column to obtain the pure products.

Catalyst reuse and stability

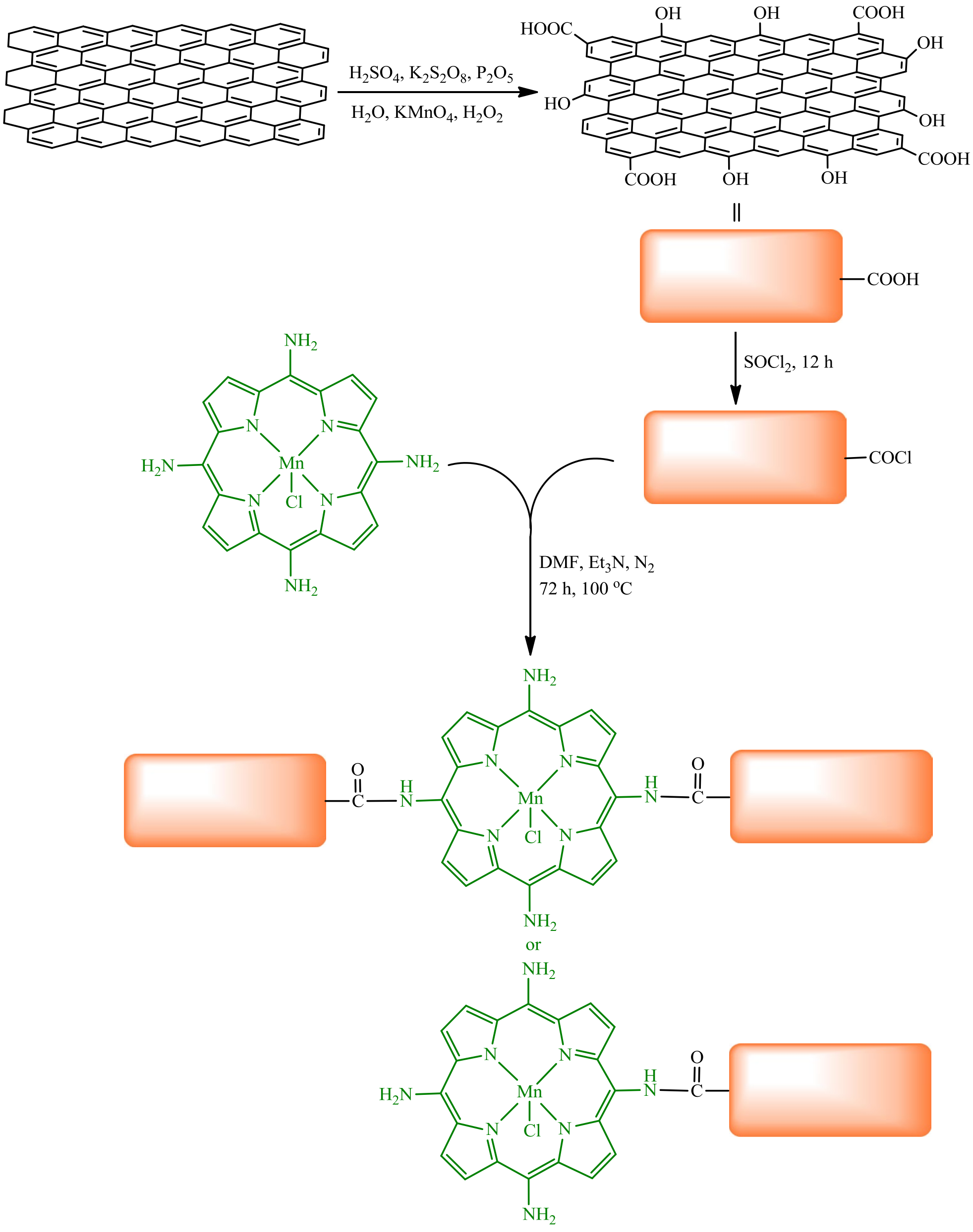
The reusability of [Mn(TNH$_2$PP)Cl]@GO was investigated in the repeated epoxidation of cyclooctene, as described above. At the end of each reaction, the catalyst was separated from the reaction mixture by simple filtration, washed with Et$_2$O and dried carefully before using it in the next run.

Results and discussion

Preparation and characterization of the catalyst, [Mn(TNH$_2$PP)Cl]@GO

Scheme 2 shows the preparation route for [Mn(TNH$_2$PP)Cl]@GO. First, the carboxylic acid groups were converted

Scheme 2 Preparation of [Mn(TNH$_2$PP)Cl]@GO



to acyl chloride to increase the reactivity of GO-COOH. In the next step, the Mn(TNH$_2$PP)Cl was reacted with GO-COCl to obtain the catalyst. The prepared catalyst was characterized by ICP, FT-IR spectroscopy, DR UV–vis spectrophotometry, FE-SEM and TEM analyses. The loading of manganese porphyrin on the catalyst, determined by measuring the Mn content by ICP, was obtained about 160 μmol per gram of the catalyst.

The most informative spectroscopic data, which confirmed the covalent anchoring of [Mn(TNH$_2$PP)Cl] on the functionalized GO, were obtained by comparison of the FT-IR spectra of GO-COOH, GO-COCl and [Mn(TNH$_2$PP)Cl]@GO (Fig. 1). The C=O stretching band of the acidic groups was appeared at 1729 cm^{-1}. This vibration shifted to 1711 cm^{-1} upon conversion to acid chloride. When the porphyrin was attached to GO-COCl, an amide vibration was observed at 1657 cm^{-1}. These observations clearly confirmed the attachment of the manganese porphyrin to the GO.

The DR UV–vis of the [Mn(TNH$_2$PP)Cl]@GO resembles the homogeneous counterpart spectrum (Fig. 2) and shows the Soret band at 466 nm which is a good indication for attachment of metalloporphyrin on the surface of GO. Since the GO shows no absorption peak in its diffuse reflectance spectrum, therefore, it is confirmed that [Mn(TNH$_2$PP)Cl] has been supported on GO.

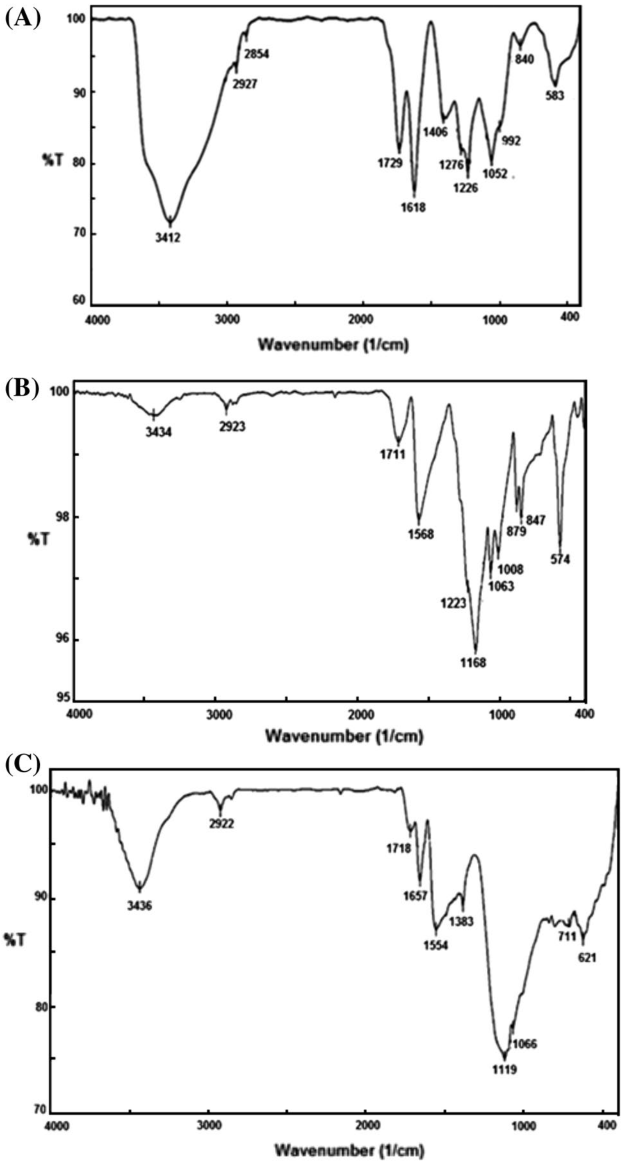


Fig. 1 The FT-IR spectrum of: **a** GO-COOH; **b** GO-COCl and **c** [Mn(TNH$_2$PP)Cl]@GO

The scanning electron micrograph of catalyst (Fig. 3a) shows the morphology of the GO used in this study. As can be seen, the catalyst has a wrinkled layered structure with thin thickness and smooth surface. Also, the EDX spectrum clearly shows the presence of Mn in the catalyst texture (Fig. 3b). The TEM image of [Mn(TNH$_2$PP)Cl]@GO (Fig. 4), clearly indicates that manganese porphyrin has been supported on the GO. The light regions belong to GO and the dark parts are the Mn porphyrins.

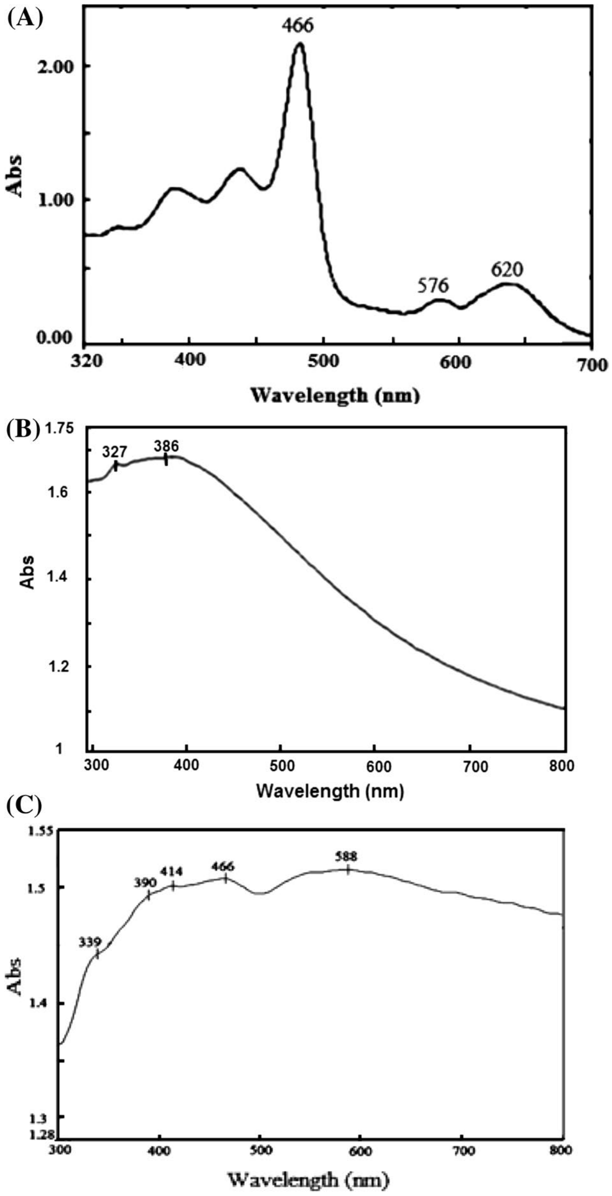


Fig. 2 **a** UV–vis spectrum of homogeneous [Mn(TNH$_2$PP)Cl], **b** diffuse reflectance UV–vis spectrum of GO and **c** [Mn(TNH$_2$PP)Cl]@GO

Catalytic experiments

After preparation and characterization of the catalyst, its catalytic activity was investigated in the epoxidation of olefins with sodium periodate at room temperature. In this manner, epoxidation of cyclooctene was chosen as model reaction, and the catalyst amount, kind of solvent and oxidant were

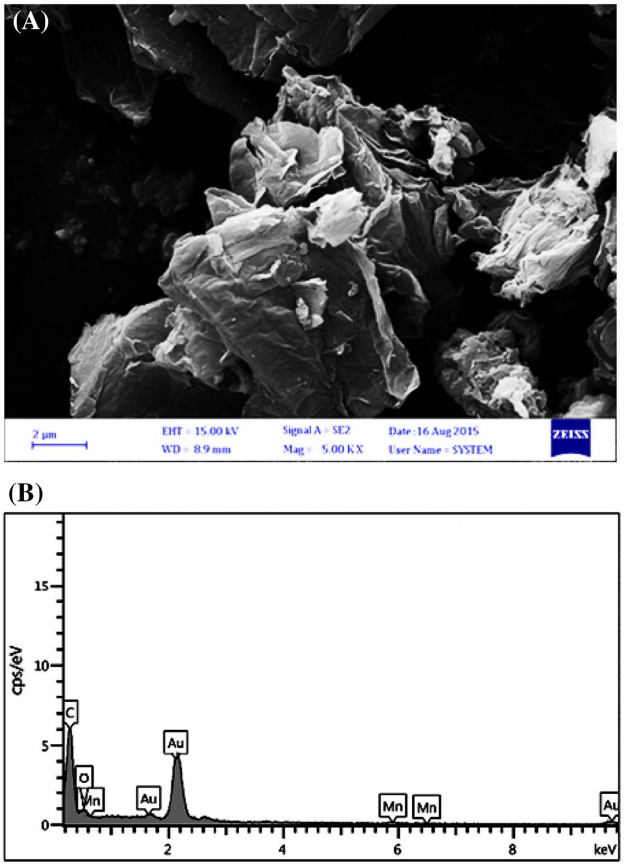


Fig. 3 **a** SEM images of [Mn(TNH$_2$PP)Cl]@GO and **b** EDX spectrum of [Mn(TNH$_2$PP)Cl]@GO

optimized in this reaction. To optimize the catalyst amount, different amounts of catalyst were used in the epoxidation of cyclooctene with NaIO$_4$. The best results were obtained with 200 mg (0.032 mmol) of the catalyst (Table 1). The ability of different single oxygen donors such as NaIO$_4$, KHSO$_5$ (Oxone) and H$_2$O$_2$ was investigated in the model reaction. In the investigation of the effect of different oxidants on the epoxidation of cyclooctene, we added the suitable co-catalyst to the reaction mixture. The results, which are summarized in Table 2, showed that NaIO$_4$ is the best oxygen source because this oxidant, which is inert in the absence of catalyst, can give good oxidation conversion in CH$_3$CN/H$_2$O. For choosing the reaction media, different solvents were checked in the model reaction. Among the different mixtures of acetonitrile, acetone, ethanol, dichloromethane with water, the 1:1 mixture of acetonitrile: water was chosen as the reaction medium (Table 3). The high catalytic activity of the catalyst in this in the acetonitrile/water mixture is attributed to the polarity of the solvent and the high solubility of NaIO$_4$ in it. Natural metalloenzymes such as peroxidase and cytochrome P-450 enzymes have axially coordinating histidine and thiolate residue, respectively. To completely mimic the action of these enzymes and also to improve the catalytic activity of these metalloporphyrin catalysts, addition of a donor ligand is necessary. In this manner, in the [Mn(TNH$_2$PP)Cl]@GO/NaIO$_4$ catalytic system, the effect of different axial ligands was investigated in the epoxidation of cyclooctene (Table 4). Pyridine and 4-methylpyridines, with weak π donating ability and pK_b values, generally show low co-catalytic activity. Among the nitrogen bases which are used as axial ligands, imidazole exhibited the highest activity in the model reaction. Strong π-donors such as imidazole and its derivatives are the best co-catalysts among the nitrogen donors listed in Table 4. The lower co-catalytic activity of 2-MeImH and 2-PhImH are due to the steric effects of the 2-substituent. Bulky and flat BzImH displays a higher co-catalytic activity in comparison with substituted imidazoles. Strong coordination of imidazole increases the electron density on the metal and promotes facile cleavage of the O–IO$_3$ bond in NaIO$_4$. In the absence of any axial ligand, only 17 % of cyclooctene oxide was observed.

Epoxidation of alkenes with NaIO$_4$ catalyzed by [Mn(TNH$_2$PP)Cl]@GO

After optimization of the reaction conditions, the [Mn(TNH$_2$PP)Cl]@GO catalyst was used for epoxidation of olefins with NaIO$_4$. The optimum conditions, which obtained in the epoxidation of cyclooctene, were catalyst, oxidant, imidazole and substrate in a molar

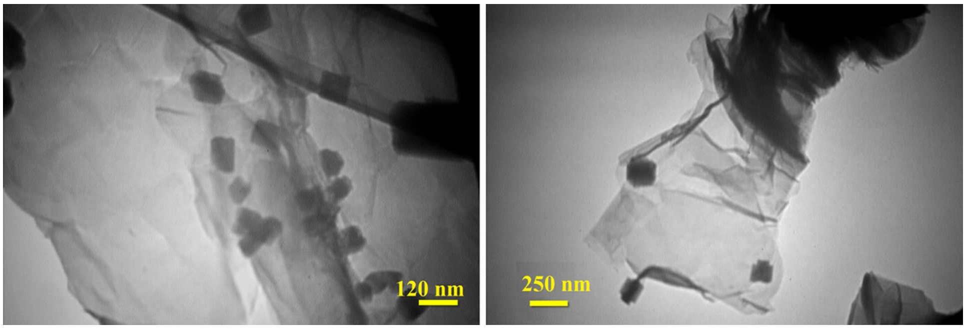


Fig. 4 TEM image of [Mn(TNH$_2$PP)Cl]@GO

Table 1 Optimization of the catalyst amounts in the epoxidation of cyclooctene

Entry	Catalyst amount (mmol)	Epoxide yield (%)[a]
1	0	6
2	100 (0.016)	43
3	150 (0.024)	70
4	200 (0.032)	95
5	300 (0.048)	95

Reaction conditions: cyclooctene (1 mmol), catalyst, oxidant (2 mmol), imidazole (0.2 mmol) and CH_3CN/H_2O (10 ml /10 ml) after 3 h

[a] GC yield

Table 2 The effect of oxidant on the epoxidation of cyclooctene catalyzed by [Mn(TNH$_2$PP)Cl]@GO at room temperature

Solvent	Oxidant	Epoxide yield (%)[a]
Acetonitrile:H_2O	No oxidant	5
Acetonitrile:H_2O	$NaIO_4$ (1 mmol)/imidazole	56
Acetonitrile:H_2O	$NaIO_4$ (2 mmol)/imidazole	95
Acetonitrile:H_2O	$KHSO_5$ (2 mmol)/pyridine	82
Acetonitrile	H_2O_2 (2 mmol)/imidazole	21
Acetonitrile	H_2O_2 (2 mmol)/NH_4Ac	17

Reaction conditions: cyclooctene (1 mmol), oxidant, catalyst (0.032 mmol), imidazole (0.2 mmol) and CH_3CN/H_2O (10 ml/10 ml) after 3 h

[a] GC yield based on starting alkene

Table 3 The effect of solvent on the epoxidation of cyclooctene with $NaIO_4$ catalyzed by [Mn(TNH$_2$PP)Cl]@GO at room temperature

Entry	Solvent	Time (h)	Yield (%)[a]
1	Acetonitrile:H_2O (1:2)	3	39
2	Acetonitrile:H_2O (1:1)	3	95
3	Acetonitrile:H_2O (2:1)	3	61
4	Acetone: H_2O	3	27
5	Ethanol:H_2O	3	43
6	Dichloromethane:H_2O	3	20

Reaction conditions: cyclooctene (1 mmol), $NaIO_4$ (2 mmol), catalyst (0.032 mmol), imidazole (0.2 mmol)

[a] GC yield based on starting alkene

Table 4 The effect of different axial ligands on the epoxidation of cyclooctene with sodium periodate catalyzed by [Mn(TNH$_2$PP)Cl]@GO

Entry	Axial ligand	Time (min)	Yield (%)[a]
1	None	3	17
2	Pyridine	3	45
3	4-Methylpyridine	3	39
4	Imidazole	3	95
5	Benzimidazole	3	72
6	2-Methylimidazole	3	57
7	2-Phenylimidazole	3	61

Cyclooctene (1 mmol), $NaIO_4$ (2 mmol), axial ligand (0.2 mmol) and catalyst (0.032 mmol), imidazole (0.2 mmol) in CH_3CN (10 ml)/H_2O (10 ml)

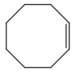
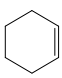
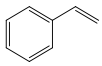
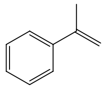
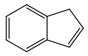
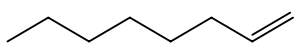
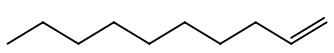
[a] GC yield based on the starting cyclooctene

ratio of 1:60:6:30. Under the optimized reaction conditions, different cyclic, linear and phenyl substituted olefins were subjected to epoxidation with $NaIO_4$. As can be seen in Table 5, the [Mn(TNH$_2$PP)Cl]@GO/$NaIO_4$ catalytic system showed a high catalytic activity in the alkene epoxidation in the presence of imidazole as the axial base. Cyclohexene was oxidized in 91 % yield, in which 83 % cyclohexene oxide was produced as the major product and 2-cyclohexen-1-one was obtained in 8 % yield. In the epoxidation of styrene, 79 % styrene oxide and 9 % benzaldehyde were produced. Oxidation of α-methylstyrene produced 80 % α-methylstyrene oxide and 11 % acetophenone. In the case of linear alkenes such as 1-octene and 1-decene, the corresponding epoxides were obtained in 68 and 52 % yields with 100 % selectivity, respectively.

Catalyst reuse and stability

The reusability of a heterogeneous catalyst is an important issue for industrial applications. While, homogeneous [Mn(TNH$_2$PP)Cl] cannot be recovered even once, the GO supported catalyst can be filtered and reused several times without significant loss of its activity. The reusability of [Mn(TNH$_2$PP)Cl]@GO was investigated in the multiple sequential epoxidation of cyclooctene with $NaIO_4$. The catalyst was separated from the reaction mixture after each experiment by simple filtration, washed with methanol and dried carefully before using it in the subsequent run. After using the catalyst five consecutive times, the epoxide yield was 86 % (Table 6). The filtrates were collected for determination of Mn leaching. The results showed that after the five runs, no manganese was detected in the filtrates by atomic absorption spectrometry. The nature of the recovered catalyst has been followed by IR. The results indicated that the catalyst, after reusing it several times, showed no change in its IR spectrum. These observations

Table 5 Epoxidation of alkenes with $NaIO_4$ catalyzed by [Mn(TNH_2PP)Cl]@GO

Entry	Olefin	Conversion (%)[a]	Epoxide yield (%)[a]	Time (h)	TOF (h^{-1})
1		95	95	3	9.89
2		91	83[b]	2.5	11.37
3		88	79[c]	3	9.16
4		91	80[d]	3	9.47
5		75	75	3	7.81
6		68	68	3.5	6.07
7		52	52	3.5	4.64

Reaction conditions: Alkene (1 mmol), $NaIO_4$ (2 mmol), catalyst (0.032 mmol), CH_3CN/H_2O (10 ml/10 ml)

[a] GC yield based on the starting alkene

[b] The by-product is allylic ketone

[c] The by-product is benzaldehyde

[d] The by-product is acetophenone

Table 6 The results of [Mn(TNH_2PP)Cl]@GO catalyst recovery and the amounts of manganese leached in the epoxidation of cyclooctene with sodium periodate

Entry	Time (h)	Epoxide yield (%)[a]	Mn leached (%)[b]
1	3	92	0
2	3	90	0
3	3	88	0
4	3	88	0
5	3	86	0

Reaction conditions: alkene (1 mmol), $NaIO_4$ (2 mmol), catalyst (0.032 mmol), CH_3CN/H_2O (10 ml/10 ml)

[a] GC yield

[b] Determined by atomic absorption spectroscopy

show that [Mn(TNH_2PP)Cl]@GO is a robust catalyst during the catalytic cycles.

Conclusion

In conclusion, [Mn(TNH_2PP)Cl]@GO/$NaIO_4$ catalytic system was used as a highly efficient system for biomimetic epoxidation of alkenes with sodium periodate under agitation with magnetic stirring. The corresponding epoxides were obtained in good to excellent yield (52–95 %) and high selectivity was highly reusable and recycled five times without appreciable decrease in its initial activity.

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