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Electronic Supplementary Information

Efficient conversion of fructose into 5-Hydroxymethylfurfural over WO_3/Reduced Graphene Oxide catalysts

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Experimental

General Information

Graphite powder and Sodium tungstate dihydrate (99%) were purchased from Sinopharm. Fructose, Glucose and HMF (99%) were purchased from Sigma–Aldrich. Ionic liquids including 1-butyl-3-methylimidazolium chloride ([BMIM])Cl), 1-butyl-3-methylimidazolium bis(trifluormethylsulfonyl)imide ([BMIM][Tf_2N]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) were purchased from Nowe Wuhu Chemical Technology Co., Ltd. All of the other chemicals were purchased from Aladdin, Alfa, Kermel Chemical Company and used without purification.

The structure of WO_3/RGO was characterized by high-resolution transmission electron microscopy (HRTEM, JEM-2100) with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out with a VG ESCALAB MK II with an Mg Kα (1253.6 eV) achromatic X-ray source. X-ray diffraction (XRD) analysis was performed with a Cu Kα X-ray source (λ = 1.54056 Å). Infrared Fourier Transform spectroscopy (FT-IR) was recorded by SP-100 Fourier transform infrared spectroscopy. Raman spectra of the catalyst were tested with a Renishaw inVia spectrometer.

Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized by the modified Hummer's method, that exfoliate graphite as starting material was oxidized by potassium permanganate and concentrated sulfuric acid. Exfoliate graphite 0.5 g was added to concentrated H_2SO_4 and H_3PO_4 solution with volume ratio of 9:1 at 0-5 °C. Potassium permanganate was slowly added to the reaction system. Next, the reaction system was heated to 50 °C and maintained for 12 hours. The reaction system was added to 60 ml of deionized water and temperature controlled at below 60 °C. Then 5 ml of 30% H_2O_2 solution were added to the reaction solution under mechanical stirring. The solution was washed with 5% HCl solution three times and deionized water three times and

vacuum dried at 50 °C for 12 hours.

Analysis of fructose and HMF concentrations

The quantitative analysis of HMF and sugars in the reaction mixture were done using the Shimadzu LC-20AT HPLC system equipped with a UV detector and with a refractive index (RI) detector [1, 2]. HMF was analyzed using UV detector with a RP-C18 column and the mobile phase consisted methanol/water = 80: 20 at a flow rate of 0.5 mL·min^{-1}. The column's temperature was set to 35 °C. In the meantime, the refractive index (RI) detector was used for the detection of HMF, sugars, levulinic acid, and formic acid. An Aminex HPX-87H column with 0.005 M H_2SO_4 was used as the mobile phase at a flow rate of 0.6 mL·min^{-1}, and the column's temperature was set to 65 °C.

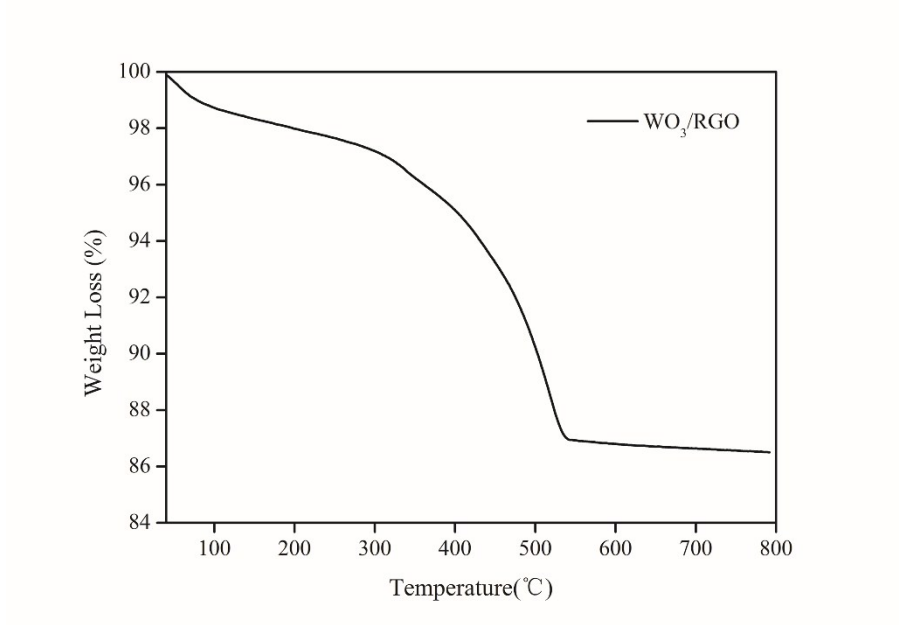


Fig. S1 TGA of the WO_3/RGO.

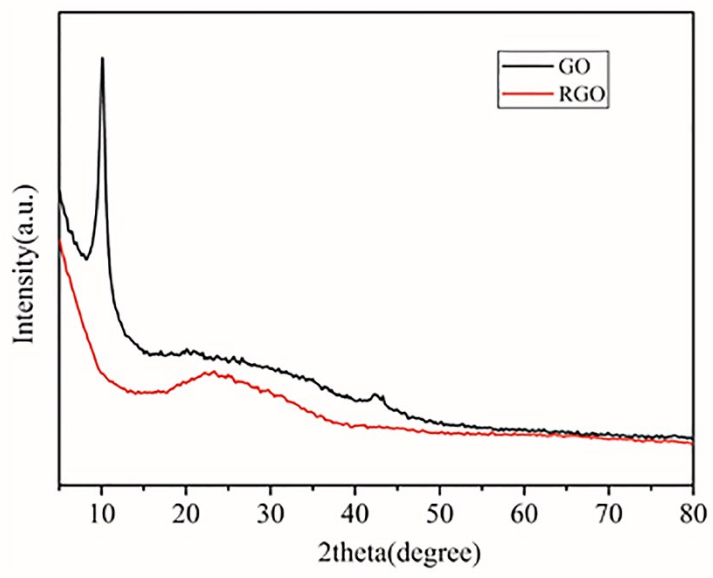
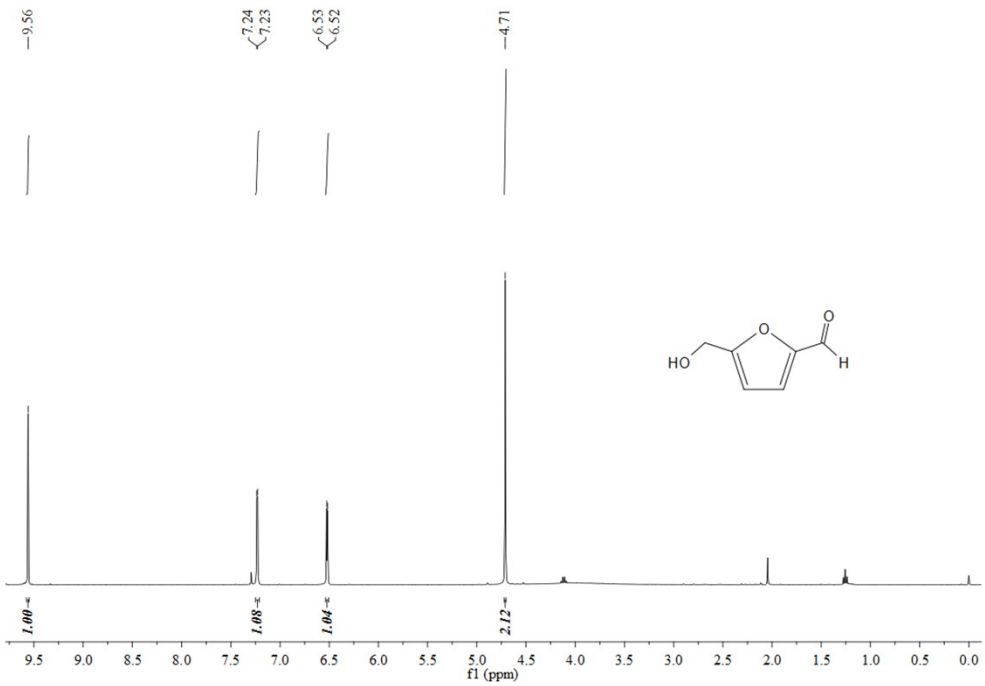


Fig. S2 XRD profile of the GO and RGO.

^{1}H NMR spectra of HMF



Notes and references

[1] Y. Jiang, L. Yang, C. M. Bohn, G. Li, D. Han, N. S. Mosier, J. T. Miller, H. I. Kenttämaa and M. M. Abu-Omar, *Org. Chem. Front*., 2015, **2**, 1388-1396.

[2] A. Ranoux, K. Djanashvili, I. W . C. E. Arends and U. Hanefeld, *ACS Catal.*, 2013, **3**, 760-763.