Institut de Recerca en Energia de Catalunya
Catalonia Institute for Energy Research

UNIVERSITAT DE BARCELONA

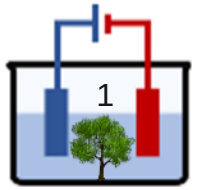
CHINA SCHOLARSHIP COUNCIL

Electrochemical Conversion of Benzaldehyde and its Device Optimization

Applicant: Li Gong

Director: Paulina R. Martínez-Alanis and Andreu Cabot

Monday, June 20, 2022



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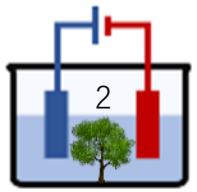


Background

It is urgent to move away from fossil fuels towards renewable sources of energy and to build a climate-friendly circular carbon economy.

Background

petroleum-based carbon sources

biomass and municipal wastes[1]

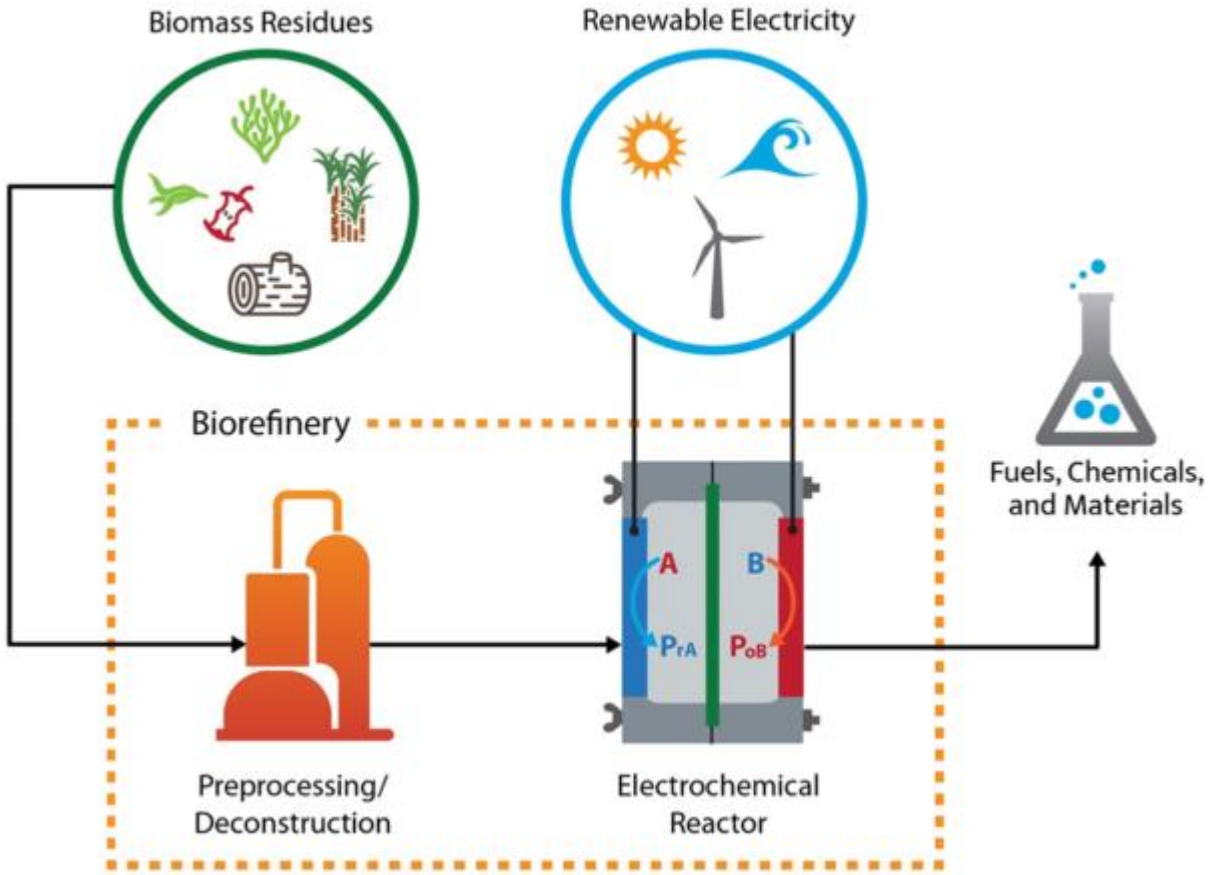


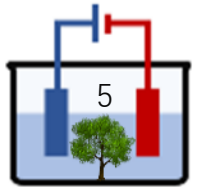
Figure 1. Biorefining with renewable electricity.[2]

1. *Green Chem., 2020, 22, 7233–7264*
2. *2. ACS Energy Lett. 2021, 6, 1205−1270*

Background

Advantages of Electrochemistry

- operates on aqueous feedstocks.
- operates near ambient conditions.
- Sometimes does not require external reagents.
- integrates with renewable energy sources such as solar and wind.



Background

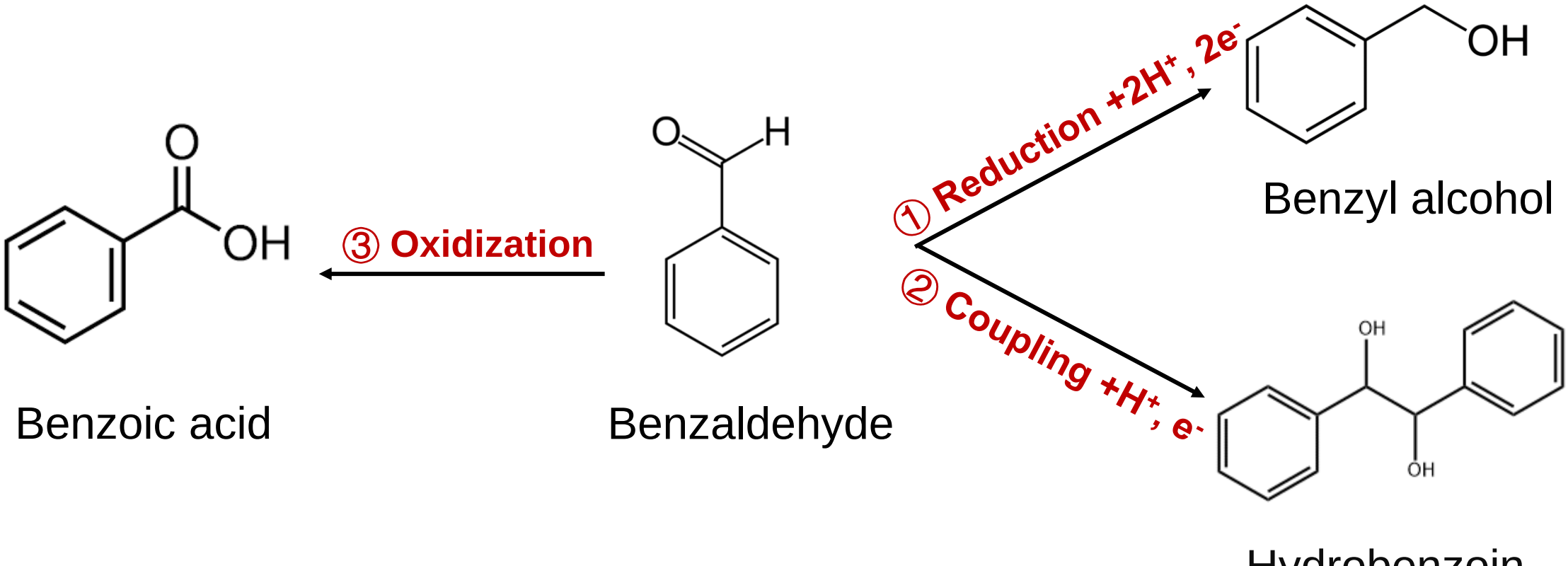
Reasons for conversion of Aldehydes

- Troublesome for Bio-oil upgrading---aldol condensation reactions. [3]
- Aging----secondary condensation and polymerization reactions.[3]
- Valorization of aldehydes into high-value added chemicals.

3. *ACS Catal. 2018, 8, 7645−7658*

Work Plan

Electrochemical conversion pathways of Benzaldehyde:



Benzoic acid

Benzaldehyde

Benzyl alcohol

Hydrobenzoin

Electrocatalytic Hydrogenation of Benzaldehyde into Benzyl alcohol

The importance of adsorption of aldehyde on the catalyst surface.[4]

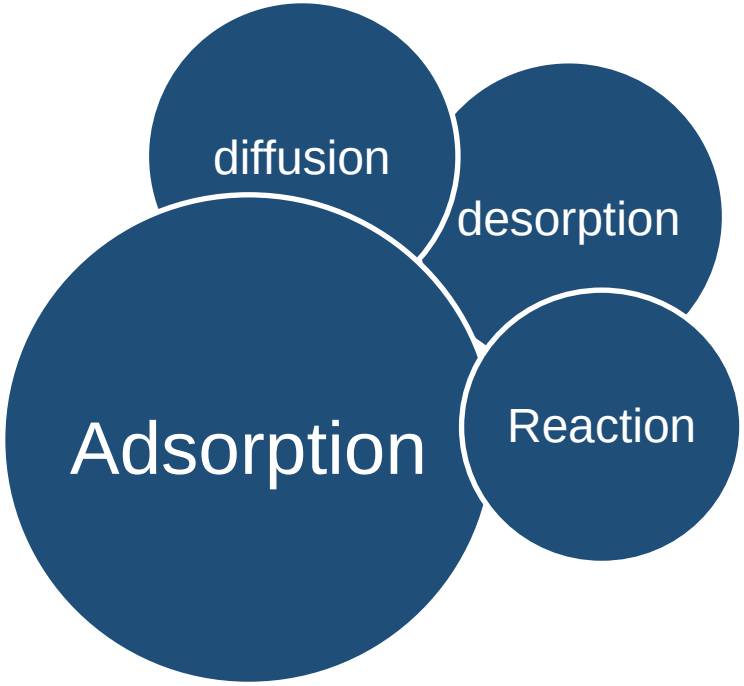


Figure 3. steps of electrocatalysis

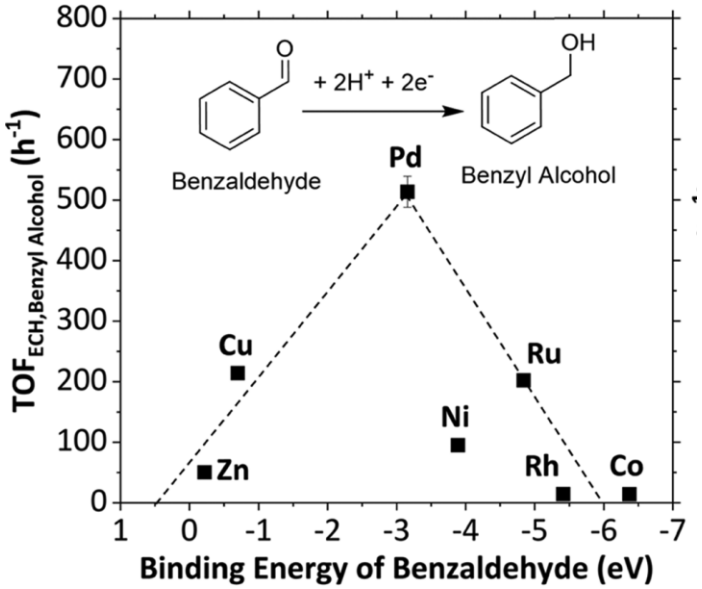


Figure 4. Volcano plots of benzaldehyde to benzyl alcohol with the computed binding energies (BEs) of benzaldehyde.[4]

4. ACS Catal. 2018, 8, 7645−7658

Electrocatalytic Hydrogenation of Benzaldehyde into Benzyl alcohol

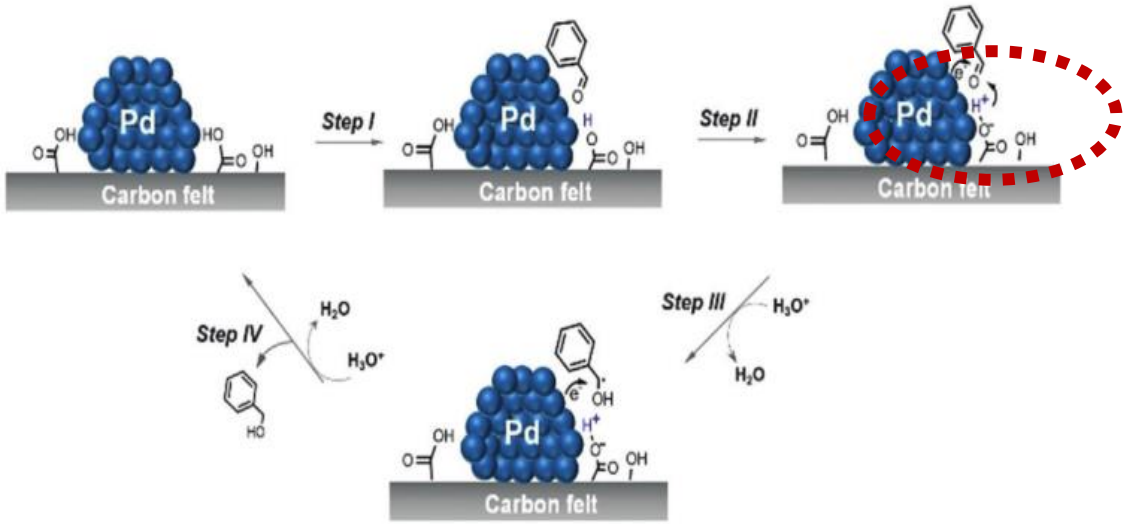


Figure 5. Hydrogenation steps of benzaldehyde depicted as proton-coupled electron additions. [5]

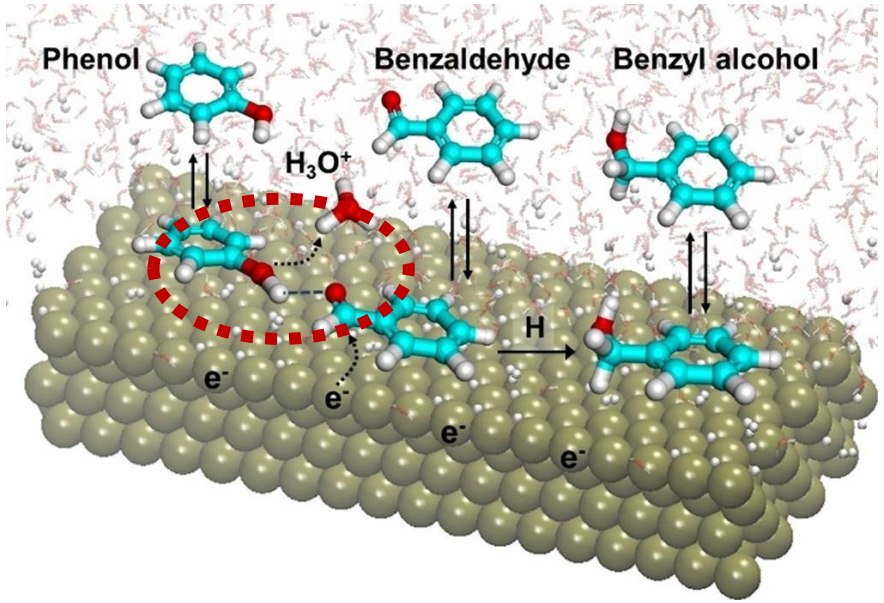
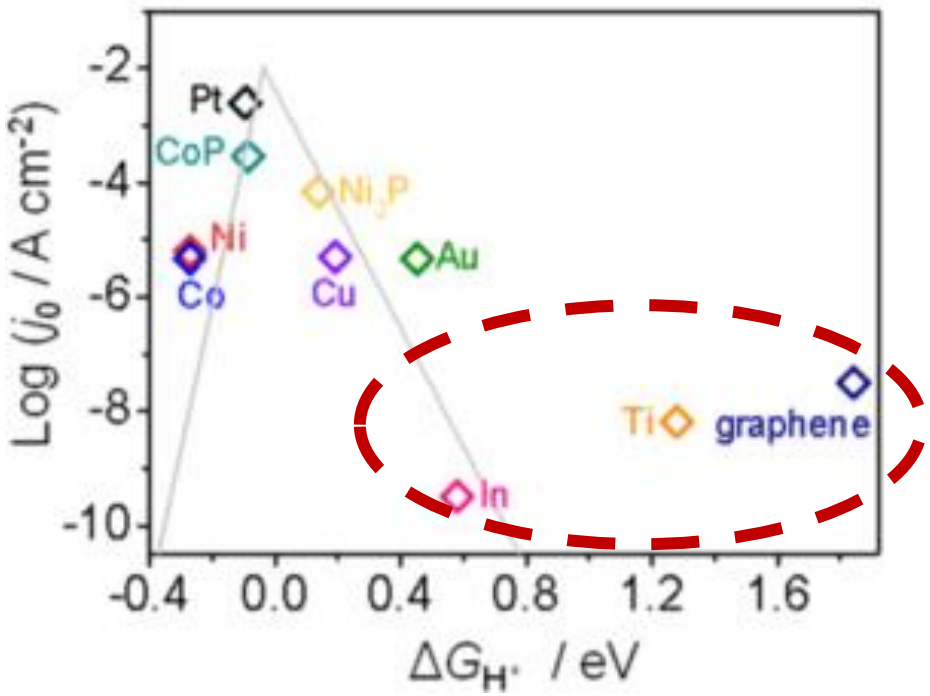


Figure 6. Electrocatalytic hydrogenation of the H-bonded complex formed upon adsorption of benzaldehyde and phenol. [6]

Oxygen-riched surface of the electrocatalyst

5. Angew. Chem. 2020, 132, 1517–1521; 6. Angew. Chem. 2021, 133, 294–300

Electroreductive C-C Coupling of Benzaldehyde into Hydrobenzoin



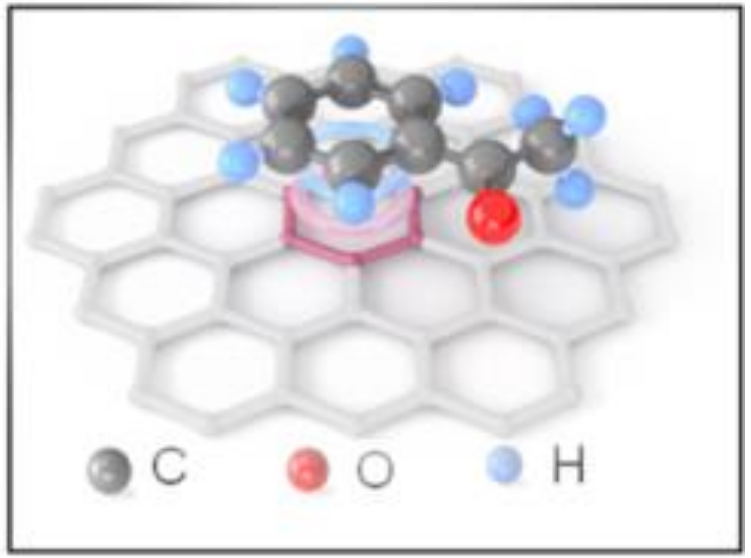


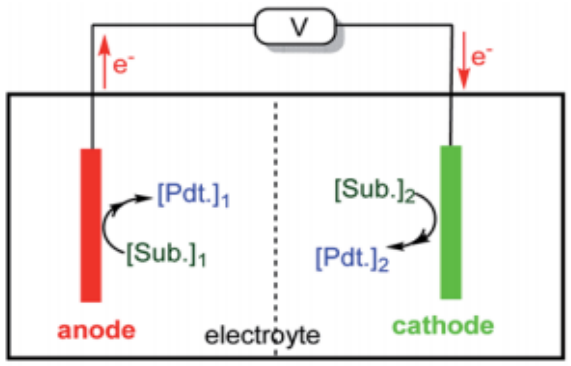
Figure 7. (a) HER calculated ΔG_{H^*}; (b) adsorption of the aryl ring on the surface of the electrode via π−π stacking.[7]

The elements for C-C coupling of Benzaldehyde :

Ti, In, Zn, Cd, Pb…

7. *ACS Catal. 2021, 11, 8958−8967*

Work Plan -------Paired Electrolysis of Benzaldehyde



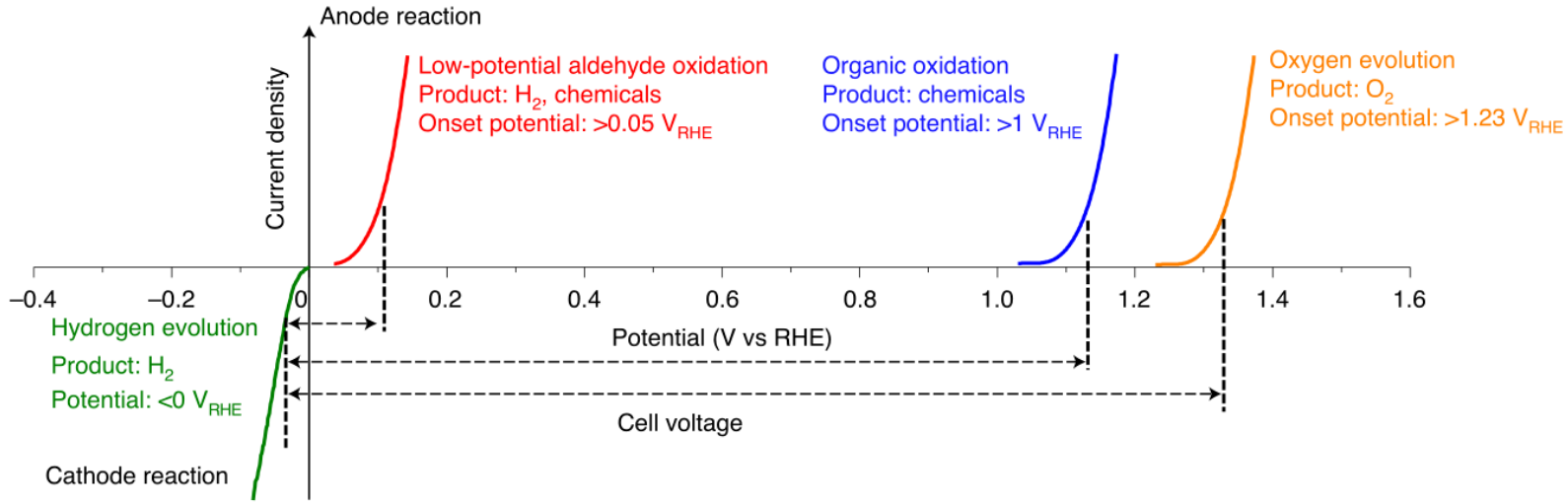


Figure 8. (left) illustration of parallel paired electrolysis[8]; (right) comparison of various anode reactions for water electrolysis.[9]

Combining oxidation and reduction of Benzaldehyde.

8. Chem. Sci., 2020, 11, 10786–10791

9. Nat Catal 5, 66–73 (2022).

Experimental Feasibility ----equipment and Characterizations

(a)

(b)

(c)

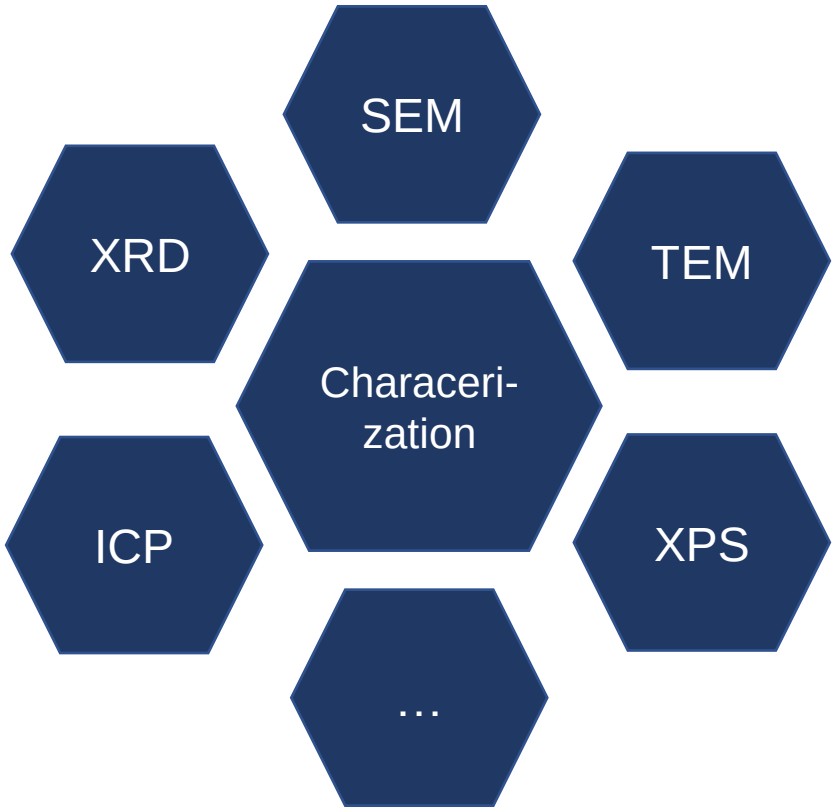


Figure 10. (a) H-cell reactor; (b) High-performance liquid chromatography (HPLC) ;
(c) Characterizations

Experimental Feasibility----Time table

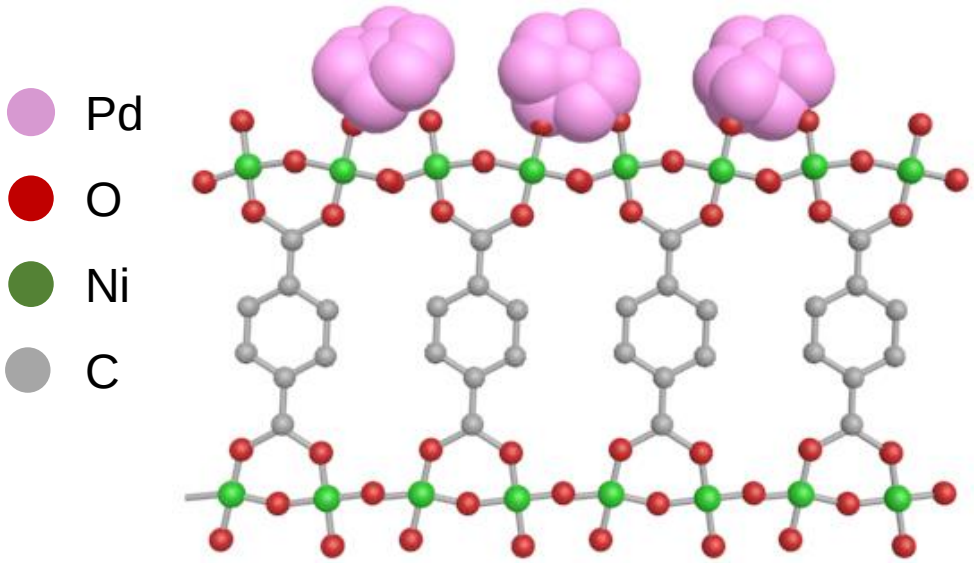
Time table

WPs	6	12	18	24	30	36
WP1 Synthesis of electrocatalysts						
WP2 Study of individual electrocatalytic reactions						
WP3 Design and engineering of electrochemical systems with coupled reactions and process parameter optimization						
WP4 Dissemination and exploitation of the project results						
WP5 Write and defend my PhD thesis						

This project is planned to take place from September 2021 until the end of May 2024.

Experimental Procedure

Work 1 Primarily proved high efficient performance of this electrocatalyst



- Pd as the active component
- MOFs as the support---high content of oxygen on the surface (EDS proved)

Figure 11. illustration of electrocatalyst Pd@Ni-MOF

Experimental Procedure

Large surface area and well distribution of Pd

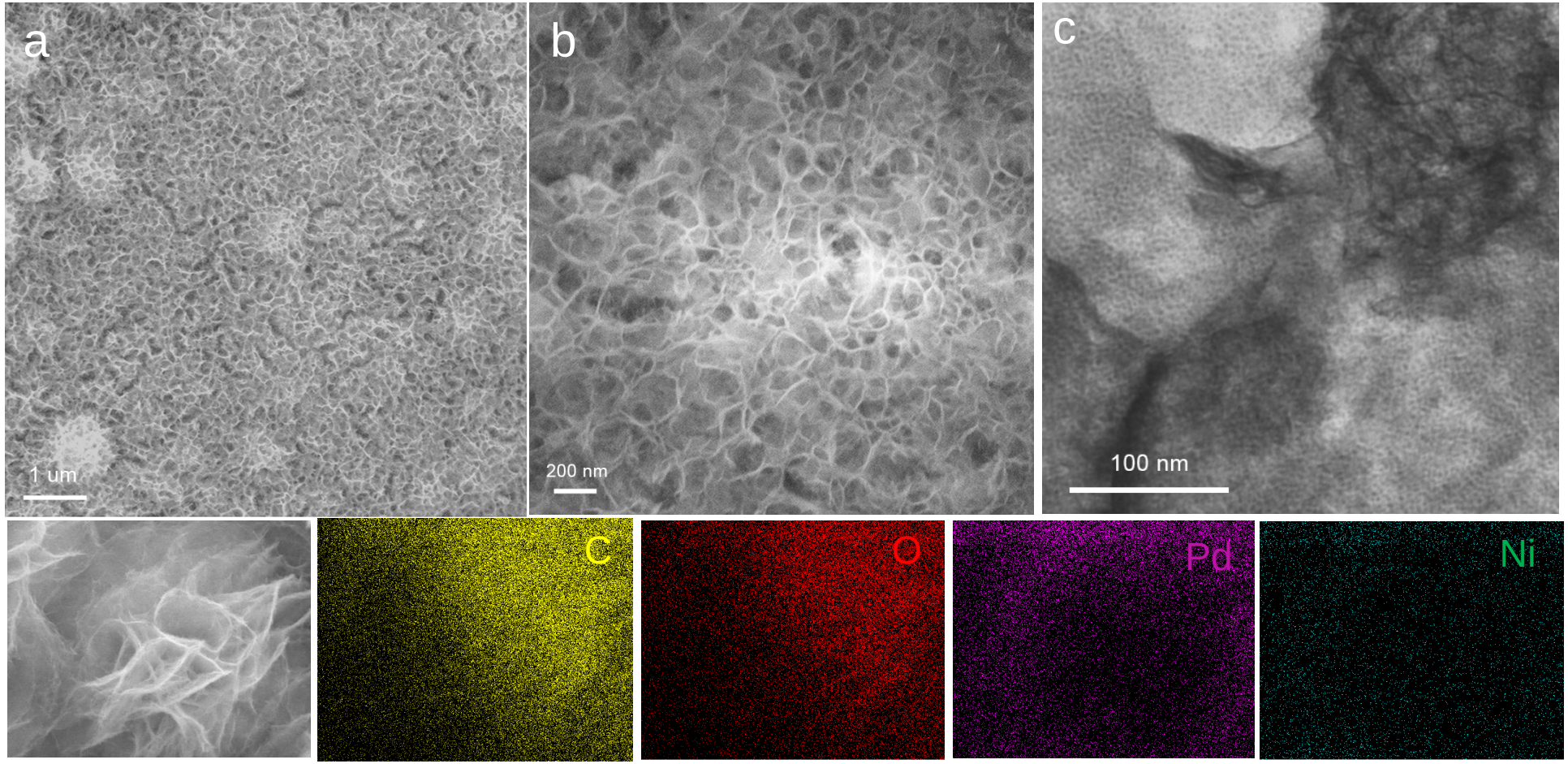
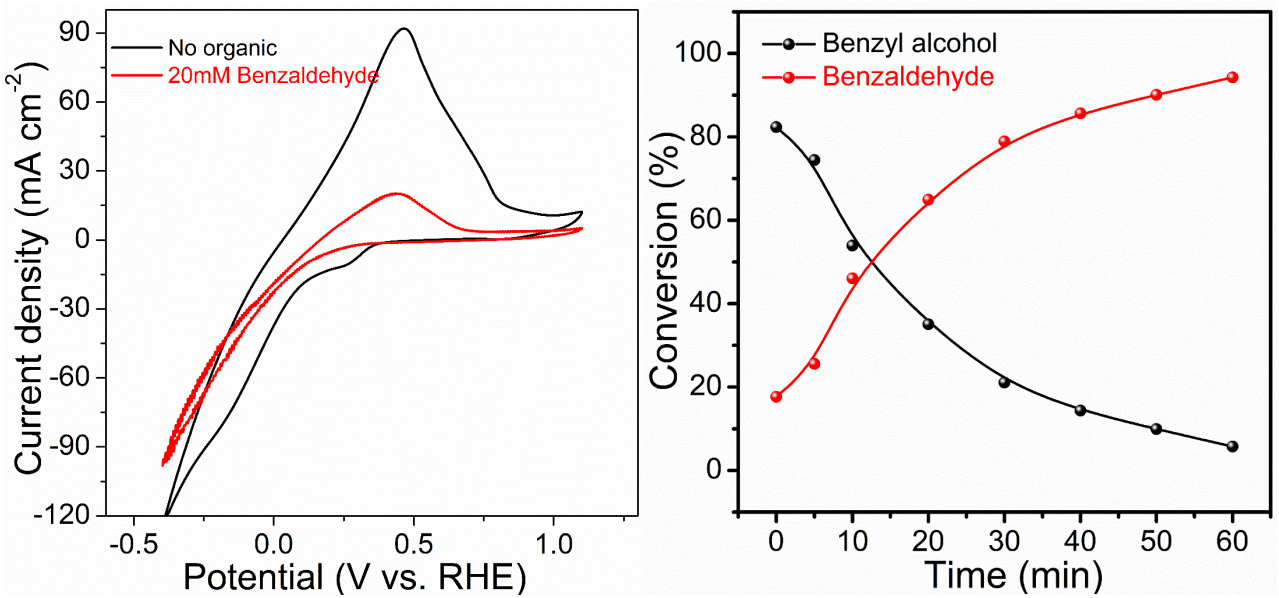


Figure 12. SEM & TEM & Mapping of Pd@Ni-MOF

Experimental Procedure

Work 1 Primarily proved high efficient performance of this electrocatalyst



- Rate=0.278 mmol cm^{-2} h^{-1}
- FE%(after optimized) ≥99.9%
- High efficiency and selectivity

Figure 13. (left) CV test of Benzaldehyde hydrogenation ; (right) conversion of Benzaldehyde (acetate buffer solution, 3 M pH=5.3, 50 mV S^{-1}, I-t at -0.1 V vs. RHE)

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