EDTA-2Na Promotes the Formation of Linear Cross-linked PtCu to Enhance the Performance of Methanol Oxidation Reaction

Yuxin Bai‡, Hongyu Pei‡, Yajie Zhang, Long Yang*

College of Chemical Engineering, Inner Mongolia University of Technology, Hohhot 010051, China.

Corresponding author: *Long Yang, E-mail:* YanglongCHN@outlook.com

Synthesis of materials

The $PtCu_2$-LCN was prepared by co-reduction of $H_2PtCl_6 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ with $NaBH_4$ in an EDTA-2Na aqueous solution. For a typical preparation of PtCu-LCN, a solution containing 0.0077 M $H_2PtCl_6 \cdot 6H_2O$, 0.0154 M $CuCl_2 \cdot 2H_2O$, and 0.062 M EDTA-2Na was added into a 100 mL beaker with 40 mL deionized water. The mixture was stirred with a magnetic stirrer. Subsequently, a freshly prepared $NaBH_4$ solution was quickly injected into the beaker. After stirring for 1 min with the magnetic stirrer, black nanocrystals were obtained. The product was centrifuged and washed with ethanol. The product was then dispersed in ethanol for further testing. All experiments were conducted at ambient temperature. $PtCu_{0.5}$-LCN was prepared by the same method with adding 0.00385 M $CuCl_2 \cdot 2H_2O$.

2-EDTA-2Na-PtCu-LCN was prepared by co-reduction of $H_2PtCl_6 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ with $NaBH_4$ in an EDTA-2Na aqueous solution. For a typical preparation of PtCu-LCN, a solution containing 0.0077 M $H_2PtCl_6 \cdot 6H_2O$, 0.0077 M $CuCl_2 \cdot 2H_2O$, and 0.124 M EDTA-2Na was added into a 100 mL beaker with 40 mL deionized water. The mixture was stirred with a magnetic stirrer. Subsequently, a freshly prepared $NaBH_4$ solution was quickly injected into the beaker. After stirring for 1 min with the magnetic stirrer, black nanocrystals were obtained. The product was centrifuged and washed with ethanol. The product was then dispersed in ethanol for further testing. 0.5-EDTA-2Na-PtCu-LCN was prepared by the same method with adding 0.031 M EDTA-2Na.

Catalyst characterization

Fourier Transform infrared spectroscopy (FTIR) were obtained using Shimadzu FTIR-8400s with scanning range 4000-500 cm^{-1}.

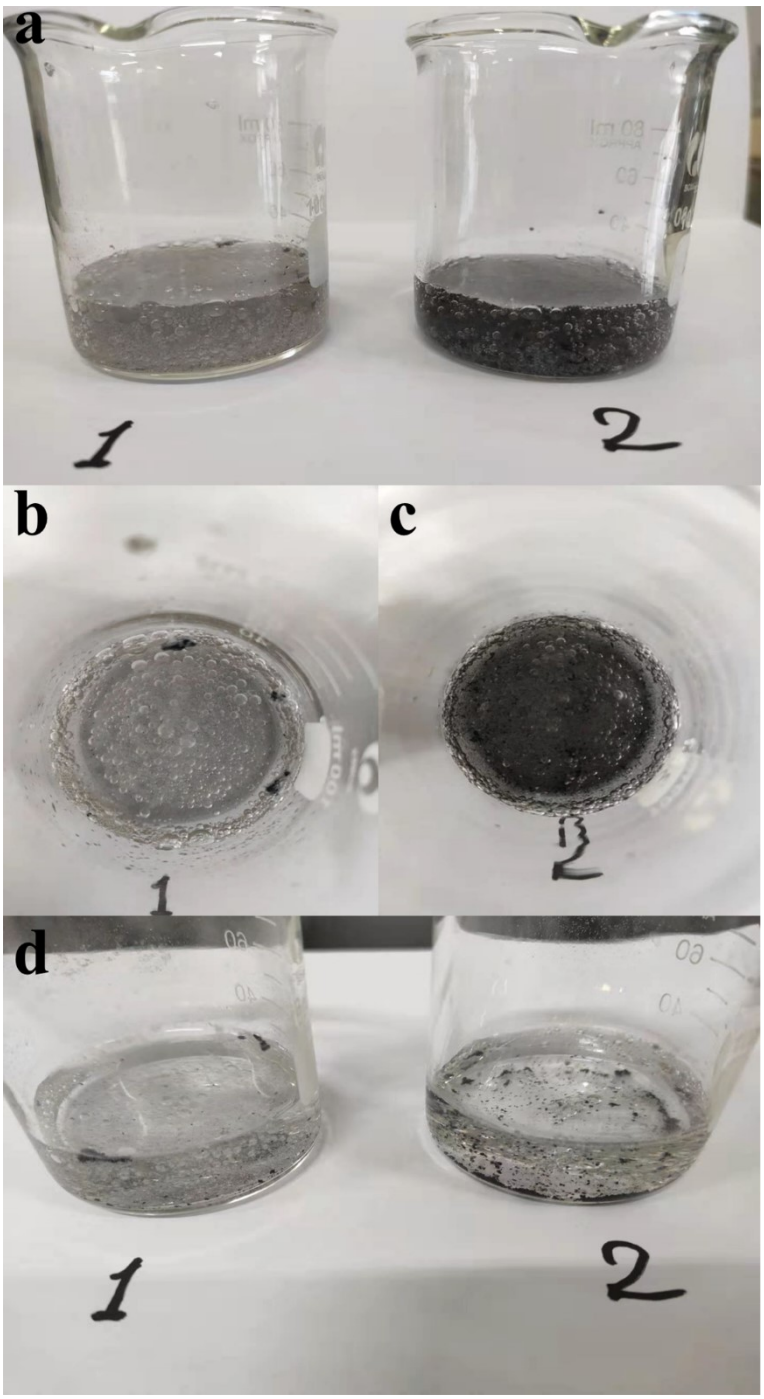

Fig. S1. The corresponding result solution of PtCu-LCN (breaker 1) and PtCu (breaker 2) after adding $NaBH_4$ just now (a, b and c) and standing for 2 hours (d).

Fig. S2. The corresponding result solution of PtCu-LCN after washing.

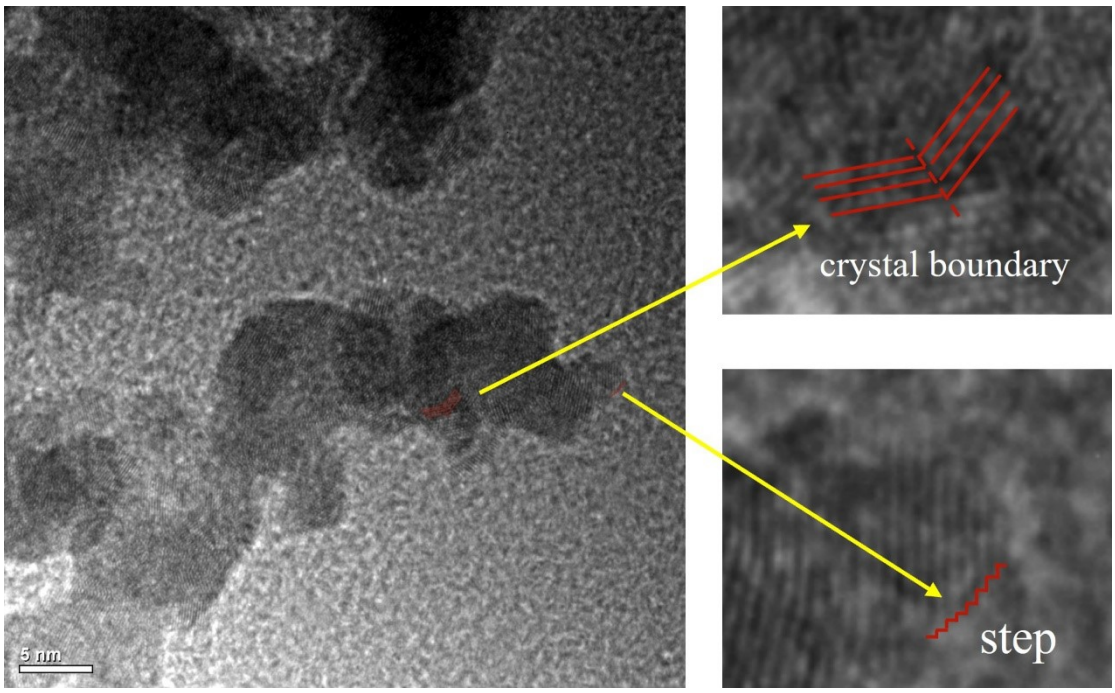

Fig. S3. TEM of PtCu-LCN and the enlarged TEM images.

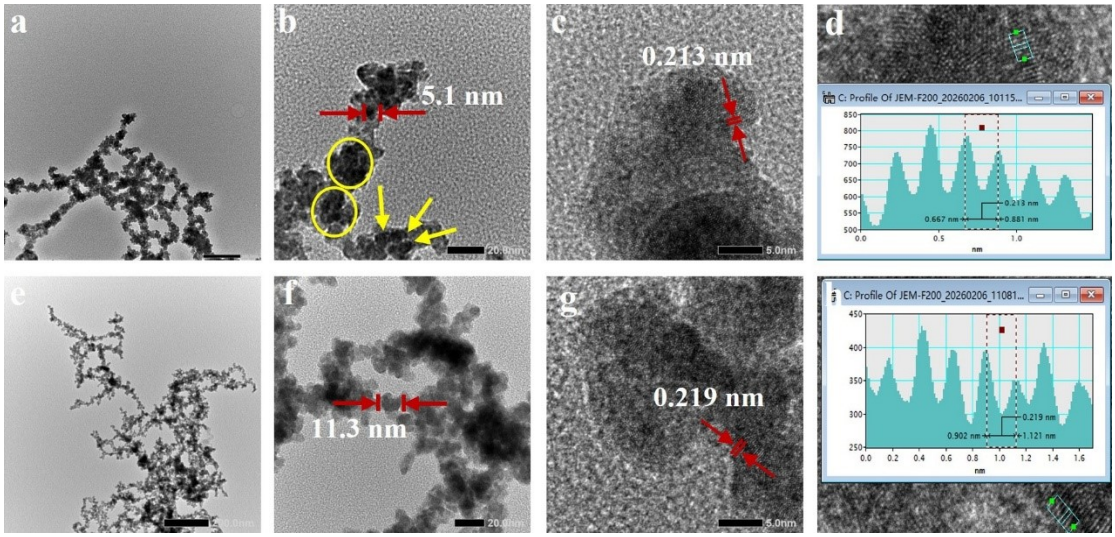

Fig. S4. TEM images of 2-EDTA-2Na-PtCu-LCN (a, b), HRTEM images of 2-EDTA-2Na-PtCu-LCN (c, d), TEM images of 0.5-EDTA-2Na-PtCu-LCN (e, f) and HRTEM images of 0.5-EDTA-2Na-PtCu-LCN (g, h).

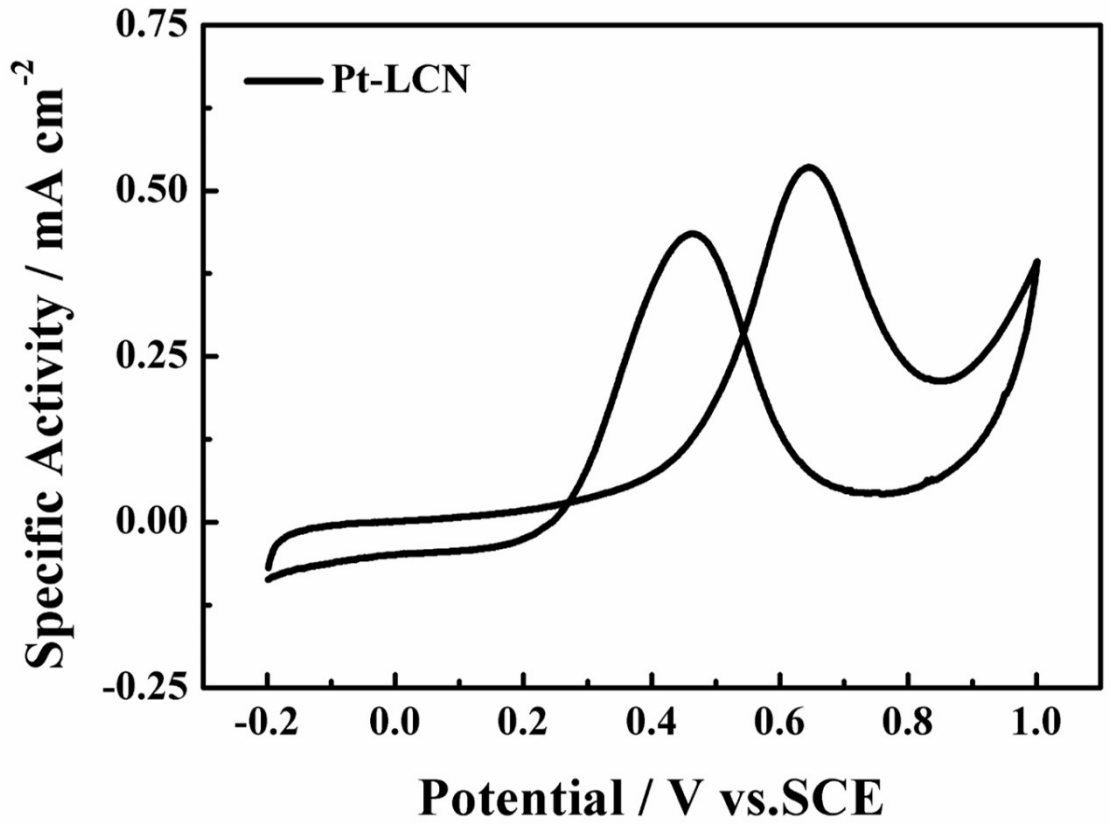

Fig. S5. CV curves of Pt-LCN.

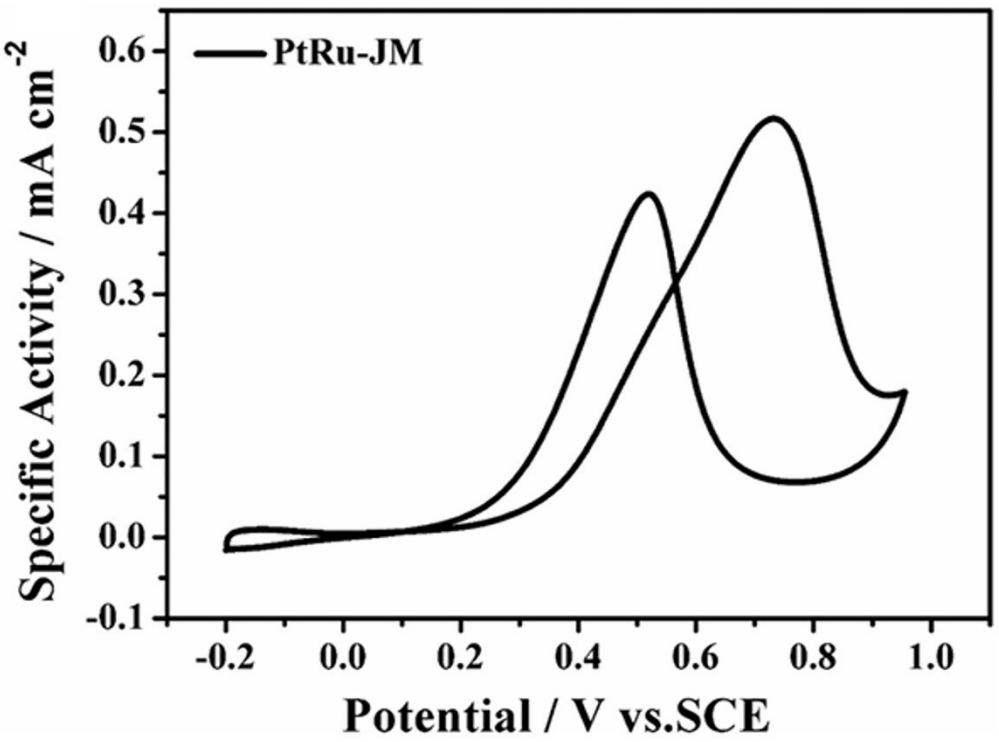

Fig. S6. Specific activity of commercial PtRu-JM.

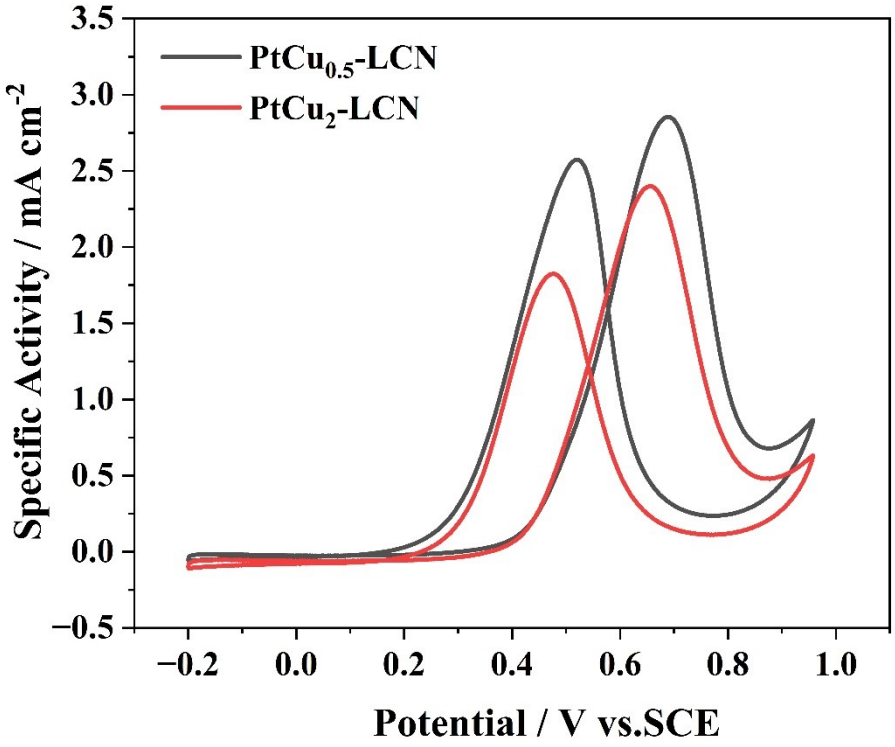

Fig. S7. Specific activity of $PtCu_{0.5}$-LCN and $PtCu_2$-LCN.

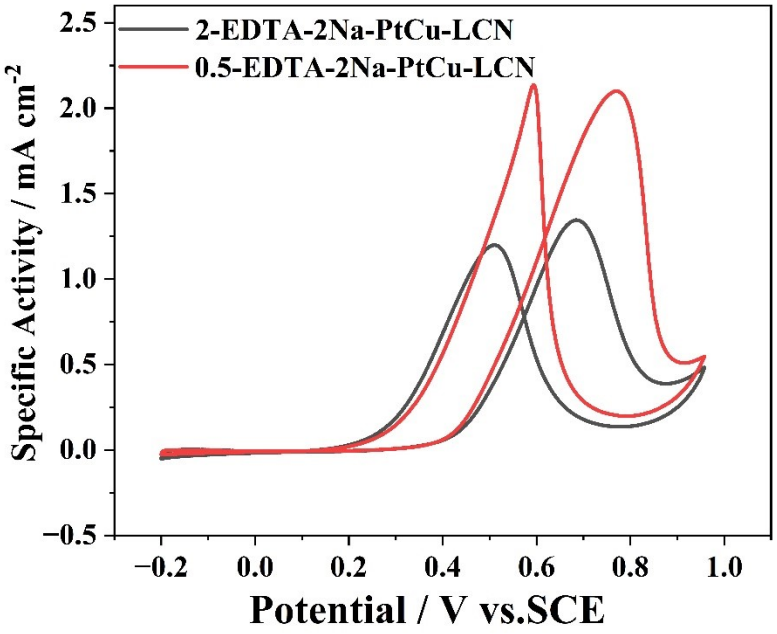

Fig. S8. Specific activity of 2-EDTA-2Na-PtCu-LCN and 0.5-EDTA-2Na-PtCu-LCN.

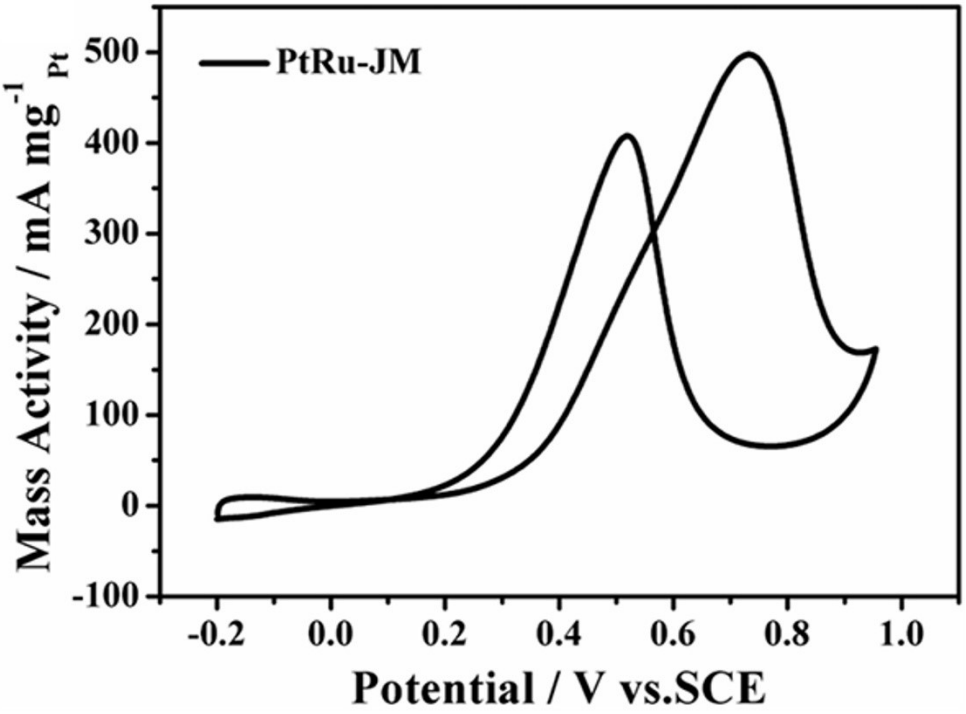

Fig. S9. Mass activity of commercial PtRu-JM.

Table. S1 Comparison of the methanol oxidation performance of PtCu-LCN with recently reported state-of-the-art catalysts.

Catalysts	Mass Activity ($mA \cdot mg_{Pt}^{-1}$)	Methanol Concent	Electrolyte	Reference
PtCu/GDY	336	1.0 M	0.5 M H_2SO_4	1
PtCu-250	755.5	0.5 M	0.5 M H_2SO_4	2
M-PtCu/G	792.9	0.5 M	0.5 M H_2SO_4	3
PtCoCu/G	750	1.0 M	0.5 M H_2SO_4	4
Pt-Cu@CeO_2/ MWCNTs	833.75	1.0 M	0.5 M H_2SO_4	5
$Pt_{0.10}$/Cu-MoC	563.25	1.0 M	1.0 M KOH	6
PtNiCu/MWCNT	871.4	0.5 M	0.5 M H_2SO_4	7
Cu-$Pt_{5.2}Ru_1$	638.2	1.0 M	0.5 M H_2SO_4	8
Cu@Pt/C 18nm	521	0.1 M	0.1 M $HClO_4$	9
PtCu-LCN	891.69	1.0 M	0.5 M H_2SO_4	**This work**

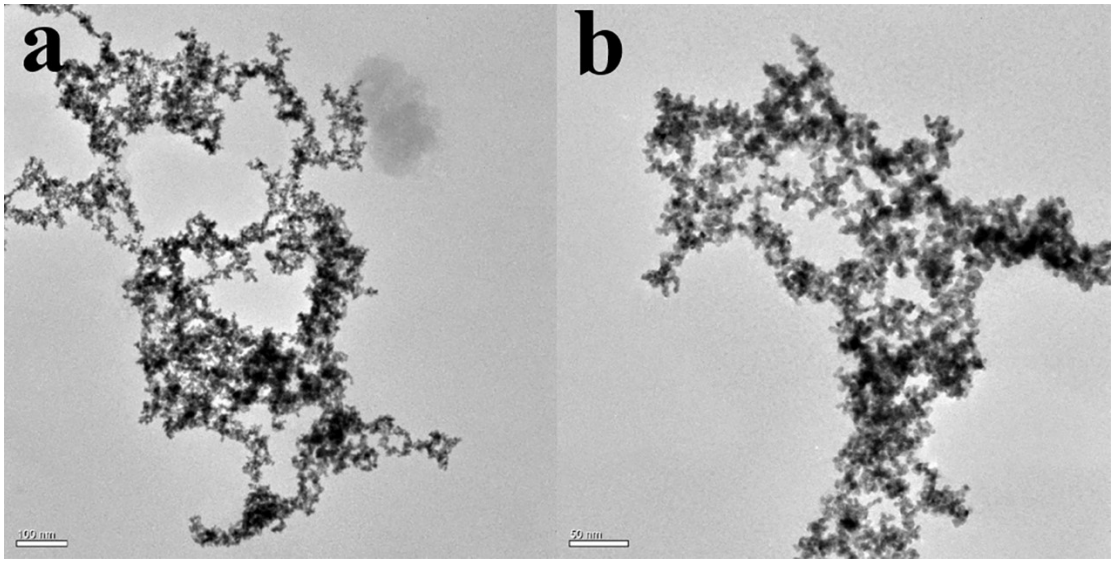

Fig. S10. TEM of PtCu-LCN after testing with 100 nm (a) and 50 nm (b).

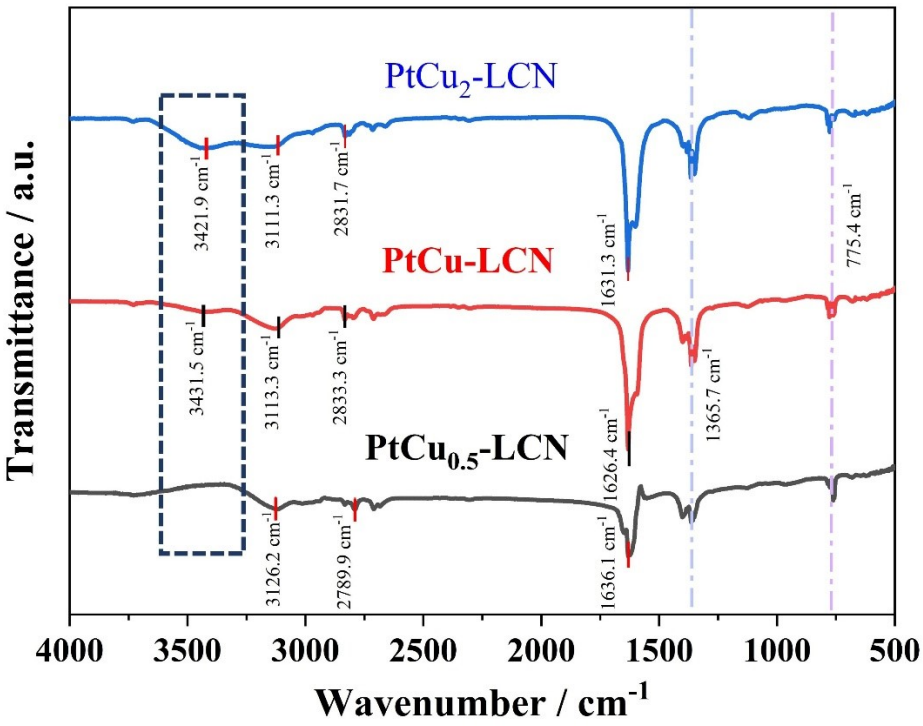

Fig. S11 FTIR image of $PtCu_2$-LCN, PtCu-LCN and $PCu_{0.5}$-LCN.

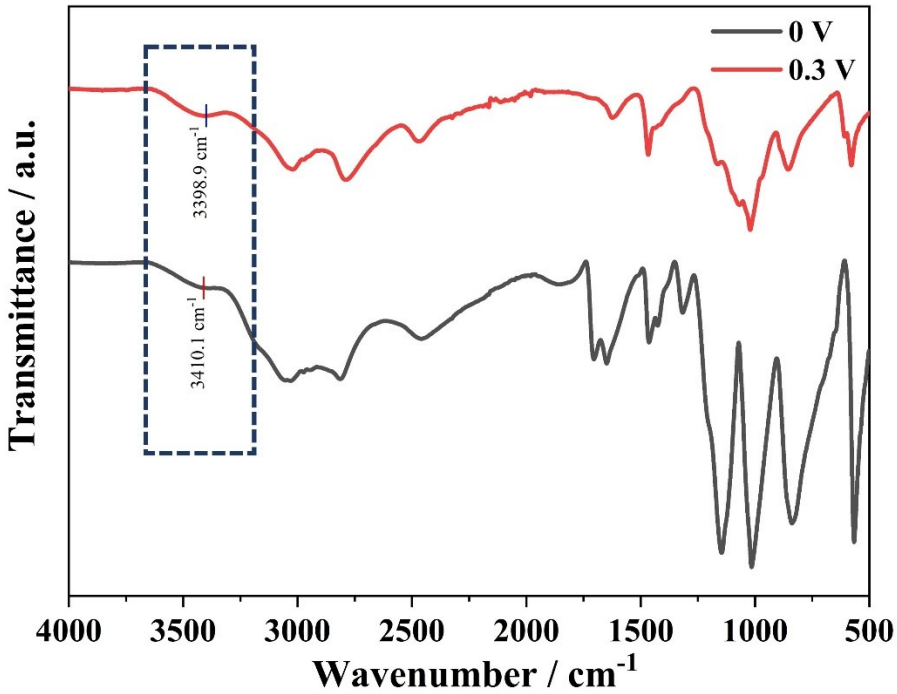

Fig. S12 FTIR image of PtCu-LCN at different potential.

References

1. C. Zhang, Y. Zhang, H. Xiao, J. Zhang, L. Li, L. Wang, Q. Bai, M. Liu, Z. Wang and N. Sui, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2021, **612**, 125960.

2. J. Cao, Y. Du, M. Dong, Z. Chen and J. Xu, *Journal of Alloys and Compounds*, 2018, **747**, 124-130.

3. X. Liang, M. Huang, F. Huang, X. Peng, K. K. Rani, L. Wang, Z. Yang, Y. Fan and D.-H. Chen, *Molecular Catalysis*, 2023, **545**, 113225.

4. R. Chen, J. Gao, J. Yang, F. Zhang and Q. Wang, *Fuel*, 2024, **371**, 131994.

5. X. Zhang, C. Wang, C. Luan, M. Liao and W. Xu, *New Journal of Chemistry*, 2024, **48**, 7964-7971.

6. Z. Wang, L. Wang, K. K. Rani, M. Waqas, D. Huang, Q. Huang, X. Liu, Z. Yang, X. Peng, D.-H. Chen, W. Chen and Y. Fan, *Journal of Alloys and Compounds*, 2023, **946**, 169354.

7. W. Zhou, R. Yan and S. Zhou, *Surfaces and Interfaces*, 2023, **40**, 103131.

8. S. Polani, M. Shviro, V. Shokhen, M. Zysler, A. Glüsen, R. Dunin-Borkowski, M. Carmo and D. Zitoun, *Catalysis Science & Technology*, 2020, **10**, 5501-5512.

9. X. Wang, Q. Lan, Y. Li and S. Liu, *MatL*, 2017, **198**, 148-151.