Supplementary information

Derivatization and Interlaminar Debonding of Graphite-Iron Nanoparticles Hybrid Interfaces Using Fenton's Chemistry

Neha Agarwal^a, Ruma Bhattacharrya^a, Narendra K. Tripathi^a, Sanjay Kanojia^a, Debmalya Roy^{a*}, Kingsuk Mukhopadhyay^a and Namburi Eswara Prasad^b

^a Directorate of Nanomaterials and Technologies, DMSRDE, GT Road, Kanpur, India

^b Director, DMSRDE, GT Road, Kanpur, India.



Fig S1: The schematic figure of the parentage of oxygenated species produced (%O1S) in graphite lattices by sonication in DI water at different concentration (blue squares) and time (red dots). The optimized 0.4 mg/ml concentration of graphite powder in DI water and 60 minutes of sonication time were selected for this study for economical and faster rate of reaction.



Fig S2: The comparative C-1S (A) and O-1S (B) XPS spectra for the starting graphite powder (black triangles) and sonicated graphite powder in DI water (blue circulars). The comparative TGA (C) spectra of the starting graphite powder (black triangles) and sonicated in DI water (blue circulars). Both XPS and TGA revealed that all types of oxygenated functional groups (C-OH, C=O, C-O-etc.) were introduced by sonication of the graphite powder in de-ionized water where the functional groups generated are 10-15 weight percentage of graphite.



Fig S3: Fe core level (2p) level XPS spectrum (A) of metal nanoparticles decorated graphite matrix where the small hunch at 706.7 eV indicates iron nanoparticles and the peaks around 710 eV indicates iron oxide nanoparticles. The scanning electron microscope (SEM) images and the transmission electron microscope (TEM) images of the nanoscale organic-inorganic interfaces (B and D) by sonication of graphite in DI water and the morphology for washed graphene with HCl/H_2O_2 followed by further sonication in DMF (C and E) respectively.



Fig S4: AFM surface curvature parameters (A) for measurement of thickness of graphene layers after sonication of Fenton's product in DMF and the surface topography of the standard graphene film casted on the HOPG substrate (B). Assuming that the deposited graphene film is uniform both in terms of composition and in thickness, the maximum fifteen numbers of layers have been calculated from the surface curvature parameters in the AFM experiment.



Fig S5: The comparative EDX spectra of the Fenton regent treated product (A) and the product after washing with hot HCl containing H_2O_2 followed by centrifugation and sonication in DMF (B). The EDX analysis confirms that the iron nanoparticles could be removed from the graphene flakes by washing, centrifugation and sonication.



Fig S6: The Comparative resistances of the free standing film made out of GO (black square), edge functionalized few layers graphene which is free from metal nanoparticles (red circles) and Fenton reaction product which has at least 15 weight percentage iron clusters by weight (blue triangles). The powder samples were mixed with aqueous solution of cetyltrimetylammonium bromide (CTAB) (5% by weight) and stirred for 15 minutes. The concentration of the aqueous solution is maintained at 0.5 mg/ml and solution is sonicated for 15 minutes to get the uniform stable aqueous dispersion. The free-standing films were prepared by vacuum filtered of aqueous colloidal suspension through Whatman Anodisc membrane filter (47 mm, 0.2 μm pore). The films were peeled off from the support and further dried in an oven at 60 °C overnight. The resistance measurements at different temperatures of the films were performed using four-probe resistance measurements in the temperature range of 20-300°C. Keithley's current source model-220 and a nano-voltmeter model-2182 were used to record the resistance at different temperatures. The ohmic contacts were made by silver paste.



Fig S7: The VSM results of the Fenton's reagent treated graphite (A) and the product after washing with hot HCl containing H_2O_2 followed by centrifugation and sonication in DMF (B) respectively at room temperature. The produced edge functionalized few layers graphene were found to be embedded with iron and iron oxide nanoparticles which developed a magnetic character in the intrinsic non-magnetic graphene.



Fig S8: Reflection loss vs Frequency in Ku band region of gigahertz frequency range of the neat epoxy (black squares), 1 weight percentage added Fenton's reagent treated graphite in epoxy (red triangles) and 1 weight percentage metal free FLG flakes in epoxy (blue circles) respectively. It was found that specifically at frequency 14.2 GHz there was sharp microwave absorption for Fenton's treated graphite compared to metal free FLG flakes and neat epoxy. This highlights the importance of the introduction of magnetic nature in graphene by the embedding iron nanoparticles.



Fig S9: The comparative FT-IR spectra of the starting graphite powder (black), sonicated graphite in DI water (blue) and Fenton's reagent treated graphite (red) respectively. It was found that sonication introduced functional groups in the graphite surfaces. The FT-IR spectrum showed that the Fenton's treated graphite generated mainly hydroxyl functional groups.



Fig S10: The MALDI spectrum of the Fenton reaction products after 48 hours (A, black) and after 120 hours (B, blue) of graphite respectively. It was found that longer reaction time produced low molecular weight masses from graphite similar to that of GO [reference 38]. Processed spectra of all samples were analyzed in Bruker Maldi TOF system & Polytools 1.0 software. The matrixes HCCA, DHB, SA were used and for the ionization sodium trifloroacetate was used. The sample and matrix along with salt were applied onto a spot on ground steel.



Fig S11: The line scans of the successive D, G and 2D bands of Raman intensities of normal GO (A) and the few layers graphene flakes by Fenton's reagent (B) where the scan direction is from 1 to 14 or 15. The line scans of no. 1 and 2 does not yielded any spectrum as it falls outside the graphene flake for Fenton reagent treated sample. For micro Raman studies, the samples were dispersed well in alcohol by sonication and drop cased on the pre-cleaned atomically smooth silicon wafer. The samples were dried in vacuum at room temperature and the dried samples were subjected to Raman analysis using a Renishaw Raman Microscope with Ar-ion laser excitation at 514 nm using 50 mW power. The lower D and 2D band intensities may be attributed to the feeble film of graphene on the Silicon wafer and the few layers configuration of graphene morphology.