

Supplementary Materials: Efficient Production of N-Butyl Levulinate Fuel Additive from Levulinic Acid Using Amorphous Carbon Enriched with Oxygenated Groups

Jinfan Yang ^{1,*}, Guangyi Li ², Lulu Zhang ¹ and Sufeng Zhang ^{2,*}

2. Results and Discussion

2.1. Catalyst Characterizations

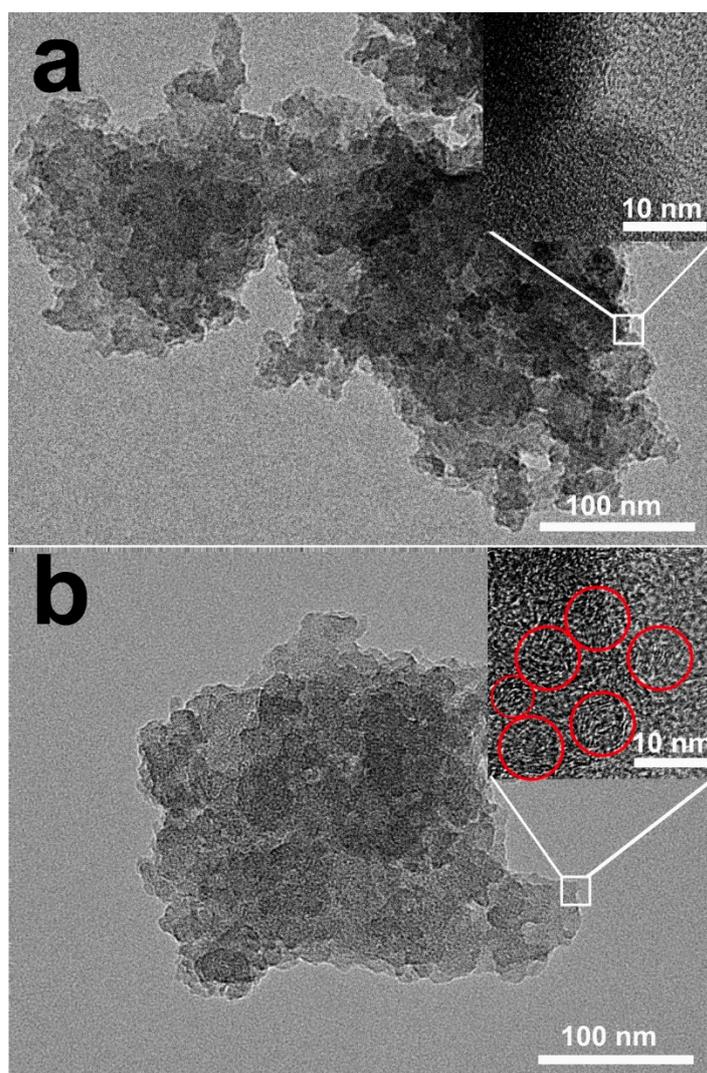


Figure S1. HRTEM images of GC400 (a) and AC400 (b).

Table S1. Acid amount of different functional groups on two samples

Catalyst	Total acid density (mmol·g ⁻¹)		-SO ₃ H ^b (mmol·g ⁻¹)	-COOH ^a (mmol·g ⁻¹)	-OH ^a (mmol·g ⁻¹)
	NH ₃ adsorption	Titration ^a			
GC400	1.1	1.22	0.66	0.15	0.41
AC400	0.44	0.46	0.21	0.03	0.22

^a Determined by BOEHM titration method. ^b Determined by elemental analysis.

BOEHM Titration

The overall amount of -SO₃H, -COOH and phenolic -OH sites on the surface of the catalyst was measured. To do this, 0.1 g catalyst was dispersed into 30 mL 4 mmol·L⁻¹ NaOH solution, sonicated for 1.5 h and then centrifuged. The resulting filtrate was titrated with 1 mmol·L⁻¹ potassium hydrogenphthalate solution using phenolphthalein as indicator. The molar amount of phenolic -OH sites per gram of catalyst was calculated by subtracting the total amount of -SO₃H and -COOH sites per gram of catalyst from the overall amount of -SO₃H, -COOH and phenolic -OH sites per gram of catalyst.

The total amount of -SO₃H and -COOH sites on the surface of the catalyst was measured as follows. 0.1 g catalyst was dispersed into 30 mL 4 mmol·L⁻¹ NaHCO₃ solution, sonicated for 1.5 h and then centrifuged. The liquid as obtained was titrated with 0.1 mol·L⁻¹ HCl (precalibrated by a standard NaOH solution) using methyl orange as indicator. The molar amount of -COOH sites per gram of catalyst was calculated by subtracting the molar amount of -SO₃H sites per gram of catalyst from the total amount of -SO₃H and -COOH sites per gram of catalyst.

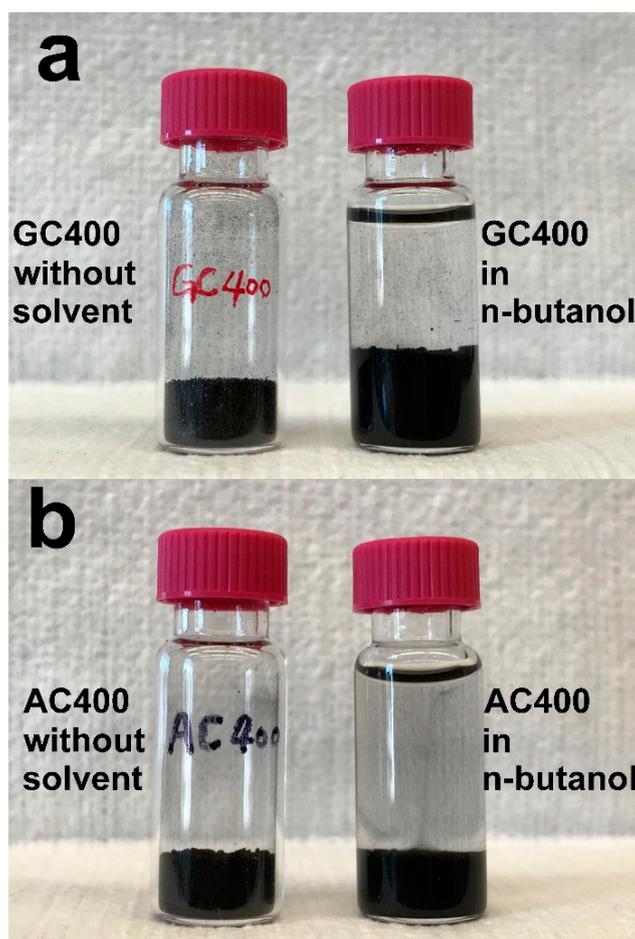


Figure S2. The behavior of GC400 (a) and AC400 (b) in contact with n-butanol.

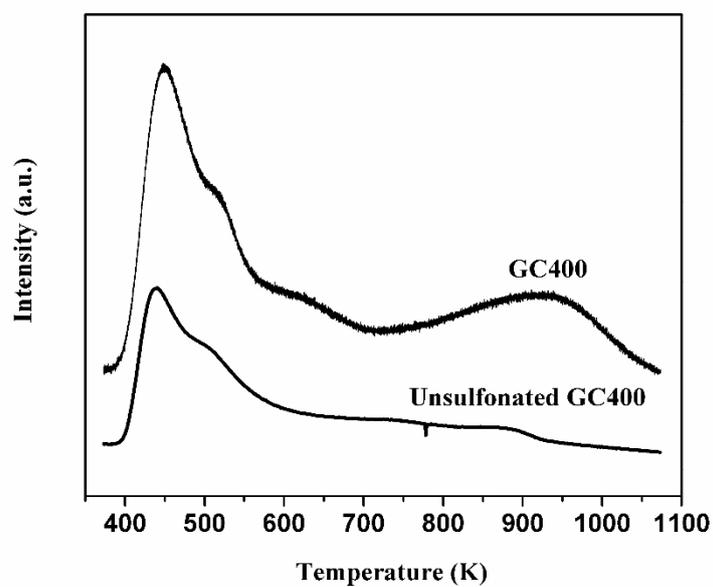
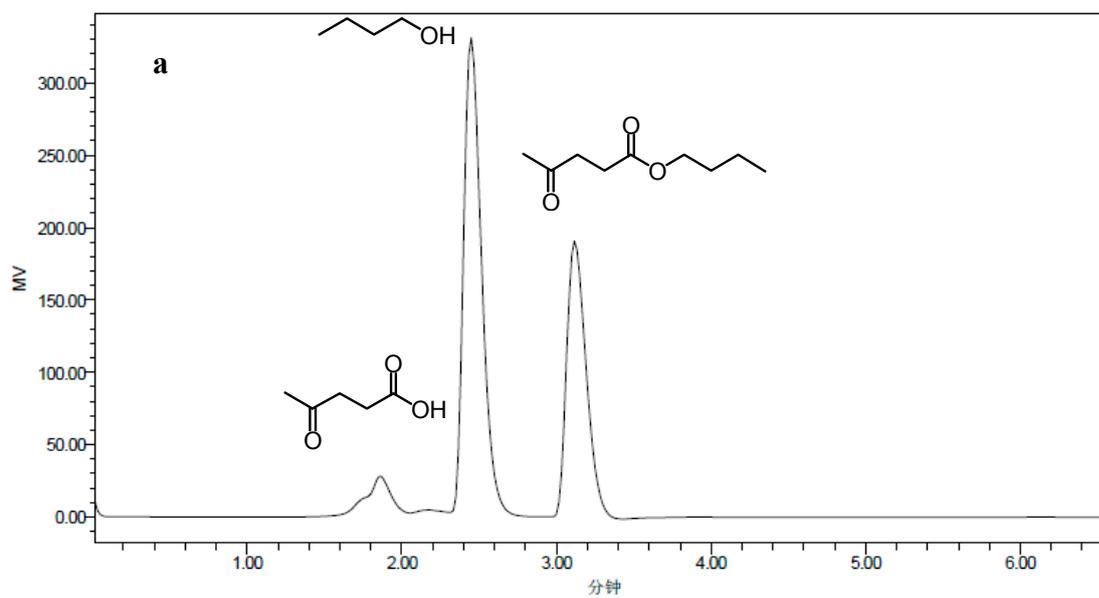


Figure S3. NH₃-TPD results of GC400 and unsulfonated GC400.

2.2. Esterification Activity over Two Sulfonated Carbon Materials



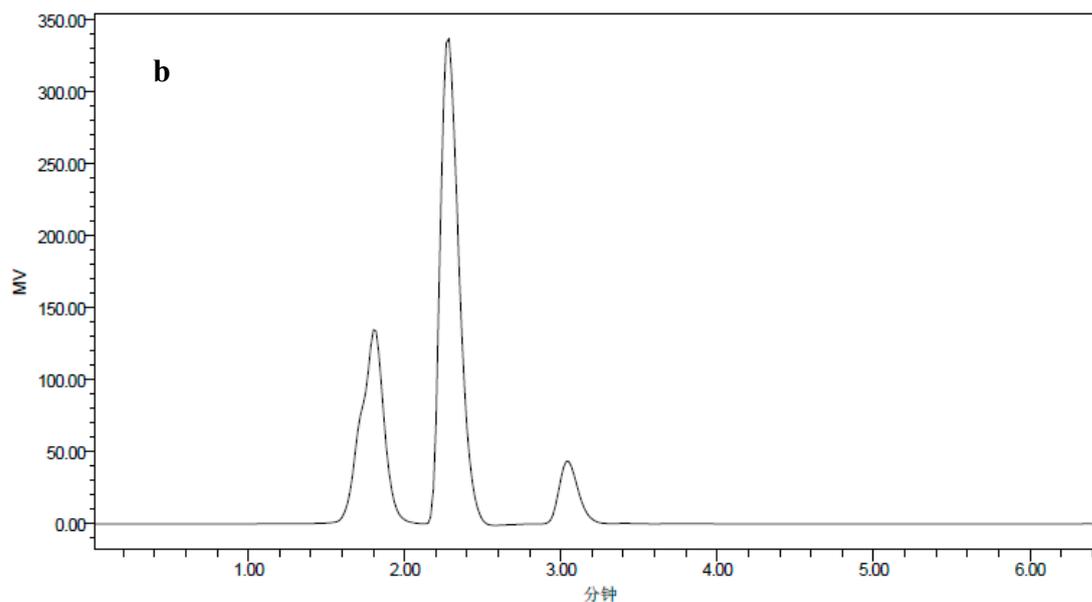


Figure S4. HPLC chromatograms of the liquid products from the esterification of LA and n-butanol over GC400 (a) and AC400 (b). Reaction conditions: 0.16 g LA, 3.7 g n-butanol and 0.16 g catalyst; 373 K, 4 h.

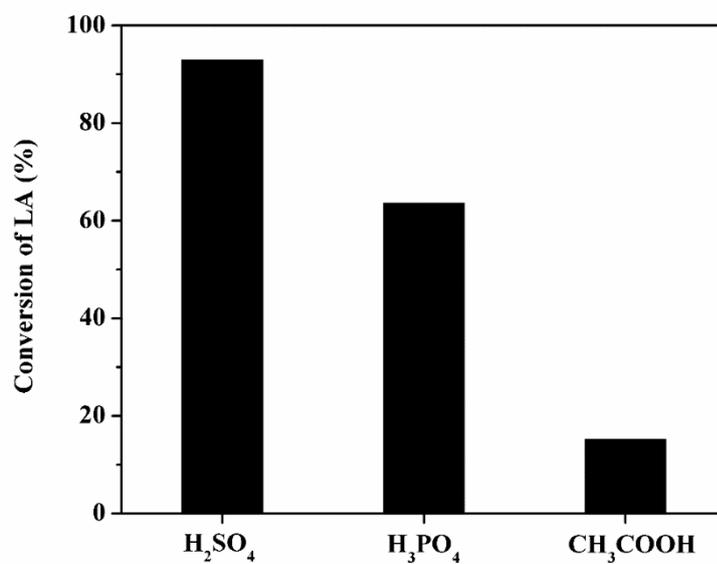


Figure S5. Conversions of LA catalyzed by different liquid acids. Reaction conditions: 1.16 g LA, 3.7 g n-butanol and 1.16 g catalyst, 333 K, 4 h. The concentrations of the acid solutions are 20 wt%.

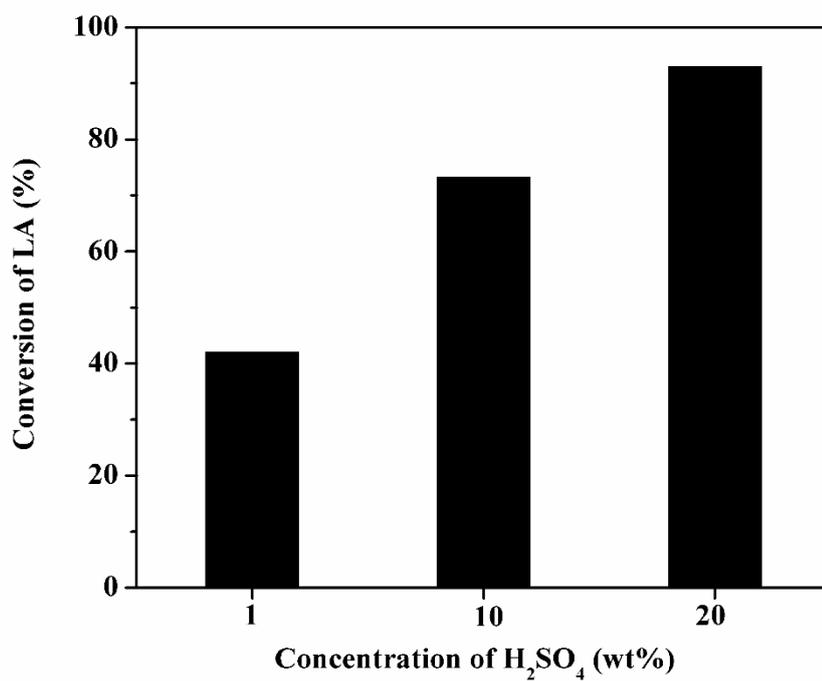


Figure S6. Conversions of LA catalyzed by different concentrations of H₂SO₄ solution. Reaction conditions: 1.16 g LA, 3.7 g n-butanol and 1.16 g catalyst, 333 K, 4 h.

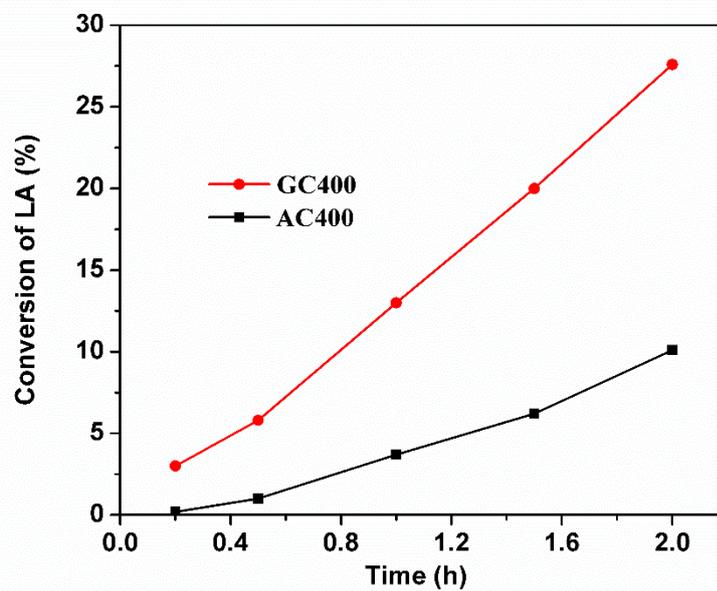


Figure S7. Conversions of LA over GC400 and AC400 when identical amounts of -SO₃H sites in reaction mixture were utilized. Reaction conditions: 1.16 g LA, 3.7 g n-butanol, 0.0232 g GC400 or 0.063 g AC400, 373 K, 2 h.

2.3. Effect of Reaction Temperature over Two Sulfonated Carbon Materials

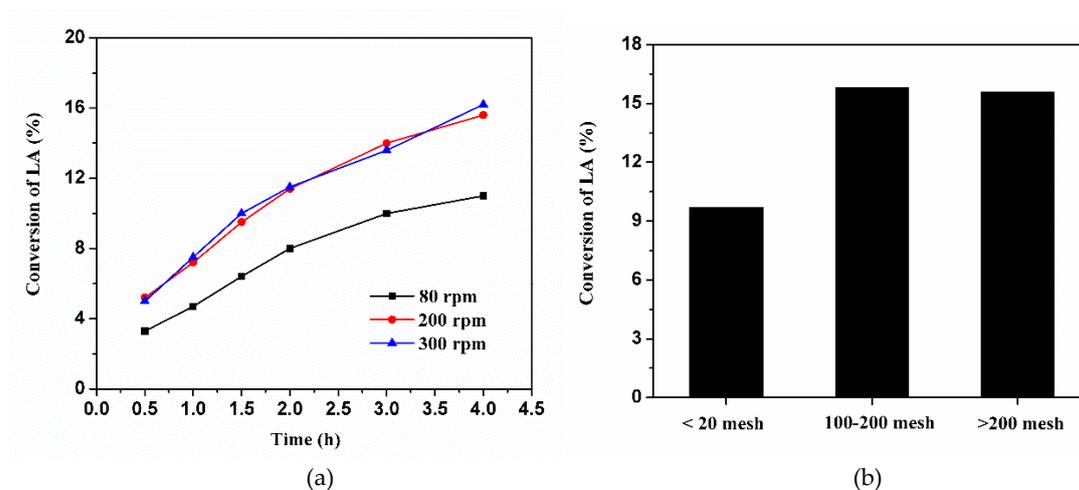


Figure S8. Effect of stirrer speed (a) and particle size (b) on esterification of LA over AC400. Reaction conditions: a. 1.16 g LA, 0.116 g catalyst (>200 mesh), 373 K, 4 h; b. 1.16 g LA, 3.7 g n-butanol, 0.116 g catalyst, 200rpm, 373 K, 4 h.

2.5. Comparison with Other Typical Solid Acids

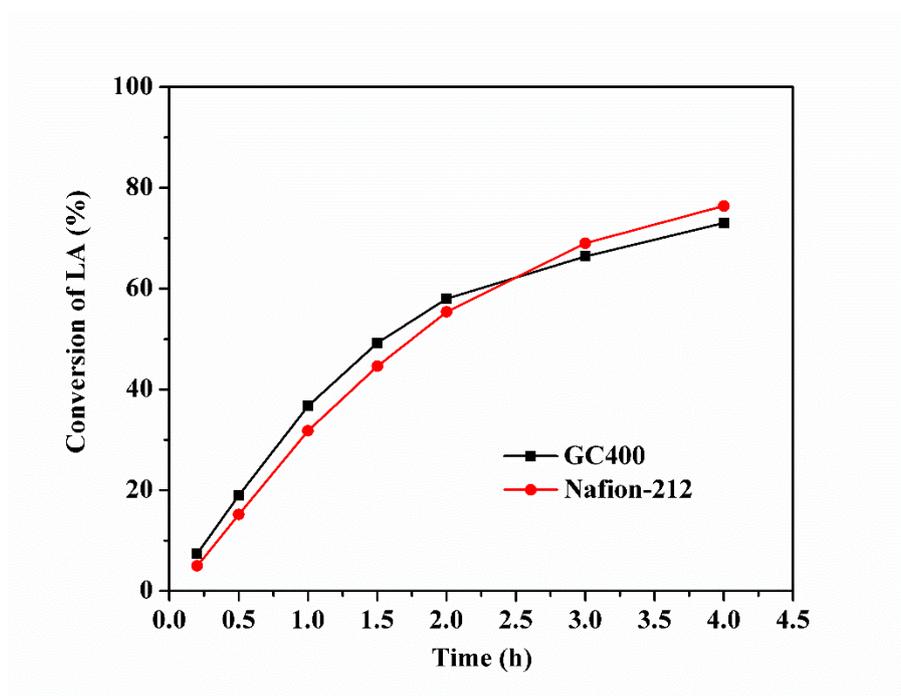


Figure S9. Conversions of LA over GC400 and Nafion-212 as the function of reaction time. Reaction conditions: 1.16 g LA, 3.7 g n-butanol and 0.058 g catalyst, 373 K.

3. Materials and Methods

3.1. Catalyst Preparation

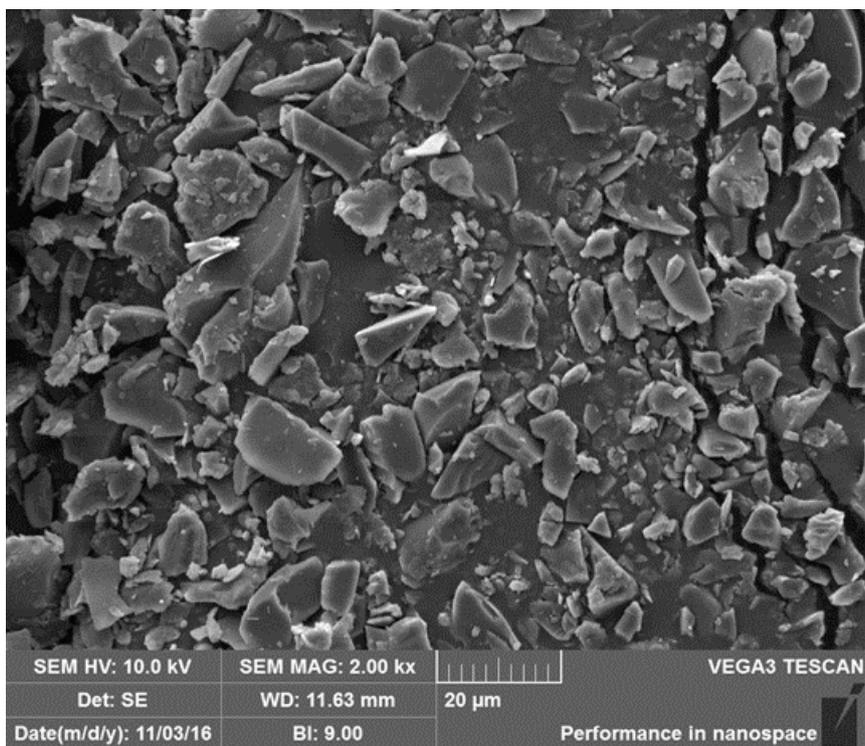


Figure S10. SEM images of GC400 sample.