Electronic supplementary information for

Graphene oxide for cellulose hydrolysis: How it works as a highly active catalyst?

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Experiment

Preparation of graphite oxide

The graphite oxide was prepared by a modified Hummers method according to previous report (ref. [7a]). 10 g of graphite powder and 5 g of sodium nitrate (5 g) were mixed with 230 mL sulfuric acid (98 wt%) in an ice bath, while maintaining agitation. Then after 30 g of potassium permanganate was slowly added to solution, the system was heated to 35 ^{o}C and kept for 0.5 h. Then 460 mL of deionized water was gradually added under violent effervescence. Afterward, the water bath was self-heated to 98 ^{o}C and the reaction was maintained at 98 ^{o}C for 40 min. The resultant bright-yellow suspension was diluted and further treated with 30 mL of H_2O_2 solution (30%). Finally, the suspension was centrifuged and carefully washed to clean out the remnant salt, and dewatered by vacuum drying (50 ^{o}C) to obtain the graphite oxide powder.

Sample treatment before XPS measurements

The samples were firstly filtrated from the reaction solution, and then dispersed in deionized water and sonicated for more than 10 min after filtration. Then the samples were washed more than five times to remove the adsorbed hydrocarbons before the XPS characterization.

Recycle test

We employed cellobiose as the substance in the recycle test to exclude the separation problems. After each run, the catalysts were filtrated from the reaction solution, dispersed in deionized water, and sonicated for more than 10 min. Then the samples were washed more than five times to remove the adsorbed hydrocarbons. Afterward, the recovered catalysts were dewatered by vacuum drying at 50 ^{o}C. The aggregated samples were grinned into powder again, and dispersed in deionized water for another 30 min sonication before the final use.

The reaction was conducted in a 50 mL autoclave in the presence of 0.27 g cellobiose, 0.04 g catalyst, and 27 mL water, at the temperature of 150 ^{o}C for 24 h.

Fig. S1 Photograph of suspended GO-ene in water with increasing concentration from left to right

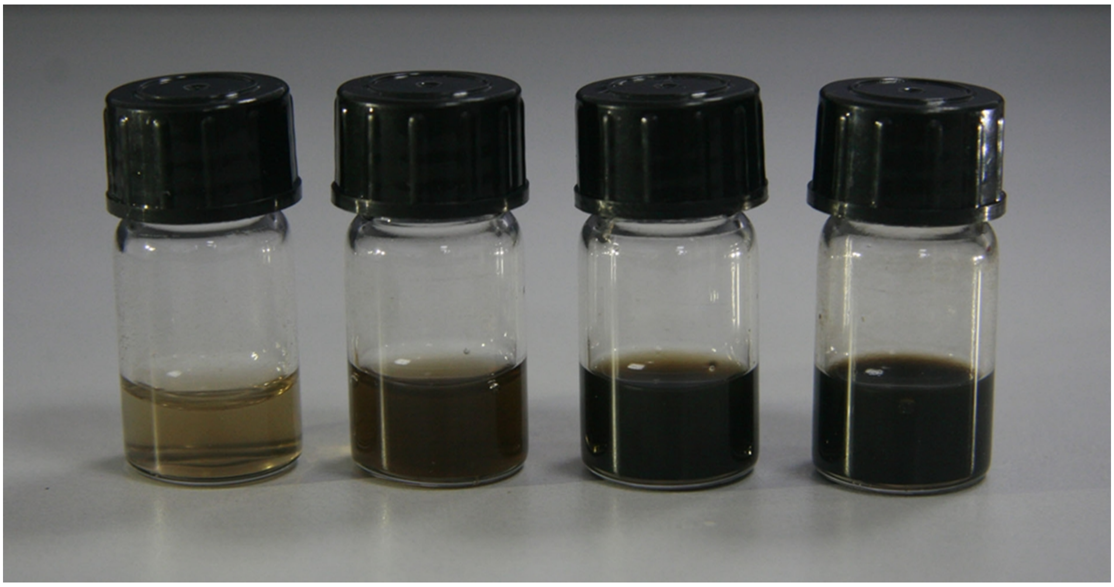

Fig. S2 MS-patterns for temperature programmed desorption (TPD) of GO-ite

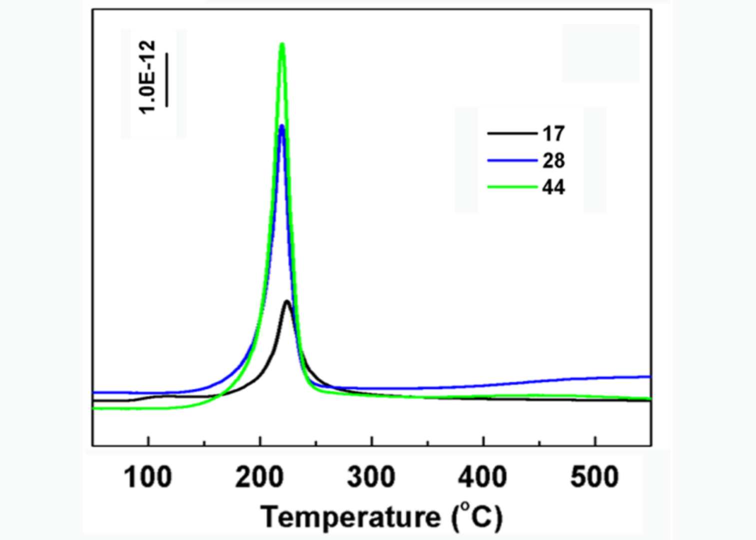

Fig. S3 S2p XPS spectra of GO-ene after 12 h hydrothermal treatment and after 12 h reaction

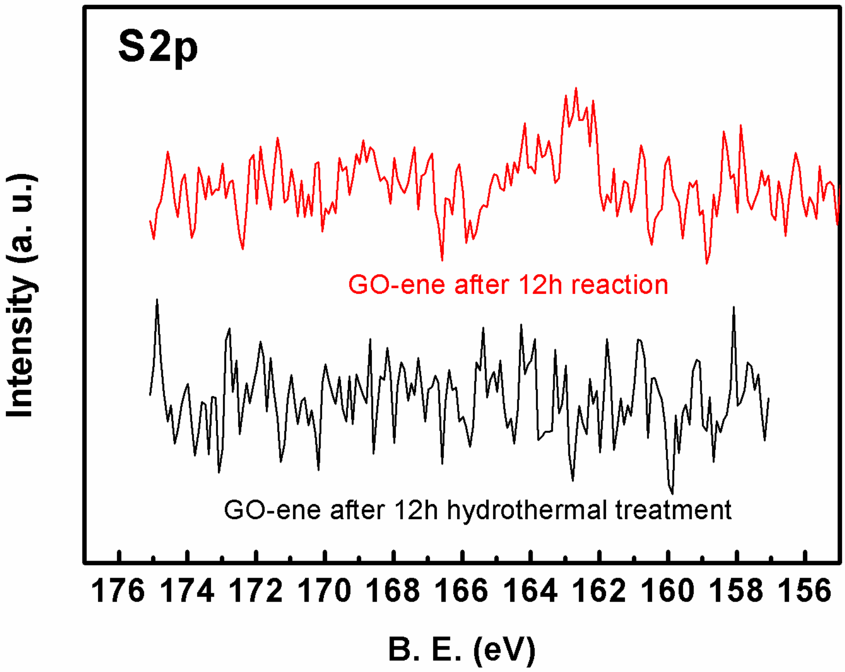

Fig. S4 Raman spectra (a) and XRD patterns (b) of GO-ene before and after hydrolysis

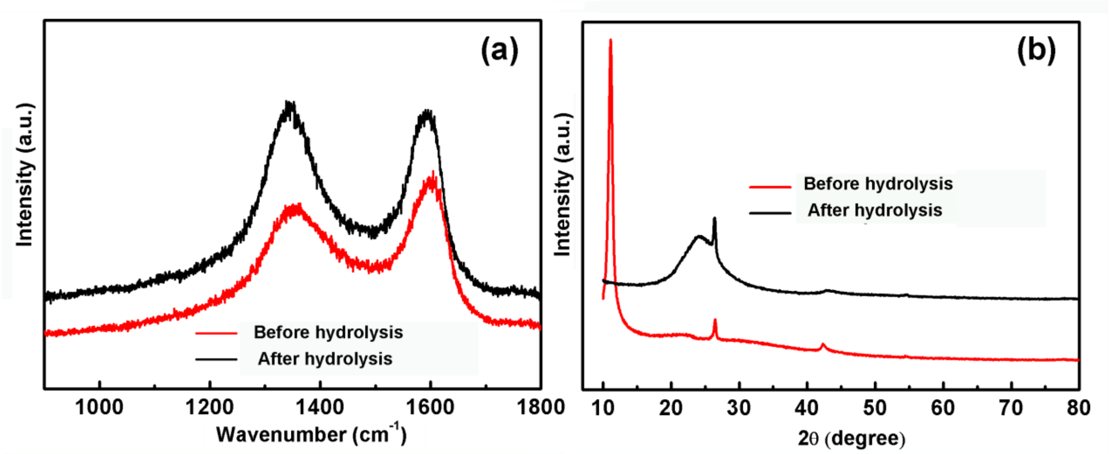

Fig. S5 ln(k) versus the reciprocal absolute temperature 1/T K^{-1} over the GO-ene (a) and GO-ite (b). The reaction temperature range was 135-160 ^{o}C.

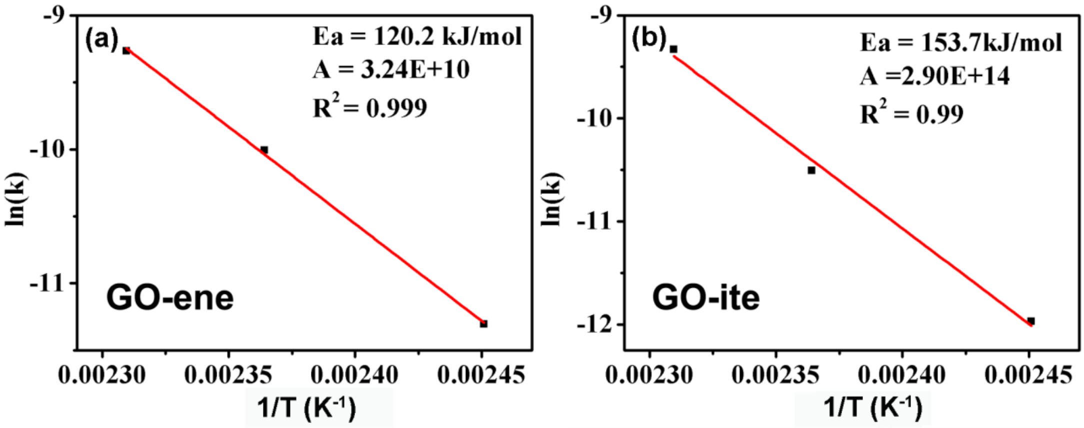

Fig. S6 TEM images of GO-ene before reaction (a-f) and after reaction (g-l)

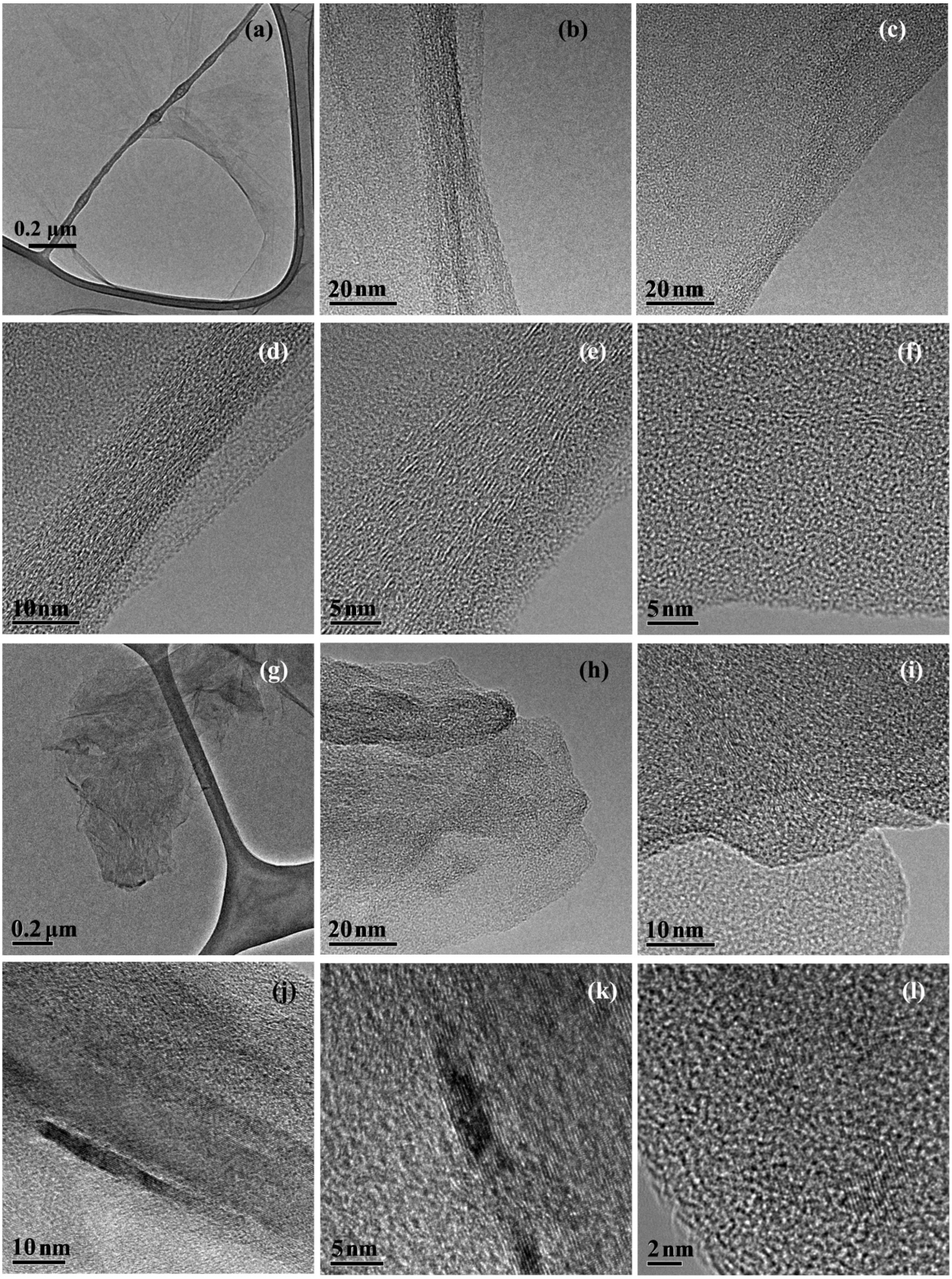

Table S1 Catalytic activity for the hydrolysis of cellulose over GO-ite and GO-ene

Entry	Catalyst	Amount (g)	Yiel. $_{GLU.}$ (%)	Conv. (%)
1	GO-ite	0.31	39.4	51.1
2	GO-ene	0.30	49.9	58.6
3	GO-ite	0.15	22.5	29.9
4	GO-ene	0.15	28.6	39.8
5	GO-ite	0.08	17.4	24.9
6	GO-ene	0.08	23.7	33.9
7	GO-ite	0.04	0.9	4.2
8	GO-ene	0.04	21.4	30.2
12	GO-ene	0.03	14.1	20.9
13	GO-ene	0.02	7.9	13.6
14	GO-ene	0.01	6.4	14.5

Table S2 Stability test for the hydrolysis of cellobiose over GO-ene

Cycle	Conversion (%)	Yield (%)			
		glucose	mannose	fructose	HMF
1	79.1	65.6	2.7	3.5	7.2
2	78.5	57.8	3.3	4.0	13.4
3	80.9	67.7	2.7	2.2	8.4
4	77.0	66.2	1.6	1.7	7.6