

## Supporting Information

### Selective CO<sub>2</sub> Electroreduction over Oxide-Derived Gallium Catalyst

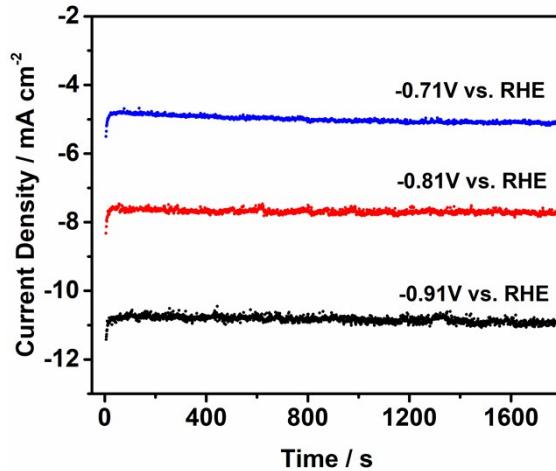
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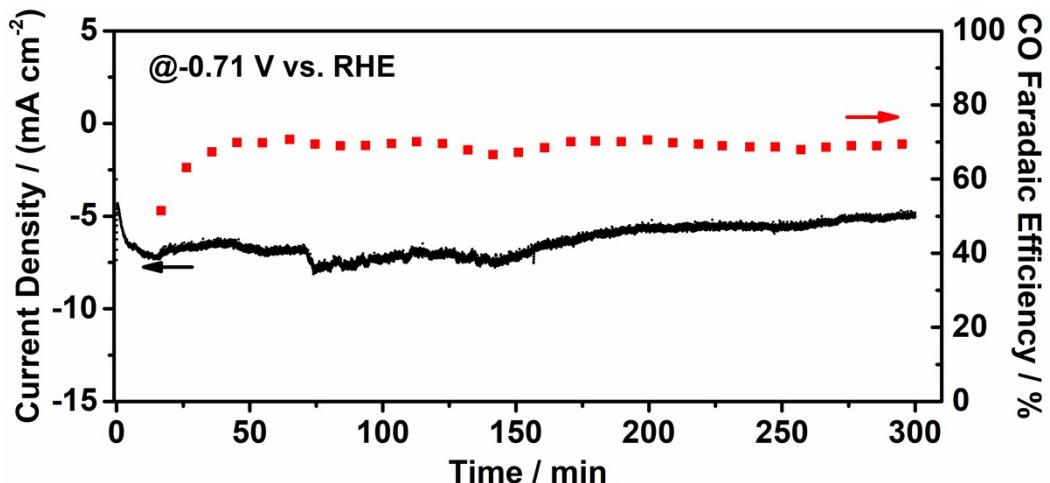
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<sup>c</sup> University of Chinese Academy of Sciences, Beijing, 100039, China

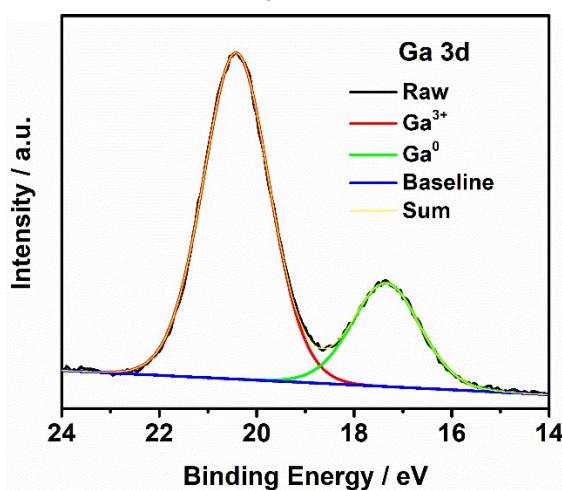
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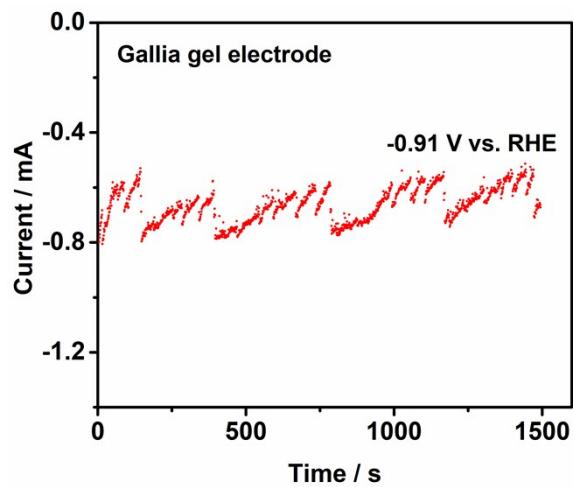
**Fig. S1.** Cathodic current density at other potentials after first tested at -0.61 V vs. RHE on Gallia gel/C electrode.



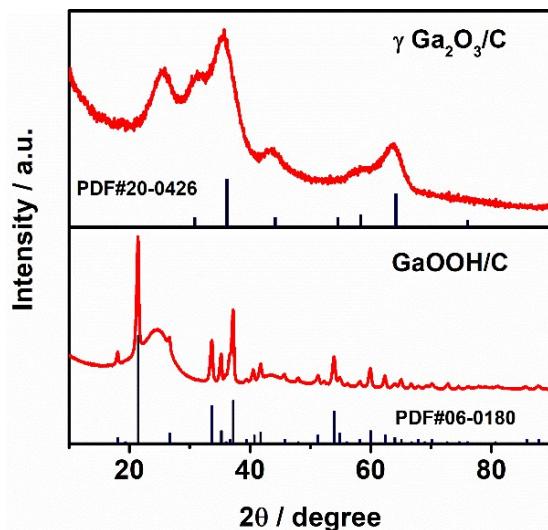
**Fig. S2** Stability test of Gallia gel/C at -0.71 V vs. RHE in CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub> solution.



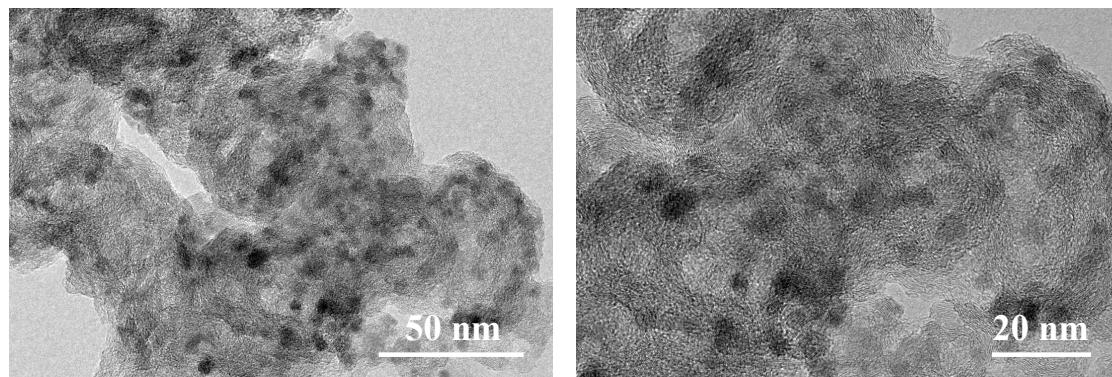
**Fig. S3.** (a) High-resolution Ga 3d XPS spectra of Gallia gel/C electrode after the CO<sub>2</sub>RR measurements with activation at -0.61 V vs. RHE.



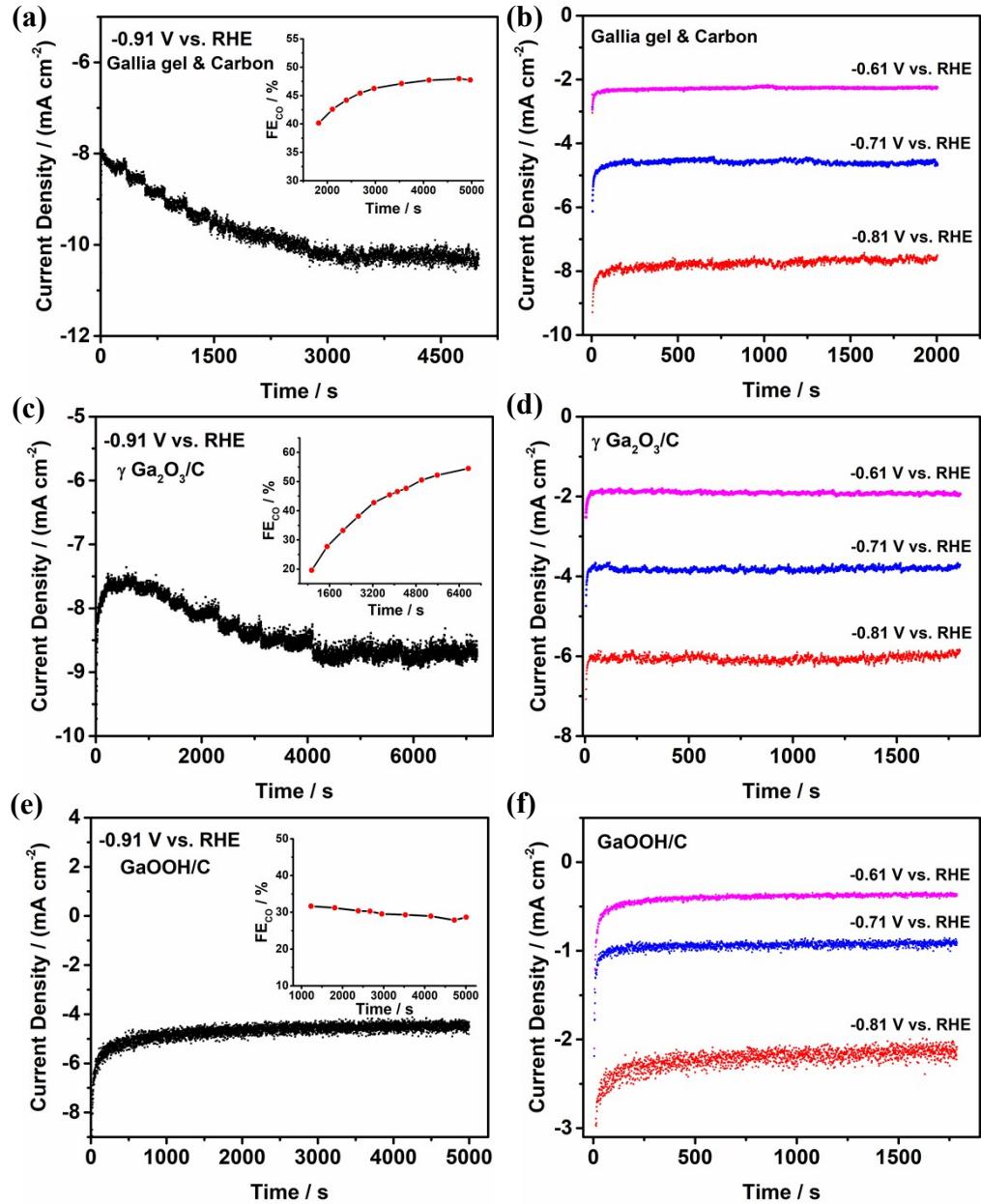
**Fig. S4.** Cathodic current plot for gallia gel electrode tested at -0.91 V vs. RHE with the same Ga loading with Gallia gel/C electrode.



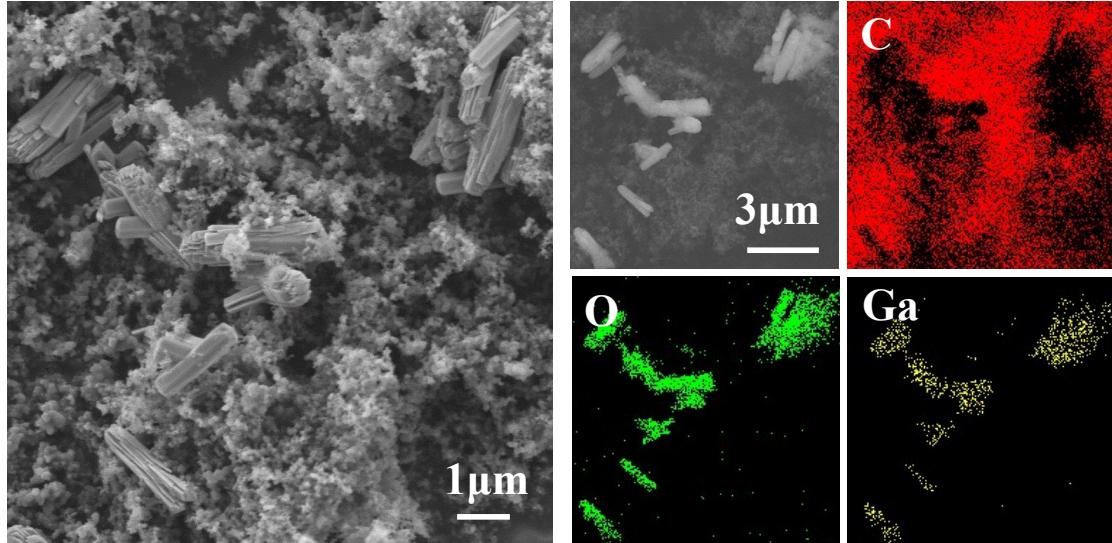
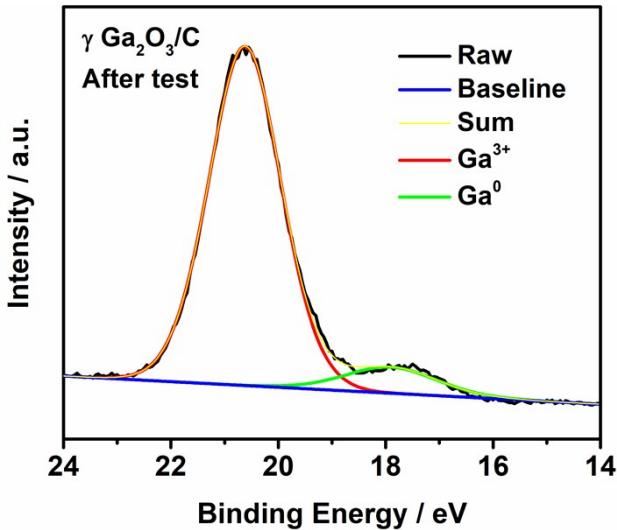
**Fig. S5.** XRD patterns for  $\gamma$   $\text{Ga}_2\text{O}_3/\text{C}$  and  $\text{GaOOH}/\text{C}$  and corresponding standard PDF documents.



**Fig. S6.** TEM images for  $\gamma$   $\text{Ga}_2\text{O}_3/\text{C}$  at different resolutions, showing well-dispersion of  $\gamma$   $\text{Ga}_2\text{O}_3$  nanoparticles.



**Fig. S7.** Cathodic current density profiles for (a) gallia gel mixed with carbon electrode, (c)  $\gamma$  Ga<sub>2</sub>O<sub>3</sub>/C electrode and (e) GaOOH/C electrode for the initial test at -0.91 V vs. RHE, insets show the variation of CO Faradaic efficiency during the corresponding electrolysis time; Corresponding I-t curves at other potentials after activation at -0.91 V vs. RHE for (b) gallia gel mixed with carbon electrode, (d)  $\gamma$  Ga<sub>2</sub>O<sub>3</sub>/C electrode and (f) GaOOH/C electrode.



**Fig. S9.** SEM image and corresponding EDS Mappings for  $\text{GaOOH}/\text{C}$ .

**Table S1.** Comparison with reported Ga-based catalysts for  $\text{CO}_2\text{RR}$

<b>Electrode</b>	<b>Potential(V)</b> <b>vs. Ag/AgCl</b>	<b>Current density</b> <b>(mA cm<sup>-2</sup>)</b>	<b>f<sub>CO</sub>%</b>	<b>f<sub>HCOO-</sub>%</b>	<b>f<sub>H2</sub>%</b>	<b>Electrolyte</b>
Gallia gel/C this work	-1.52	10.7	65.0	0	35.0	0.1 M KHCO <sub>3</sub>
Gallia gel/C this work	-1.32	4.8	77.0	0	23.0	0.1 M KHCO <sub>3</sub>
Ga <sup>1</sup>	-1.64	5.0	23.2	0	79.0	0.1 M KHCO <sub>3</sub>
Ga <sup>2</sup>	-1.60	4.5	5.9	0	91.0	0.1 M KHCO <sub>3</sub>
Si-doped Ga <sub>2</sub> O <sub>3</sub> <sup>3</sup>	-1.80	< 1	0.7	88.9	9.3	3.0 M KCl

## References

- Y. Hori, H. Wakebe, T. Tsukamoto and O. Koga, *Electrochim. Acta*, 1994, 39, 1833-1839.
- N. Hidetomo, I. Shoichiro, O. Yoshiyuki, I. Kazumoto, M. Masunobu and I. Kaname, *Bull. Chem. Soc. Jpn.*, 1990, 63, 2459-2462.
- T. Sekimoto, M. Deguchi, S. Yotsuhashi, Y. Yamada, T. Masui, A. Kuramata and S. Yamakoshi, *Electrochem. Commun.*, 2014, 43, 95-97.