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Electronic Supplementary Information

Cooperative catalysis by Acid-Base Bifunctional Graphene

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Experimental Section

Preparation of acid-base bifunctional Graphene Oxide hybrids

Graphene oxide (GO) was prepared and purified by Hummers method,[1] and the resulting suspension was obtained by dispersing GO (300 mg) in ethanol (150 mL) under sonication. Then, excess of 3-[2-(2-Aminoethylamino) ethylamino] propyl-trimethoxysilane (AEPTMS) (3 mmol, 0.885 g) was added to the obtained GO suspension, and refluxed for 6 h at 78 ^{o}C with continuous stirring. The yielded suspension was filtered and washed with ethanol for several times to get a purified GO–AEPTMS suspension.

4-Benzenediazoniumsulfonate was synthesized by diazotization of sulfanilic acid. Sulfanilic acid (2.082 g, 12 mmol) was dispersed in 1 M HCl aqueous solution (60 mL) with continuous stirring at 3–5 ^{o}C in a three-necked ground flask. Then, 10 % excess of $NaNO_2$ (13.2 mmol) was added slowly, and a clear solution was obtained after all the $NaNO_2$ was added. After stirring for another 1 h at the same temperature, the white precipitate formed was filtered off and washed with deionized water. 4-Benzenediazoniumsulfonate obtained was then mixed with the GO–AEPTMS and stirred for 1 h at room temperature, followed by washing with deionized water and ethanol.

Catalytic ability towards Deacetalization–Nitroaldol reaction

The catalytic ability of the acid-base bifunctional graphene oxide was examined through the Deacetalization–Nitroaldol reaction. This reaction was carried out in a mixture of benzaldehyde dimethyl acetal (2 mmol) and Nitromethane (CH_3NO_2, 10 mL) at 90 ^{o}C under N_2 atmosphere for 4 h. The GO–AEPTMS/SO_3H hybrids (40 mg, ~0.072 mmol of amine) as catalysts were added. The mixture was extracted with ethyl acetate (3×10 mL) after reaction, and dried over anhydrous sodium sulfate (Na_2SO_4). The resulting mixture was analyzed by gas chromatography (GC).

Characterization

The samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR, Thermo Nicolet Nexus FTIR), X-ray Photoelectron Spectroscopy (XPS, Perkin-Elmer, PHI 1600 spectrometer), Raman Spectroscopy (NT-MDT NTEGRA Spectra), Scanning Electron Microscopy (SEM, Hitachi S 4800), Energy Dispersive X-ray Spectroscopy (EDS, Hitachi S4800) and atomic force microscopy (AFM) (CSPM 5000). The catalysis results were measured by GC (Agilent 6890N GC-FID system).

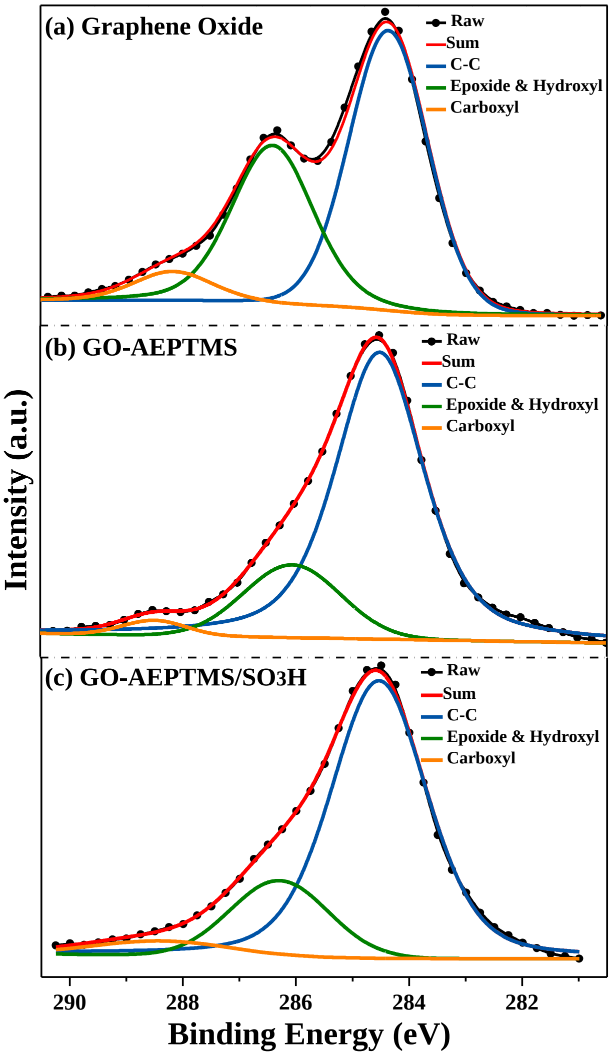

Figure 1S. C 1s XPS spectra of (a) GO (b) GO–AEPTMS hybrids and (c) GO–AEPTMS/SO_3H hybrids, respectively.

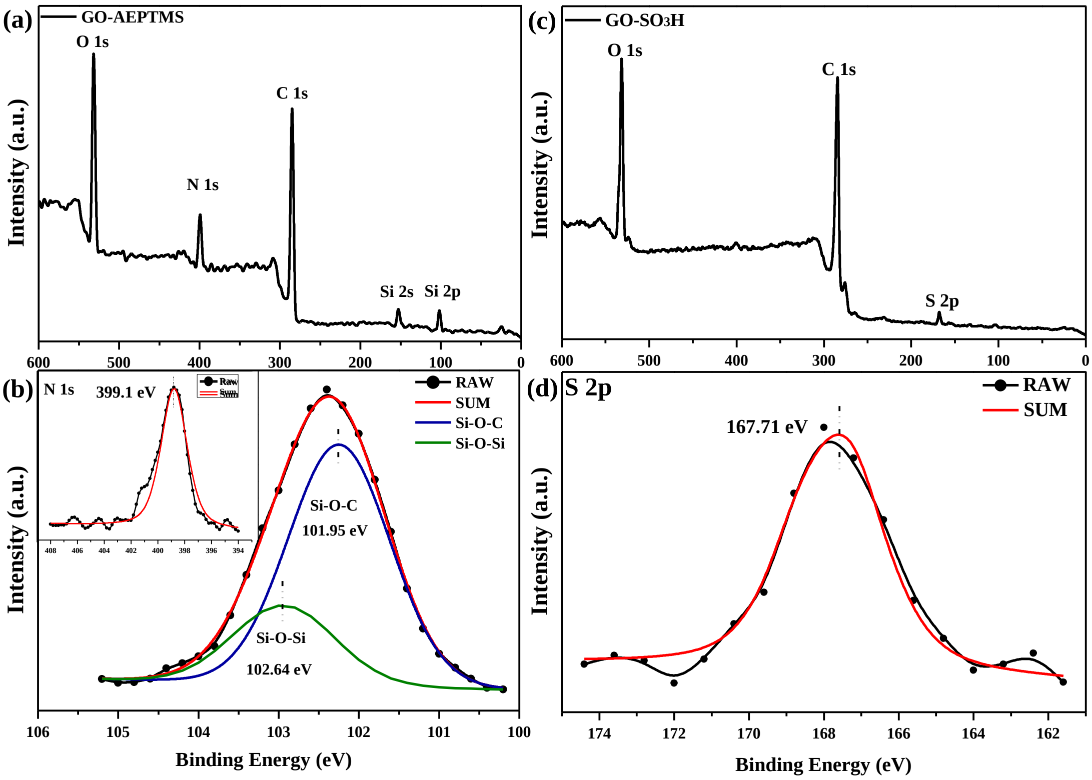

Figure 2S. (a) Full range, (b) Si 2p and (insert) N 1s XPS spectra of GO–AEPTMS hybrids, as well as (c) full range and (d) S 2p XPS spectra of GO–SO$_3$H hybrids. The peak area ratio of Si–O–C in Si 2p of GO–AEPTMS is 75.7 %.

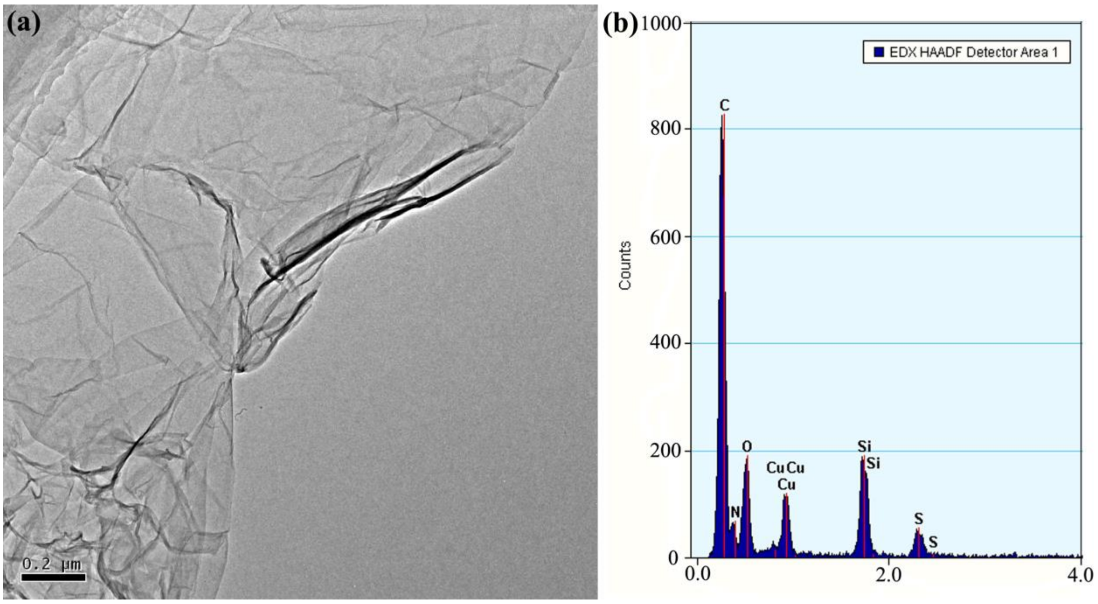

Figure 3S. (a) Typical TEM image of GO–AEPTMS/SO$_3$H hybrids, and (b) corresponding EDX result.

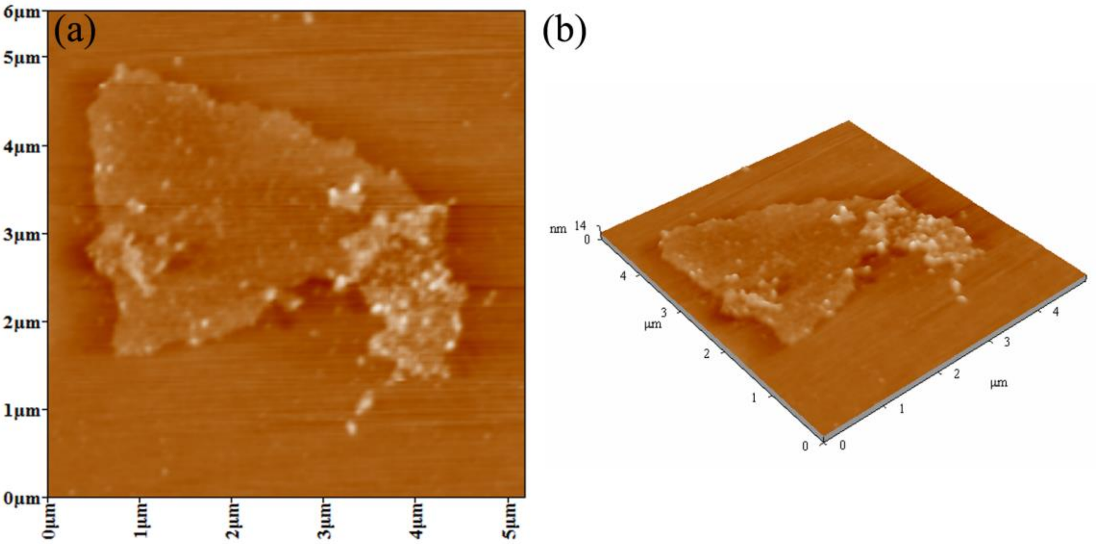

Figure 4S. AFM image of (a) GO–AEPTMS/SO_3H, and (b) corresponding 3D image.

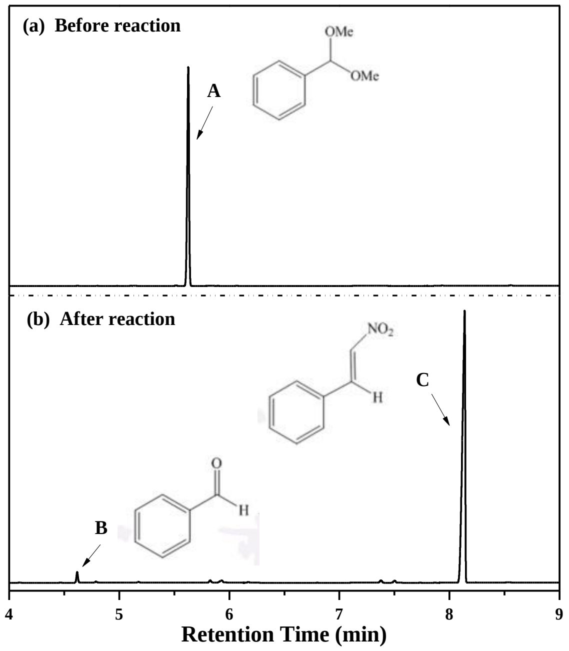

Figure 5S. GC results (a) before and (b) after Deacetalization–Nitroaldol reaction sequence.

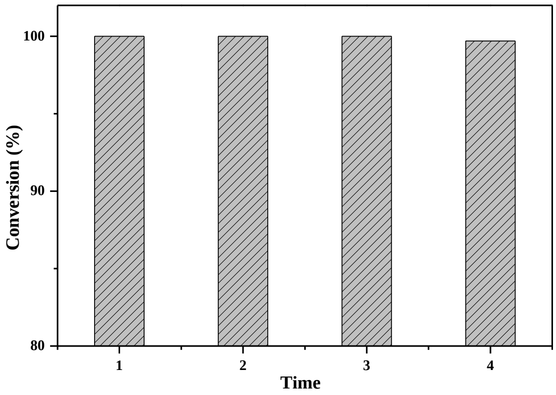

Figure 6S. Reusability of the acid-base bifunctional catalysts

Table 1S. Deacetalization–Nitroaldol reaction sequence catalyzed by different hybrids under same reaction condition.

Catalyst	GO–SO_3H/AEPTMS	GO–AEPTMS	GO–SO_3H	GO	GO–AEPTMS /GO–SO_3H
Conversion of A (%)	56.5	100	100	60.3	trace
Yield of B (%)	56	16.95	95.84	52.81	trace
Yield of C (%)	0.5	15.64	0	0	0

Reference:

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, 80, 1339-1339.