Electronic Supplementary Material (ESI) for Green Chemistry. This journal is © The Royal Society of Chemistry 2019

Electrochemical Valorization of Carboxylates in Aqueous Solution for the production of Biofuels, Fine Chemicals, and Hydrogen

Gang Yuan, a,d Li Wang, a,d Xiangwen Zhang, a,d Rafael Luque, b,c,* and Qingfa Wang a,d,*

Corresponding Author

* Rafael Luque E-mail: <u>rafael.luque@uco.es</u>
* Qingfa Wang E-mail: <u>qfwang@tju.edu.cn</u>

- ^a Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, 92 Weijin Road, Tianjin 300072, P. R. China, E-mail: qfwang@tju.edu.cn
- ^b Departamento de Quimica Organica, Universidad de Cordoba, Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal IV-A, Km. 396, Cordoba E-14014, Spain, E-mail: rafael.luque@uco.es
- c Peoples Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya 12 str. Moscow 117198, Russia.
- ^d Collaborative Innovation Centre of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin 300072, P. R. China.

1. Supplementary Results

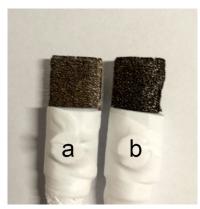


Figure S1. Digital photos of (a) pristine Ti sponge (TS) and (b) Pt@TS.

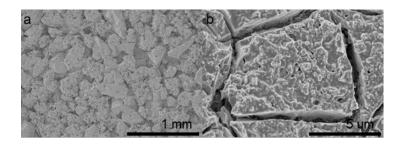


Figure S2. SEM images of pristine TS at (a) low and (b) high magnifications.

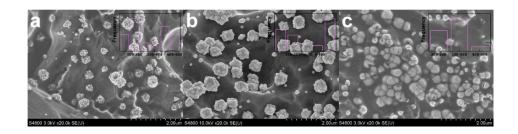


Figure S3. Representative SEM images of *as-prepared* Pt@TS electrodes with the addition of (a) 1 mM, (b) 2 mM, and (c) 5 mM H_2 PtCl₆.

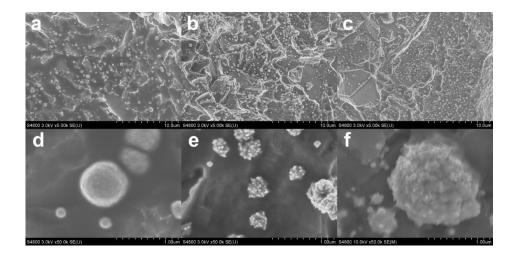


Figure S4. Representative SEM images of *as-prepared* Pt@TS electrodes at (a, d) 4 °C, (b, e) 30 °C, and (c, f) 60 °C.

The following reactions took place in the electrochemical cell during the electrolysis:

Anodic reaction:
$$2RCOO^- \rightarrow R-R + 2CO_2 \uparrow + 2e^-$$
 (R1)

Solution reaction:
$$CO_2 + OH^- \rightarrow HCO_3^-$$
 (R2)

Cathodic reaction:
$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$$
 (R3)

Overall reaction:
$$2RCOO^- + 2H_2O \rightarrow R-R + 2HCO_3^- + H_2\uparrow$$
 (R4)

The electrolyte was acidified with concentrated H₂SO₄ after electrolysis.



Figure S5. Digital photographs of the solution after Kolbe electrolysis. The unreacted CA and hydrophobic products (i.e. tetradance, heptane, and the isomers of heptene) gathered together on the surface of the solution. An obvious phase boundary was formed between the aqueous solution of bicarbonates and hydrophobic biofuels products.

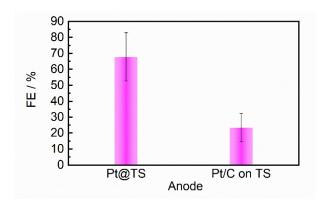


Figure S6. FE comparison of Pt@TS and Pt/C on TS anodes in the aqueous solution of 0.5 M CA and 0.5 M KOH.



Figure S7. Digital photo of flat Pt electrode after electrolysis test. It could be clearly seen that the surface of the electrode was covered with the organic containment which is consistent with the result from the literature.¹

Reference

1. Y. Peng, Y. Ning, X. Ma, Y. Zhu, S. Yang, B. Su, K. Liu and L. Jiang, *Advanced Functional Materials*, 2018, **28**, 1800712.