Electronic Supplementary Information

Design of nanostructured 2D (photo-)electrocatalysts for biomass valorization coupled with H_2 production

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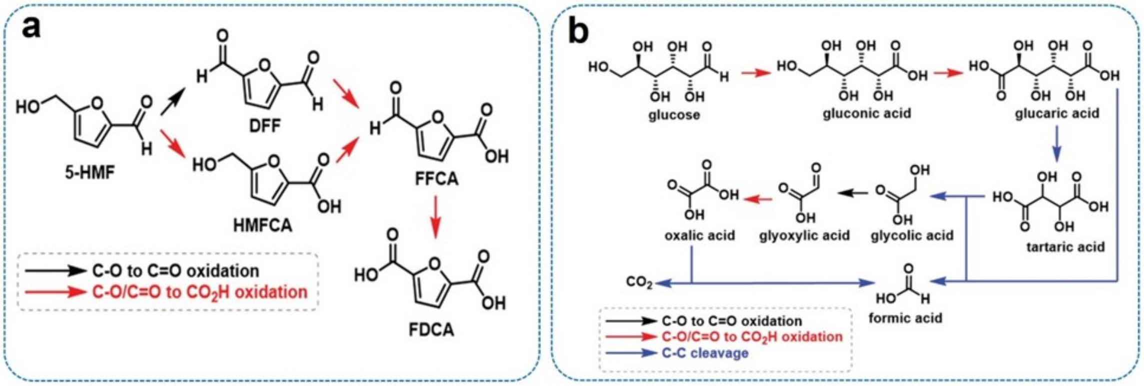

Fig. S1. Schematic illustration of catalytic mechanism for (a) HMF and (b) glucose. These figures have been reproduced from Ref.[1] with permission from Wiley, copyright 2021.

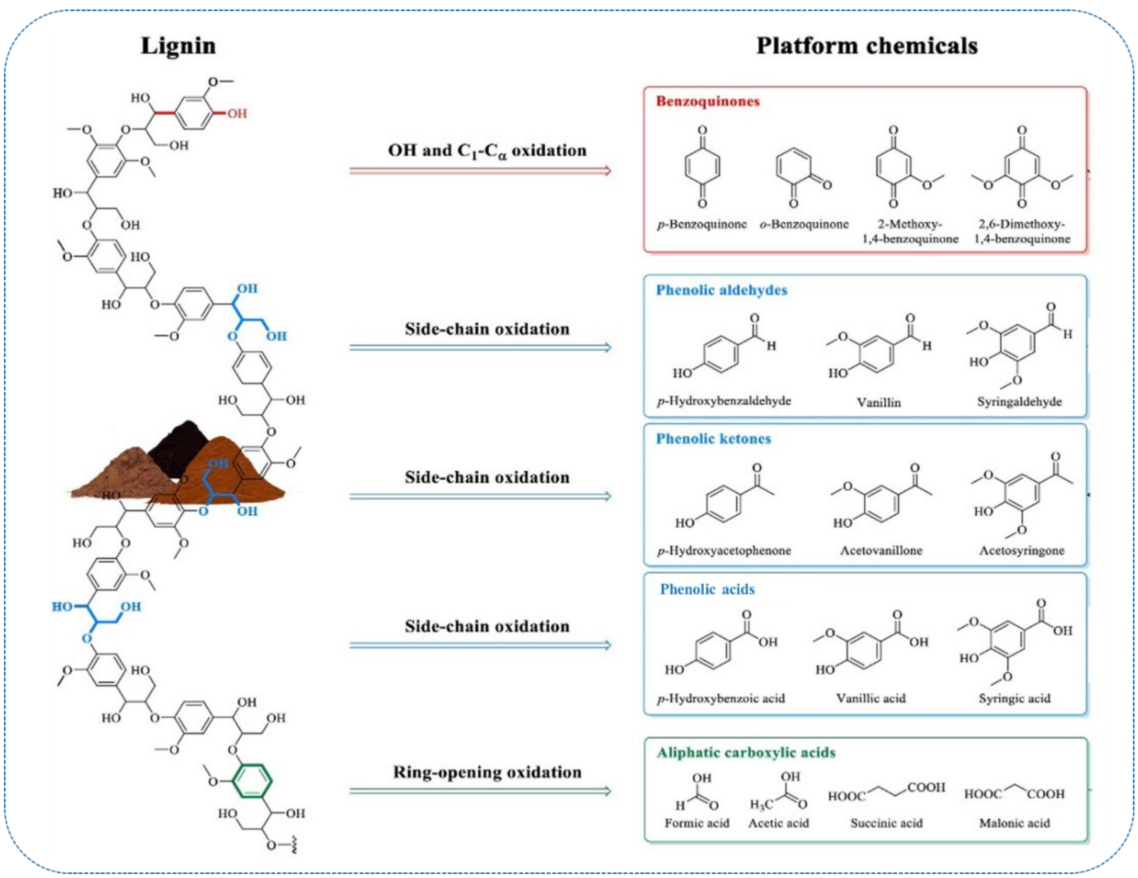

Fig. S2. Schematic illustration of catalytic oxidation pathways for lignin. This figure has been reproduced from Ref.[2] with permission from Elsevier, copyright 2019.

Table S1: An overview of biomass and valorization involved in this review.

Biomass	Source	Catalytic reactions and products	Products applications	Developed catalysts	Ref.
HMF	• Dehydration of simple sugars like fructose • Biomass: cellulose and lignocellulosic materials	• C1 oxidation (aldehyde groups): 2,5-Furandicarboxylic Acid (FDCA) and 2,5-Diformylfuran (DFF) • C6 oxidation (Hydroxymethyl Group): 5-Hydroxymethyl-2-furancarboxylic Acid (HMFCA) • C1 reduction (Aldehyde Group): 2,5-Bis(hydroxymethyl)furan (BHMF) • C6 reduction (Hydroxymethyl Group): 2,5-Dimethylfuran (DMF)	• Bio-based Plastics (e.g. FDCA) • Fine Chemicals (e.g. DFF and BHMF) • Biofuels (e.g. DMF)	• Ni, Co, Mo-based • Metal nanoparticles: Pt, Pd • Semiconductors: $BiVO_4$, WO_3, Fe_2O_3	3-15
Glucose	• Food Processing Residues • Lignocellulosic biomass:	• C1 oxidation (aldehyde groups): gluconic acid (GNA) • C6 oxidation (hydroxymethyl groups): glucaric acid (GRA) • C1-C2 cleavage: formic acid (FA) and arabinose (AR) • C2-C3 cleavage: acetic acid (AA) • C3-C4 cleavage: lactic acid (LA), and glycerol (GLY) • Isomerism: Fructose	• Food and Beverage Industry: As a sweetener and energy source • Pharmaceuticals: For medical treatments and supplements • Biofuels: As a feedstock for ethanol	• Ni-based • Metal nanoparticles: Pt, Pd, • Semiconductors: Bi_2WO_6, $BiVo_4$	16-25
Lignin	• Wood • Agriculture residues • Grasses	• OH and C_1-C_α oxidation: Benzoquinones (p-Benzoquinone, o-Benzoquinone, 2-Methoxy-1,4-benzoquinone, and • 2,6-Dimethoxy-1,4-benzoquinone) • Side-chain oxidation: Phenolic aldehydes (p Hydroxybenzaldehyde, Vanillin, and Syringaldehyde) • Side-chain oxidation: Phenolic ketones (p-Hydroxyacetophenone, Acetovanillone, and Acetosyringone)	• Animal Feed: As a binding agent • Biofuels: As a renewable energy source • Chemicals: For producing macromolecules used in bitumen, biofuels, and bio-refinery	• Ni-based • Metal oxide: IrO_2, PbO_2 • Semiconductors: TiO_2, g-C_3N_4, CdS	2, 26-36

	• Side-chain oxidation: Phenolic acids (p-Hydroxybenzoic acid, Vanillic acid, and Syringic acid) • Ring-opening oxidation: Aliphatic carboxylic acids (Formic acid, Acetic acid, Succinic acid, and Malonic acid)	catalysts	

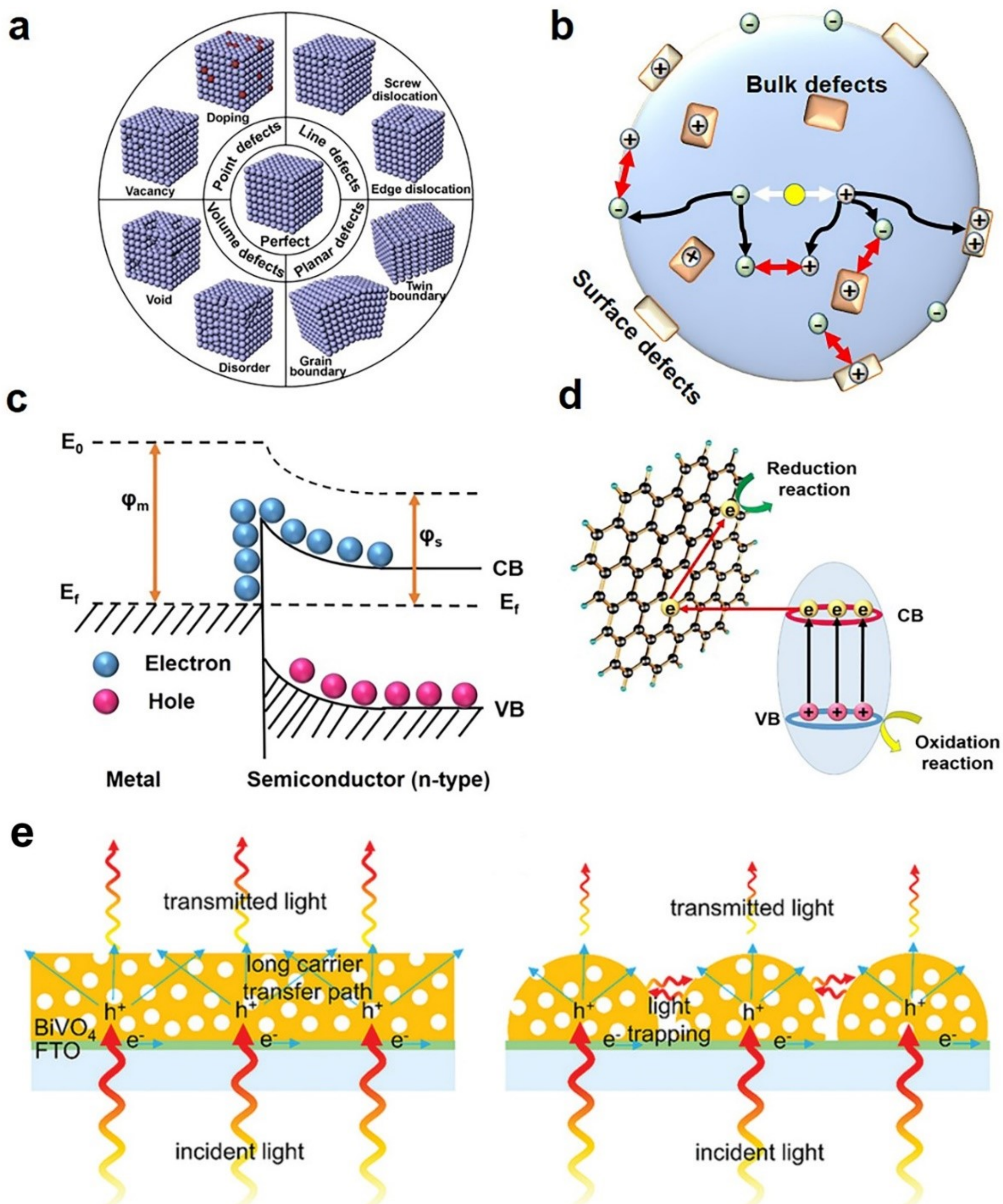

Fig. S3. Schematic illustration of (a) the defects with different atomic arrangement structures (This figure has been reproduced from Ref.[37] with permission from Elsevier, copyright 2018), (b) recombination pathways of photo-generated electrons and holes on semiconductors with surface and bulk defects, (c) Schottky barrier (where ϕ_s and ϕ_m represent work function of semiconductor and metal, respectively.), and (d) the charge transfer mechanism for graphene-semiconductor heterostructure, (e) schematic of light penetration a flat film and nanosphere arrays (These figures have been reproduced from Ref.[38] with permission from American chemical society, copyright 2017.)

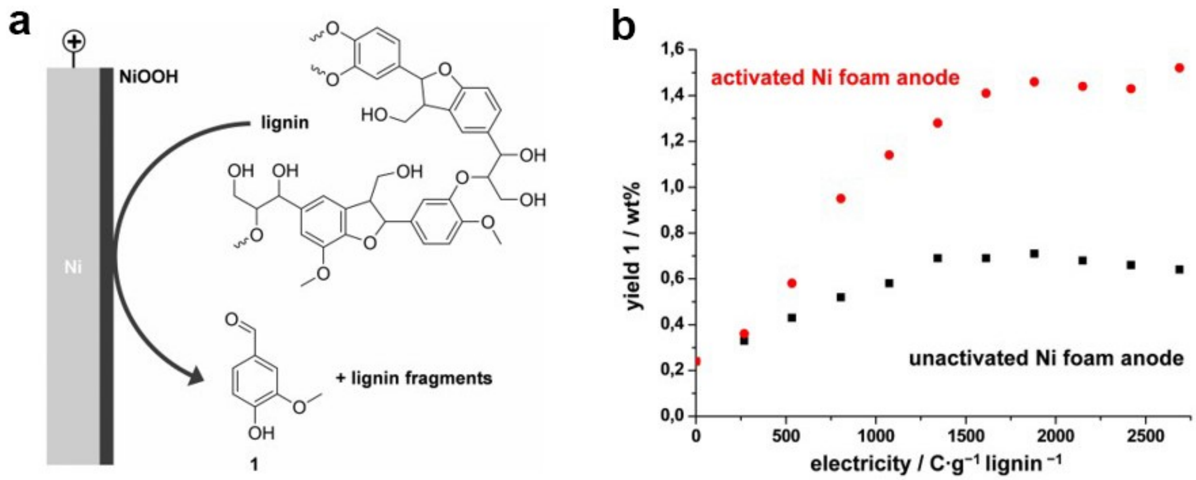

Fig. S4. Schematic illustration of (a) electrochemical lignin oxidation on Ni foam electrode and (b) influence of applied potential on lignin degradation. These figures have been reproduced from Ref.[39] with permission from European chemical societies publishing, copyright 2018.

Table S2. A comprehensive study of reported articles on HMF-, glucose-, and lignin-assisted H_2 production. ($E_{OER//HER}$ and $E_{BOR//HER}$ show required potential for conventional water electrolysis and hybrid water electrolysis, respectively.)

Anode||Cathode	Electrolyte	$E_{OER//HER}$ - $E_{BOR//HER}$ / Current density ($mA\ cm^{-2}$)	Products Yields	Hydrogen production yields	Ref.
Heteroatom doping					
BiCoO-NA/NF || BiCoO-NA/NF	1 M KOH + 10 mM HMF	0.1 V / 50	FDCA FE: 97.7% Yield: 362.5 µmol h^{-1}	Yield: 7.33 µmol h^{-1}	40
$Ni_{0.9}Cu_{0.1}(OH)_2$|| Pt wire	1.0 M KOH + 5 mM HMF	0.29 V / 100	FDCA FE: 91.2%	-	41
Co@NPC-800 || Co@NPC-800	1 M KOH+ 0.1 M glucose	0.18 V / 10	Lactic acid and formic acid FE: 45.4% and 15.2%	FE: 98.9%	42
Fe-Ni_2P@C/NF || Fe-Ni_2P@C/NF	1 M KOH + 20 mM glucose	0.11 V / 100	Lactic acid and formic acid Yield: 52.1 % and 35.6 %	FE: 98.2%	43
Defect/vacancy engineering					
$NiVW_v$-LMH || Pt foil	1.0 m KOH+ 10 mM HMF	0.26 V / 50	FDCA Yield: 99.2 %	-	44
$CuMn_2O_4$-NH_3 || Pt wire	1.0 M KOH + 10 mM HMF	0.05 V / 20	FDCA	-	45

			FE: 96%		
Pt/def-TiO_2 RNAs || Pt foil	1 M KOH + 10 mM glucose Light condition: Xenon lamp (300 W, AM 1.5G filter, 100 mW cm^{-2})	0.4 V / 1.2	gluconic acid (GLU) and glucaric acid (GLA) Yield: 84.3% and 9.2%	FE: 99%	46
Co-catalysts engineering					
Ni_3N-V_2O_3 || Ni_3N-V_2O_3	1.0 M KOH +10 mM HMF	0.13 V / 10	FDCA Selectivity: 98.7% Yield: 96.1%	FE: 100%	47
Ir-NiFeO@NF || Ir-NiFeO@NF	1.0 M KOH + 10 mM 1-phenylethanol	0.15 V / 100	Benzoic acids	0.45 mmol h^{-1} cm^{-2} FE: 100 %	48
Heterostructure design					
Ni/$Ni_{0.2}Mo_{0.8}N$/NF || Ni/$Ni_{0.2}Mo_{0.8}N$/NF	1 M KOH + 50 mM HMF	1.4 V / 50	FDCA Yield: 98.5%	-	49
Ni_xSe_y–NiFe LDH@NF || Pt sheet	Anolyte (1.0 M KOH + 10 mM HMF)/ catholyte (1.0 M KOH)	1 V / 40	FDCA FE: 96.7% Yield: 99.3%	-	50

Cu_xS@NiCo-LDHs || Cu_xS@NiCo-LDHs	1 M KOH (pH 13.8) + 10 mM HMF	2.2 V / 100	FDCA FE: 100%	FE: 100%	[51]
Fe_3O_4/Au/CoFe-LDH || Fe_3O_4/Au/CoFe-LDH	1 M KOH + 0.5 M glucose	1 V / 50	Gluconate FE: 100 % @ 50 mA cm^{-2}	99.6 % @ 50 mA cm^{-2}	[52]
β-PbO_2/MWNTs || Pt black cathode	Anolyte: 1 M NaOH + 10 g L^{-1} lignin catholyte: 1M NaOH	-	-	98.7 % @ 20 mA cm^{-2}	[53]
NiCo/TiO_2 || Pt-loaded carbon clothe	Anolyte: 1 M NaOH + 50 g/L lignin Catholyte: 1 M NaOH	0.5 V / 10	-	FE: 100 %	[54]
Surface engineering					
t-NiCo-MOF) || $MoNi_4$	1.0 M KOH + 10 mM HMF	0.3 V / 100	FDCA FE: 98%	-	[55]
NiS@NOSC || NiS@NOSC	1.0 M KOH + 10 mM HMF	1.5 V / 50	FDCA Yield: 99.6%	FE: 100%	[56]
CoNW/NF || CoNW/NF	1.0 M KOH + 100 mM HMF	0.3 / 50	FDCA Yield: 96.8% FE: 96.6%	FE: 100%	[57]
	0.5 M NaCl (pH: 7) + 0.1 M		Gluconic and Glucaric acids, Erythrose and		

	glucose Light condition: AM 1.5 G		Arabinose Total FE: 64%		
CNF-60 || CNF-60	1.0 M KOH + 0.15 M glucose	0.26 V / 10	-	-	59
$NiSn_{20\%}$ || $NiSn_{20\%}$	Anolyte: 1.0 M NaOH + 10 g l^{-1} Lignin Catholyte: 1.0 M NaOH	0.5 V / 10	Vanillin production rate: 300 g/kg lignin min^{-1}	72 ml h^{-1}	60
2D materials/ 3D supports					
Co_3O_4/CF || Co_3O_4/CF	1.0 M KOH + 10 mM HMF	0.2 V / 50	FDCA FE: 92.9 %	FE: 99.8 %	61
$Co(OH)_2$-CeO_2 || Pt wire	0.1 M PBS + 10 mM HMF	0.2 V / 10	2-furancarboxylic acid (HMFCA) Selectivity: 89.4 % Yield: 85.8 %	114.39 μmol cm^{-2} h^{-1}	62
CF@CoNC-2T || CF@CoNC-2T	1 M KOH + 100 mM glucose	0.88 V / 100	Gluconic acid (GNA) and glucaric acid (GRA)	FE: 100 %	63
$NiFeO_x$ || $NiFeN_x$	1 M of KOH + 100 mM glucose	2.5 V / 100	Glucaric acid (GRA) FE: 87% Yield: 83%	-	64

NF@Co_3S_4/(α,β)-NiS || Pt sheets	1.0 M KOH + 1 mM 2-phenoxy-1-phenylethanol (PPE)	0.7 V / 60	Benzoate FE: 83.3%	-	65

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