

Electronic Supplementary Information (ESI) for
Synthesis and characterization of sulfonated graphene as a
highly active solid acid catalyst for ester-exchange reaction

Lin Wang^a, Dianlong Wang^{*a}, Suoqin Zhang^b and Hua Tian^{*b}

^a School of Chemical Engineering & Technology, Harbin Institute of Technology, No. 92, Xidazhi Road, Nangang District, Harbin 150001, China; E-mail: chinalinkwang@126.com, dlwang@hit.edu.com.

^b Department of Chemistry, Jilin University, No. 2699, Forward Street, Changchun 130012, China; E-mail: tianhuawl@yahoo.com.cn.

General information

All of reagents were purchased from Aladdin Company and used without further purification. The morphology and energy-dispersive X-ray spectroscopy elemental mapping of sulfonated graphene were observed on a field emission scanning electron microscopy (FESEM, Hitachi, S-4800, 15 kV). FT-IR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer by using KBr disks in the range of 4000–450 cm⁻¹. Raman spectra were obtained with a Renishaw Raman system model 1000 spectrometer. Thermogravimetric (TG) analysis was performed on a Perkin-Elmer STA 6000 with a heating rate of 10 °C min⁻¹ in a temperature range from 30 to 800 °C under atmosphere. The X-ray photoelectron spectrum (XPS) was carried out with PHI 5700 ESCA System and binding energies were calibrated using the C1s peak at 284.6 eV. Gas chromatograph (GC) analyses were made by a Shimadzu GC 9A gas chromatograph (carrier gas: N₂; injector: 240 °C; FID detector:

240 °C) on a HP-INNOWax capillary column (30 m). The initial temperature was 100 °C, the temperature ramp rate was 10 °C min⁻¹, and the final temperature was 240 °C. High Performance Liquid Chromatography(HPLC) measurements were performed at room temperature using Agilent 1200 Series enginery: Quaternary Pump G1311-90010, Multiple Wavelength Detector SL G1315-90012 and AgilentExtend-C18(4.6 x 250mm) column. Flash chromatography separations were carried out on columns using 230-400 mesh silica gel (petrol ether/ethyl acetate 8:1).

Experimental procedure for synthesis of graphite oxide and graphene

Graphite oxide was synthesized from natural graphite powders according to modified Hummers method[1]. 6.5 g of graphite powders was added into 150 mL of cold (0 °C) concentrated H₂SO₄, and then 19.5 g of KMnO₄ was added gradually with stirring and cooling, and the temperature of the solution was not allowed to go up to 20 °C. After the mixture was stirred for 40 min, 460 mL of distilled water was added slowly to an increase in temperature to 98 °C. The temperature was then held at 35±3 °C for 2 h. Subsequently, 1.4 L of distilled water and 100 mL of 30 % H₂O₂ solution were added, and then the slurry was held at room temperature for 24 h. The graphite oxide was collected by filtration, washed with 5 % HCl aqueous solution until sulfate could not be detected with BaCl₂, and dried at 50 °C for 72 h. Graphene was obtained after graphite oxide being put into a muffle oven preheated to 1073 K for 60 s.

Experimental procedure for synthesis of chemically modified graphene

200 mg of graphene was added into a 100 mL round-bottom flask. The system was outgassed under dynamic vacuum at 120 °C for 2h, to remove any adsorbed moisture.

The flask was then flushed using Ar, and then 40 mL of n-hexane was added. After graphene was dispersed by ultrasonication for 15 min, 40 mL of n-butyllithium (n-BuLi, 1.5 M in n-hexane) was added. Then, the mixture was stirred at room temperature under Ar overnight. The mixture was subsequently transferred into a 500 mL beaker containing 100 mL of cold ethanol to neutralize the excess n-BuLi. The obtained precipitate was further collected by filtration, washed with 1M HCl solution and deionized water, and dried at 80 °C.

Experimental procedure for synthesis of sulfonated graphene

76 mg of chemically modified graphene was suspended in 30 ml of dichloromethane. The slurry was then dispersed by ultrasonication for 15 min, and then 10 ml of chlorosulfonic acid was added dropwise into the above slurry at 0 °C. After stirring for 1h, the system was allowed to go up to room temperature and held overnight. Then, the reaction was stopped by neutralisation with 20 wt% NaOH. The obtained precipitate was collected by filtration, washed with 1M HCl solution and deionized water, and dried at 80 °C.

General procedure for catalytic Tests

The catalytic ability of catalysts was examined through the ester-exchange reaction between alcohols and ethyl acetate. In brief, the ester-exchange reaction was carried out as follow: a mixture solution of an alcohol (0.3 mmol) and ethyl acetate (2 mL) was stirred in the presence of a catalyst at reflux temperature (80 °C). The progress of the reaction was monitored by HPLC or GC. Upon completion of the reaction, the catalyst was separated by filtration and reused. The organic phase was concentrated to

afford the crude product. If further purification was needed, it was passed through a short column of silica gel.

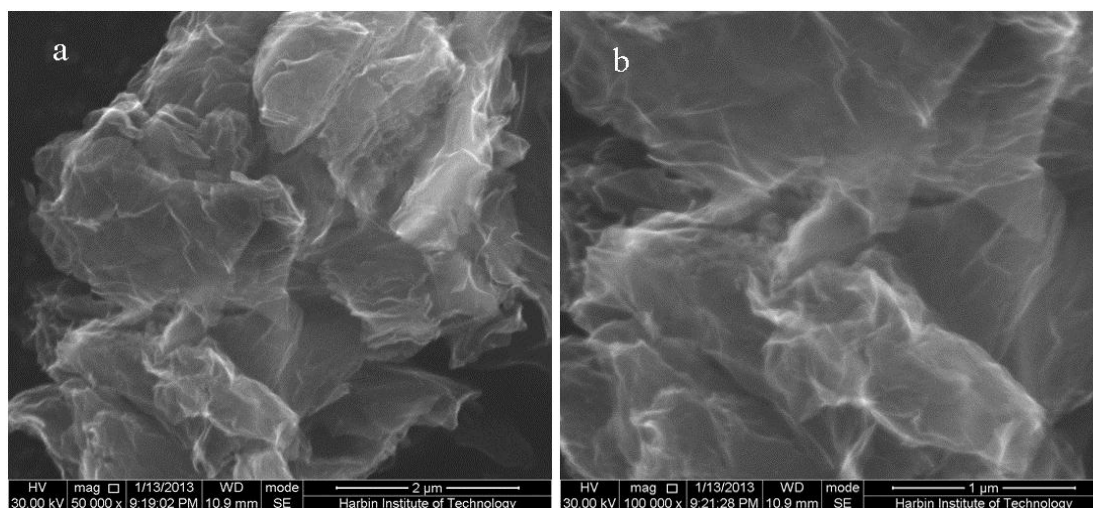


Fig. S1 SEM images of sulfonated graphene

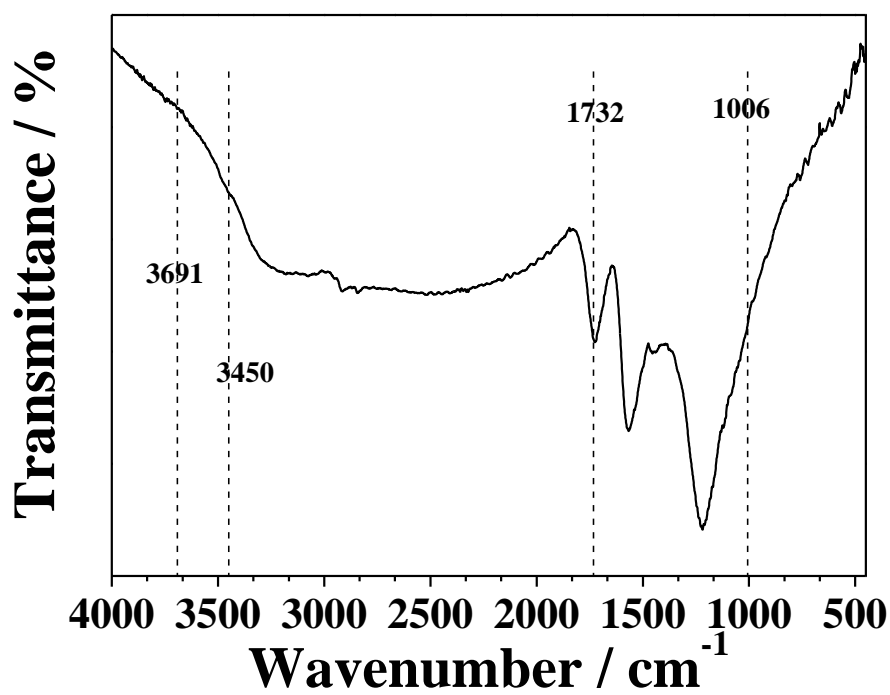


Fig. S2 FT-IR spectrum of graphene

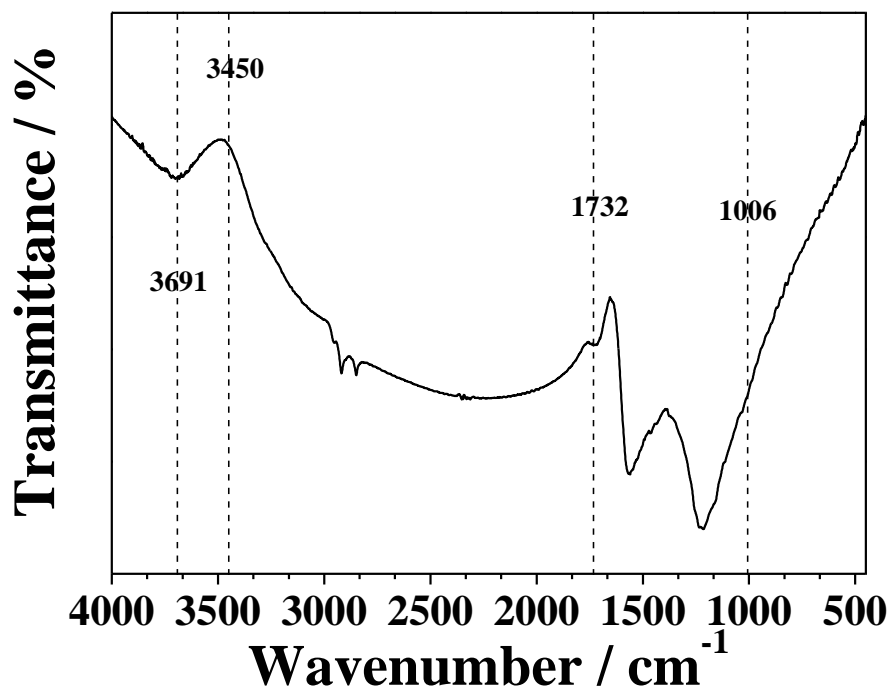


Fig. S3 FT-IR spectrum of chemically modified graphene

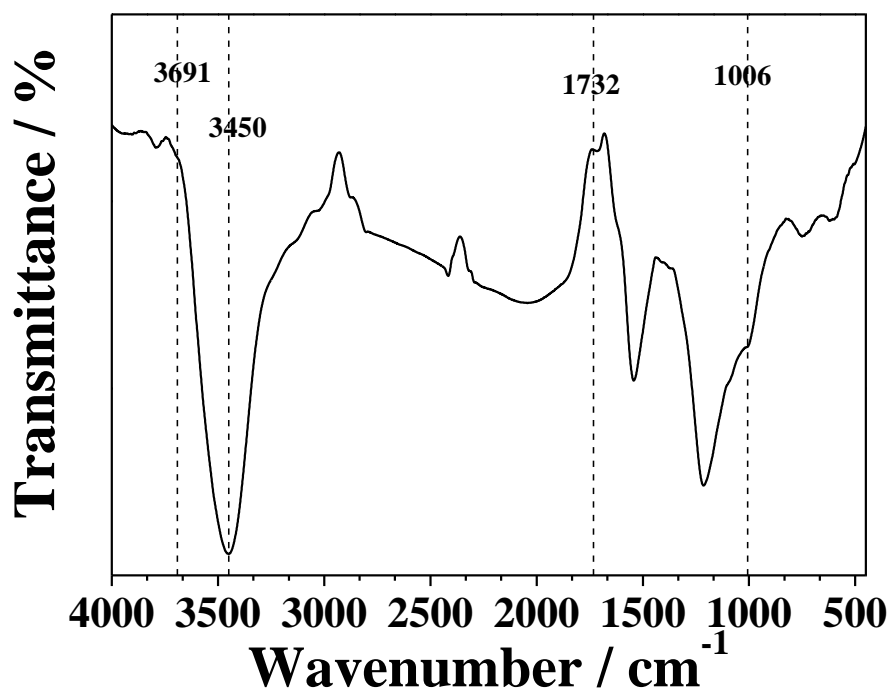


Fig. S4 FT-IR spectrum of sulfonated graphene

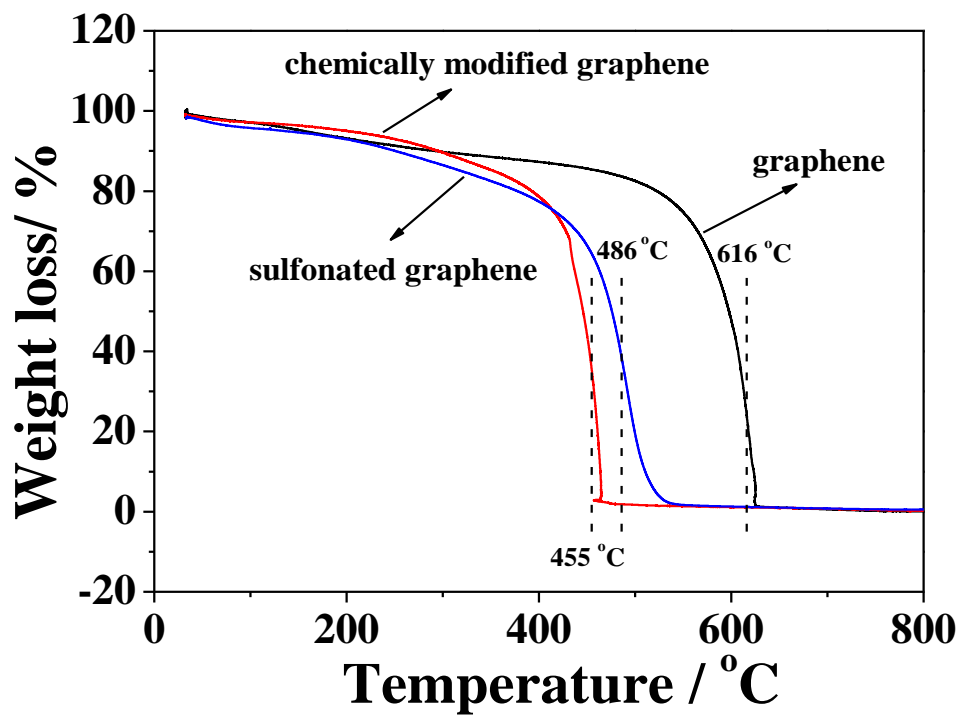


Fig. S5 TG curves of graphene, chemically modified graphene and sulfonated graphene.

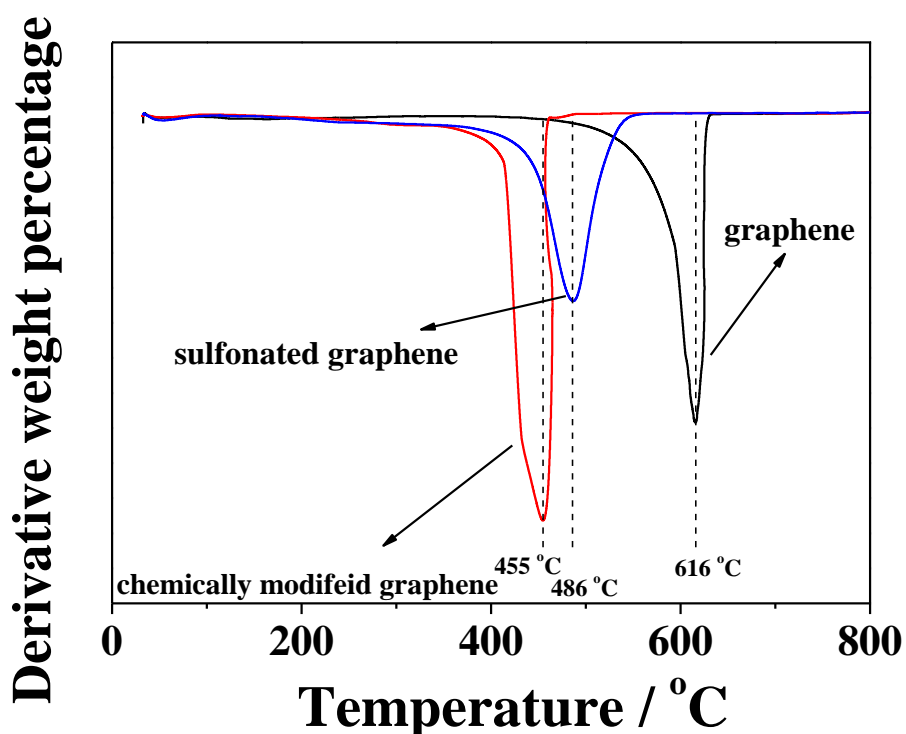


Fig. S6 dTG curves of graphene, chemically modified graphene and sulfonated graphene.

References

1. W. S. Hummers and R. E. Offeman, *Journal of the American Chemical Society*, 1958, **80**, 1339.