

# Levulinic Acid Hydrogenation to $\gamma$ -valerolactone over Single Ru Atoms on $\text{TiO}_2$ @Nitrogen Doped Carbon Support



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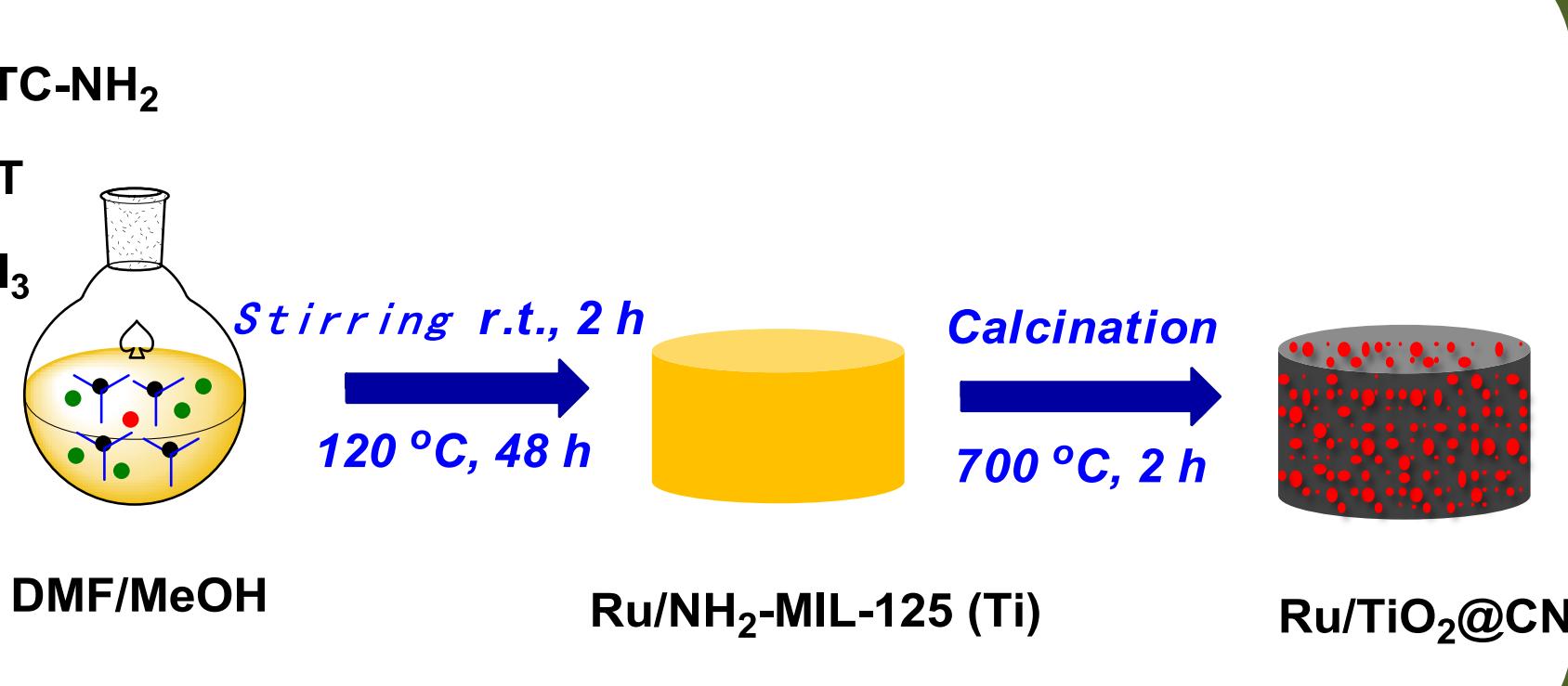
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## Introduction

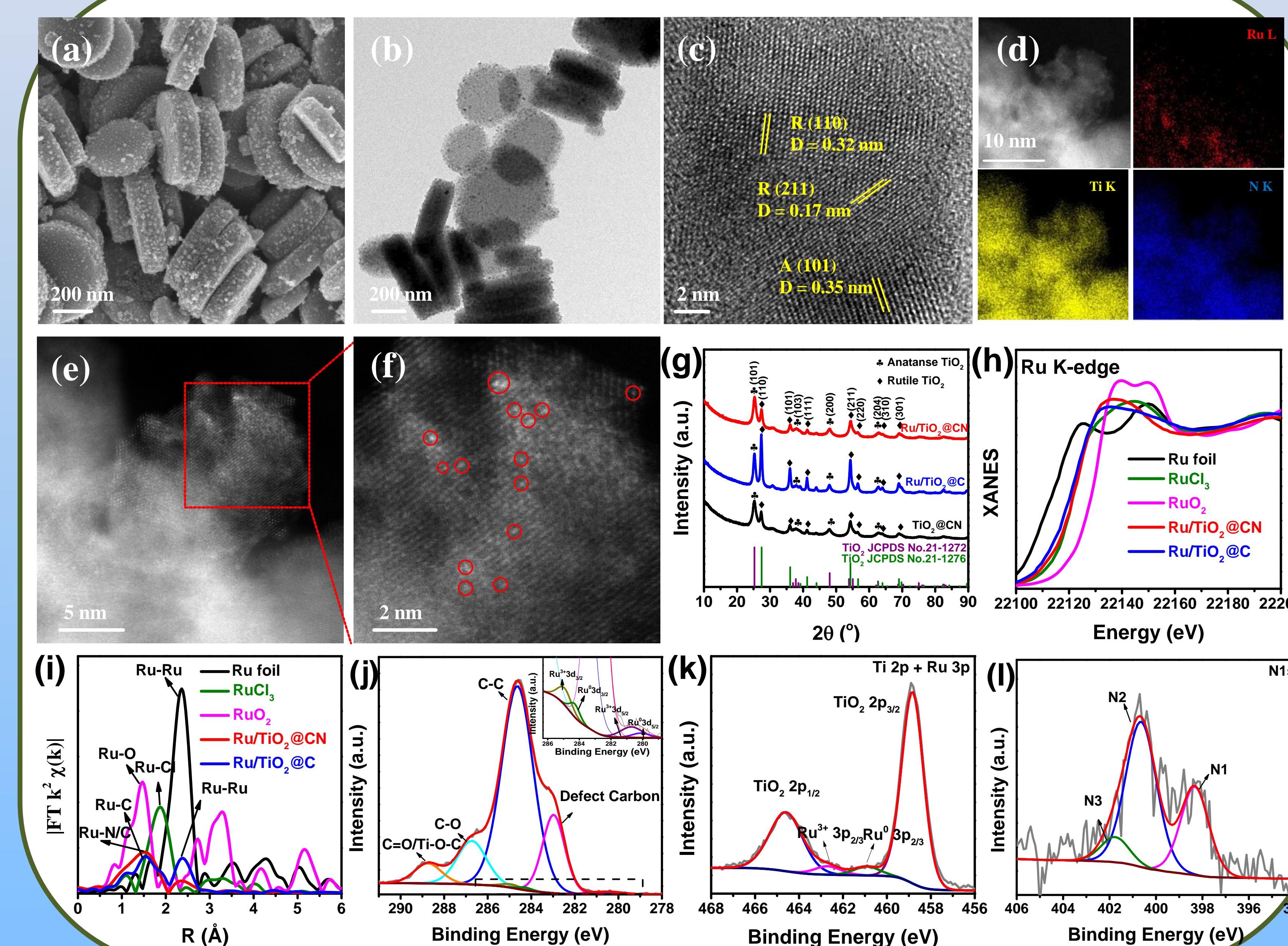
With the diminishing of the fossil resource and increasing of the energy demand, it is urgent to find new sustainable alternative energies. Biomass, which is the widespread, cheap and carbon-neutral renewable resource in nature, has attracted more and more attentions in recent years.<sup>1</sup> As the dominant component of biomass, cellulose is widely found in forest biomass, agricultural waste, and paper pulp, and can be transformed into fuels and chemicals via biological and chemical methods, thus can partially replace the fossil resource. Levulinic acid (LA) is recognized by the U.S. Department of energy as one of the “top 10” most promising platform molecules derived from biomass.<sup>2,3</sup> Many value-added chemicals can be synthesized directly from LA, such as  $\gamma$ -valerolactone (GVL), 1,4-pentanediol, pentaenoic acid, and 2-methyl-tetrahydrofuran.<sup>4-16</sup> Among these products, GVL has received widespread attention due to its excellent physical and chemical properties. It can be used as solvent, flavoring agent, food ingredients, pharmaceutical intermediates, fuel additive and so on.<sup>17-20</sup> Recently, SACs have received more and more attention in biomass conversions.<sup>44-46</sup>

## Method

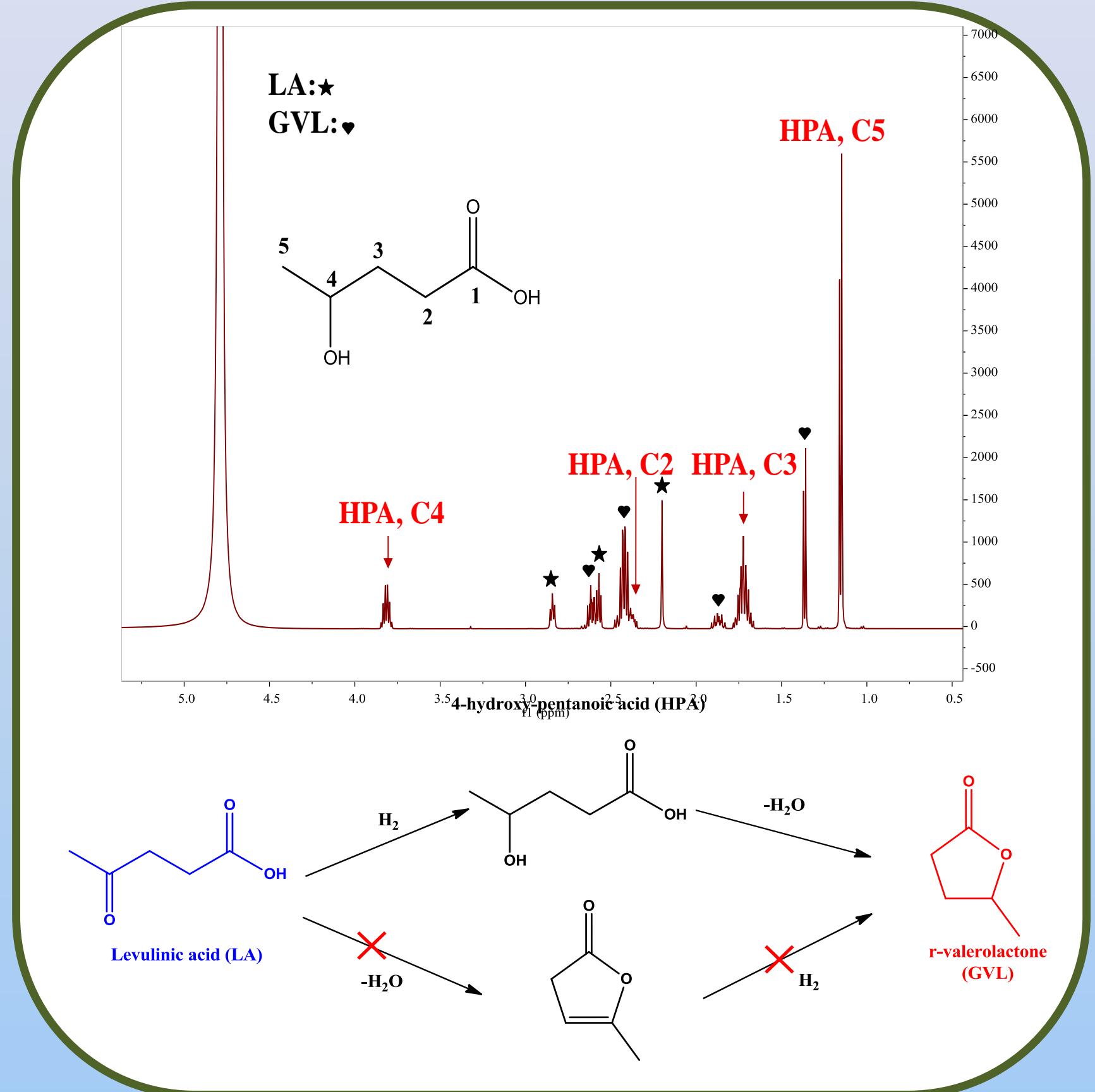


**Scheme 1.** Schematic illustration for the preparation of the Ru/TiO<sub>2</sub>@CN catalyst.

## Results



**Fig. 1** Structural characterization of the Ru/TiO<sub>2</sub>@CN catalyst: (a) SEM image; (b and c) TEM images; (d) HAADF-STEM image and corresponding element maps for Ru (red), Ti (yellow) and N (blue); (e and f) HAADF-STEM and enlarged images of the Ru/TiO<sub>2</sub>@CN catalyst, with single Ru atoms highlighted by red circles; (g) XRD patterns of the Ru/TiO<sub>2</sub>@CN and Ru@TiO<sub>2</sub>@C samples; (h) XANES spectra of Ru/TiO<sub>2</sub>@CN and Ru/TiO<sub>2</sub>@C for Ru K-edge; (i) Fourier transformed (FT) k<sup>2</sup>-weighted  $\chi(k)$ -function of the EXAFS spectra for Ru K-edge; XPS spectra of Ru/TiO<sub>2</sub>@CN catalyst. (j) Ru 3d and C 1s, (k) Ti 2p, (l) N 1s, pyridinic N (N1), pyrrolic N (N2), and graphitic N (N3).



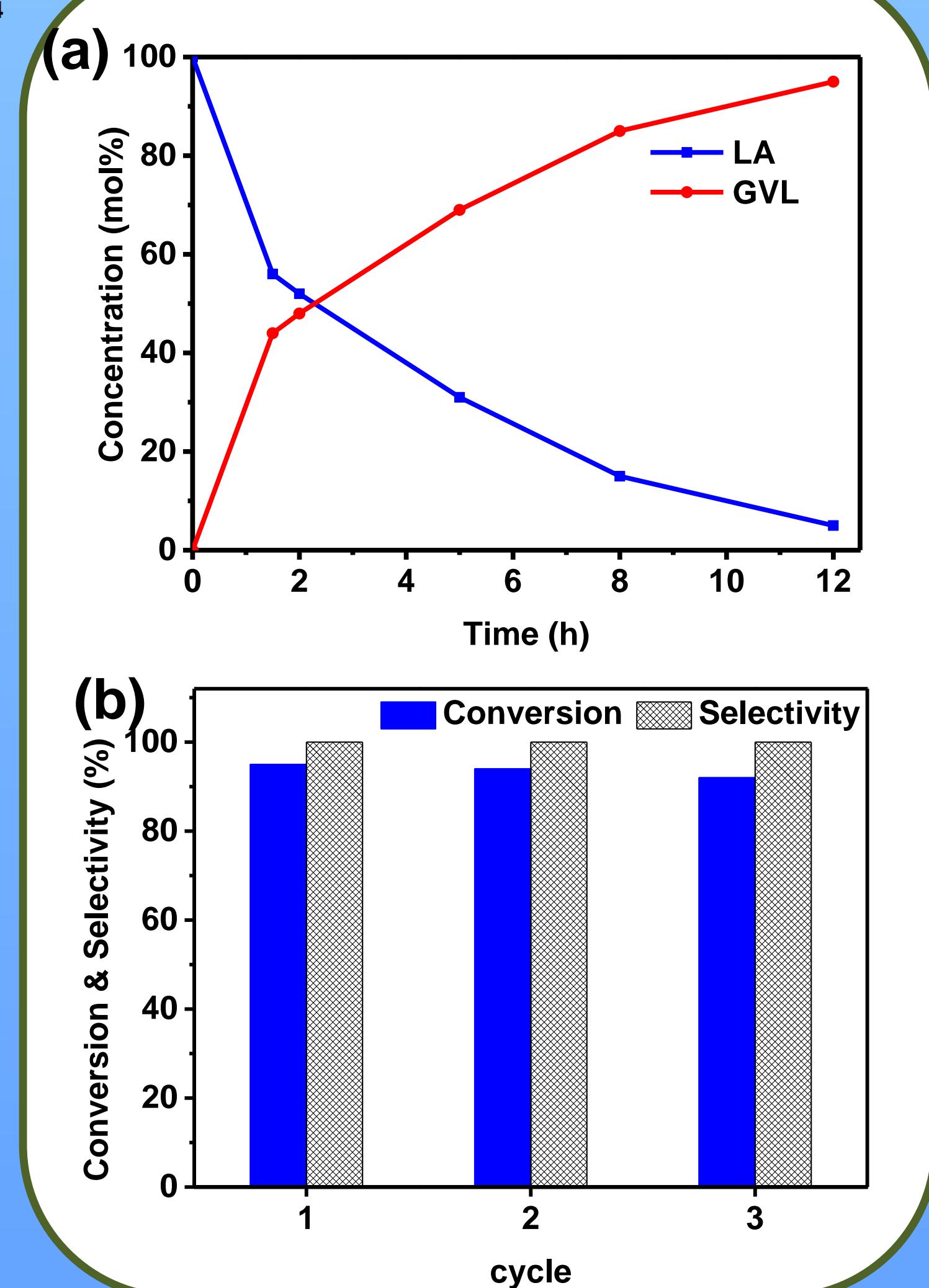
**Fig. 3** Determination of the intermediate in the transformation of LA. Reaction conditions: D<sub>2</sub>O (1 mL).

## Conclusion

In summary, we designed and fabricated Ru/TiO<sub>2</sub>@CN catalyst, in which single Ru atoms are supported on TiO<sub>2</sub>@CN. At room temperature, the conversion of LA reaches 100% with GVL selectivity of 100% via hydrogenation and dehydration processes. The TOF of the catalyst was about 35 times higher than that of the commercial Ru/C catalyst, and the selectivity of GVL is also higher. Detailed study indicates that LA is first converted to HPA via hydrogenation process, and then HPA was quickly dehydrated into GVL. The performance is much better than the reported Ru-based catalysts. We believe that the highly efficient and selective catalyst has great potential of application.

## References

- P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538; K. Barta and P. C. Ford, *Acc. Chem. Res.*, 2014, **47**, 1503; C. Z. Li, X. C. Zhao, A. Q. Wang, G. W. Huber and T. Zhang, *Chem. Rev.*, 2015, **115**, 11559; A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411; M. Mascal, S. Dutta and I. Gandarias, *Angew. Chem., Int. Ed.*, 2014, **53**, 1854. ....



**Fig. 2** (a) Effect of reaction time and (b) Recycling experiments of the Ru/TiO<sub>2</sub>@CN catalyst in the transformation of LA.

**Table 1** Catalytic Performance of Ruthenium in the hydrogenation of LA<sup>a</sup>

Entry	Catalysts	Catalyst (mg)	S/M <sup>b</sup>	Time	Conv. (%)	Selectivity (%)		mol <sup>c</sup> TOF <sup>d</sup> g <sup>-1</sup> gRu <sup>-1</sup>
						GVL	Others <sup>c</sup>	
1 <sup>e</sup>	Ru/TiO <sub>2</sub> @CN	10	3610	8	78	100	0	234
2	Ru/TiO <sub>2</sub> @CN	10	3610	12	95	100	0	285
3	Ru/TiO <sub>2</sub> @CN	10	3610	13	100	100	0	278
4	Ru/TiO <sub>2</sub> @C	10	2021	12	83	99	1	141
5	Ru/TiO <sub>2</sub> @CN-500	10	3887	12	-	-	-	-
6	Ru/TiO <sub>2</sub> @CN-900	10	2197	12	3	100	0	6
7	Ru/TiO <sub>2</sub>	10	4211	12	13	100	0	10.5
8	TiO <sub>2</sub> @CN	10	-	12	-	-	-	-
9 <sup>f</sup>	Ru/TiO <sub>2</sub> @CN	10	3610	12	40	89	11	-
10 <sup>g</sup>	Ru/TiO <sub>2</sub> @CN	10	3610	12	66	86	14	-
11 <sup>h</sup>	Ru/TiO <sub>2</sub> @CN	10	3610	12	2	100	-	-
12 <sup>i</sup>	Ru/C	10	101	12	100	94	6	7.91
13 <sup>j</sup>	PtO <sub>2</sub>	400	286	44	87	-	-	6.5
14 <sup>k</sup>	Ru/FLG	15	1460	8	99.3	97.7	2.3	178
15 <sup>l</sup>	Ru/C	250	348	50	100	97.5	2.5	6.8

<sup>a</sup>Reaction conditions: LA (0.5 mmol), H<sub>2</sub>O (1 mL), 30 °C, H<sub>2</sub> (6 MPa).<sup>b</sup>/M is the molar ratio of substrate (LA) to active metal (Ru).<sup>c</sup>Other byproducts include  $\gamma$ -hydroxyvaleric acid, angelica lactone and other unknown products. <sup>d</sup> Turnover Frequency (TOF) of GVL = moles of produced GVL)/(mass of Ru)(reaction time), mol<sub>GVL</sub>g<sub>Ru</sub><sup>-1</sup> h<sup>-1</sup>. <sup>e</sup>H<sub>2</sub>, 4 MPa, 20 °C. <sup>f</sup>Methanol. <sup>g</sup>Ethanol. <sup>h</sup>1, 4-Dioxane. <sup>i</sup> 5% Ru/C. <sup>j</sup>Reaction conditions in the literature 32: 500 mmol LA, 0.4 g PtO<sub>2</sub>, 150 mL ethyl acetate, room temperature, 2.3–3.0 bar H<sub>2</sub>, 44 h. <sup>k</sup>Reaction conditions in the literature 27: 4.3 mmol LA, 2% Ru/FLG (few-layer graphene), 10 mL H<sub>2</sub>O, 4 MPa H<sub>2</sub>, 20 °C. <sup>l</sup>Reaction conditions in Ref 40 (43 mmol LA, 5% Ru/C, 25 °C, 12 bar H<sub>2</sub>, 50 h).