

Electronic Supplementary Information

Eco-efficient preparation of N-doped graphene equivalent and its application to metal free selective oxidation reaction

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Chemicals and characterization: Graphite powder (20 μm flake size), sulfuric acid (95-97%), hydrogen peroxide (30 wt%), potassium permanganate, hydrazine hydrate (65 % in water), and all organic reactant were obtained from Sigma-Aldrich chemicals. For all the experiment deionized water (18.2 mS conductivity) was used. PTFE capillaries (id 500 μm) was used for micro reactor process. Wide angle X-ray diffractograms of the synthetic samples were recorded using Rigaku D/max 2500/PC X-ray diffractometer with $\text{Cu K}\alpha(1.54056)$ radiation. The thermal degradation processes were investigated using a thermo gravimetric analyser (SDT Q600) under a nitrogen or air atmosphere with a heating rate of 1 $^{\circ}\text{C}/\text{min}$ from 30 to 830 $^{\circ}\text{C}$. The surface morphology of thoroughly dried sample was studied by a JEOL JEM 2100F transmission electron microscope (TEM). The transmission electron microscope with tungsten, electron source operated at an accelerating voltage of up to 120 kV. The TEM sample was prepared by dispersing dry powder of MR-60 in ethanol solvent. For scanning electron microscopy (SEM), gold sputter coating were carried out on desired samples at pressure ranging in between 1 and 0.1 Pa. Sample was loaded in the machine, which was operated at 10^{-2} to 10^{-3} Pa with EHT 15.00 kv with 300 V collector bias using Philip XL30 SEMs were recorded. All XPS measurements were taken in a SIGMA PROBE (ThermoVG)

using a monochromatic Al-K α X-ray source at 100 W. Gyrogen 1236 MG for centrifugation, power sonic 405 (frequency 40 KHz, voltage 240, 50/60 Hz) for sonication were used.

Generation of graphene oxide (GO): Graphite oxide was obtained by the oxidation of graphite flake using modified Hummer methods.¹ In general, 10 g of graphite flake was added in 500 ml of concentrate H₂SO₄ and stirred on ice bath for 1 h and then 40 g of KMnO₄ was slowly added. This reaction mixture was further stirred for 2 h, then ice bath was removed and continued stirring for 24 h. And the reaction mixture was put back on ice bath and added 500 ml of deionised water slowly, and then 30% hydrogen peroxide till the solution colour changed to orange/gold. Orange colour solution was centrifuged at 600 rpm for 10 min to separate the unexfoliated graphite oxide. Then the supernatant solution was transferred into other centrifuging tube and centrifuged at 4000 rpm for 30 min to get golden coloured solid. The solid material was washed with deionised water several time using centrifuge till the solution pH reached 6.6. Finally the solid material was dried under reduced pressure.

Synthesis of reduced graphene oxide by batch process (rGO-b): 300 mg of GO powder was dissolved in 200 ml of deionised water to make colloidal suspension and 1 ml hydrazine monohydrate (65% in water) was added. The reaction mixture was put into a free heated oil bath at 80 °C and stirred for 24 h. After cooling the reaction mixture to room temperature it was centrifuged at 4000 rpm for 10 minute to get the black coloured precipitate rGO-b, and further dried under vacuum.

Synthesis of N-doped rGO by microsonochemical method (MR-X): For in-situ reduction of GO, a solution of GO (300 mg GO powder in 300 mL water) and a solution of hydrazine hydrate (1 ml hydrazine monohydrate (65% in water) + 299 ml water) were separately introduced into the PTFE capillary microreactor (id 500 μ m, varied length, flow rate of hydrazine solution and GO solution (30 μ L/min.)) with T-mixer using syringe pumps (Fig. 1).

However, right after mixing of graphene oxide and hydrazine solution, a tube blocking problem was encountered, presumably due to the rGO aggregation. And T-mixer and the tubing were kept in an ultrasonic bath (power 330 W, frequency 40 KHz, temperature 65 °C) which eventually resolved the aggregation of rGO with better mixing. The reduced graphene oxide (rGO) samples as a black precipitate were collected at controlled retention times in range 30~70 min by varying the capillary length in a constant flow rate 30 μ L/min., designated as MR-X (X: retention time), (Table S1) centrifuged and washed with water for three times and eventually washed with acetone. Washed MR-X samples, were dried at 120 °C for 24 h for further experiment and analysis.

Table S1. Optimization of the reduced graphene oxide, synthesized by a microsonochemical process.

Entry	Channel length (cm)	Channel volume (μ l)	Residence time (min.)	N-doped rGO Product
1	917	1800	30	MR-30
2	1222	2400	40	MR-40
3	1528	3000	50	MR-50
4	1834	3600	60	MR-60
5	2139	4200	70	MR-70

Reaction condition: flow rate of hydrazine solution (30 mL/min); flow rate of GO solution (30 mL/min); temperature 65 °C; sonication power 330W and sonication frequency 40 KHz.

Catalytic reaction for selective ketone synthesis: Typically, reactant (1.0 mmol) MR-60 (30 mg), TBHP (3.0 mmol, 65 wt% in water), and water (3 mL), internal standard anisole (1.0 mmol) for scheme 12, were filled in glass reactor sealed with teflon lid. The reaction mixture was heated to constant temperature (80 °C) in the oil bath and continuously stirred for desired time. After completion of reaction, 10 mL CH_2Cl_2 was added and centrifuge for 10 min to separate the catalyst. The organic layer was analysed by GC-MS.

Catalytic reaction for selective acid synthesis: Reactant (0.5 mmol), MR-60 (30 mg), TBHP (5.0 mmol, 65 wt% in water), and water (1 mL), internal standard anisole (1.0 mmol) for scheme 2, were filled in glass reactor sealed with teflon lid. The reaction mixture was heated to constant temperature (80 °C) in the oil bath and continuously stirred for desired time 12 h. After completion of reaction, 10 mL CH₂Cl₂ was added and centrifuge for 10 min to separate the catalyst. The organic layer was analysed by GC-MS.

Catalytic reaction for selective ester synthesis: Reactant (0.5 mmol), MR-60 (30 mg), TBHP (5.0 mmol, 65 wt% in water), and methanol (0.5 mL), internal standard anisole (1.0 mmol) for scheme 3, were filled in glass reactor sealed with teflon lid. The reaction mixture was heated to constant temperature (80 °C) in the oil bath and continuously stirred for desired time 12 h. After completion of reaction, 10 mL CH₂Cl₂ was added and centrifuge for 10 min to separate the catalyst. The organic layer was analysed by GC-MS.

Catalytic reaction for selective ether synthesis: Reactant (0.5 mmol), MR-60 (30 mg), and methanol (0.5 mL), internal standard anisole (1.0 mmol) for scheme 4, were filled in glass reactor sealed with Teflon lid. The reaction mixture was heated to constant temperature (80 °C) in the oil bath and continuously stirred for desired time 12 h. After completion of reaction, 10 mL CH₂Cl₂ was added and centrifuge for 10 min to separate the catalyst. The organic layer was analysed by GC-MS.

Catalytic reaction for selective amide synthesis: Reactant (1 mmol), MR-60 (30 mg), and water (3 mL), TBHP (3.0 mmol, 65 wt% in water), internal standard anisole (1.0 mmol) for scheme 5, were filled in glass reactor sealed with Teflon lid. The reaction mixture was heated to constant temperature (80 °C) in the oil bath and continuously stirred for desired time 12 h. After completion of reaction, 10 mL CH₂Cl₂ was added and centrifuged for 10 min to separate the catalyst. The organic layer was analysed by GC-MS.

Catalytic oxidation for multiple bond: Reactant (1 mmol), MR-60 (30 mg), and water (3 mL), TBHP (10 mmol, 65 wt% in water), internal standard anisole (1.0 mmol) for scheme 6, were filled in glass reactor sealed with teflon lid. The reaction mixture was heated to constant temperature (80 °C) in the oil bath and continuously stirred for desired time 12 h. After completion of reaction, 10 mL CH₂Cl₂ was added and centrifuge for 10 min to separate the catalyst. The organic layer was analysed by GC-MS.

Table S2: Catalytic efficiency of different graphite derivatives for the oxidation of 1-methylindolin-2-one in the aqueous phase of conventional flask.

1-methylindolin-2-one $\xrightarrow[\text{Water}]{\text{TBHP, Catalyst}}$ 1-methylindoline-2,3-dione + 2-(methylamino)benzoic acid

Entry	Catalyst	Time (h)	Conv. (%) ^e	Yield (%) ^d	
				1-methyl indole-2,3-dione	2-(methylamino) benzoic acid
1	NA	50	NA	NA	NA
2	Graphite	32	13	12.1	NA
3	GO	40	5	5	NA
4	rGO-b	32	42	40.9	NA
5	MR-30	32	48	45.2	NA
6	MR-40	32	70	67.1	NA
7	MR-50	32	82	78.3	0.8
8	MR-60	32	95	92.3	1.0
9 ^a	MR-60	32	NA	NA	NA
10 ^b	MR-60	32	NA	NA	NA
11 ^c	MR-60	12	96	92	1.0

Reaction conditions: 1-methylindoline-2-one (1.0 mmol), catalyst (0.01 g), TBHP (3.0 mmol, 65 % in water), water (3 mL), pressure tube (8 mL), temperature 80 °C [NA] not available; [a] without TBHP; [b] with TEMPO (10 mmol); [c] catalyst (0.03) and other condition are same; [d & e] determined by GC-MS using anisole as an internal standard.

Started: 13-03-19 08:36:15 Analysis Adsorptive: N2
 Completed: 13-03-19 11:33:36 Analysis Bath: 77.35 K
 Report Time: 13-03-20 22:26:59 Thermal Correction: No
 Sample Weight: 0.1887 g Smoothed Pressures: No
 Warm Freespace: 17.0866 cm Cold Freespace: 52.2605 cm
 Equil. Interval: 10 secs Low Pressure Dose: None

BET Surface Area Report

BET Surface Area: 67.12 ± 0.1936 m²/g
 Slope: 0.064549 ? 0.000185
 Y-Intercept: 0.000305 ? 0.000025
 C: 212.400123
 VM: 15.419247 cm³/g STP
 Correlation Coefficient: 9.999876e-01

Molecular Cross-section: 0.1620 nm

Relative Pressure	Vol Adsorbed (cm ³ /g STP)	1/[VA*(Po/P - 1)]
0.065243552	15.4092	0.004530
0.079992139	15.8875	0.005473
0.121141048	17.0032	0.008107
0.161627044	17.9859	0.010719
0.201453920	18.9259	0.013330

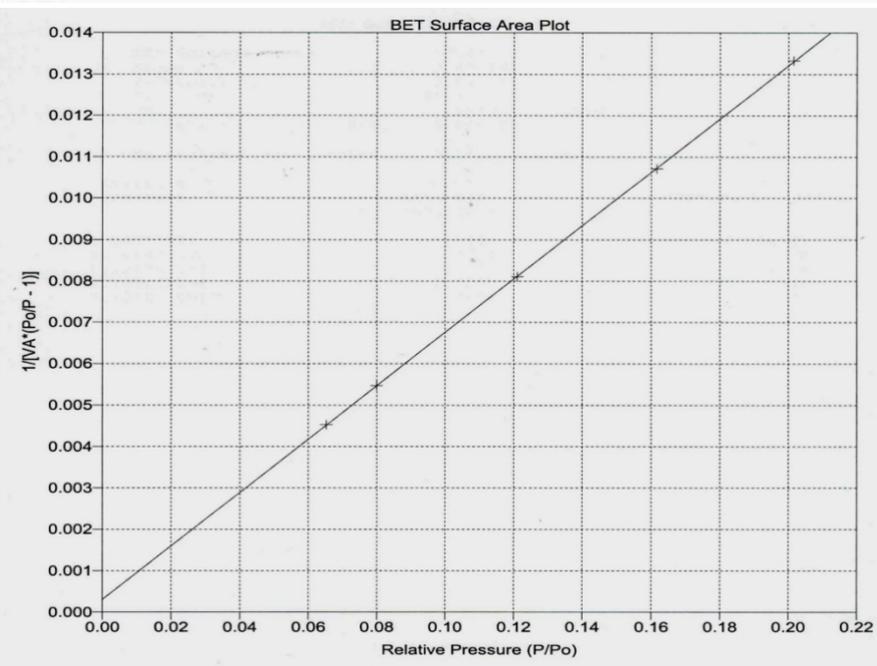


Fig. S1. BET surface area analysis data of MR-60 platelets.

XRD and XPS

Superior quality of MR-60 obtained by the microsonochemical method could be further inferred from the interlayer distance as determined by powder X-ray diffraction (XRD), and the extent of restoration of delocalized π conjugation as identified by X-ray photoelectron spectroscopy (XPS).² The interlayer distance or d-spacing rGO-b was reduced to 3.81 Å ($2\theta = 23.60^\circ$) from 9.0 Å ($2\theta = 9.82^\circ$) of fully oxidized GO as shown in Table S2 and Fig. S2b, which lies in the typical interlayer distance range of rGO (3.7-3.8 Å).^{3,4} In contrast, the value for MR-60 was 3.62 Å ($2\theta = 24.7^\circ$), revealing better recovery to the layered structure as indicated by the lower d-spacing than for rGO-b. High-resolution C1s spectra in Fig. S2 c reveal that MR-60 sample has clearly stronger C-C peak with weaker peaks of the oxidized carbon species than those of rGO-b sample. At the same time, high resolution O1s spectra in Fig. S2d show that all O1s peaks are sharply lowered in MR-60 sample when compared with rGO-b, indicating that the delocalized π conjugation was restored in MR-60 sample (Fig. S2 c&d, Fig. S3c-h in the SI).

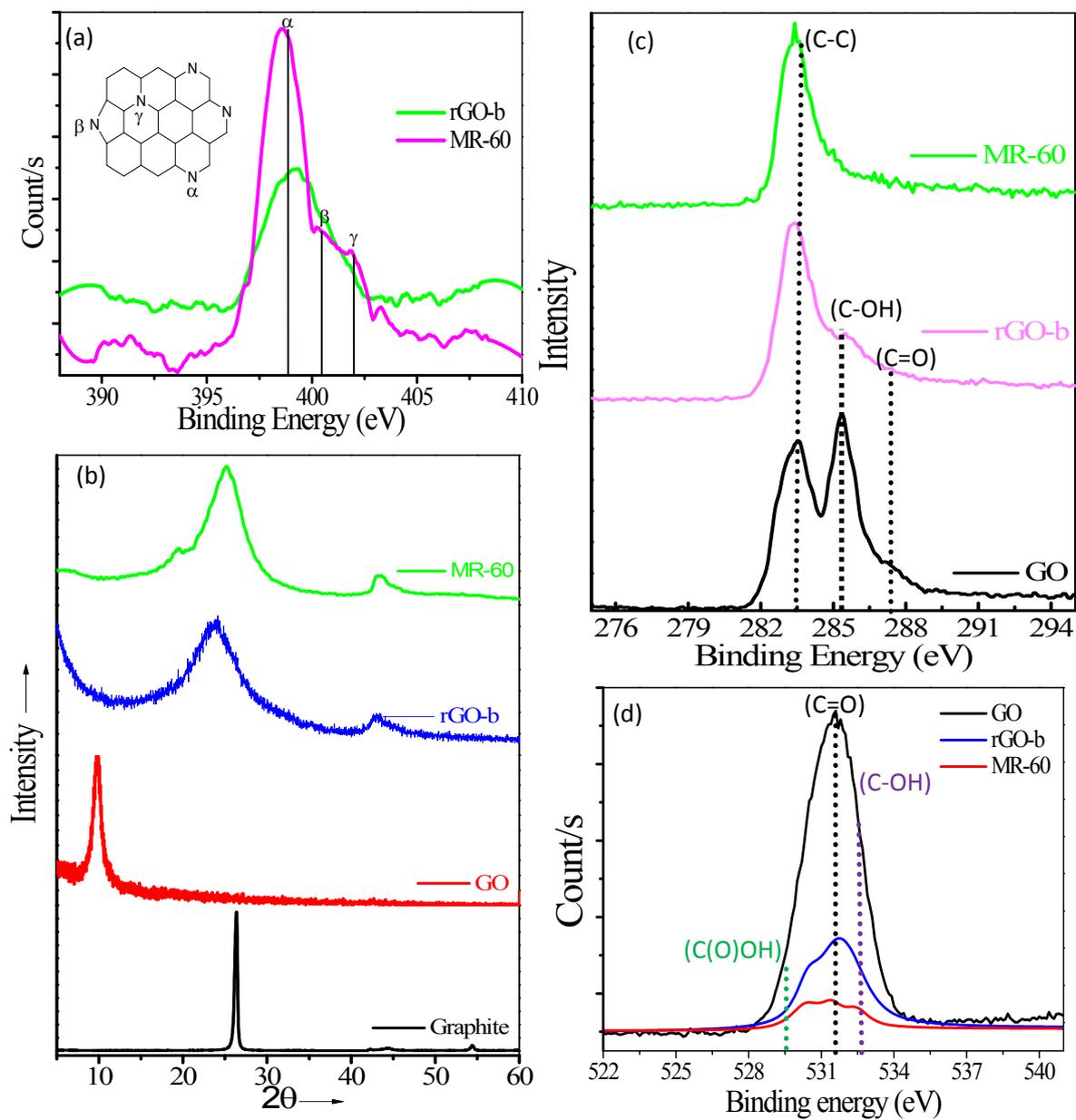


Fig. S2. Molecular structural characterization of graphite derivatives; (a) XPS N_{1s} spectra of rGO-b and MR-60, (b) Powder XRD patterns of Graphite, GO, rGO-b and MR-60; (c & d) High resolution C_{1s} and O_{1s} spectra of the GO, rGO-b and MR-60 respectively.

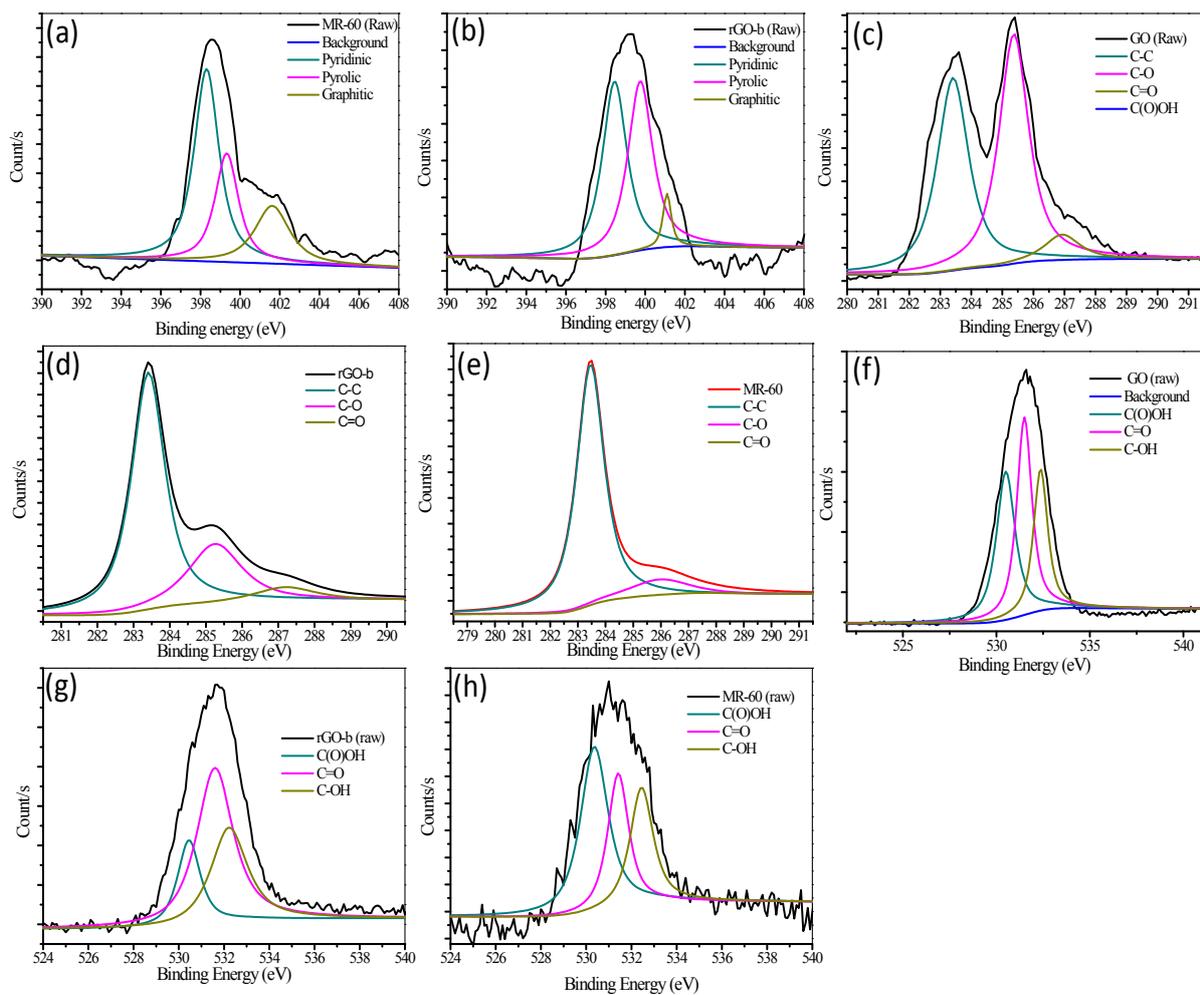


Fig. S3. Deconvoluted XPS spectra; (a&b) N1s spectra of rGO-b and MR-60; (c-e) C1s spectra of GO, rGO-b and MR-60, respectively; (f-h) O1s spectra of GO, rGO-b and MR-60, respectively.

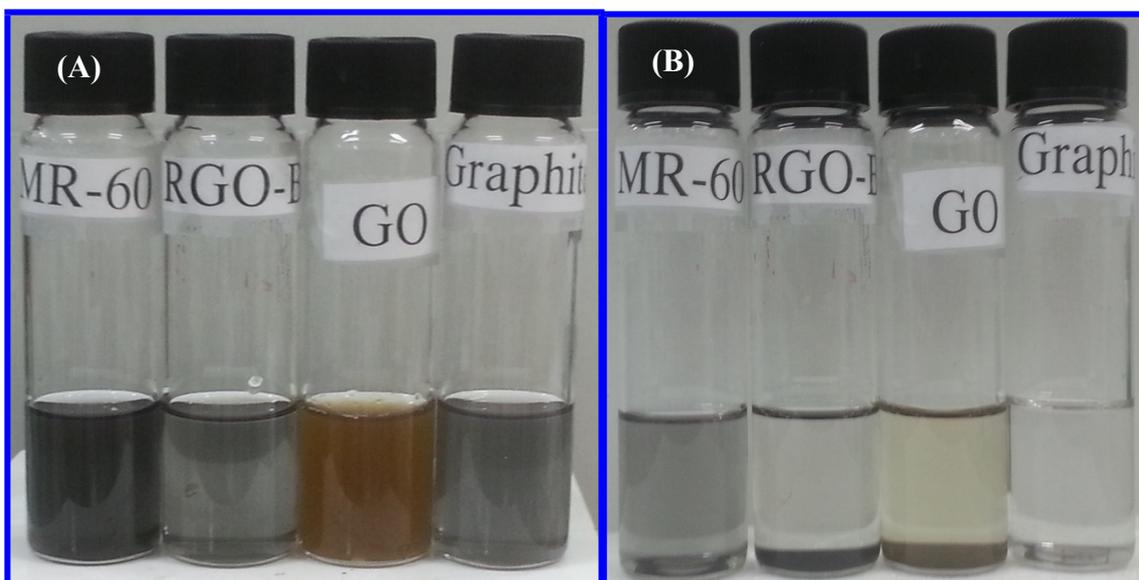


Fig. S4. Dispersion stability test of graphite and there derivatives. (A) Photograph of MR-60, rGO-b, GO, graphite dispered in DMF prepared by 1 h sonication (4 mg in 20 ml DMF) (B) Photograph were taken after 1 month since the graphite derivativeswere dispersed in DMF.

Dispersibility test

Excellent reduction quality could also be confirmed from dispersibility of reduced graphene platelets in organic medium, which depends on the degree of deoxygenation of GO platelets.³ It is known that GO platelets can well dispersed in polar water, while rGO platelets can easily dispersed in dimethylformamide (DMF).⁵ In the dispersion stability test in DMF, platelets in rGO-b sample agglomerated and precipitated within one day. In contrast, the platelets in MR-60 sample were well dispersed and remained stable even after 1 month (Fig. S4), which is an additional evidence for highly deoxygenated graphene platelets.

Thermal stability test

Thermogravimetric analysis (TGA) (Fig. S5 a&b) shows that the weight loss by MR-60 was much less (13.2 wt% loss) compared to the rGO-b (22 wt% loss) and GO (80 wt% loss) when heated to 800 °C in nitrogen atmosphere, revealed high thermal stability of MR-60 presumably due to high level of deoxygenation and enhanced Vander Waals forces between layers.⁶

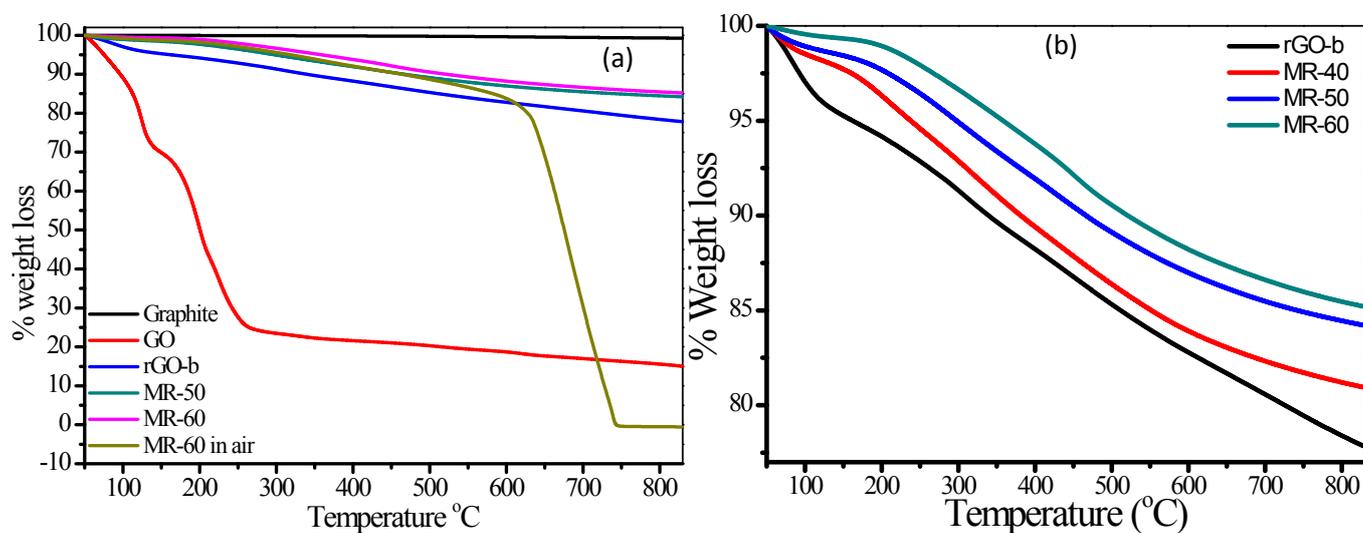
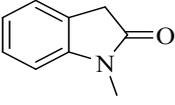
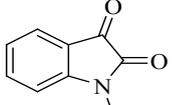
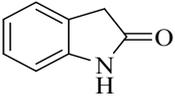
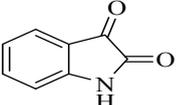
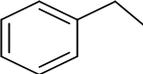
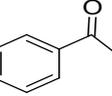
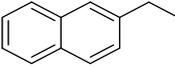
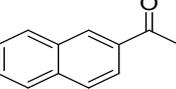
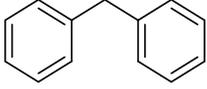
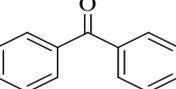
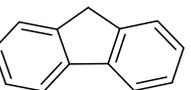
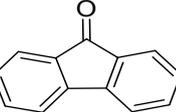
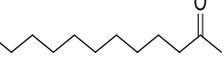
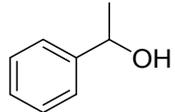
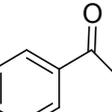
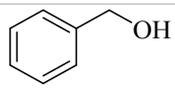
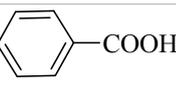
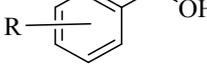
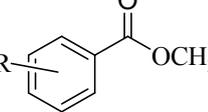
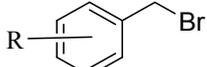
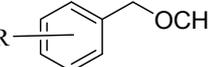
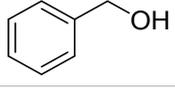
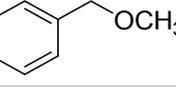
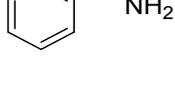
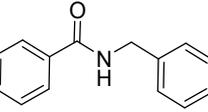


Fig. S5. Thermal decomposition behaviour of different graphite derivatives; (a) TGA of graphite, GO, rGO-b, MR-50, MR-60; (b) detailed weight loss behaviour of different reduced graphene oxide samples.

Electrical conductivity measurements. Three samples pellets were measured for the electrical conductivity of graphite (~45500 S/m), rGO-B (~1630 S/m), and MR-60 (~9035 S/m) by using the standard 4-point contact method.² Surprisingly, the result revealed that the electrical conductivity of the MR-60 samples is enhanced by 5 fold compared to the rGO-b samples. Improvement of conductivity reveals that graphene oxide is highly reducing by the using simple microsonochemical process.

Table S3: Comparative selective oxidation study of C-H bond compounds.

Entry	Reactant	Product	Catalyst	Time [h]	Conv. [%]	Select. [%]	Ref.
1			MR-60 ^a Cobalt(II) Schiff's base ^b	12 3	96 -	92. 94	This study ⁷
2			MR-60 ^a Cobalt(II) Schiff's base ^b	10 3	73 -	74 67	This study ⁷
3			MR-60 ^c ZJU-18 ^d LCN-8.9 ^a MnCl-TPyP ^e MR-60 ^f	12 18 24 12 0.66	99 99 98.6 -	92 99 91.3 73.6 95	This study ⁸ ⁹ ¹⁰ This study
4			MR-60 ^c LCN-8.9 ^a	12 24	99 99	95.3 95.9	This study ⁹
5			MR-60 ^c ZJU-18 ^d LCN-8.9 ^a	12 18 24	99 18 99	97 99 99	This study ⁸ ⁹
6			MR-60 ^c ZJU-18 ^d LCN-8.9 ^a	16 18 24	99 43 97.6	92 99 97.5	This study ⁸ ⁹
7			MR-60 ^c Mn-ALPO ^g	40 24	70 16	48 3.2	This study ¹¹
8			MR-60 ^c 0.5%Pd@C ^h	10 11	99 16.6	99 95	This study ¹²
9			MR-60 ⁱ Au/C ^j	12 12	99 99	99 99	This study ¹³
10			R = H; MR-60 ^k R = H; Co ₃ O ₄ /C@N ^l R = H; Pd ^m R = CH ₃ , Au ⁿ R = H; Ir ^o R = OCH ₃ , Cu ^p	12 24 24 24 24 24	99 - - - - -	85 97 99 99 75 95	This study ¹⁴ ¹⁵ ¹⁶ ¹⁷ ¹⁸
11			MR-60 ^q FeSO ₄ ^r	12 12	99 22	99 -	This study ¹⁹
12			MR-60 ^q Re (I) ^s	12 12	99 99	99 99	This study ²⁰
13			MR-60 ^c Ru(COD)Cl ₂ ^t	12 32	75 -	68.3 21	This study ²¹

Reaction conditions: [a] substrate (1.0 mmol), catalyst (0.03 g), TBHP (3.0 mmol, 65 % in water), water (3 mL), at 80 °C, [b] substrate (1.0 mmol), catalyst (1 mmol), oxygen stream, 100 ml methanol; [c] substrate (0.5 mmol), catalyst (0.03 g), TBHP (1.5 mmol, 65 % in water), water (1.5 mL), at 80 °C; [d] substrate (0.1 mmol), catalyst (0.005 mmol), TBHP (0.15 mmol), acetonitrile (1 mL), acetic acid (0.2 mL), and water (0.2 mL), at 65

°C; [e] substrate (0.1 mmol), catalyst (0.5 mmol), TBHP (0.5 mmol), water (5 mL), at 80 °C; [f] microreactor condition; [g] dodecane (49.7 g), catalyst (0.5 g), air 1.5 MPa, at 373 K; [h] substrate (4 mL), catalyst (20 mg), air 1 atm, temperature 120 °C; [i] substrate (0.5 mmol), catalyst (0.03 g), TBHP (5 mmol, 65 % in water), water (1 mL), at 80 °C; [j] substrate (1600 mol), catalyst (1 mol), air 1 atm, at 60 °C; [k] substrate (0.5 mmol), catalyst (0.03 g), TBHP (6.0 mmol, 65 % in water), methanol (0.5 mL) at 80 °C; [l] substrate (0.5 mmol), catalyst (2.5 mol% Co), 1 bar O₂, 0.2 Equivalent K₂CO₃, 60 °C; [m] 0.5 mmol of benzylic alcohol, 5 mol%, Pd(OAc)₂, 2 eq. Na₂CO₃, 2 mL of MeOH, 40 °C, in air; [n] Substrate (0.5), PI-Au (1 mol %), MeOH:water (500:1), K₂CO₃ (0.5 mol), O₂ (1 atm) at RT; [o] Substrate (2 mmol); methanol (8 mmol); Ir complex (0.04 mmol), MAE (0.12 mmol), and base (0.1 mmol) in acetone (1 mL) at rt (ca. 25 °C); [p] substrate (0.3 mmol), catalyst (20 mol), TBHP (1.8 mmol), DMSO (2 mL), additive (0.12 mmol) base (2 equivalent) at 120 °; [q] substrate (0.5 mmol), catalyst (0.03 g), methanol (0.5 mL) at 80 °C; [r] substrate (3 mmol), catalyst (1 equivalent), methanol (5 mmol) at 110 °C; [s] 1.0 mmol of substrate, 5.0 mmol of methanol, and 0.03 mmol of ReBr(CO)₅, at 160 °C; [t] 5% Ru(COD)Cl₂, 5% salt, 20 % KOtBu, 5% PCyP₃HBF₄, mesitylene at 163 °C.

Catalyst Recycling test:

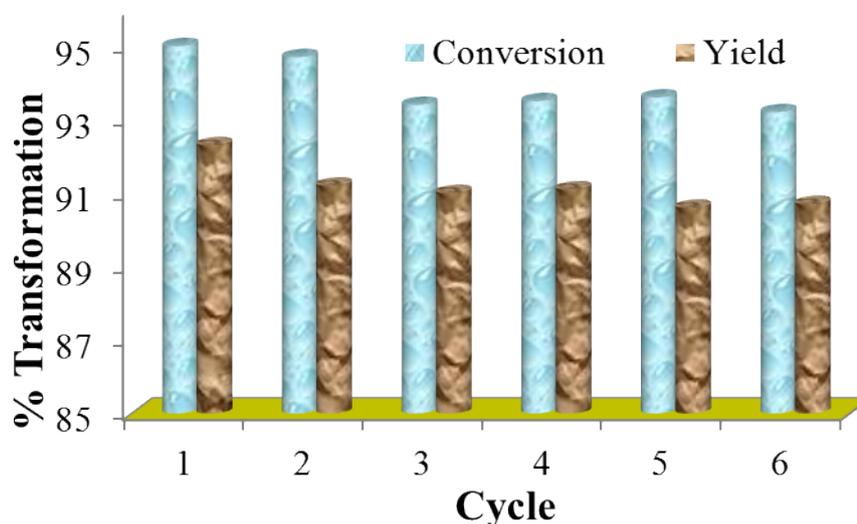


Fig. S6. Recovery and reuse of MR-60 catalyst.

Table S4: Catalyst recovery in every cycle.

Cycle	Reactant (mmol)	Catalyst amount (g)	Recovered catalyst amount (g)
1	0.1	0.03	0.029
2	0.1	0.029	0.029
3	0.1	0.029	0.029
4	0.1	0.029	0.028
5	0.1	0.028	0.028
6	0.1	0.028	0.028

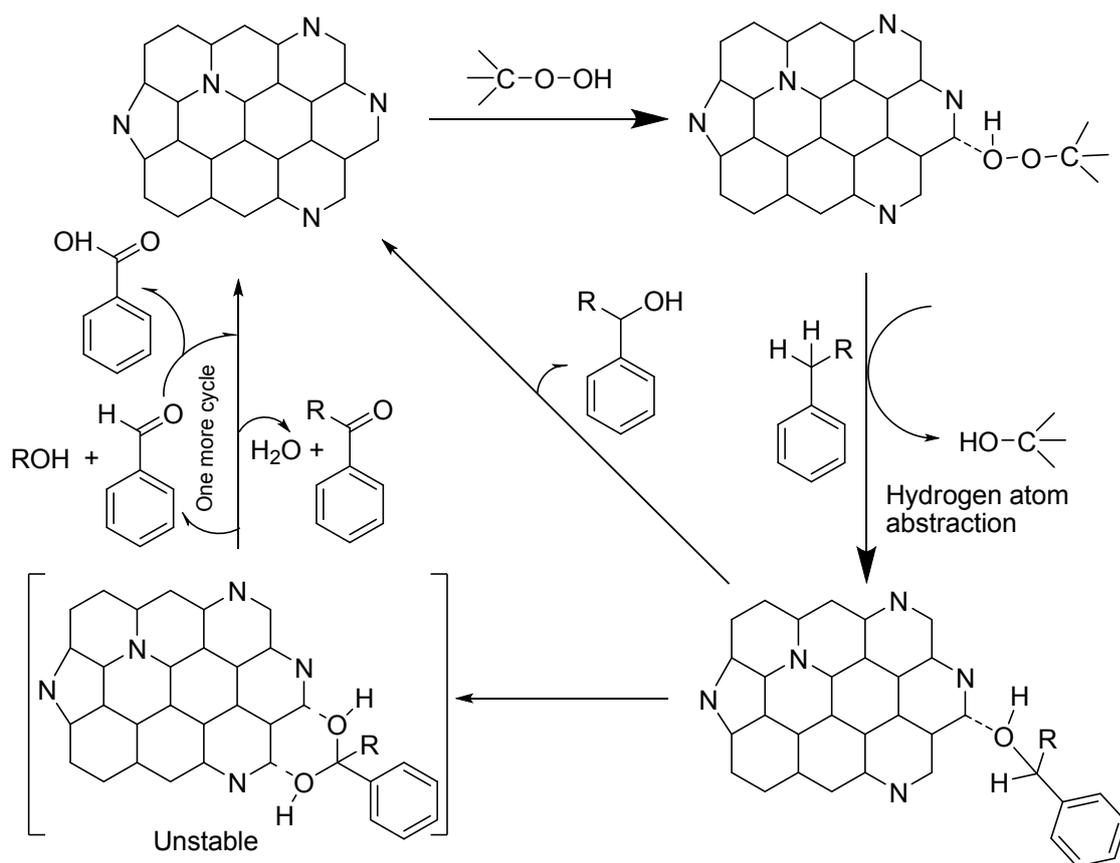


Fig. S7. Proposed radical reaction mechanism for the oxidation of C-H bond activation, based on the previous N-doped graphene report.⁹

Catalytic reaction under microreactor: A typical microreactor setup is as shown in Fig. S8, it contains a sonicator heated at 65 °C and an oil bath heated at 80 °C. For oxidation of ethylbenzene, a solution of ethylbenzene (1 mmol) in CH_2Cl_2 (0.9 mL), water 3 mL, *tert*-butyl hydroperoxide (TBHP) (3.00 mmol in 65% in water) and MR-60 catalyst (0.03 g) were introduced in to the capillary microreactor (inner diameter (id) 500 μm , length 20 cm) with a X-junction using three separate syringe pumps. The flow rate of the water and TBHP (6 $\mu\text{l}/\text{min}$) was kept three times the rate of ethylbenzene (2 $\mu\text{l}/\text{min}$), in accordance with the stoichiometry of the reagent and substrates. After mixing of MR-60 catalyst and ethylbenzene in X-junction blocking problem was encountered due to heterogeneous catalyst system. To overcome the blocking problem the X-junction and tubing were kept in ultrasonic bath (power 330 W, frequency 40 KHz, 65 °C for 5 min.) and resulting reaction mixture smoothly

passed through PTFE tubing (volume 40 μL , time 5 min), and continuously transferred to additional set of PTFE tubing (id 500 μm , length 143 cm, volume 280.77 μL , time 35 min) for the completion of reaction. A residence time of 35 min was found to be enough for oxidation of ethylbenzene. After completion of reaction, 10 mL CH_2Cl_2 and internal standard anisole (1.0 mmol) were added and centrifuged for 10 min to separate the catalyst. Ethylbenzene was completely converted to acetophenone with high selectivity as analyzed by GC-MS.

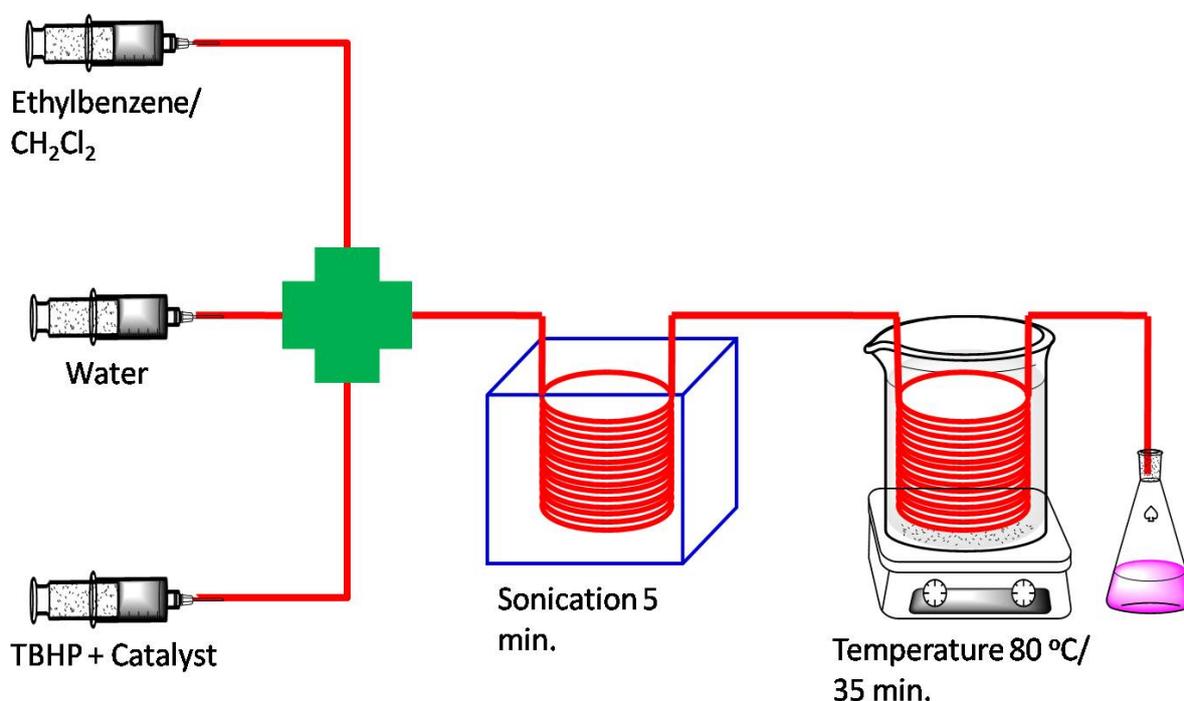


Fig. S8. Schematic presentation of selective catalytic oxidation of ethylbenzene via continuous flow microreactor process.

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