Electronic Supplementary information (ESI)

Few-Layer Graphene-Graphene Oxide Composite containing Nanodiamonds as Metal-Free Catalyst

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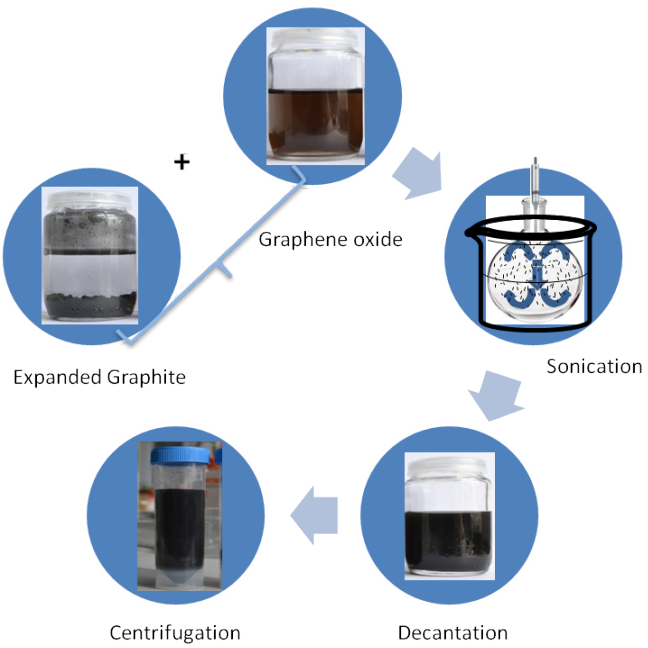
1. Synthesis of graphene oxide (GO) and GO-mediated exfoliation of expanded graphite (EG) in water

Graphene oxide (GO) powder was prepared from graphite flakes using modified Hummers method [1, 2]. Briefly, 5 g of graphite (Sigma-Aldrich, cat # 332461, ~ 150 μm) and 3.75 g of $NaNO_3$ were placed in a flask. Then, 375 mL of H_2SO_4 (95%) was added dropwise while the system was kept under stirring in an ice-water bath, and 25 g of $KMnO_4$ were slowly added during 1 h. Stirring was continued for 2 h in the ice-water bath. The ice bath was then removed and the mixture was stirred at room temperature until it became pasty brownish and then 250 mL deionized (DI) water was slowly added to the system. The reaction temperature was rapidly increased to 98°C, and the color changed to brown after 2 h. Finally, 15 mL of 30 wt% aqueous solution of H_2O_2 was added to complete the oxidation process. The ions of oxidant and other inorganic impurities were removed by repeating cycles of centrifugation, followed by the removal of the supernatant liquid, and the solid was redispersed using 3 wt % HCl aqueous solution. After filtration, the solid was dispersed again in water using ultrasonication for 2 h and centrifuged at 6000 rpm for 30 min to remove the multilayered- carbon species.

For the synthesis of FLG-GO complex, GO suspension with a concentration of 1 mg/mL was obtained by dispersing GO powders in distilled water with the aid of ultrasonic bath for 30 min. Then the mixture of EG/GO with different weight ratios, i.e. 1:1, 3:1 and 5:1 were subjected to sonication. The typically procedure is the following: 600 mg of expanded graphite (EG) dispersed in 280 mL DI water was placed in a 500 mL capped-round bottom flask and pre-sonicated with a tip sonicator with a power of 30 W for 30 min to swelling the EG. It was then mixed with a 200 mL GO suspension (1mg/mL) and followed by sonication for various time, from 1 to 5 hours. The reaction temperature was kept at around 40-50 °C by adding water to the sonicator bath. After the sonicating step, the as-prepared suspension was left to stand 2 days for settling down unstable expanded graphite aggregates, and the supernatant was extracted by pipette, and then further centrifuged at 3000 rpm for 30 min. The aqueous GO-stabilized FLG with a concentration of 0.35 mg/mL is turned out to be a stable suspension for few days without any observable aggregation. It was then used for characterization and further application.



Schematic1. Solution-processed few-layer graphene/graphene oxide by exfoliating expanded graphite in the presence of GO suspension under sonication.

Reference:
1. W. S. Hummers, R. E. Offeman. Preparation of graphitic oxide. *J. Am. Chem. Soc.* 1958, 80, 1339.
2. Y. Liang, D. Wu, X. Feng, K. Mullen. Dispersion of graphene sheets in organic solvent supported by ionic interactions. Adv. Mater. 2009, 21, 1679-83.

2. Self-organized decoration of nanodiamonds on the surface of FLG-GO

The commercial nanodiamonds (NDs) with diameter in the range of 4-10 nm in a powder form were supplied by the Hightech Co (Finland) and were used without any further purification. For the preparation of a FLG-GO@NDs composite, typically 200 mg pristine NDs was dispersed in 200 mL DI water and sonicated with a tip sonicator for 15 min. It was then well-mixed with a 286 mL of the as-synthesized FLG-GO complex suspension (0.35 mg/mL) by droplet under stirring condition. Nanodiamond particles were steadily absorbed homogeneously on the surface of FLG-GO sheets and the formed composite was settled down after few minutes. The mixture was then filtered and dried in the oven at 100 °C for 6 hours to get the constant weight of FLG-GO@NDs composite.

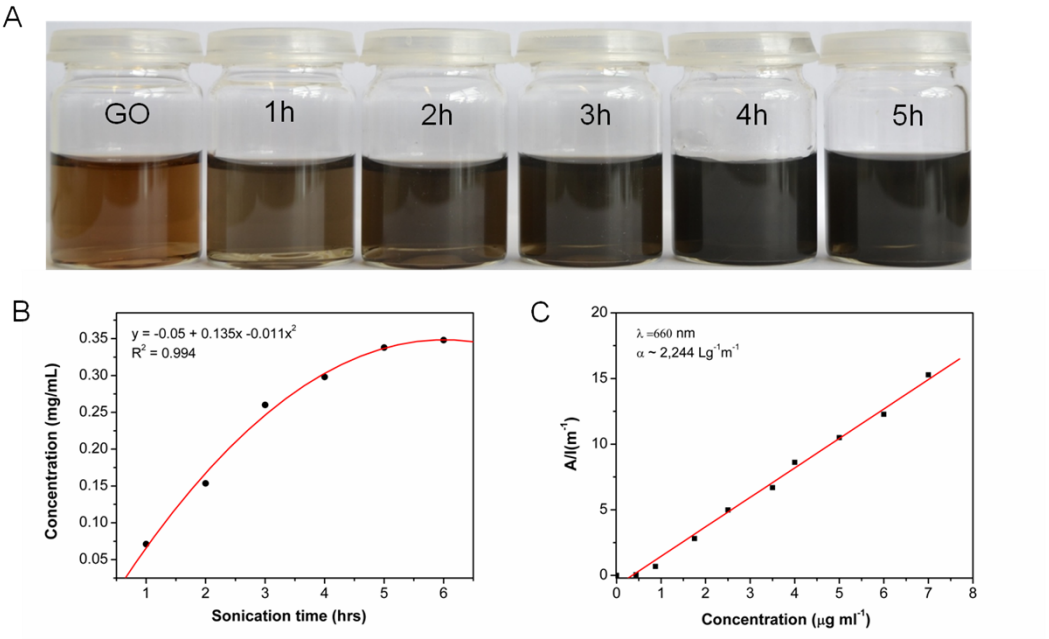


Figure S1. A digital photo of diluted FLG-GO complex suspension as a function of sonication time (A), their concentration (B), this curve has obtained from the absorbance value as a function of concentration. The linear fit (C) confirms the Lambert-Beer behavior with an average absorption of α =2,244 $Lg^{-1}m^{-1}$ by recording the diluted 50 times of maximum concentration at optical absorbance of 660 nm.

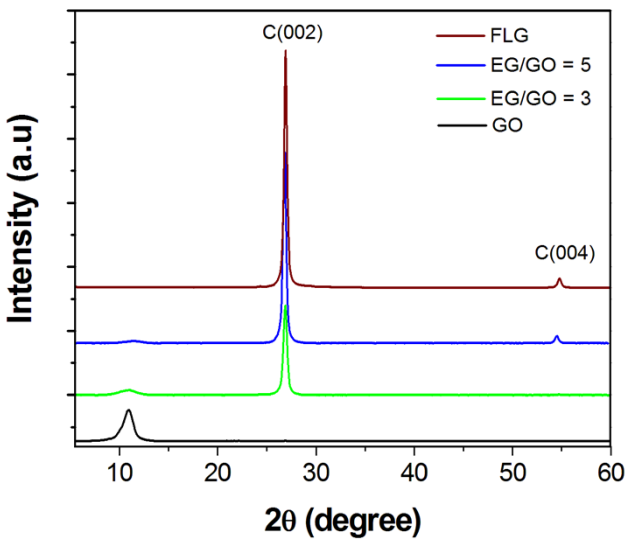


Figure S2. The XRD patterns of different EG/GO mixtures with different EG/GO weight ratio as compared to GO and FLG

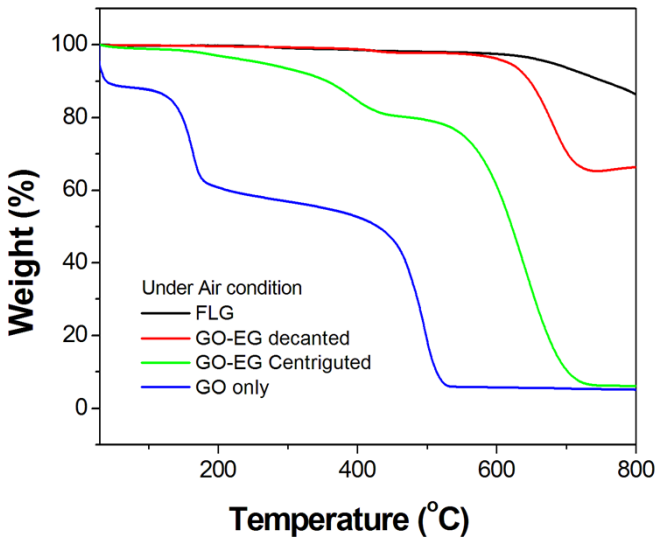


Figure S3. TGA curves of FLG-GO complex (green), as compared to GO (blue), sediment GO-multilayer graphene (red) and expanded graphite (black).

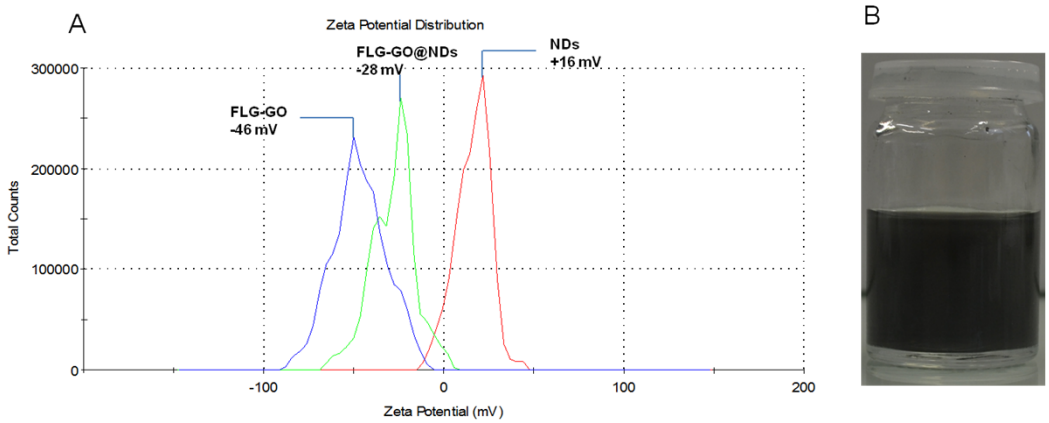


Figure S4. (A) Zeta potential distribution confirms the electrostatic interaction between FLG-GO and NDs, (B) a digital photo showing no NDs are adsorbed on the FLG surface.

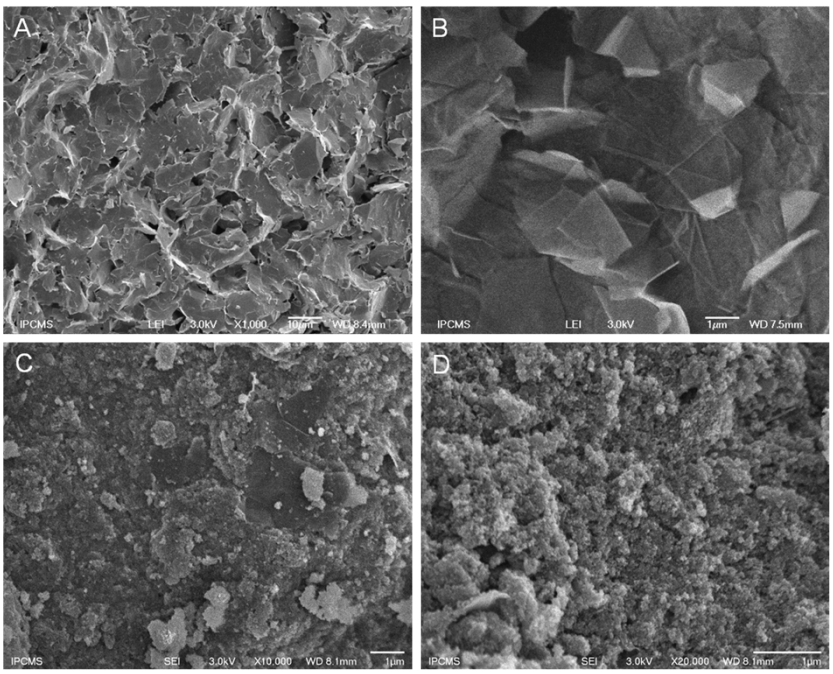


Figure S5. SEM images of FLG-GO complex powders (A, B), nanodiamond particles adsorbed on the surface of FLG-GO (C, D).

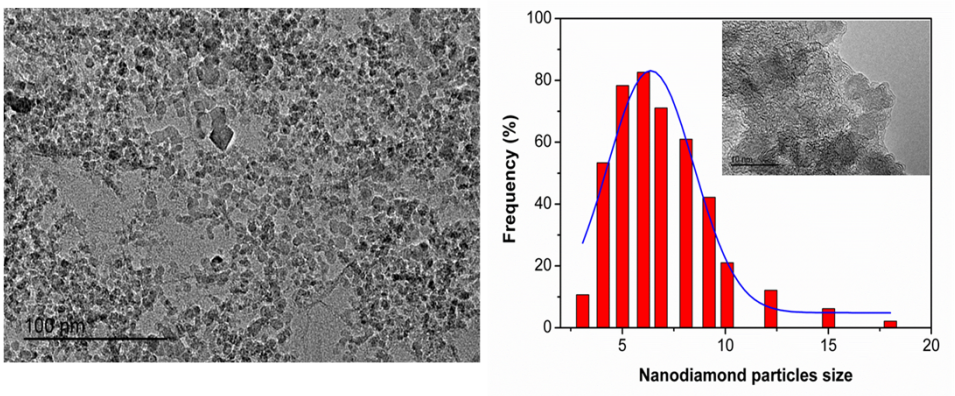


Figure S6. Representative TEM micrograph of the ND/GO/FLG and frequency distribution of ND particles size on the surface of FLG-GO complex using *Image-Pro plus* software measured from TEM images

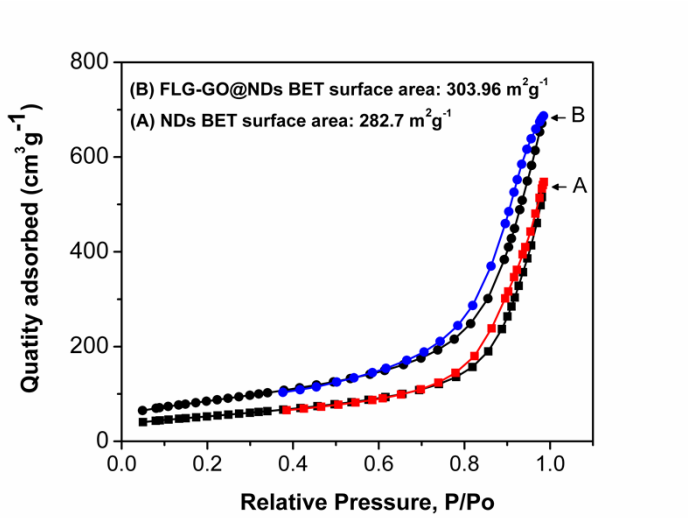


Figure S7. Nitrogen absorption-desorption isotherms of pristine NDs (A) and FLG-GO@NDs composite (B).

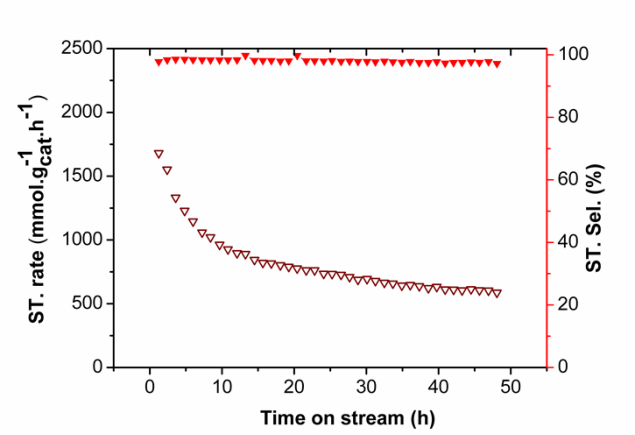


Figure S8. DH activity of the controlled GO@NDs composite (without FLG)

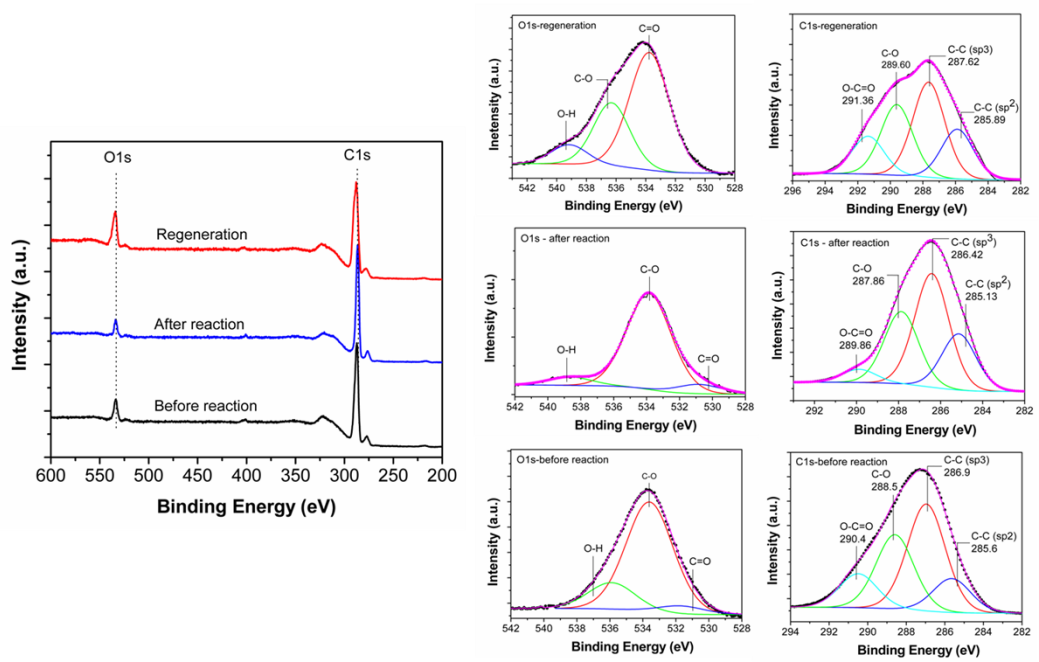


Figure S9. XPS measurements showing the structural changes between carbon and oxygen species during the dehydrogenation test.

A

Sample	O-C (At.%)	O=C (At.%)	O-H (At.%)
As-received FLG-GO@NDs	42.48	27.1	30.4
Pre-treated at 550 °C FLG-GO@NDs	79.28	13.81	7.91
After using FLG-GO@NDs	78.2	13.88	7.92

B

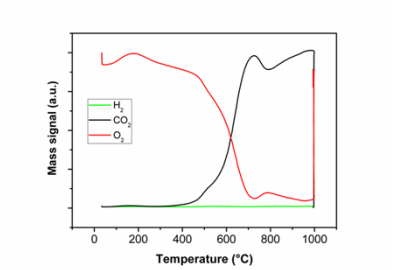


Figure S10. A compared O1S XPS component of catalytic materials before and after reaction (A). A TPO spectrum of post-reaction catalyst (B)