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## **FULL PAPER**

# Simultaneous production of biofuels, hydrogen and fine chemicals via Kolbe electrolysis of biomass-derived fatty acids over Pt nanocrystals in an electrochemical cell

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**Abstract:** Electrochemical valorization of non-food biomass-derived carboxylates into fuels is promising for the conversion, storage, and distribution of renewable electricity. Herein, we demonstrate that biofuels, hydrogen, and bicarbonate can be simultaneously produced in an electrochemical cell by one-step electrolysis of free fatty acids under ambient conditions on 3D self-supported ultralow Pt loading (2 wt%) electrode. The three valuable products can naturally separate from each other during the electrolysis in the alkaline aqueous solution. The experimental suggests that Pt(100) and Pt(110) are favorable for the production of non-Kolbe and Kolbe hydrocarbons, respectively. DFT calculation further clarifies the adsorption and stabilization of the reaction intermediates on Pt(100) and Pt(110).

### Introduction

The depletion of petroleum-based carbon sources, concerns regarding CO<sub>2</sub> emission, and the increasing need for energy and chemicals are pushing scientists to search for technologies to produce carbon-neutral fuels and renewable chemicals. To address the challenges, efforts in searching green alternative resources (e.g. solar, tide, and wind)<sup>[1]</sup> and developing efficient catalysts to produce biofuels have been made.<sup>[2]</sup> Alternative resources, however, suffer from a fluctuating nature and need to be converted into a storable form.<sup>[3]</sup> Thus, an effective production of biofuels and fine chemicals with these energy resources is important for a sustainable energy future.<sup>[4]</sup>

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Supporting information for this article is given via a link at the end of the document. Biodiesel is a well-known biofuel commonly produced at a large scale using biomass-derived triglycerides (TG) as feedstocks. Comparing to biodiesel ( $C_xH_yO_2$ ), hydrocarbons ( $C_xH_y$ ) retain almost all energy from the precursors.<sup>[5]</sup> Recently, instead of biodiesel production, the conversion of TG to hydrocarbons has been investigated.<sup>[6]</sup> However, the synthesis of hydrocarbons from a refined TG feedstock is not economically feasible. The cost can be reduced by using algal oil as a feedstock, which is rich in free fatty acids (FFAs). To date, the majority of such feedstocks were converted to biodiesel by the esterification of FFAs.<sup>[7]</sup> Alternatively, FFAs can be decarboxylated to provide hydrocarbons, which can be used directly in an internal engine as "green drop-in fuels".

The decarboxylation of FFAs to fuel range products has been carried out mainly through two approaches: hydrothermal treatment and Kolbe electrolysis. The former can achieve a high selectivity with alkali hydroxide and noble metals as catalysts at elevated temperature (e.g. 400 °C) and high pressure (e.g. 3 MPa).<sup>[8]</sup> In contrast, Kolbe electrolysis only uses electricity to decarboxylate FFAs into hydrocarbons at room temperature and pressure.<sup>[9]</sup> It offers a less energy-intensive way for the decarboxylation of FFAs and an effective approach for the conversion and storage of the surplus renewable sourced electricity. In a conventional Kolbe electrolysis process, methanol solution has been used to decarboxylate FFAs over a bulk Pt plate anode, in which 90 % reactant conversion and 32-58 % decarboxylation yield was achieved.<sup>[10]</sup> Comparing to toxic methanol, water fulfills the major criteria of "green chemistry".<sup>[11]</sup> When conducting the electrolysis in aqueous solution, the organic hydrocarbon products can spontaneously separate out from the reaction mixture, which provides an easy and costeffective approach for product collection/separation.[10b, 12] The remaining aqueous solution is rich in fine chemicals, arising from the reaction between CO2 and the alkaline electrolyte. The cathodic "byproduct" gaseous hydrogen (H2) is clean energy and easy to be collected from the system. The roles of Pt nanocrystals morphology and facets on their electrocatalytic FFAs decarboxylation performance in Kolbe electrolysis using Pt as an anode have not been studied yet, which restrict the development of the low-cost, high efficient Pt-based electrodes. In fact, the catalytic properties of Pt-based electrocatalysts depend strongly on their crystal structure and crystal face facets orientation.<sup>[13]</sup> For example, it was reported that Pt(100) has much stronger adsorption of anions than Pt(111).<sup>[14]</sup> Comparing to single crystal electrodes, industrial electrocatalysts are usually extended crystal facets on support to maximize the accessible surface and charge transfer between electrodes and reactants.<sup>[15]</sup> On the other hand, medium-chain n-carboxylates (C6-C12) were identified as important platform chemicals.[10b, 16]

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In this study, Pt nanocrystals with different ratios of Pt(100) to Pt(110), which were controllably electrodeposited on carbon fiber paper (CFP), were used as anodes for the decarboxylation of n-octanoate (C<sub>8</sub>) in aqueous solution. These nanoscale Pt anodes show enhanced activity and stability towards electrocatalytic decarboxylation of n-octanoate, compared with conventional Pt sheet. The decarboxylation performs well at high FFAs concentration (0.5 M), proving the scale-up ability of this procedure. The synchronous produced H<sub>2</sub> at the cathode and bicarbonate in the solution can naturally separate from each other. Moreover, the dependence of the decarboxylation pathways on Pt facets was studied in detail by experiments and DFT calculations.

### **Results and Discussion**



**Figure 1.** Typical SEM images of as-prepared Pt nanoparticles: (a) Pt-NP and (b) Pt–NT; insets are the corresponding SEM images at high magnifications; the scale bars in (a) and (b) are 5  $\mu$ m and 10– $\mu$ m, respectively; both of the scale bars in the inset of (a) and (b) are 100 nm.

Pt nanopolyhedra (Pt-NP) and Pt nanothorns (Pt-NT) were directly electrodeposited on CFP as self-supporting anodes. Figure 1 shows typical SEM (scanning electron microscopy) images of the Pt-NP and Pt-NT anodes with different morphology and sizes. The 3D porous network structure of CFP backbone remains after electrodeposition (Figure S1). In both cases, Pt nanocrystals are homogenously dispersed on CFP (Figure 1a and 1b, size distribution in Figure S2). Pt-NP is composed of Pt nanopolyhedra and Pt nanocubes (Figure 1a inset). Pt-NT only contains Pt nanothorns with several prism branches around the center (Figure 1b inset).

TEM (transmission electron microscope) images of Pt-NP (Figure 2a) and Pt-NT (Figure 2b) clearly show their shapes which are similar to the SEM observations. The HRTEM (high resolution transmission electron microscope) images in Figure 2c-d reveal their highly polycrystalline structure and the presence of Pt(111) and Pt(110) in Pt-NP and Pt(111) and Pt(100) in Pt-NT. The SAED (selected area electron diffraction) patterns (inset in Figure 2c-d) further confirmed the presence of Pt(111), Pt(100) and Pt(110) facets. Their crystal facet distribution was also proved by cyclic voltammetry (CV) in N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> and XRD. Figure 2e shows the cyclic voltammograms normalized by the electrochemical active surface area (ECSA), which was decided from the charge of hydrogen adsorption/desorption on Pt surfaces.

Two sharp peaks at 0.12 V and 0.23 V with a small shoulder be attributed to around 0.28 V can hvdrogen adsorption/desorption at (110) and short-range order (100) domains, respectively.<sup>[17]</sup> The broad peak at 0.23 V observed for Pt-NT reveals that it is rich in Pt(100) facets. For Pt-NP, the peak current density at 0.12 V and 0.23 V are almost same (26.2 µA (cm-Pt)<sup>-2</sup> and 28.2 µA (cm-Pt)<sup>-2</sup>), indicating that the Pt-NP surface consists of roughly equal (110) and (100) facets. The preferential orientation was also confirmed by XRD (Figure 2f). The sharp peaks at 39.8°, 46.2°, 67.5°, and 81.3° are assigned to Pt(111), (200), (220), and (311), respectively, suggesting a high crystallinity Pt with a face-centered cubic structure. The absence of hydrogen adsorption/desorption peaks from Pt(111) and Pt(311) in CV indicates that the exposed surface of the Pt nanoparticles is dominated by Pt(110) and Pt(100). The ratios of peak intensity  $(I_{200} / I_{220})$  are 1.1 ± 0.23, 1.9 ± 0.31, and 0.4 ± 0.27 for Pt-NP, Pt-NT, and Pt/C, respectively, which are close to the results obtained from XRD (details in Table S1). This further indicates that the content of Pt(100) in Pt-NP is roughly equivalent to that of Pt(110), whereas Pt-NT is dominated by Pt (100) facets.



**Figure 2.** (a, b) TEM image of a nanopolyhedron Pt particle and a nanothorn Pt particle, respectively; Inset of (b) is a portion of a nanothorn Pt particle at enlarged view; (c, d) Corresponding HRTEM image of (a) and (b). Insets of (c, d) are the corresponding SAED patterns. (e) Cyclic voltammograms and (f) XRD patterns of Pt-NP (black line), Pt-NT (red line) and Pt/C (blue line).

The electrocatalytic decarboxylation (2.1-2.5V vs SHE)<sup>[18]</sup> was conducted in aqueous solution, where water oxidation (1.23 V vs SHE) is a competitive reaction. We monitored the distribution of the gaseous products during the electrolysis with a gas analysis system (Omni Star GS320, Pfeiffer, Germany). The results (Figure 3) suggested that water oxidation is totally suppressed by decarboxylation at the given conditions in good agreement with

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literature reports.<sup>[18]</sup> Figure 3 shows that only CO<sub>2</sub> and H<sub>2</sub> were detected in the gas mixture when the electrolysis was carried out in a one-pot electrochemical cell, which come from the decarboxylation of octanoate and reduction of water, respectively. On the other hand, the O<sub>2</sub> signal, which comes from intentionally injected air, has the same trend with N<sub>2</sub>, verifying that no more O<sub>2</sub> was formed under electrolysis conditions. With water oxidation being suppressed, the following reactions can take place in the electrochemical cell:

Anodic reaction: 
$$2\text{RCOO}^{-} \rightarrow \text{R-R} + 2\text{CO}_2\uparrow + 2\text{e}^{-}$$
 (1)  
 $\text{CO}_2 + \text{OH}^{-} \rightarrow \text{HCO}_3^{-}$  (2)

Cathodic reaction:  $2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$  (3) Overall reaction:

$$2\mathsf{RCOO}^{-} + 2\mathsf{H}_2\mathsf{O} \to \mathsf{R} + 2\mathsf{HCO}_3^{-} + \mathsf{H}_2\uparrow \tag{4}$$



Figure 3. Real-time gaseous products detection during the electrolysis of n-octanoate at 0.25 A  $\rm cm^{-2}.$ 

It is worth mention that the fresh electrolyte is homogenous and clear. As the electrolysis proceeds, the oil products accumulate on the top of the solution with a discerned phase boundary (Figure S3). This suggests that the integrated production of spontaneously separated biofuels, fine chemicals, and H<sub>2</sub> can be achieved in this cell under ambient conditions.





Figure 4 illustrates the decarboxylation performance of Pt-NP and Pt-NT anodes. As comparisons, unmodified CFP or Pt/C on CFP anodes were also tested under the identical reaction conditions, for which only 5.0% and 8.7% hydrocarbon yields were respectively observed. Pt-containing anodes show higher yields than that on bare CFP, suggesting that the introduction of Pt on CFP can enhance its decarboxylation activity. Both Pt-NP and Pt-NT have better decarboxylation performance and higher Pt(100) to Pt(110) ratios than Pt/C while their Pt contents are roughly the same. Pt-NT was significantly more active for catalytic octanoate decarboxylation as compared to Pt-NP. The current efficiency (CE), hydrocarbons yield and selectivity were found to be ca. 2-3 times higher than that of Pt-NP. These results indicate that Pt-NP and Pt-NT are good Kolbe anodes, Pt facets play a pivotal role on their Kolbe reaction performance, and Pt(100) facets are more active for Kolbe electrolysis with respect to Pt(110).



Figure 5. Reusability of Pt-NP or Pt-NT: Hydrocarbons (a) selectivity and (b) CE; (c) TON and (d) TOF. (reaction conditions: 0.5M aqueous solution of octanoate, 0.25 A cm<sup>-2</sup>).

To further evaluate the suitability of Pt-NT and Pt-NP as decarboxylation anodes, reusability is determined by employing the anode from a previous run in a new run without any treatments. Every run was conducted at a current density of 0.25 A cm<sup>-2</sup> until 1 F mol<sup>-1</sup> of charge is consumed in aqueous electrolyte containing 0.5 M octanoic acid and 0.5 M KOH. The new run is carried out in a different cell using a fresh electrolyte. The reusability was assessed by measuring the selectivity, CE, TON and TOF. Figure 5 shows the electrocatalytic decarboxylation performance of Pt-NP and Pt-NT anodes with different used times. Pt-NT showed good reusability. The hydrocarbons selectivity, CE, TON and TOF were above 35%, 35%, 3000, and 2000  $h^{\text{-1}}$  respectively, after three times, with a performance loss less than 40%. Both anodes indeed show some activity loss after the third run due to product adsorption and surface blockage, as confirmed by BET results (Table S2) and SEM images (Figure S4 and S5). The morphology remained unchanged, while their surface area and pore volume only exhibited minor changes after reuses. Nevertheless, neither Pt-NT nor Pt-NP seemed to suffer from rapid deactivation under

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the investigated reaction conditions. Pt-NT, especially provideed high activity and reusability towards catalytic decarboxylation of carboxylates. It is interesting to note that the hydrocarbons selectivity over Pt-NP increases with reuses (Figure 5a). The corresponding SEM images of the anode after 1<sup>st</sup> run (Figure S5) show that some Pt polyhedra are transformed into Pt nanocubes under the reaction conditions, which leads to an increase of Pt(100) thereby enhancing Pt(100)/Pt(110) ration in Pt-NP. This implies that Pt(100) is more favorable for the electrocatalytic decarboxylation of carboxylate to hydrocarbons than Pt(110), consistent with the findings from Figure 4.

Optimum Pt-NT (more active and recyclable than Pt-NP) was subsequently adopted for further investigations in the effects of Pt loading and Pt facets on its decarboxylation performance. The loading and facets of Pt in Pt-NT anodes were tailored by varying the electro-deposition duration. Pt mass loading increases along with prolonged electrodeposition time, while the size and morphology of Pt-NTs remained almost unchanged (see the comparison in Figure S6). The ratios of Pt facets in obtained Pt-NT anodes were characterized by CV (Figure S7), and results have been complied in Table S3. Pt(110) facets were not detected until the electrodeposition time reached 20 min, and the ratio of Pt(100) to Pt(110) increased with prolonged deposition time. Pt loading and ratio of Pt(110) to Pt(100) in Pt-NT affect its decarboxylation performance, as shown in Figure 6. The hydrocarbons yield, selectivity and CE at 0.07 mg Pt loading were 6.5%, 11.0%, and 23.8%, respectively and at 0.31 mg loading were 27.8%, 41.4%, and 52.2%, respectively. A positive correlation between electrocatalytic decarboxylation performance of Pt-NT and its Pt loading was found. On the other hand, Pt loading increased while its hydrocarbon selectivity decreases when prolonging the electrodeposition time from 20 min to 25 min. It may be caused by more side reactions occur at high Pt(110) to Pt(100) ratio. Some of the products identified by GC-MS included 1-heptanol, 1-heptanal, and heptyl caprylate. The highest TON and TOF values were achieved at 0.07 mg Pt loading and the lowest values at 0.31 mg Pt loading. It seems that the utilization of Pt is more effective where Pt is uniformly dispersed on CFP (Figure S7) and the ratio of Pt(110) to Pt(100) is low (Table S3). These findings confirm that Pt facets in the anodes affect their activity toward octanoate electro-catalytic intrinsic decarboxylation.



Figure 6. (a) CE, selectivity and yield of hydrocarbons and (b) TON and TOF of Pt-NT anodes with different electrodeposition time.

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Scheme 1. Overview of the reaction pathways of the electrocatalytic decarboxylation of octanoate.

Based on above results and the Levy's work.<sup>[19]</sup>, the reaction pathways of Kolbe electrolysis are displayed in Scheme 1. It shows that the hydrocarbon products can be divided into two groups by carbon numbers, C7 group and C14 group (i.e. Kolbe dimers). Figure S8 shows that the portion of C7 hydrocarbons in the products mixture is lower over Pt-NP as compared to Pt-NT. Pt mass loading of the two anodes are almost identical, while the ratio of Pt(110) to Pt(100) is significantly higher than in Pt-NP with respect to Pt-NT. These results pointed out that Pt(110) is more favorable to yield C14 hydrocarbons, while Pt(100) is more favorable to yield C7 hydrocarbons. Moreover, C14 to C7 ratio in the final products increased with an increase of the electrodeposition time for Pt-NT (Figure S9). The amount of Pt(110) and the ratio of Pt(110) to Pt(100) increases along with electrodeposition time (Table S3). The relationship of Pt facets and reaction pathways was further studied by DFT calculations. The magnetization of Pt(100) is 0.8 time higher than that of Pt(110), as seen in Table S4. A strong paramagnetic center can firmly bind the initially formed radicals, inhibits their desorption, and, therefore, promotes their conversion to carbonium ions.<sup>[20]</sup> Besides, the OH\* adsorption is stronger on Pt(110) as compared to Pt(100), as shown in Table S4. The adsorption of OH\* stabilizes the formed surface radicals.<sup>[21]</sup> These DFT calculations demonstrate that Pt(110) facets favor the stabilization of radical intermediates and therefore C-C coupling reaction to yield C14 dimers. Comparably, Pt(100) facets are favorable for the generation of carbonium ions and the formation of C<sub>7</sub> products.

### Conclusions

In summary, self-supported nanoscale Pt anodes were firstly employed for the valorization of biomass-derived fatty acids (C<sub>8</sub> in this case) in aqueous media at room temperature via Kolbe electrolysis. Pt-NT and Pt-NP (Pt content below 2 wt.%) with different morphology and ratio of Pt(100)/Pt(110) were directly grown on CFP substrates by electrodeposition. Pt electrodes could be reused up to 3 times without significant activity loss with Pt-NT comparably more active than Pt-NP. Pt(100) facets were found to favor the generation of hydrocarbons (C<sub>7</sub>) with one carbon atom less than the carboxylate precursor (C<sub>8</sub>), while Pt(110) facets favor the formation of Kolbe dimers (C<sub>14</sub>). This work opens a new door for the selective production of hydrocarbons with different chain lengths by designing novel nanoscale Pt

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anodes with preferred orientations for selective electrochemical reactions.

### **Experimental Section**

#### **General remarks**

All electrochemical experiments were conducted with an undivided glass cell (30 mL) by using a Versa STAT 3 (Princeton Applied Research) electrochemical workstation in a three-electrode arrangement. A 1 cm x1 cm Pt mesh (99.995%; Ida, China) was used as the counter electrode throughout the study. If not stated otherwise, all potentials in this paper are referenced to a saturated calomel electrode (SCE) electrode (244 mV vs SHE). All experiments were performed at least in triplicate and the respective standard deviations were provided.

#### Materials

Potassium hydroxide (KOH, 90%; Aladdin, China), n-octanoic acid (99%; Macklin, China), H<sub>2</sub>PtCl<sub>6</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub> (both 99%, Alfa Aesar, USA), Pt/C (20 wt%, Hesen, China) and argon (99.9%; Liufang, China) were used as purchased, without purification. Ultrapure water (18.2 M $\Omega$  cm<sup>-1</sup>; home made by a Millipore, Milli-Q Advantage A10 system) and ethanol (95%, Jiangtian, China) were used as the solvent and wash work. 1-heptene, n-heptane, n-tetradecane and n-dodecane (all 99%; Sigma–Aldrich, Germany), were used for the GC internal calibration.

#### Preparation of the electrodes

Electrodeposition of Pt nanoparticles was prepared in 2 mM H<sub>2</sub>PtCl<sub>6</sub> + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution according to the method described in literature and our previous work.<sup>[22]</sup> Pt nanopolyhedra (denoted as Pt-NP) were synthesized via cyclic voltammetry from 0.4 V to -0.25 V vs SCE at 50 mV s<sup>-1</sup> for 50 cycles; Pt nanothorns (denoted as Pt-NT) were obtained by square wave potential between -0.2 V and 0.8 V vs SCE at 10 Hz for 20min.Carbon fiber paper (CFP, from Toray) was used as the current collector and support of the above Pt nanoparticles. In addition, the Pt/C anode was prepared by a drop-dry method on a piece of CFP (Pt/C@CFP, 1cm×1cm, the Pt mass loading was ca. 0.3 mg cm<sup>-2</sup>) as in the literature.<sup>[23]</sup>

#### Catalytic activity evaluation

The catalytic activities of the as synthesized Pt-NT and Pt-NP for Kolbe electrolysis were evaluated in an electrolytic cell. The electrolyte was a 25 ml aqueous solution of 0.5 M n-octatonic acid and 0.5 M KOH in each experiment. Ultrapure water was used as the solvent. As a comparison, commercial Pt/C on CFP and blank CFP were also used for the electrolysis. The electrolysis was conducted at 250 mA until the total charge consumption at 1 Faraday per mole (F mol<sup>-1</sup>).<sup>[24]</sup>

#### Materials characterization

The size and morphology of all of the materials were measured with a JSM-6700F FE- scanning electron microscopy (JEOL, Japan) at an acceleration voltage of 3 kV. X-ray diffraction (XRD) patterns were analyzed by a Bruker AXS D8 Discover X-ray diffractometer with Cu K $\alpha$  radiation. The specific surface area was calculated according to the Brunauer-Emmett-Teller (BET). The pore volume and pore size distribution were obtained from the Horvath-Kawazone Differential Pore Volume Plot. The mass loading of Pt nanoparticles on CFP before and

after catalytic test was determined with an inductively coupled plasma optical emission spectrometer (ICP-OES).

#### Electrolysis products analysis

#### Qualitative analysis

Qualitative analysis was conducted by GC-MS. About 0.02  $\mu$ l of each sample was injected in the split-injection mode with a split ratio of 100:1. The split/split-less injector was connected to a HP-5MS column (30 m, 0.25mm ID, and 0.25, Agilent) that interfaced with a mass spectrometer (5975N mass spectrometry, Agilent). The temperatures of the injector, interface and ion source were 250, 280, and 230 °C, respectively. Helium was used as the carrier gas set at a constant velocity of 36 cm/s in velocity mode. Initially, the oven temperature was maintained at 40 °C for 1 min, and increased at a rate of 20 °C min<sup>-1</sup> to 200 °C. At last increased at a rate of 40 °C min<sup>-1</sup> to 310 °C and held for 1 min. The mass range scanned was 20 to 300 m/z. Peak identification was accomplished by comparing mass spectra to the National Institute of Standards and Technology (NIST) 2005 mass spectral library (NIST, Gaithersburg, MD).

#### Quantitative analysis

Quantitative analysis was carried out by a GC (Agilent 7890A, Agilent Technologies, United States of America) equipped with a flame ionization detector (FID). The separation is achieved on a LH PONA column (50 m x 0.2 mm; i.d.  $0.5 \mu$ m). For mixed standards, the GC oven is programmed from 40 °C (hold time: 12 min) to 160 °C at a rate of 15 °C min<sup>-1</sup> (hold time: 10 min), and then increased to 280 °C at a rate of 15 °C min<sup>-1</sup> (hold time: 2 min). The concentration of the hydrocarbons (i.e. n-heptane, 1-heptene, n-tetradecane) and n-octanoic acid were determined by internal calibrate curves with n-dodecane as an internal standard.

#### Calculation

The conversion (%) of n-octanoic acid, yield (%), and selectivity (%) of electrocatalytic deoxygenation products were calculated based on the following three equations:

Conversion	(%) = $\frac{mol \ of \ n-octanoic \ acid \ consumed}{mol \ of \ intial \ n-octanoic \ acid} \times 100\%$	(1)
Vield (%) –	mol of C14 formed×2+mol of C7 formed $\times 100\%$	(2)

	mol of n–octanoic acid consumed		(-)
Selectivity (%	$b) = \frac{yield  of  hydrocarbons}{conversion  of  n-octanoic  acid}$	× 100%	(3)

The turnover number (TON) and turnover frequency (s<sup>-1</sup>, TOF) of the Pt-NP and Pt-NT electrodes were calculated based on the following two equations<sup>[25]</sup>:

$=\frac{mol of C14 formed \times 2+mol of C7 formed}{mol of Pt nanoparticles on the surface} \times 100\%$	
reaction time (h)	

The current efficacy (CE) of products formation was calculated based on the following two equations

$$CE (\%) = \frac{mol of C14 formed \times 2+mol of C7 formed}{total charge passed/F} \times 100\%$$
(6)

where the number of electron transfer for  $C_{14}$  product formation is 2, for  $C_7$  product formation is 1, and F is the Faraday constant (96485 C mol<sup>-1</sup>).

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#### **DFT Calculation**

In this work, we compared OH\* adsorption properties on Pt(110) and Pt(100) surface studied by density functional theory (DFT) with the Vienna ab initio simulation package (VASP) with Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation (GGA) functional.

The optimized lattice parameter of Pt is 3.957 Å. Pt(110) modeling with five layers and Pt(100) with six layers, both surface with the bottom two layers fixed and other layers together with adsorbed molecular were set free. Spin-polarized was considered. Monkhorst-Pack grids with  $3x 3 \times 1$  k-point sampling were used for both Pt(110) and Pt(100) surfaces.

Total energies were converged lower than 10<sup>-6</sup> eV, 0.02 eV/Å.

Gas-phase species OH\* with  $\Gamma\text{-point}$  calculations were performed in 15 x 15 x 15 Å  $^3$  boxes.

Ead= E (OH\*/Pt surface) - ( EOH(gas) + EPt surface )

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**Keywords:** biomass valorization • renewable resources • Kolbe electrolysis • electrodeposition • DFT calculations

- a) S. Chu, A. Majumdar, *nature* 2012, *488*, 294; b) S. Chu, Y. Cui, N. Liu, *Nature materials* 2017, *16*, 16.
- a) J. C. Serrano-Ruiz, R. Luque, A. Sepúlveda-Escribano, *Chemical Society Reviews* 2011, *40*, 5266-5281; b) A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, *science* 2006, *311*, 484-489; c) M. E. Himmel, S.-Y. Ding, D. K. Johnson, W. S. Adney, M. R. Nimlos, J. W. Brady, T. D. Foust, *science* 2007, *315*, 804-807.
- [3] E. Troncoso, M. Newborough, International journal of hydrogen energy 2011, 36, 120-134.
- [4] a) Y. Zheng, Y. Jiao, M. Jaroniec, S. Z. Qiao, Angewandte Chemie International Edition 2015, 54, 52-65; b) D. Kang, T. W. Kim, S. R. Kubota, A. C. Cardiel, H. G. Cha, K.-S. Choi, Chemical reviews 2015, 115, 12839-12887.
- [5] L. Petrus, M. A. Noordermeer, *Green chemistry* **2006**, *8*, 861-867.
- a) I. Kubičková, D. Kubička, Waste and Biomass Valorization 2010,
   1, 293-308; b) H. Chen, Q. Wang, X. Zhang, L. Wang, Applied Catalysis B: Environmental 2015, 166, 327-334.
- [7] a) D. Kusdiana, S. Saka, in Proceedings of the Twenty-Fifth Symposium on Biotechnology for Fuels and Chemicals Held May 4– 7, 2003, in Breckenridge, CO, Springer, 2004, pp. 781-791; b) K. Okitsu, Y. Sadanaga, N. Takenaka, Y. Maeda, H. Bandow, Bioresource Technology 2010, 101, 5394-5401.

- [8] A. A. Peterson, F. Vogel, R. P. Lachance, M. Fröling, M. J. Antal Jr, J. W. Tester, *Energy & Environmental Science* 2008, 1, 32-65.
- a) B. A. Frontana-Uribe, R. D. Little, J. G. Ibanez, A. Palma, R. Vasquez-Medrano, *Green Chemistry* 2010, *12*, 2099-2119; b) H. Kolbe, *Justus Liebigs Annalen der Chemie* 1849, 69, 257-294.
- a) H. Schäfer, Chemistry and Physics of Lipids 1979, 24, 321-333;
   b) C. Urban, J. Xu, H. Sträuber, T. R. dos Santos Dantas, J. Mühlenberg, C. Härtig, L. T. Angenent, F. Harnisch, Energy & Environmental Science 2017, 10, 2231-2244; c) H.-J. Schäfer, in Electrochemistry IV, Springer, 1990, pp. 91-151.
- P. Anastas, N. Eghbali, *Chemical Society Reviews* 2010, *39*, 301-312.
- a) S. R. Kubota, K. S. Choi, *ChemSusChem* 2018, *11*, 2138-2145;
   b) P. Nilges, T. R. dos Santos, F. Harnisch, U. Schröder, *Energy & Environmental Science* 2012, *5*, 5231-5235.

a) V. R. Stamenkovic, B. S. Mun, K. J. Mayrhofer, P. N. Ross, N. M. Markovic, *Journal of the American Chemical Society* 2006, *128*, 8813-8819; b) L. Zhang, W. Niu, G. Xu, Nano Today 2012, 7, 586-605; c) W. Niu, J. Liu, J. Huang, B. Chen, Q. He, A.-L. Wang, Q. Lu, Y. Chen, Q. Yun, J. Wang, C. Li, Y. Huang, Z. Lai, Z. Fan, X.-J. Wu, H. Zhang, Nature Communications 2019, 10, 2881.

- [14] V. Stamenkovic, N. Markovic, P. Ross Jr, Journal of Electroanalytical Chemistry 2001, 500, 44-51.
- [15] a) X. Liang, Y. Zhou, J. Li, A. W. Weimer, *Journal of Nanoparticle Research* 2011, *13*, 3781-3788; b) J. Lai, F. Lin, Y. Tang, P. Zhou, Y. Chao, Y. Zhang, S. Guo, Advanced Energy Materials 2019, 9, 1800684.
- [16] M. T. Agler, B. A. Wrenn, S. H. Zinder, L. T. Angenent, *Trends in biotechnology* 2011, *29*, 70-78.
   [17] Y.-J. Fan, C.-J. Fan, C.-H. Zhen, S.-P. Chen, S.-G. Sun,
  - Y.-J. Fan, C.-J. Fan, C.-H. Zhen, S.-P. Chen, S.-G. Sun, *Electrochimica acta* **2006**, *5*2, 945-950.
- [18] A. Vijh, B. Conway, *Chemical Reviews* **1967**, *67*, 623-664.
- [19] P. Michaud, M. Panizza, L. Ouattara, T. Diaco, G. Foti, C. Comninellis, *Journal of applied electrochemistry* 2003, 33, 151-154.
- [20] S. D. Ross, M. Finkelstein, The Journal of Organic Chemistry 1969, 34, 2923-2927.
- [21] D. Bijl, H. Kainer, A. C. Rose-Innes, *Nature* **1954**, *174*, 830.
- [22] a) G. Wang, B. Huang, L. Xiao, Z. Ren, H. Chen, D. Wang, H. D. Abruña, J. Lu, L. Zhuang, *JACS* 2014, *136*, 9643-9649; b) H. Zhang, X. K. Gu, C. Canlas, A. J. Kropf, P. Aich, J. P. Greeley, J. W. Elam, R. J. Meyers, J. A. Dumesic, P. C. Stair, *Angew. Chem. Int. Ed.* 2014, *53*, 12132-12136; c) J. M. Encinara, A. Pardal, *Fuel Process. Technol.* 2012, *103*, 9-15.
- [23] J. M. Marchetti, A. F. Errazu, Energy Conversion & Management 2008, 49, 2160-2164.
- [24] T. R. dos Santos, F. Harnisch, P. Nilges, U. Schroder, ChemSusChem 2015, 8, 886-893.
- [25] A. J. Bissette, S. P. Fletcher, Angew. Chem. Int. Ed. 2013, 52, 12800-12826.

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## **FULL PAPER**

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#### Harvest from inexhaustible

**nature**: Intermittent renewable electricity can be stored in chemical bonds by atomic economy production of fuels and chemicals from the aqueous solution of biomass over efficient and stable nanoscale electrodes.



Gang Yuan, Chan Wu, Guorong Zeng, Xiaopo Niu, Guoqiang Shen, Li Wang, Xiangwen Zhang, Rafael Luque \*, Qingfa Wang\*

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Simultaneous production of biofuels, hydrogen and fine chemicals via Kolbe electrolysis of biomass-derived fatty acids over Pt nanocrystals in an electrochemical cell