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Graphical abstract:

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Graphene based magnetic nanohybrids as promising catalysts for the green synthesis of

β-amino alcohol derivatives.

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Abstract

The principle of green chemistry evolves around designing products and processes with catalyst retrieval as its foremost aim. In this regard, the present report encompasses the synthesis of graphene based magnetic nanohybrids (CoFe@rGO) and their catalytic evaluation for epoxide ring opening reactions. Numerous techniques were employed for sample characterization. Powder X- Ray diffraction patterns confirm the single phase cubic structure corresponding to $CoFe_2O_4$ with Fd-3m space group. The average crystallite size was observed to be in the range of 8-12 nm for all the samples which was calculated in accordance with Debye-Scherrer equation. The FE-SEM and HR-TEM techniques were utilized to obtain detailed structural analysis of the nanohybrids displaying layered structure of GO decorated with CoFe₂O₄ nanoparticles. The EDX spectra confirm the elemental purity of the synthesized materials. Magnetic measurements were investigated by vibrating sample magnetometer, displaying the increase in saturation magnetization values with increase in CoFe₂O₄ concentration from 32.7 emu/g for CoFe@rGO (5%) to 38.6 emu/g for CoFe@rGO (20%). The catalytic presentation of the synthesized nanohybrids was evaluated for epoxide ring opening reactions under solvent free conditions displaying 100% conversion rates within 6 minutes of reaction time.

Keywords: Graphene based nanohybrids; magnetic nanocatalyst; heterogeneous catalyst; epoxide ring opening; alcohol based products.

Highlights:

- Synthesis of Graphene based magnetic nanohybrids (CoFe@rGO) using hydrothermal technique.
- Enhanced catalytic performance owing to large surface areas and active catalytic sites.
- Magnetically retrievable catalyst displaying great recyclability.
- Epoxide ring opening reactions with amines under solvent free conditions.

1. Introduction

Heterogeneous catalysis has procured gigantic appreciation in the contemporary span, owing to ease of separation, regeneration and reusability of the catalyst. Payable to their prodigious returns heterogeneous catalysts have been extensively used for numerous applications such as organic transformations, environmental remediation etc. [1]. Diversity of materials like semiconductors, metal oxides, iron based materials and inorganic matrices can be utilized as heterogeneous catalyst [2- 4]. Recently, carbon based inorganic matrices like graphene oxide (GO), carbon nanotubes (CNTs) have drawn immense attention of the scientific community owing to their large surface areas, surface defects, admirable electrical conductivity and high mechanical strength. The chemically active sites of these materials are predominantly answerable for their catalytic performance; moreover these sites allow easy functionalization and immobilization with various materials [5-7].

Amongst various inorganic moieties, implementation of graphene oxide (GO) as heterogeneous catalyst is worthwhile owing to its large specific surface area, high thermal stability, flexible structure, exceptional mechanical and electronic properties [8]. GO consists of various functional groups like hydroxyl, carboxylic and epoxide which facilitates the interactions with reactants and participates as heterogeneous catalyst in various reactions [9, 10]. Bhattacharya *et al.* [11] reported metal-free transamidation of aliphatic amide with aromatic amine catalysed by graphene oxide (GO) providing a clean and practical method for the formation of amines in good yields and with high selectivity. Shaikh *et al.* [12] demonstrated metal-free GO as a proficient catalyst for the oxidative polymerization of 2-naphthols in aqueous basic media and the homocoupling of 2-naphthols in organic media in high yields. Selective oxidation of 5-hydroxymethylfurfural (HMF) to 2,5- diformylfuran (DFF) using GO as carbocatalyst was reported by Lv. *et al.* [13].

Besides, the impending use of GO as a catalyst for innumerable reactions, it dwells certain drawbacks such as challenging separation from reaction mixture, poor dispersion, inconstant multilayer thickness which restricts its practical use. Moreover, it is challenging to recycle GO, which causes cost escalation and fetch secondary pollution [14, 15]. Fabricating hybrids of GO with magnetic nanocatalyst can curb these downsides as well as shadow the central aim of green chemistry, offering high catalytic performance, simplified seclusion of products, easy recovery and recyclability of the catalyst [16]. But agglomeration of magnetic nanocatalyst seems inescapable which declines their dispersal in solution phase thus limiting their catalytic performance. Thus, functionalization of magnetic nanocatalyst with GO can unravel the motive by reducing the agglomeration of magnetic particles providing large

surface areas [17, 18]. Numerous research associates have explored the catalytic exhibition of composites of graphene oxide and magnetic nanomaterials. Maleki and Rahimi [19] developed Fe₃O₄@GO as a capable heterogeneous nanocomposite for the synthesis of various derivatives of quinazoline and quinazolinone fused heterocyclic compounds via modest multicomponent reactions. Bahadorikhalili et al. [20] synthesized β-Cyclodextrin functionalized PEGylated mesoporous silica nanoparticles-graphene oxide hybrid and explored its catalytic performance for the synthesis of benzimidazoles and 1,2,3-triazoles. Tanhei et al. [21] designed a novel 3-D graphene- magnetic palladium nanohybrid for Suzuki and Heck cross-coupling reactions to produce 86% yield over 10 cycling tests. Lee *et al.* [22] employed nanocomposites of ZnFe₂O₄ with GO and rGO (reduced graphene oxide) for the synthesis of propene through oxidative dehydrogenation of propane. Eris et al. [23] fabricated polyaniline – rGO decorated platinum catalyst and utilised for methanol oxidation reactions displaying good catalytic activity and durability of the catalyst. Numerous organic conversions have been reported in literature, out of which epoxide ring opening reactions are highly beneficial as epoxides are versatile chemical intermediates which can be commonly transformed via ring opening reactions with different nucleophiles such as water, alcohols, amines and other substrates to produce a comprehensive range of bifunctional products. Specifically, alcohol based products find great applications in pharmaceutical and solvent industry [24-28].

In present study, nanohybrids of cobalt ferrite and reduced graphene oxide (CoFe@rGO) were utilized as heterogeneous catalyst for epoxide ring opening reactions, due to the availability of large number of catalytic sites and magnetically separable nature. The catalytic performance was evaluated by varying the concentration of cobalt ferrite in the synthesized materials keeping the amount of GO constant. Although graphene based nanocomposites have been utilized for numerous applications, but to the best of our knowledge, such nanohybrids have been seldom used for ring opening reactions under solvent free conditions following the principles of green chemistry. Comparison has been made from literature, for epoxide ring opening reactions using different catalysts on the basis of reaction completion time, % yield and recyclability of the catalyst.

2. Experimental section

2.1 Materials used

Cobalt nitrate hexahydrate ($Co(NO_3)_3.6H_2O$, 98%), Ferric nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, 98%) and Potassium permanganate ($KMnO_4$) were obtained from Central

Drug House (CDH). Graphite flakes were purchased from Otto chemicals. Sodium nitrate (NaNO₃) and Hydrogen peroxide (H₂O₂, 30% w/v) were provided by Fisher scientific. Sulphuric acid (H₂SO₄) and liquor ammonia (Liq. NH₃) were purchased from Merck. All the mentioned chemicals were of analytical grade and were used as bought without any further refining. All the solutions were prepared in ultrapure water obtained from an ultrafiltration system (Milli-Q, Millipore).

2.2 Synthesis of nanocatalyst

2.2.1 Synthesis of Graphene Oxide (GO)

GO was synthesized using graphite flakes via modified Hummer's method [10]. In this method, 3g of natural graphite flakes were added to 70 ml conc. H_2SO_4 , followed by addition of fixed amount of NaNO₃ (1.5g) and KMnO₄ (9g) for about half an hour along with continuous stirring, maintaining the temperature of the reaction mixture using ice bath at - 4°C. Further, the reaction mixture was magnetically stirred for 24 h at room temperature. Subsequently, the mixture was diluted by addition of distilled water and finally, 18 ml H_2O_2 was added slowly until the colour of the solution changes from brown to yellow which indicates complete oxidation of graphite to graphene oxide. The resulting mixture was repeatedly washed with distilled water until the pH of the solution became neutral; the obtained product was then filtered and dried at 80 °C for 10 h.

2.2.2 Synthesis of CoFe@rGO nanohybrids

A facile hydrothermal method was employed for the synthesis of CoFe@rGO nanohybrids [29], as depicted in Scheme 1. Primarily, GO was dispersed in distilled water using ultrasonic technique. The stoichiometric amounts of metal nitrates (Co(NO₃)₃ and Fe(NO₃)₃; 0.02M) were dissolved in minimum amount of water and pH of the solution was adjusted to 7.5 using liquid ammonia. Subsequently, aqueous GO suspension was added to metal nitrate solution followed by continuous stirring for 2 h. The solution was then transferred to a Teflon autoclave maintained at 160 °C for 15 h. The obtained precipitates were thoroughly washed with distilled water and acetone; followed by drying at 60 °C overnight. The concentration of CoFe was varied as 5, 10, 15 and 20% and keeping the amount of GO constant. The obtained nanohybrids were labelled as CoFe@rGO (5%). CoFe@rGO (10%), CoFe@rGO (15%) and CoFe@rGO (20%).

2.3 Physical techniques

Various techniques were employed for the characterization of the synthesized nanohybrids. For crystalline phase identification, Powder X-ray diffraction (XRD) analysis was performed using Panalytical's X'pert Pro diffractometer equipped with CuKα radiation

 $(\lambda=1.54\text{ Å})$ with scanning angle (20) range varying from 10° - 80°. The Fourier Transform Infra-red (Perkin Elmer Spectrum 400, FT-IR/FT-FIR spectrometer) spectroscopy was employed for all the samples in the range of 4000-400 cm⁻¹; the samples were prepared using KBr pellets, in order to confirm the functional groups present in the synthesized materials. The surface morphology of the synthesized nanohybrids was perceived using Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi-SU8010) and High Resolution-Transmission Electron Microscope (HR-TEM, FEI Tecnai (G2 F20) operating at 200 keV). Vibrating sample magnetometer (VSM, Microsense EZ7) was used for magnetic measurements. Thin layer chromatography (TLC) was performed using pre-coated silica 60 F254, 0.25 mm aluminium plates (Merck) and the progress of the reactions was visualized and studied under UV chamber. Confirmation of the desired product formation was scrutinized by Nuclear Magnetic Resonance (NMR) spectrometer (BRUKER AVANCE II 400 MHz) using CDCl₃ as solvent and TMS as an internal standard.

2.4. Catalytic assessment

The catalytic study for the aminolysis of the epoxides was investigated using GO and CoFe@rGO nanohybrid. The reactions were performed under solvent free conditions amongst equimolar amounts of epoxide (1 mmol) and amine (1 mmol) using GO and CoFe@rGO nanohybrid as catalyst (10 mg) at 80 °C. The progress of the reaction was monitored using thin layer chromatography (TLC). After the completion of the reaction, the catalysts were magnetically separated from the reaction mixture and thoroughly washed with distilled water and acetone in order to remove the organic or inorganic part. The recovered catalysts were then dried and recycled for further use. The final isolated products were analysed using ¹H NMR and the obtained records were matched with those reported in literature [30].

3. Results and Discussion

3.1. Characterization of the nanohybrids

3.1.1 FT-IR Spectroscopy

The FT-IR spectra depict the presence functional groups present in the crystal lattice through their vibrational modes. Here, FT-IR spectroscopy was used to investigate the existence of oxygen containing functionalities and their variations after the formation of nanohybrids. The FT-IR spectra of pure GO and CoFe@rGO nanohybrids are depicted in Fig. 1. In case of GO, a broad peak around 3400 cm⁻¹ corresponding to stretching vibration of O-H bonds of hydroxyl and carboxyl moieties was observed. Furthermore, five peaks around 1725, 1620, 1415, 1220, 1088 cm⁻¹ were observed which could be ascribed to stretching

modes of C=O, aromatic C=C, carboxyl C-O, epoxy C-O, alkoxy respectively [31]. The spectra of CoFe@rGO nanohybrids reveals all the signature peaks of GO except the peaks of oxygen containing functional groups around 1625-1725 cm⁻¹ and 1150 cm⁻¹ in Fig.1 (b-e), suggesting complete reduction of GO to rGO. Moreover, a new peak around 590 cm⁻¹ appeared indicating the formation of metal-oxygen bond in CoFe@rGO nanohybrids [32].

3.1.2. Powder XRD Analysis

Powder XRD analysis was executed in order to determine the structural parameters and phase purity of synthesized nanohybrids. The XRD patterns of GO and CoFe@rGO nanohybrids are presented in Fig. 2. In case of GO, a strong diffraction peak at $2\theta = 10.5^{\circ}$ corresponding to (011) crystal plane was observed. For CoFe@rGO hybrid, diffraction peaks corresponding to (220), (311), (400), (511) and (440) planes were perceived, hence confirming the formation of single phase cubic structure of CoFe₂O₄ with Fd-3m space group. Furthermore, in case of nanohybrids the diffraction plane of GO at (011) plane was absent indicating complete reduction of GO to rGO [33, 34]. However, in the nanohybrids the diffraction peak corresponding to rGO at $2\theta = 25^{\circ}$ was not observed that could be attributed to the damage and disorder generated in its layered structure by the crystal growth of ferrite nanoparticles in its interlayers [35-37].

The average crystallite size of the synthesized materials was calculated using most intense peak broadening of (311) plane using Debye-Scherrer equation [38]

$$D_{hkl} = k\lambda/\beta \cos\theta \tag{1}$$

Where D_{hkl} is the crystallite size, λ is the wavelength of radiation used, β is full width at half maxima of the diffraction peak (FWHM), k is Scherrer's constant with a value of 0.9 and θ is the angle of diffraction. The values of crystallite size in the range of 8-12 nm were observed for all the samples and are listed in Table 1. Le Bail refinement method was employed to estimate the lattice parameter (a) values of the synthesized materials which are tabulated in Table 1.

3.1.3 Structural analysis

To gain insight into the structure and morphology of nanohybrids, FE-SEM analysis was carried out. The typical FE-SEM micrographs of CoFe@rGO (20%) at resolution 500 nm and 300 nm are presented in Fig. 3. The FE-SEM micrographs revealed that rGO has layered structure and cobalt ferrite (CoFe₂O₄) nanoparticles were randomly distributed on the surface and edges of graphene sheets. Furthermore, it can be clearly perceived from the FE-SEM micrographs that CoFe₂O₄ remain intact to the surface of rGO besides long period of

sonication and stirring suggesting strong interaction between rGO and $CoFe_2O_4$ nanoparticles. Owing to layered structure, rGO possess large surface area which in turn proliferates the exposure of active sites of ferrites which ultimately enhances the catalytic efficiency of nanohybrids [5, 23, 39, 40].

HR-TEM studies were carried out for the detailed structural analysis of the synthesized nanohybrids. Fig.4 (a), (b) and (c) displays low resolution TEM images of hydrothermally synthesized CoFe@rGO (20%) nanohybrid. The images reveal that the ferrite nanoparticles were successfully sheathed over GO. Fig. 4 (d) displays the lattice spacing of 0.25 nm corresponding to (311) plane of CoFe@rGO nanohybrid. The interplanar distance values obtained from the HR-TEM images well matched with the corresponding XRD diffraction planes of CoFe@rGO(20%) nanohybrid.

The crystalline nature of the samples can be predicted from concentric electron diffraction rings corresponding to different planes in the SAED pattern. Typical SAED (selected area electron diffraction) pattern of CoFe@rGO(20%) nanohybrid is shown in Fig. 4(e). The presence of the concentric diffraction rings illustrates the highly crystalline nature of the synthesized nanohybrid and all the planes observed from the SAED patterns matched well with the planes observed in the powder XRD patterns.

Furthermore, the elemental composition of the synthesized nanohybrids was confirmed from EDX spectra as presented in Fig. 4 (f) which demonstrates the presence of desired elements. The presence of peaks corresponding to C and Cu were observed due to carbon coated copper grid, which was utilized for the analysis. No additional peak corresponding to other elements was perceived hence, confirming the purity of the synthesized nanohybrid.

3.1.4 Magnetic measurements

The magnetic characteristics of the synthesized nanohybrids were assessed by recording room temperature hysteresis loops using vibrating sample magnetometer as depicted in Fig. 5. The saturation magnetization (M_s) values were observed to increase with increase in cobalt ferrite concentration from 32.7 emu/g for CoFe@rGO (5%) to 38.6 emu/g for CoFe@rGO (20%). The enhancement in the M_s values could be attributed to coherent magnetic nature of CoFe₂O₄. The values of saturation magnetization (M_s), coercivity (H_c), remanence (M_r) and squareness ratio (S_q) for all the synthesized nanohybrids are listed in Table 2.

3.2 Catalytic investigation of GO and CoFe@rGO nanohybrids for epoxide ring opening reaction

The epoxide ring opening reactions were performed under solvent free conditions and substrate scope was investigated via reactions between epoxides and aromatic amines at 80 C using GO and CoFe@rGO as heterogeneous catalysts. The substrate scope of GO and CoFe@rGO (20%) catalysed ring opening reactions amongst various epoxides (2, 4, 6) and aromatic amines bearing electron withdrawing and electron releasing groups are listed in Table 3-5. The isolated products were obtained in excellent yields showcasing 100% conversion within minutes; the yields were calculated using column chromatography. In case of halogen substituted aromatic amines, longer reaction times were observed as listed in entries b-g in Table 3-5. Amongst halogens, the reaction time was observed to be shortest for iodine substituted amines followed by bromine and then by chlorines substituted amines. As observed, completion time for the epoxide ring opening reaction was equivalent, irrespective of the position of attached halogen. In case of p-OCH₃ and p-CH₃ anilines, rapid completion times as well as excellent isolated yields (93 to 94%) were observed as mentioned in entries h and i from Table 3-5. On comparing the results for the reaction of epoxides (cyclohexene oxide (2) and cyclopentene oxide (4)) with various aromatic amines similar completion times were observed except for the case of unsymmetrical epoxide i.e., styrene oxide (6) little longer completion time was detected with all the aromatic amines. As inferred from all the reaction results, CoFe@rGO (20%) nanohybrid showcased better catalytic performance compared to that of pristine GO towards epoxide ring opening reactions which could be attributed to large surface area of the nanohybrid showcasing better dispersal in the solution phase. In case nanohybrids, both CoFe and GO act synergistically, hence augmenting the catalytic performance towards epoxide ring opening reactions.

3.3 Characterization of product

The formation of all the desired products was confirmed and characterized using ¹HNMR spectroscopy. The ¹HNMR spectra and data of obtained products using GO and CoFe@rGO nanohybrids as catalyst are provided as supplementary data (Fig. S1-S27).

3.4 Probable mechanistic pathway

The catalytic performance of GO is due to its capacity to function as an acid. GO transfers a proton to the epoxide when the epoxide gets adsorbed on the surface of the GO. This results in the increased electrophilicity at one of the epoxide carbon atoms which prompts the attack of nucleophile and consequently, ring opening of epoxide takes place. The schematic representation of the reaction mechanism for epoxide ring opening using GO as catalyst is shown in the Fig. 6. The epoxide ring opening reaction catalysed by GO is represented in equation (2) :



In case of nanohybrids (CoFe@rGO), the adsorption of reactant molecule occurs at the surface of the nanohybrid due to the presence of acidic sites on the surface. The plausible mechanism for epoxide ring opening in the presence of CoFe@rGO as catalyst is depicted in Fig. 7. On adsorption of the epoxide molecule at the surface of nanohybrid, epoxide gets activated for the nucleophilic attack by the amine derivatives. This results in the formation of intermediate (I) which can interchange with the intermediate (II) by proton transfer and finally results in the formation of the desired product. The epoxide ring opening reaction catalysed by CoFe@rGO is represented in equation (3) :



The results obtained in Tables 3 to 5 can be justified on the basis of the above mentioned plausible mechanism. The higher reactivity of –OMe substituted amine is due to its high nucleophilicity which results in the facile attack on the epoxide-nanohybrid complex to form the desired product in lesser time. So, based on the nucleophilicity of different groups, the order of reactivity for various amines follows the trend OMe > Me > H > I > Br > Cl.

The presently prepared materials were compared with previous reports in terms of completion time, % yield, use of solvent and magnetically separable nature which directly relates with recyclability of the materials. [41-47]. The present study displays superior results for epoxide ring opening reactions as compared to previously reported materials as mentioned in Table 6.

3.5 Recyclability

Admirable stability and recyclability are the significant features of the synthesized nanohybrids, CoFe@rGO. The recyclability of the nanohybrids was examined for six catalytic cycles employing CoFe@rGO (20%) as catalyst. Owing to the magnetic nature of the nanohybrid, it was separated from reaction mixture using an external magnet and washed with distilled water and acetone. The obtained material was then dried and reused for subsequent reactions. No significant decrease in the % yield was observed even after six catalytic cycles signifying excellent reusability of the nanohybrid (Fig. 8). After each catalytic run, the recovered catalyst was characterized using FT-IR and powder X-ray diffraction; no significant change in the nanohybrid was observed suggesting high durability of the nanohybrids. The FT-IR spectra and the powder XRD pattern of the recovered nanohybrid are provided as supplementary data (Fig. S28-S29). The prepared materials were found to be superior in comparison with the previously reported materials in terms of recyclability.

4. Conclusions

To conclude, graphene based magnetic nanohybrids (CoFe@rGO) were synthesized using a facile hydrothermal method and were characterized using various techniques. Powder XRD pattern confirms the formation of single phase cubic structure of CoFe₂O₄ with Fd-3m space group, absence of diffraction peak (011) indicates the complete reduction of GO to rGO in the nanohybrids. From FE-SEM and HR-TEM images, ferrite nanoparticles sheathed over reduced graphene oxide were observed. The saturation magnetization values were observed to be more than 30 emu/g for all the prepared samples and were observed to increase with increase in cobalt ferrite content. The catalytic performance of Graphene oxide (GO) and magnetic nanohybrids (CoFe@rGO) was exploited for ring opening reactions of epoxides with amines under solvent free conditions. The nanohybrids (CoFe@rGO) emerged out as better candidates for the conversion of different aromatic amines to corresponding amino alcohols with 100% conversion rate within 6 minutes of reaction time. Owing to the magnetically separable nature of the prepared samples, excellent recyclability for upto 6 catalytic runs was observed. The present report exhibited short reaction time, simple work up procedure, great recyclability and solvent free greener approach for the given reaction as compared with previous reports. Thus, the synthesized magnetic nanohybrids could be potentially used as green catalyst for the formation of various pharmaceutical and intermediate chemicals in near future.

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References:

- N. Arora, A. Mehta, A. Mishra, S. Basu, 4-Nitrophenol reduction catalysed by Au-Ag bimetallic nanoparticles supported on LDH: Homogeneous vs. heterogeneous catalysis, Appl Clay Sci. 151 (2018) 1-9.
- M. N. Chen, L. P. Mo, Z. S. Cui, Z. H. Zhang, Magnetic nanocatalysts: Synthesis and application in multicomponent reactions, Curr. Opin. Green and Sustainable Chem. 15 (2019) 27-37.
- R. Bonyasi, M. Gholinejad, F. Saadati, C. Najera, Copper ferrite nanoparticles modified starch as a highly recoverable catalyst for room temperature click chemistry: Multicomponent synthesis of 1,2,3-trizoles in water, New J. Chem. 42 (2018) 3078-3086.
- S. Vasantharaj, S. Sathiyavimal, P. Senthilkumar, F. L. Oscar, A. Pugazhendhi, Biosynthesis of iron oxide nanoparticles using leaf extract of Ruellia tuberosa: antimicrobial properties and their applications in photocatalytic degradation, J Photochem Photobiol B: Biology. 192 (2019) 74-82.
- Y. Yıldız, S. Kuzu, B. Sen, A. Savk, S. Akocak and F. Şen. Different ligand based monodispersed Pt nanoparticles decorated with rGO as highly active and reusable catalysts for the methanol oxidation, Int. J. hydrog. Energy, 42(18) (2017) 13061-13069.
- Z. Ozturk, F. Sen, S. Sen and G. Gokagac. The preparation and characterization of nano-sized Pt–Pd/C catalysts and comparison of their superior catalytic activities for methanol and ethanol oxidation, J. Mater. Sci., 47(23) (2012) 8134-8144.
- E. Erken, Y. Yıldız, B. Kilbaş and F. Şen. Synthesis and characterization of nearly monodisperse Pt nanoparticles for C1 to C3 alcohol oxidation and dehydrogenation of dimethylamine-borane (DMAB), J. Nanosci. Nanotechnol., 16(6) (2016) 5944-5950.
- A. Hassani, G. Celikdag, P. Eghbali, M. Sevim, S. Karaca, O. Metin, Heterogeneous sono-fenton like process using magnetic cobalt ferrite reduced graphene oxide (CoFe₂O₄-rGO) nanocomposite for the removal of organic dyes from aqueous solution, Ultrason Sonochem. 40 (2018) 841-852.

- K. H. Thebo, X. Qian, Q. Wei, Q. Zhang, H. M. Cheng, W. Ren, Reduced graphene oxide/metal oxide nanoparticles composite membranes for highly efficient molecular separation, J. Mater. Sci. Technol. 34 (2018) 1481-1486.
- S. Yadav, N. Goel, V. Kumar, K. Tikoo, S. Singhal, Removal of fluoroquinolone from aqueous solution using graphene oxide: experimental and computational elucidation, Environ Sci Pollut Res. 25 (2018) 2942-2957.
- S. Bhattacharya, P. Ghosh, B. Basu, Graphene oxide (GO) catalysed transamidation of aliphatic amides: An efficient metal-free procedure, Tetrahedron Lett. 59 (2018) 899-903.
- M. Shaikh, A. Sahu, A. K. Kumar, M. Sahu, S. K. Singha, K. V. S. Ranganath, Metalfree carbon as a catalyst for oxidative coupling: solvent-enhanced poly-coupling with regioselectivity, Green Chem. 19 (2017) 4533-4537.
- G. Lv, H. Wang, Y. Yang, T. Deng, C. Chen, Y. Zhu, X. Hou, Graphene Oxide: A Convenient Metal-Free Carbocatalyst for Facilitating Aerobic Oxidation of 5-Hydroxymethylfurfural into 2, 5-Diformylfuran, ACS Catal. 5 (2015) 5636-5646.
- K. Ha, G. Chen, G. Zeng, A. Chenb, Z. Huang, J. Shi, Three-dimensional graphene supported catalysts for organic dyes degradation, Appl Catal B-Environ. 228 (2018) 19-28.
- 15. P. Fei, J. Qiao, J. Huo, J. Liu, M. Zhong, B. Su, Barium(II)-doped zinc ferrite-reduced graphene oxide nanohybrids for superior adsorption and magnetic properties, New Carbon Mater. 32(5) (2017) 402-410.
- 16. R. Ghadari, H. Namazi, M. Aghazadeh, Synthesis of graphene oxide supported copper-cobalt ferrite material functionalized by arginine amino acid as a new high performance catalyst, Appl Organometal Chem. 32 (2018) 3965-3975.
- H. Javed, A. Rehman, S. Mussadiq, M. Shahid, M. A. Khan, I. Shakir, P. O. Agboola, M. F. A. Aboud, M. F. Warsi, Reduced graphene oxide-spinel ferrite nano-hybrids as magnetically separable and recyclable visible light driven photocatalyst, Synth. Met. 254 (2019) 1-9.
- A. A. Hammad, M. A. E. Aziz, M. S. Hasanin, S. Kamel, A novel electromagnetic biodegradable nanocomposite based on cellulose, polyaniline, and cobalt ferrite nanoparticles, Carbohydr. Polym. 216 (2019) 54-62.
- A. Maleki, J. Rahimi, Synthesis of dihyroquinazolinone and octahydroquinazolinone and benzimidazoloquinzolinone derivatives catalyzed by an efficient magnetically recoverable GO based nanocomposite, J. Porous Mater. 25 (2018) 1789-1796.

- 20. S. Bahadorikhalili, L. Ma'mani, H. Mahdavi, A. Shafiee, Copper supported βcyclodextrin functionalized PEGylated mesoporous silica nanoparticle-graphene oxide hybrid: An efficient and recyclable nano-catalyst for straightforward synthesis of 2-arylbenzimidazoles and 1, 2, 3-triazoles, Micropor Mesopor. Mat. 262 (2018) 207-216.
- M. Tanhaei, A. Mahjoub, R. Nejat, Three-Dimensional Graphene-Magnetic Palladium Nanohybrid: A Highly Efficient and Reusable Catalyst for Promoting Organic Reactions, Catal. Lett. 148 (2018) 1549-1561.
- 22. Y. Lee, S. Kwon, J. Yu, G. J. K. Bull, The Catalytic Activities of New Metal Oxide Catalysts Modified by Graphene Oxide to Produce Propene and its Economic Evaluation, Korean Chem. Soc. 39 (2018) 461-468.
- 23. S. Eris, Z. Daşdelen, Y. Yıldız, Y. and F. Sen. Nanostructured Polyaniline-rGO decorated platinum catalyst with enhanced activity and durability for Methanol oxidation, Int. J. Hydrog. Energy, 43(3) (2018) 1337-1343.
- 24. G. Kumar, R. Kumar, G. O. Ildiz, R. Fausto, A. Husain, Structure, spectroscopic properties and catalytic activity for epoxide ring-opening of nickel methylxanthate, J. Mol. Struct 1177 (2019) 33-46.
- 25. A. Parulkar, R. Joshi, N. Deshpande, N. A. Brunelli, Synthesis and catalytic testing of Lewis acidic nano-MFI zeolites for the epoxide ring opening reaction with alcohol, Appl Catal A-Gen. 566 (2018) 25-32.
- 26. N. Deshpande, A. Parulkar, R. Joshi, B. Diep, A. Kulkarni, N. A. Brunelli, Epoxide ring opening with alcohols using heterogeneous Lewis acid catalysts: Regioselectivity and mechanism, J. Catal. 370 (2019) 46-54.
- 27. J. Agarwal, R. K. Peddinti, Water mediated, highly efficient and improved protocol for the synthesis of vesamicol, its analogues and β blockers through the highly chemoselective aminolysis of epoxides, ChemistrySelect 4(26) (2019) 7745-7750.
- 28. A. Sharma, J. Agarwal, R. K. Peddinti, Direct access to the optically active VAChT inhibitor vesamicol and its analogues via the asymmetric aminolysis of mesoepoxides with secondary aliphatic amines, ORG BIOMOL CHEM. 15 (2017) 1913– 1920.
- A. Alazmi, V. Singaravelu, N. M. Batra, J. Smajic, M. Alyami, N. M. Khashab, P. M. F. J. Costa, Cobalt ferrite supported on reduced grapheme oxide as a T2 contrast agent for magnetic resonance imaging, RSC Adv. 9 (2019) 6299-6309.

- 30. J. Agarwal, A. Duley, R. Rani, R. K. Peddinti, Aminolysis of epoxides using iridium trichloride as an efficient catalyst, J. Synth. Org. Chem. 16 (2009) 2790-2796.
- 31. S. Sheshmani, B. Falahat, F. R. Nikmaram, Preparation of magnetic graphene oxideferrite nanocomposites for oxidative decomposition of Remazol Black B, Int. J. Biol. Macromol. 97 (2017) 671-678.
- 32. W. Wang, S. Guo, D. Zhang, Z. Yang, One-pot hydrothermal synthesis of reduced graphene oxide/zinc ferrite nanohybrids and its catalytic activity on the thermal decomposition of ammonium perchlorate, J. Saudi Chem. Soc. 23 (2019) 133-140.
- 33. R. Shu, G. Zhang, J. Zhang, X. Wang, M. Wang, Y. Gan, J. J. Shi, J. He, Synthesis and high-performance microwave absorption of reduced graphene oxide/zinc ferrite hybrid nanocomposite, Mater. Lett. 215 (2018) 229-232.
- 34. S. Bai, X. Shen, X. Zhong, Y. Liu, G. Zhu, X. Xu, K. Chen, One pot solvothermal preparation of reduced graphene oxide-ferrite hybrids for organic dye removal, Carbon. 50 (2012) 2337-2346.
- 35. Z. Shahnavaz, P. M. Woi, Y. Alias, A hydrothermally prepared reduced graphene oxide-supported copper ferrite hybrid for glucose sensing, Ceram. Int. 41 (2015) 12710–12716.
- 36. M. M. Mohameda, I. Ibrahimb, T. M. Salama, Rational design of manganese ferritegraphene hybrid photocatalysts: Efficient water splitting and effective elimination of organic pollutants, Appl. Catal. A: Gen. 524 (2016) 182–191.
- 37. S. Kapoor, V. Kumar, K.B. Tikoo, B. Chudasama, N. Goel, S. Singhal, Strategically designed reduced graphene oxide based magnetic responsive nanocatalysts for the attenuation of recalcitrant pollutants, Ceram.Int. https://doi.org/10.1016/j.ceramint.2019.09.262.
- Y. Koaeoglu, F. Alan, M. Tan, R. Yilgin, M. Ozturk, Low temperature hydrothermal synthesis and characterization of Mn doped cobalt ferrite nanoparticles, Ceram. Int. 38 (2012) 3625-3634.
- 39. K. Karami, N. S. Mousavi, A Palladium complex immobilized onto magnetic GO-MnFe₂O₄ surface as an effective and recyclable catalyst for reduction of pnitrophenol, Dalton Trans. 47 (2018) 4175-4182.
- 40. Kausar, P. Mukherjee, A. R. Das, Practical carbocatalysis by graphene oxide nanosheets in aqueous medium towards the synthesis of diversified dibenzo [1,4] Diazepine scaffolds, RSC Adv. 6 (2016) 88904-88910.

- 41. M. Meguro, N. Asaob and Yoshinori Yamamoto, Ytterbium Triflate and High Pressure-mediated Ring Opening of Epoxides with Amines. J. Chem. Soc. Perkin Trans. 1 (1994) 2597.
- 42. F. Carree, R. Gill and J. Collin, Samarium iodides catalyzed meso-epoxides ring opening by aromatic amines. Tetrahedron Lett. 45 (2004) 7749–7751.
- T. Ollevier and G. L. Compin, Bismuth triflate-catalyzed mild and efficient epoxide opening by aromatic amines under aqueous conditions. Tetrahedron Lett. 45 (2004) 49–52.
- 44. U. Das, B. Crousse, V. Kesavan, D. B. Delpon and J. P. Begue, Facile Ring Opening of Oxiranes with Aromatic Amines in Fluoro Alcohols. J. Org. Chem. 65 (2000) 6749-6751.
- 45. F. Carree, R. Gill and J. Collin, Enantioselective Ring Opening of meso-Epoxides by Aromatic Amines Catalyzed by Lanthanide Iodo Binaphtholates. Org. Lett. 6 (2005) 1023-1026.
- 46. J. Cossy, V. Bellosta, C. Hamoria and J. R. Desmursd, Regioselective ring opening of epoxides by nucleophiles mediated by lithium bistrifluoromethanesulfonimide. Tetrahedron Lett. 43 (2002) 7083–7086.

Samples	$D_{hkl}(\pm 2 nm)$	a (Å)
GO	11.4	8.250
CoFe@rGO (5%)	8.7	8.418
CoFe@rGO(10%)	9.9	8.374
CoFe@rGO (15%)	9.9	8.320
CoFe@rGO (20%)	9.9	8.371

Table 1. Crystallite size $D_{hkl}\ (nm)$ and Lattice parameter, a (Å) for GO and CoFe@rGO nanohybrids.

Catalyst	M _r (emu/g)	H _c (Oe)	$S_q \times 10^{-2}$	M _s (emu/g)
CoFe@GO(5%)	3.00	140	9.1	32.7
CoFe@GO(10%)	4.60	180	13	35
CoFe@GO(15%)	5.00	190	13	36
CoFe@GO(20%)	3.20	155	8.3	38.6

Table 2. Remanence (M_r) , coercivity (H_c) , squareness ratio (S_q) , saturation magnetization (M_s) of the synthesized nanohybrids.

30(20%)

 Table 3. GO and CoFe@rGO (20%) catalysed epoxide ring opening reaction of

 cyclohexene oxide (2) with various aromatic amines (1a-i)



				GO	CoFe@rGO(20%)			
Amine	-X	Product	Time (min)	Conversion	Yield	Time (min)	Conversion (%)	Yield
1 a	Н	3 a	4	100	92	3	100	92
1b	2-Cl	3 b	14	100	86	12	100	86
1c	4-Cl	3c	14	100	86	12	100	86
1d	2-Br	3d	12	100	90	8	100	90
1e	4-Br	3e	12	100	90	8	100	89
1f	2-I	3f	9	100	89	7	100	88
1g	4-I	3g	9	100	88	7	100	88
1h	4-Me	3h	3	100	93	2	100	93
1i	4- OMe	3i	3	100	94	2	100	94

 Table 4. GO and CoFe@rGO (20%) catalysed epoxide ring opening reaction of

 cyclopentane oxide (5) with various aromatic amines (1a-i)



GO

CoFe@rGO (20%)

Amine	-X							
-		Product	Time (min)	Conversion 100%	Yield (%)	Time (min)	Conversion (%)	Yield (%)
1a	Н	5a	4	100	92	3	100	93
1b	2-Cl	5b	14	100	88	12	100	89
1c	4-Cl	5c	14	100	88	12	100	88
1d	2-Br	5d	12	100	86	8	100	86
1e	4-Br	5e	12	100	88	8	100	86
1f	2-I	5 f	9	100	85	6	100	86
1g	4-I	5g	9	100	85	7	100	85
1h	4-Me	5h	3	100	93	2	100	94
1 i	4-OMe	5i	3	100	93	2	100	94

 Table 5. GO and CoFe@rGO (20%) catalyzed epoxide ring-opening reaction of styrene

 oxide (8) with various aromatic amines (1a-i)



			GO			CoFe@rGO (20%)			
Amine -X	-X	Product	Time	Conversion	Yield	Time	Conversion	Yield	
		(min)	100%	(%)	(min)	(%)	(%)		
1a	Н	7a	8	100	90	6	100	90	
1b	2-Cl	7b	24	100	84	20	100	84	
1c	4-Cl	7c	24	100	84	20	100	84	
1d	2-Br	7d	20	100	84	18	100	85	
1e	4-Br	7e	20	100	85	18	100	85	
1f	2-I	7 f	18	100	82	15	100	83	
1g	4-I	7g	18	100	82	15	100	82	
1h	4-Me	7h	6	100	90	5	100	92	
1i	4-OMe	7 i	6	100	92	5	100	92	

Catalyst	Solvent	Time	Yield (%)	Magnetically recoverable	References
Yb(OTf) ₃	THF	10 h	94	No	[41]
SmI ₂ (THF) ₂	CH_2Cl_2	18 h	75	No	[42]
10% Bi(OTf) ₃	H ₂ O	7-9 h	83	No	[43]
Hexafluoro-2- propanol	-	4 h	84	No	[44]
Samarium Iodo Binaphthoxide	CH ₂ Cl ₂	18 h	55	No	[45]
LiNTf ₂	-	20 h	89	No	[46]
CoFe@rGO (20%)	-	6 min	90	Yes	This work

 Table 6. Comparison of reaction time and % yield employing different catalysts for ring opening reactions

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Scheme 1. Schematic representation for the synthesis of CoFe@rGO nanohybrids via Hydrothermal route.

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Fig. 1. FT-IR spectra of (a) GO, (b) CoFe@rGO (5%), (c) CoFe@rGO (10%), (d) CoFe@rGO (15%) and (e) CoFe@rGO (20%) nanohybrid.



Fig. 2. Powder XRD patterns of GO and CoFe@rGO nanohybrids.



Fig. 3. Typical FE-SEM micrographs of CoFe@rGO(20%) nanohybrid at (a) 500 nm and (b) 300 nm magnification.

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Fig. 4 Low Resolution TEM images at different magnification (a,b,c), High Resolution TEM image (d), SAED pattern (e) and EDX spectra (f) of CoFe@rGO(20%) nanohybrid.

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Fig. 5. Room temperature hysteresis loops for CoFe@rGO at varying CoFe concentration.

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Fig. 6. Schematic representation of the reaction mechanism for the epoxide ring opening using GO as catalyst

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Fig. 7. Schematic representation of the reaction mechanism for the epoxide ring opening using CoFe@rGO as catalyst.



Fig. 8. Typical recyclability plots using CoFe@rGO (20%) nanohybrid for the ring opening of epoxide.

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Highlights:

- Synthesis of Graphene based magnetic nanohybrids (CoFe@rGO) using hydrothermal technique.
- Enhanced catalytic performance owing to large surface areas and active catalytic sites.
- Magnetically retrievable catalyst displaying great recyclability. •
- Epoxide ring opening reactions with amines under solvent free conditions. •

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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