Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

for

Graphene Oxide: an Efficient and Reusable Carbocatalyst for Aza-Michael Addition of Amines to Activated Alkenes

S1: Experimental Section

Synthesis of Graphene oxide: In a typical experiment, graphite powder (2.5 gm), $NaNO_3$ (2.5 gm) and H_2SO_4 (115 ml) were mixed in reaction vessel. $KMnO_4$ (15 gm) was added gradually under stirring conditions on ice bath and then reaction mixture was at room temperature for 24 hours under contineuos stirring. Subsequently, 200 ml water was added slowly and temperature of the reaction mixture was raised to 98 °C using an oil bath. After another 24 hours, 500 ml water was added, followed by addition of 30% H_2O_2 (50 ml). Finally, oxidation product was filtered and purified by rinsing with 125 ml of 5% HCl solution. The filtrate cake was repeatedly washed with copious amount of HPLC grade water until the pH was about 6. This processed dark brown oxidized material was dried in oven at 90 °C. The dried product was grounded with a mortar and pestle to the fine powder. Dispersion of Graphene oxide powder in water (0.05 mg/ml) was made by sonication and used as carbocatalyst.

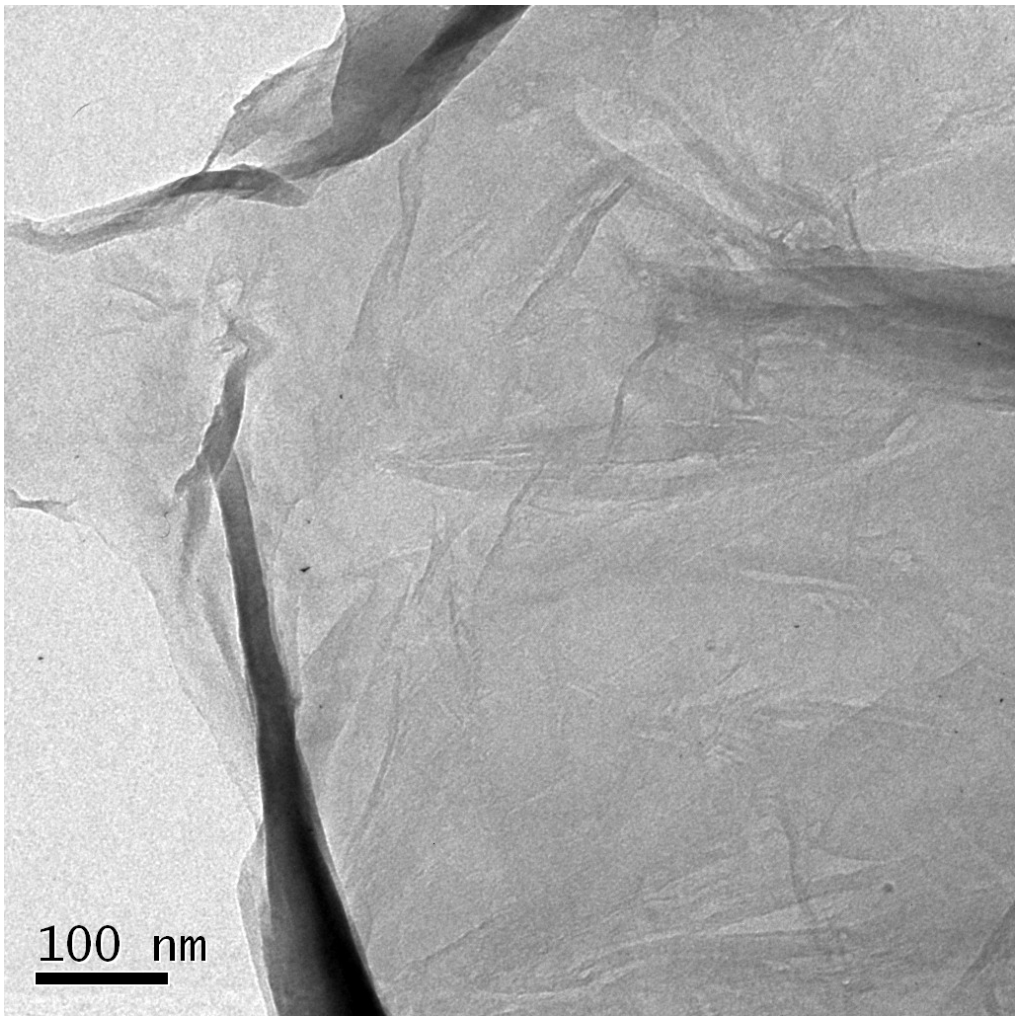
General experimental procedure for aza-Michael addition reaction: A reaction mixture containing amine (1 mmol), α,β-unsaturated compound (1.2 mmol) and carbocatalyst in water (0.5 ml) was stirred at room temperature. The completion of the reaction was monitored by TLC (SiO2). After completion of the reaction, the reaction mixture was diluted with dichloromethane followed by subsequent separation of organic and aqueous layers by separating funnel. Organic layer was dried over MgSO4 and concentrated under reduced pressure and obtained crude product was purified by column chromatography using EtOAc/hexane (6:4) as eluent.

S2: Graphene Oxide Characterization by HR-TEM

In order to further probe the morphology and dispersion of Graphene oxide, HR-TEM measurement was performed. Aqueous dispersion of graphene oxide was used for HR-TEM. Bends and wrinkles on graphene oxide nanosheets at several places as can be seen in Figure

S1 are originated by various defects and functional groups carrying sp^3 hybridized carbon atoms, which are introduced during the oxidation process. In general, graphene oxide nanosheets tend to assembled with each other and forms multilayer agglomerate. However, in HR-TEM image, the presence of topological features along with overlapping area of graphene oxide nanosheets reveals that they are highly dispersed in water.

Figure S1: HR-TEM image of graphene oxide nanosheets

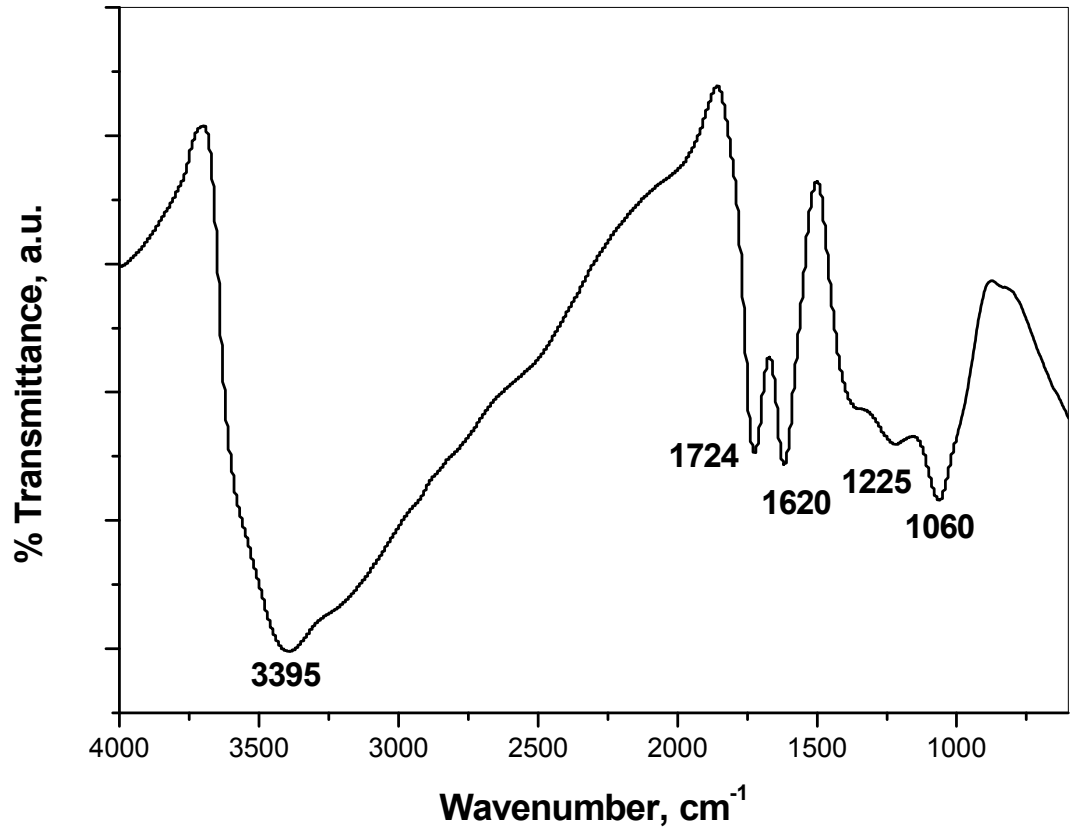


S3: Graphene Oxide Characterization by FTIR

Figure S2 shows FTIR transmittance spectra of graphene oxide in KBr. An intense and broad peak centred at 3395 cm^{-1} attributes to the stretching mode of O-H bond. The O-H groups in

graphene oxide bonded to the various sites of carbon skeleton varying from sheets centre to its border, which may cause shifts in frequency of O-H vibration, resultant peak broadening. The presence of intercalated water molecules between graphene oxide sheets also participate in broadening of O-H band. The strong band at 1724 cm^{-1} attributes to stretching vibration of C=O in carboxylic acid and carbonyl groups. The peak at 1620 cm^{-1} was assigned to the vibrations of the adsorbed water molecules and also the contributions from the skeletal vibrations of unoxidized graphitic domains. The band at 1225 cm^{-1} is usually attributed to the C-OH stretching vibrations and band at 1060 cm^{-1} assigned to C-O(epoxy) groups.[S1-S4]

Figure S2: FTIR transmittance spectra of graphene oxide



S4: References

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