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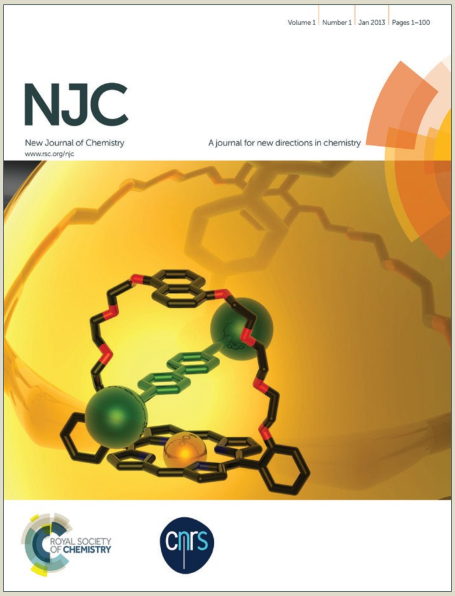

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# Carbocatalysis: N-doped reduced graphene oxide catalyzed esterification of fatty acids with long chain alcohols

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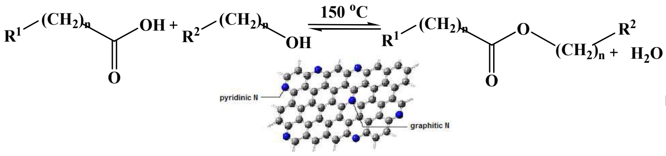
**Nitrogen doped reduced graphene oxide (N-rGO), 5.8% N readily synthesized from thermal annealing of graphene oxide (GO) in ammonium hydroxide at 453 K was demonstrated to be a superior metal-free non-acidic carbo-catalyst for the esterification of fatty acids with different alcohols. The effect of various reaction parameters such as reaction temperature, reaction time, catalyst amount etc. has been studied. The developed catalyst was found to be highly stable and exhibited consistent reusability for seven cycles without any significant decrease in the product yields.**

## Introduction

Graphene oxide, an oxidized form of graphene has been established to be promising candidate for developing reduced graphene oxide, chemically functionalized graphene and graphene-based composites for various applications in the fields of electronics, optics and catalysis.[1] Chemical doping is an effective approach to modulate the electrical and catalytic properties of graphene and its derivatives. Doping of carbon network of graphene with heteroatoms such as nitrogen, boron, phosphorus has gained considerable interest in recent years and widely been used in electrochemical applications, such as fuel cells, lithium ion batteries, supercapacitors and for catalytic applications.[2] Particularly, N-doped graphene has been reported to be metal free catalyst for aerobic selective oxidation of benzylic alcohols,[3] and the selective oxidation of ethylbenzene at 353 K to generate acetophenone[4]; however, it has never been investigated for the esterification of organic acids with alcohols.

Esterification of fatty acids with alcohols to give corresponding esters is an important reaction and extensively used in the synthesis of biofuels.[5] Esterification reactions are a classic example of reversible reactions and are mostly catalyzed by homogeneous acid catalysts such as sulphuric acid, which are corrosive, non-recyclable and produce undesirable wastes. The disposal of these undesired materials not only enhance the cost of the overall process but also leads to an environmental concern.[6] Thus, the use of solid catalysts in biofuel production has become an area of current research interest.[7,8] Biodiesel production using solid catalysts offer several advantages such as facile recovery of the catalyst, cheaper production costs due to the reusable nature of the catalyst and also reduce the corrosion and environmental problems. In this regard, several solid acid catalysts such as metal oxides,[9,10] sulfonic acid functionalized mesoporous materials,[11,12] polymers,[13] zeolites,[14] clays[15] and carbon based catalysts[16] have been reported for the esterification of fatty acids. Recently sulfonic acid functionalized ionic liquids[17] sulfated zirconia[18] and sulfonated graphene oxide[19] have been reported for the esterification of fatty acids. Along with the recent development of heterogeneous catalysis, the emerging application of carbon materials such as fullerene, carbon nanotube, and graphene which are non-polluting, reusable and can easily be modified, as metal-free catalyst is receiving increasingly interest in the area of organic synthesis.

Herein, we describe a first successful application of nitrogen doped reduced graphene oxide (N-rGO; 5.8 wt% N) as a non-acidic catalyst for the esterification of fatty acids (Scheme 1).



Scheme 1: Esterification of fatty acids

## Results and discussion

### Synthesis and characterization of the catalyst

Graphene oxide (GO) sheets were synthesized from graphite powder using a modified Hummers method. Nitrogen-doped graphene oxide was prepared through a simple process by direct thermal reduction of a GO and ammonium hydroxide at 453 K °C for 5 h by following the literature procedure.[20] The nitrogen content in the synthesized material was determined by elemental analysis and was found to be 5.8 wt%. The collected sample was denoted as N-rGO and characterized by FTIR, XRD, SEM, TEM, XPS and TG analysis.

Fig. 1(A) shows X-ray diffraction (XRD) patterns of GO/N-rGO samples. A sharp peak at 2θ = 10.8° without a graphite peak at ca. 2θ = 26.01° confirmed the successful fabrication of GO. After treating with ammonia, the peak at 2θ = 10.8° disappeared and new peaks at 25.3° appeared, indicating that GO was reduced to rGO *via* the thermal reduction.

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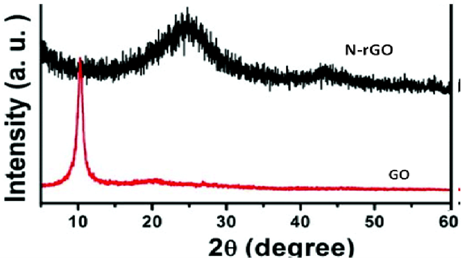

**Fig. 1:** XRD of the GO and N-rGO

X-ray photoelectron spectroscopy (XPS) was performed to analyze the elemental composition and nitrogen bonding configurations in N-rGO. In addition to carbon and oxygen peaks in the XPS survey scan spectra of N-rGO (Fig. 2a), a nitrogen peak is clearly exists, confirming the successful formation of N-doped rGO. Furthermore, sharp peaks of C1s in N-rGO at 284.85 and 284.58 eV in Fig. 2b, corresponding to graphitic or $sp^2$ carbon atoms, suggesting that most of the carbon atoms are presented in the conjugated forms. Furthermore, small peaks at 286.39 and 289.07 eV which can be attributed to different C–O bonding configurations, suggesting deoxygenation of the GO during the N-doping. Instead, two additional peaks at 285.89 and 287.48 eV are identified and can be attributed to the N-$sp^2$ C and N-$sp^3$ C bonds, respectively. These results demonstrate that substitution of the N-atoms occurs at the edges or defective sites of the graphene sheets and nitrogen atoms were successfully incorporated into the graphene lattice.

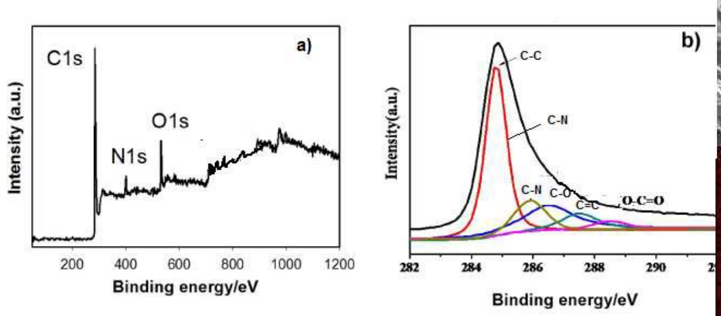

**Fig. 2:** XPS spectra of N-rGO

Furthermore, in FTIR of N-rGO, the peaks due to oxygen containing functional groups such as –OH (3432), C=O from carboxyl/ carbonyl (1736 $cm^{-1}$) and C–O–C (988 and 1227 $cm^{-1}$) were gradually decreased, suggesting the deoxygenation of graphene oxide at higher temperature. Further, new peaks ascribed to C=C (1545 $cm^{-1}$) and C–N (1338 $cm^{-1}$) were appeared in the spectra of N-rGO, confirming the successful doping of nitrogen atoms in the graphene framework. In addition, a peak corresponding to N–H from $NH_4^+$ (1458 cm-1) was found, which was probably resulting from the reaction of oxygen functionalities of graphene oxide (carbonyl, carboxyl etc) with ammonia to give $NH_4^+$ and then deoxygenation of GO (Fig 3).

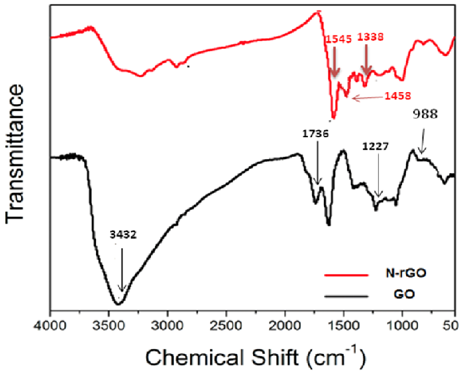

**Fig. 3:** FTIR of GO and N-rGO

The nanostructural features and morphology of the synthesized material was determined by SEM and HRTEM analysis as shown in Fig. 4. The Fig. 4a, clearly shows the plenty of wrinkle and folded regions which are mainly attributed to the $sp^3$ carbons, linked to the oxygen functionalities in the basal plane and various structural defects of rGO nanosheets. Furthermore in elemental mapping, the thorough and uniform distribution of nitrogen atoms, confirming the successful synthesis of N-rGO.

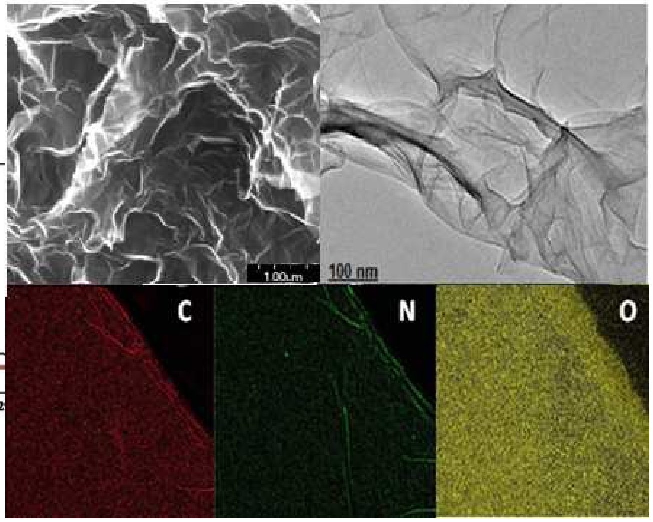

**Fig. 4:** SEM, HRTEM and elemental mapping of N-rGO

The Raman spectra of synthesized GO and N-rGO as shown in Fig 6, clearly indicated two bands, a graphite lattice (G band) at 1569 $cm^{-1}$ and stronger graphite edges (D band) at 1306.0 $cm^{-1}$. The ID/IG ratio was found to be increased in N-rGO (ID/IG=1.34) in comparison to the graphene oxide (ID/IG=0.86), which is in good agreement with the literature value[20].

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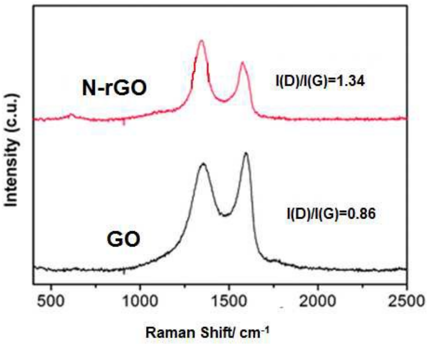

**Fig. 5:** Raman spectra of synthesized GO and N-rGO

The higher thermal stability of the N-rGO was determined by TG analysis by heating the material under air (Fig. 6). The initial weight loss about 1-2 % in N-rGO was obtained in the range of 373-423 K, which can be attributed to the evaporation of water physically absorbed between the layers of N-rGO. Then the material was found to be stable upto 623 K and exhibited major weight loss in the range of 673–1073 K, which can be attributed to the formation of carbon monoxide (CO) and carbon dioxide ($CO_2$) as suggested in the literature.[20]

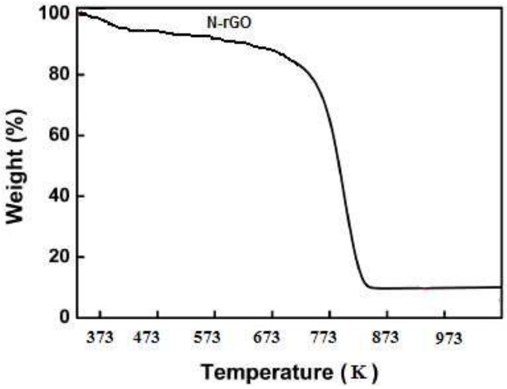

**Fig. 6:** TGA of N-rGO

## Catalysis

Synthesized N-doped reduced graphene oxide (N-rGO; 5.8 wt % N) sample was initially tested for the esterification of oleic acid with octanol by varying the reaction parameters such as reaction temperature, reaction time, catalyst concentration etc. To evaluate the effect of the reaction temperature, esterification of oleic acid was performed by varying the temperature from 373 to 433 K (Fig 7). As shown, the higher reaction temperature was found to be favourable for the reaction and at 423 K the maximum conversion to corresponding ester (98.6%) was achieved. Further increase in reaction temperature did not affect the reaction rate and the conversion remained almost same. Thus we have chosen 423 K as the optimum reaction temperature for further study.

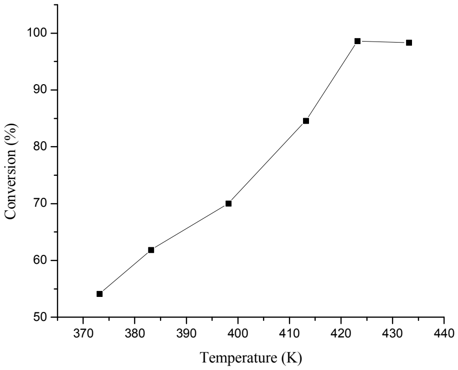

**Fig. 7:** Effect of temperature on reaction conversion for the esterification of oleic acid with octanol; catalyst 5 wt %, time 6h

To evaluate the effect of catalyst concentration, the esterification experiments were performed by varying the concentration of the catalyst from 1.5-10 wt%. The results of these experiments are summarized in Fig. 8. It is clearly shown that the reaction was found to be increased with the catalyst concentration from 1.5 to 5 wt%. However, further increase in catalyst concentration from 5 to 10 wt % affected the reaction adversely and provided lower yield of the corresponding ester under identical reaction conditions. This decrease in the conversion at higher catalyst concentration is most likely due to the excess availability of Lewis basic sites with lone pair electrons such as pyridinic which have a great potential to interact with the acid substrates. The coordination of the basic N-sites with oleic acid led to proton transfer from the acidic hydroxyl groups (Brönsted acid sites) and form quaternary pyridinium species. This kind of acid-base coordination on the catalyst surface will hamper the reaction of oleic acid with alcohol and therefore provides loss in activity and subsequently poor product yield. Based on these studies, we have considered 5 wt % as the optimum catalyst concentration for further study.

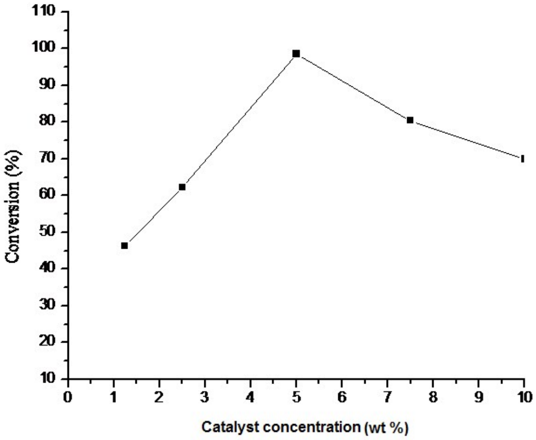

**Fig.8:** Effect of catalyst concentration on reaction conversion for the esterification of oleic acid with 1-octanol at 423 K temperature and 6h reaction time

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### *Kinetic studies*

The kinetic behaviour of the reaction was tested for esterification of oleic acid with 1-octanol over N-rGO catalyst. Two parameters have been considered for the kinetic studies i.e effect of oleic acid concentration and reaction time on the reaction rate. In all the experiments, reaction mixtures were analysed at fixed interval of times and the residual acid was titrated against an alcoholic solution of KOH (0.01 mol $L^{-1}$) to follow the progress of the reaction.

### The effect of oleic acid concentration

According to the existing literature reports, esterification reactions follow first order dependence on the fatty acid concentration. Thus we assume that equation 1 can be used to describe the substrate concentration variation with relation to time:

$$\mathrm{Ln[oleic\ acid]}_t = -kt + \mathrm{In\ [oleic\ acid]}_0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\mathrm{eq.\ 1})$$

The plot of oleic acid concentration $\{\ln(C_0/C)\}$ versus time (Fig. 9) shows a linear relationship of oleic acid conversion with respect to time. This observation indicates that esterification of oleic acid follows first-order dependence with respect to time. It is important to mention that a high molar excess of octanol in relation to oleic acid was used to assure that the alcohol concentration would essentially be remained constant during the reaction.

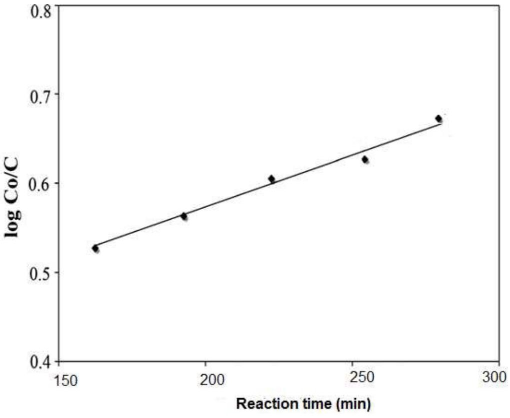

Fig. 9: First order plot for esterification of oleic acid with 1-octanol over N-rGO catalyst

### Effect of reaction time

The effect of reaction time on the esterification reaction was studied by collecting the samples at regular interval of time and analyzing by $^1$H NMR spectroscopy. From Fig. 10 it is clear that initially the reaction is very fast with 53.04 % conversion in 1 hr and as the reaction proceeds, maximum conversion 98.6 % is observed in 6 h afterwards no significant change is seen.

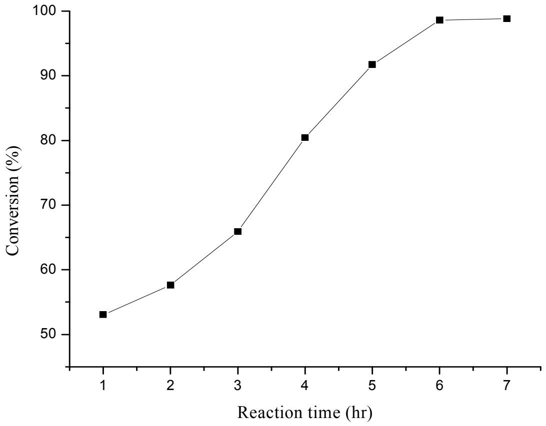

**Fig. 10:** Effect of time on reaction conversion for the esterification of oleic acid with octanol using 5 wt% catalyst and 423 K temperature

In order to extent the scope of the reaction, we further studied the esterification of fatty acid mixtures obtained by saponification of various non-edible oils such as Bischofia javanica and Toona silita seed oils. Fatty acid composition of these oils has been determined by gas chromatography as given in Table 1 (entry 5 & 9). For esterification fatty alcohols i.e. octanol, hexanol, 2-ethyl hexanol, decanol were used. All the substrates were efficiently converted to corresponding esters with excellent conversion under the optimized experimental conditions (Table 1). The identity of the products was confirmed by $^1$H and $^{13}$C NMR analysis as given in Fig 11.

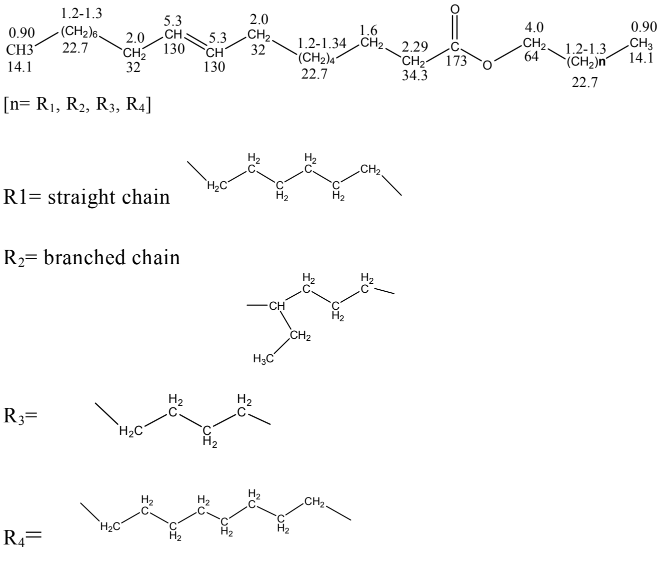

Fig 11: $^1$H NMR and $^{13}$C NMR assignment of fatty esters [(E)-octyl octadec-9-enoate; (E)-2-ethylhexyl octadec-9-enoate; (E)-hexyl octadec-9-enoate; (E)-decyl octadec-9-enoate.

To evaluate the effect of amount of nitrogen content in N-rGO catalyst on esterification reaction, we synthesized more amounts

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of samples without nitrogen and with different nitrogen content N-rGO (4.2 to 8.2 wt % N). The synthesized catalysts were tested for the esterification of oleic acid with 1-octanol under optimized experimental conditions. It was observed that undoped rGO catalyst did not show any activity even at higher temperature (450 K) and original substrates were recovered even after prolonged reaction time (15 h). However, the reaction was found to be increased with increasing the N-content from 4.2 to 5.8 wt% N in N-rGO catalysts with no significant change from 5.8 to 6.2 wt% N. In case of N-rGO catalyst having 8.2 wt% N, the reaction was found to be slow and afforded poor conversion (62.4 % with respect to oleic acid). These studies suggested that N-doping in the range of 5.5-6.2 wt% N) was found to be optimum and excess doping exhibited adverse effect on the catalytic activity.

Reusability of the heterogeneous catalyst is important for the large-scale operation and from an industrial point of view[21]. After completion of the reaction, the catalyst was separated by centrifugation, dried and reused for subsequent runs. The recovered catalyst was used for seven subsequent runs for the esterification of oleic acid with 1-octanol by following the described experimental conditions. The results of these recycling experiments are shown in Fig 12. As shown, the yield of the corresponding ester and reaction time remained almost same, indicating that the catalyst is highly stable and can be reused for several runs without any significant loss catalytic activity.

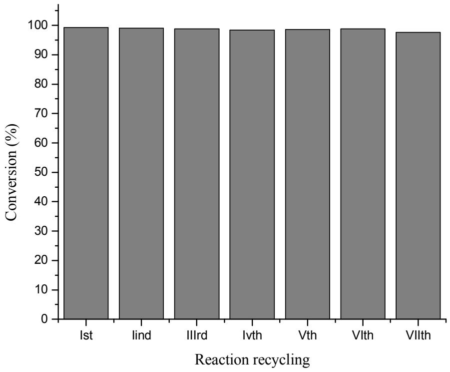
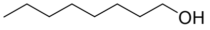
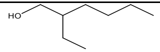
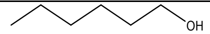
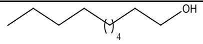
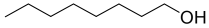
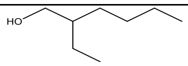
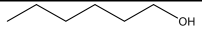
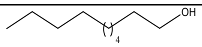
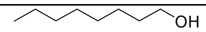
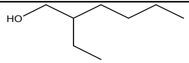
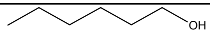
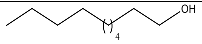


Fig. 12: Results of recycling experiments

Although, the exact mechanism of the reaction is not known at this stage; however based on the literature,[22] we assume that the N-rGO catalyst may provide dual role in activating the acid as well as alcohol molecule. The basic sites (electron rich) on the N-rGO may abstract proton from alcohol molecule to give corresponding alkoxide ion. Whereas, the pyrollic-N and gaphitic sp2 N which possesses good electron withdrawing capability, activate the acid carbonyl group by coordinating with the oxygen atom of carbonyl group and make the adjacent carbon atom net positive. The nucleophilic alkoxide ions will attack to the electrophilic carbon followed by usual esterification reaction path to give corresponding ester.

**Table 1:** Esterification of different fatty acids and alcohols[a]

| Entry | Fatty acids | Fatty alcohol | Conv. (%)[b] | Yield (%)[c] |
|---|---|---|---|---|
| 1. | $CH_3$-$(CH_2)_7$CH=CH-$(CH_2)_7$-COOH |  | 98.6 | 98 |
| 2. | $CH_3$-$(CH_2)_7$CH=CH-$(CH_2)_7$-COOH |  | 96.8 | 96 |
| 3. | $CH_3$-$(CH_2)_7$CH=CH-$(CH_2)_7$-COOH |  | 97.7 | 97 |
| 4. | $CH_3$-$(CH_2)_7$CH=CH-$(CH_2)_7$-COOH |  | 99.2 | 98.5 |
| 5. | Bischofia javanica fatty acids (Major component- C18:2; other component-C16:0, C18:1, C18:3) |  | 96.1 | 98.8 |
| 6. | Bischofia javanica fatty acids (Major component- C18:2; other component-C16:0, C18:1, C18:3) |  | 95.3 | 95 |
| 7. | Bischofia javanica fatty acids (Major component- C18:2; other component-C16:0, C18:1, C18:3) |  | 97.2 | 96.8 |
| 8. | Bischofia javanica fatty acids (Major component- C18:2; other component-C16:0, C18:1, C18:3) |  | 97.4 | 97 |
| 9. | Toona cilita fatty acids (Major component- C16:0) |  | 89 | 87 |
| 10. | Toona cilita fatty acids (Major component- C16:0) |  | 86 | 84 |
| 11. | Toona cilita fatty acids (Major component- C16:0) |  | 88 | 87 |
| 12. | Toona cilita fatty acids (Major component- C16:0) |  | 89 | 88 |

[a]Reaction conditions: catalyst 5 wt%, reaction time 6h, temperature 423 K; [b]conversion of fatty acid to ester was calculated by means of the acid value (AV). The acid value of the reaction mixture was determined by the acid base titration technique. The conversion of FFA (reduction in acid value) was calculated using the following equation: $X_{FFA} = a_i - a_t / a_i$ ;where $a_i$ is the initial acidity and $a_t$ is the acidity at time t (6 h); [c]Isolated yield

## Experimental Section

### Techniques used

The vibrational spectra of samples were recorded on Perkin–Elmer spectrum RX-1 IR spectrophotometer from 450 cm$^{-1}$ to 4000cm$^{-1}$. The micro fine structure of materials was determined by High Resolution Transmission Electron Microscopy using FEI-TecnaiG$^2$ Twin TEM working at an acceleration voltage of 200 kV. For TEM analysis well dispersed aqueous samples were deposited on carbon coated copper grid. Electron diffraction patterns were evaluated using the Process-Diffraction software package. The diffraction pattern and phase structure of materials was determined by XRD using a Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu $K_\alpha$ radiation ($\lambda$= 1.5418 nm). Thermo-gravimetric analysis was carried out for determining the thermal stability of the samples by using a thermal analyzer TA-SDT Q-600 in the temperature range 40 to 900 °C with heating rate of 10 °C/min under nitrogen flow. XPS measurements were obtained on a KRATOS-AXIS 165 instrument equipped with dual aluminum–magnesium anodes by using MgKa radiation (hν =1253.6 eV) operated at 5 kV and 15 mA with pass energy 80 eV and an increment of 0.1 eV.

**Synthesis of N-rGO:** Graphene oxide (GO) was synthesized

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from graphite flakes using modified Hummers method. The synthesized graphene oxide was dispersed in water (50 mL, 0.75 mL$^{-1}$) using ultrasonic bath. The resulting suspension was added with aqueous ammonia (4 mL, 28 wt %) under magnetic stirring and then the mixture was transferred into Teflon-lined autoclave for heating at 453-473 K for 6 h. The resulting nitrogen doped reduced graphene oxide was sonicated for 30 min to remove the excessive or physisorbed ammonia before dried at 60 °C for 24 h.

**Esterification of oleic acid:** The esterification experiments were carried out in a 25 ml round bottomed flask equipped with a magnetic stirrer and reflux condenser. In a typical experiment, oleic acid (1 mmol), octanol (1 mmol) and N-rGO catalyst (5 wt % of total weight) was taken and the resulting mixture was stirred and heated at 423K under neat conditions. The progress of the reaction was monitored by TLC ($SiO_2$). After the reaction, the heterogeneous catalyst was separated by centrifugation, dried and reused for recycling experiments. Conversion of fatty acid to the corresponding ester was calculated by means of the acid value (AV). The acid value of the reaction mixture was determined by the acid base titration technique. The conversion of FFA (reduction in acid value) was calculated using the folowing equation:[23]

$X_{FFA} = a_i - a_t / a_i$ ; where $a_i$ is the initial acidity and $a_t$ is the acidity at time t (6 h). Further the crude product was purified by passing through a short column containing activated basic alumina using ethyl acetate as eluent. The solvent was removed under reduced pressure and the product was analyzed by $^1H$ and $^{13}C$ NMR.

**Esterification of fatty acid mixtures of Bischofia javanica and Toona silita seed oil:**

To explore the activity of the synthesized catalyst, fatty acids of Bischofia javanica and Toona silita oil were obtained by saponification. Extracted oil (2 g) was saponified with NaOH (1.1 M) and acidified with HCl with stirring until the pH became 2, followed by extraction with $CCl_4$ (20 mL x 3), washing with water (20 mL x 3) and solvent recovery by vacuum distillation to give white semi solid fatty acids. The fatty acid mixture was esterified with different fatty alcohols i.e. octanol, 2-ethyl hexanol, hexanol, decanol under optimized conditions i.e. (N-rGO catalyst: 5 wt%, reaction time: 6 h and reaction temperature 423 K). Conversion of fatty acid to the corresponding ester was calculated by acid base titration technique. Further, the corresponding ester products were purified by passing through basic alumina and analyzed by $^1H$ and $^{13}C$ NMR. Yields: 87-98%; **IR** (neat, cm$^{-1}$): 2933 (C-H), 1739 (C=O), 1173 (C-C(=O)-O); **$^1$H NMR** ($CDCl_3$, δppm): 0.90 [t, (-C$\underline{H}_3$)], 1.2-1.3 [ m, (-C$\underline{H}_2$)], 1.6 [m, (-CO-$CH_2$-C$\underline{H}_2$)], 2.0 [m, -C$\underline{H}_2$-CH=CH-C$\underline{H}_2$), 2.29 [t, (-CO-C$\underline{H}_2$)], 4.0 [t, (-O-C$\underline{H}_2$)], 5.3 [b, (-C$\underline{H}$=C$\underline{H}$-)]; **$^{13}$C NMR** ($CDCl_3$, δppm): 14.1 [2x($\underline{C}H_3$)], 22.7 [2x(C$\underline{H}_2$-$CH_3$)], 32 [($\underline{C}$-C=C-$\underline{C}$)], 34.3 [($\underline{C}$-CO)], 64 (-O-C$\underline{H}_2$-), 130 [2 ($\underline{C}$=$\underline{C}$)], 173[(-$\underline{C}$OO)].

## Conclusion

We have demonstrated for the first time the application of nitrogen doped reduced graphene oxide (N-rGO) as an efficient metal free non acidic carbocatalyst for the esterification of fatty acids with different fatty alcohols under mild experimental conditions. The developed catalyst exhibited excellent catalytic activity and was found to be robust that could easily be recovered and recycled for several runs without any significant decrease in the catalytic activity. The developed methodology represents a green and sustainable approach for the esterification and can further be used for other organic transformations.

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## Notes and references

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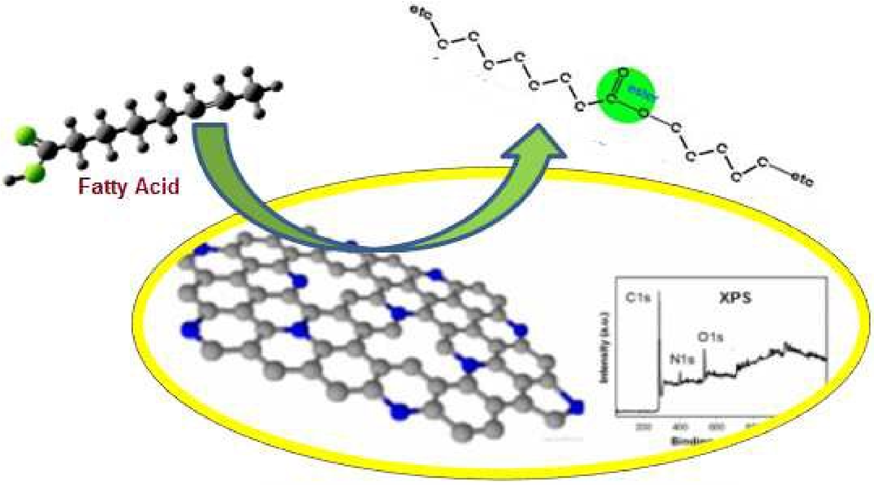

Nitrogen doped reduced graphene oxide (N-rGO) was found to be an efficient metal free and heterogeneous catalyst for esterification of different fatty compounds including acid oils with long chain alcohols.