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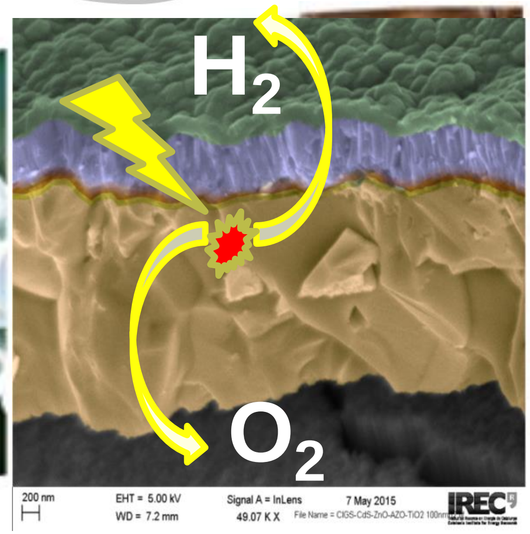

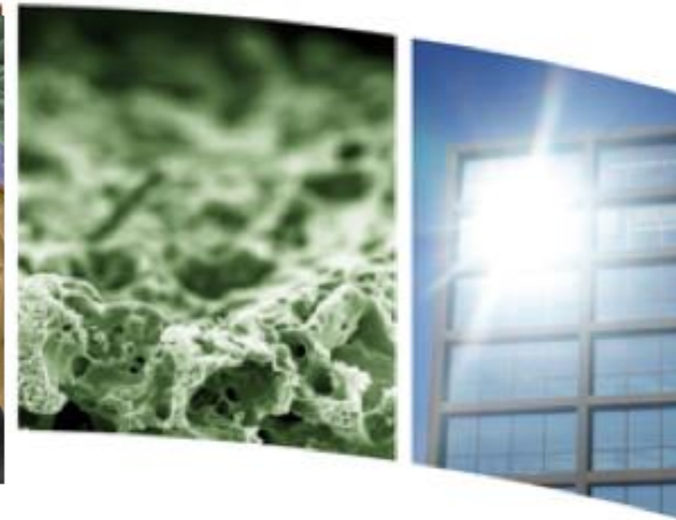

What would it take for renewably based electrosynthesis products to substitute those obtained from petrochemical processes?

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The conversion of H2O, CO2, N2 into value-added chemicals and/or fuels, using renewable energy and earth-abundant elements as well as environmental friendly materials is a key priority.

The circular economy of CO2, N2, H2 constitutes one of the major world challenges

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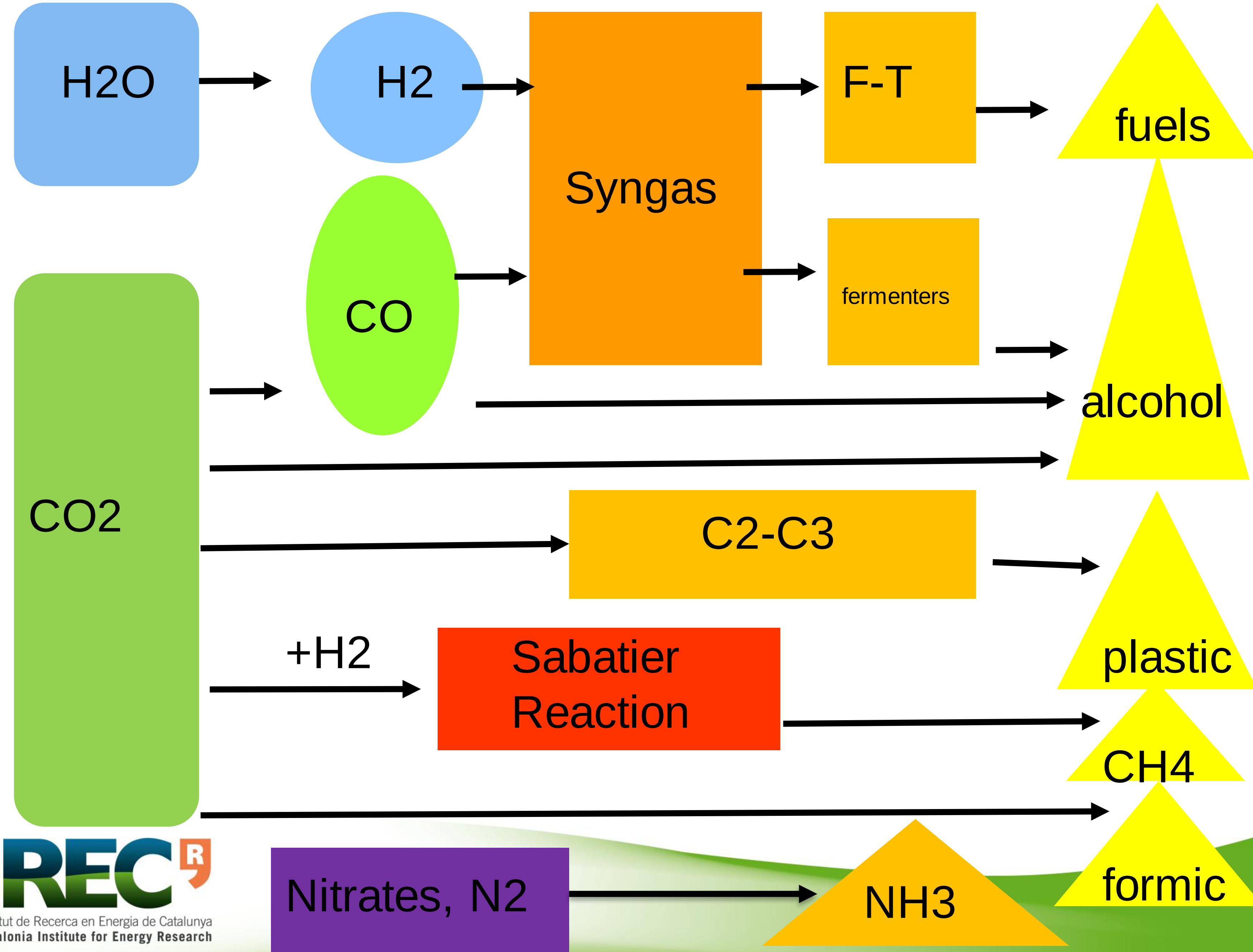

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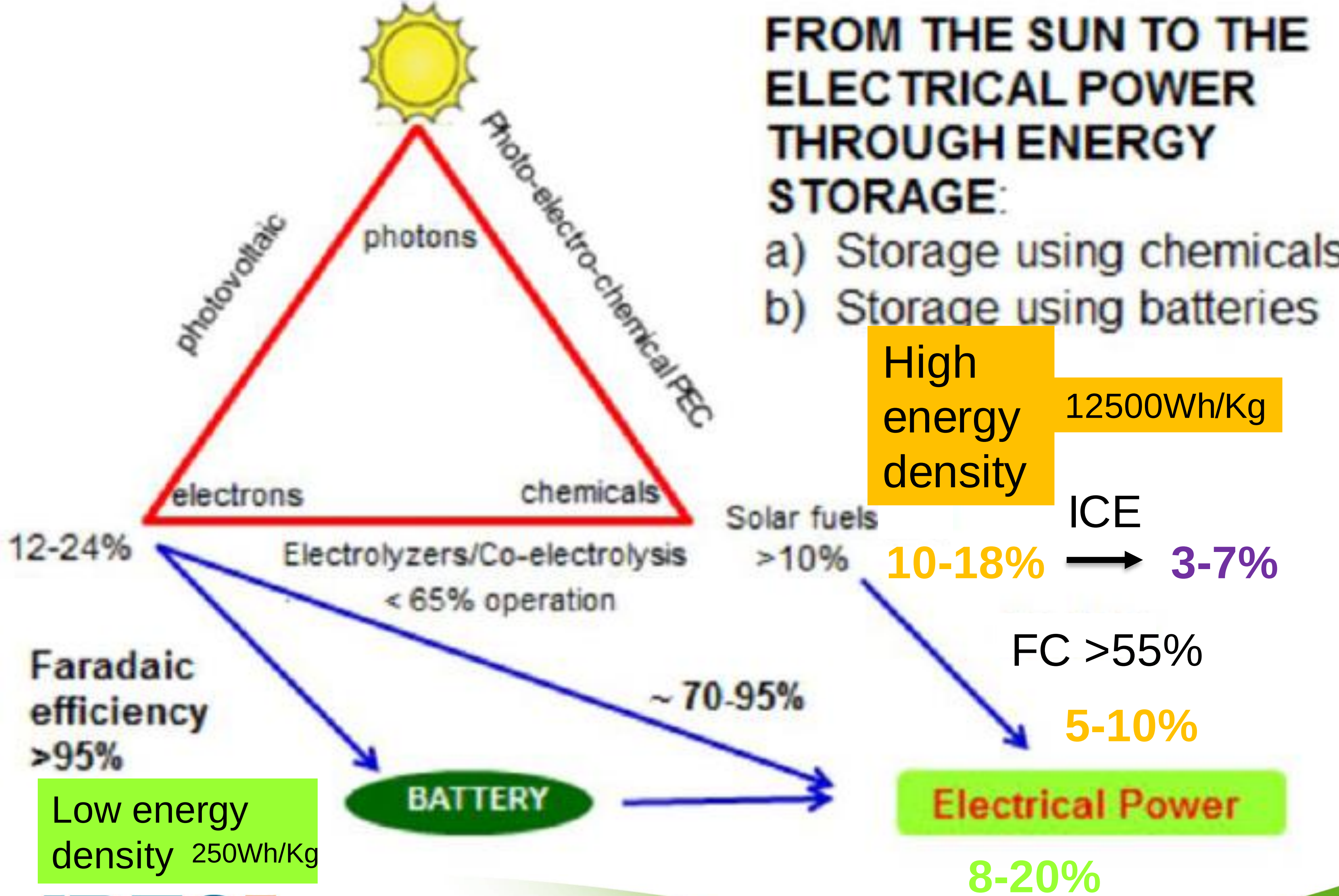

Solar Irradiation to Electrical Energy State of the Art (SoA)

Source: IREC

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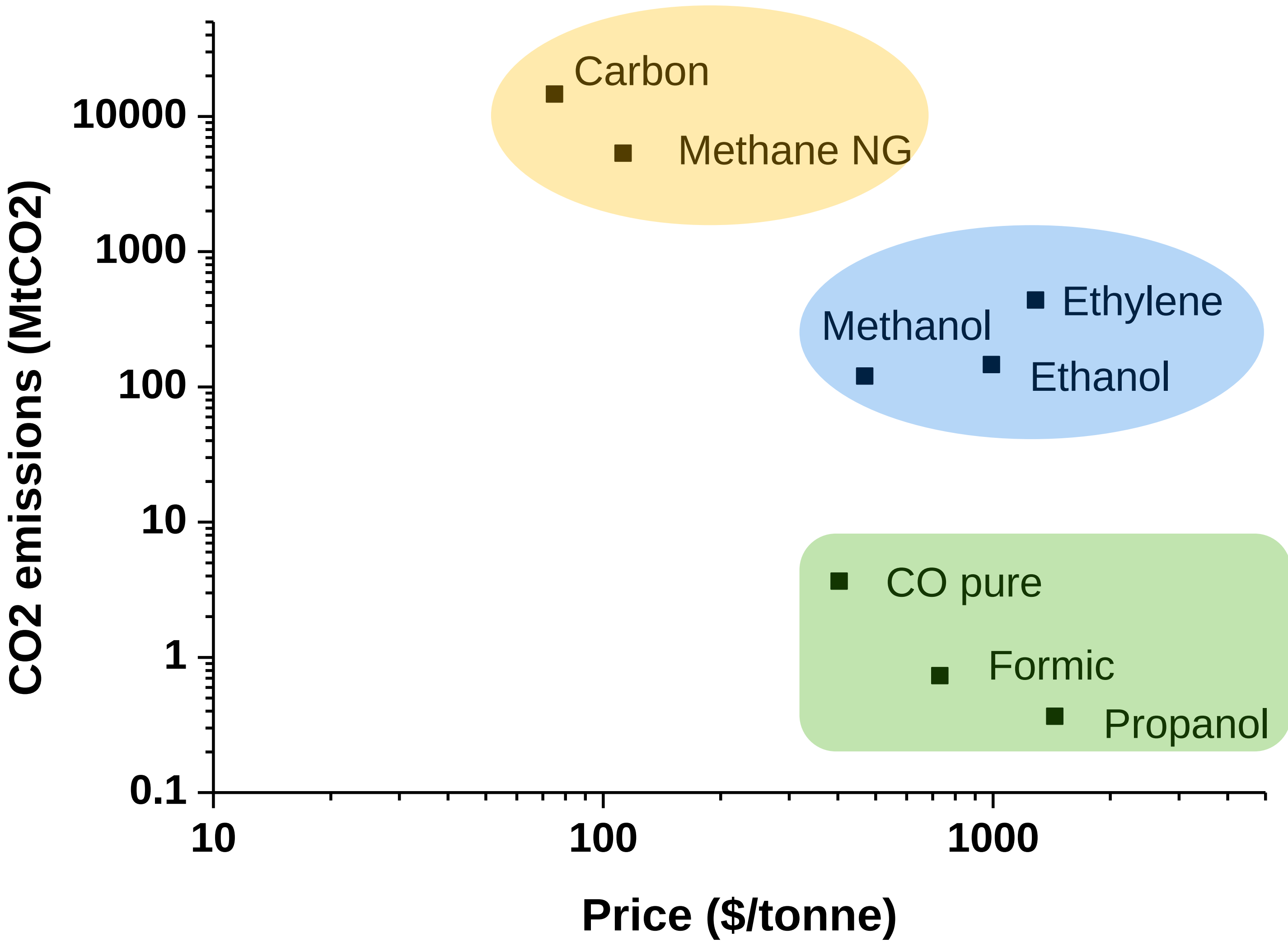

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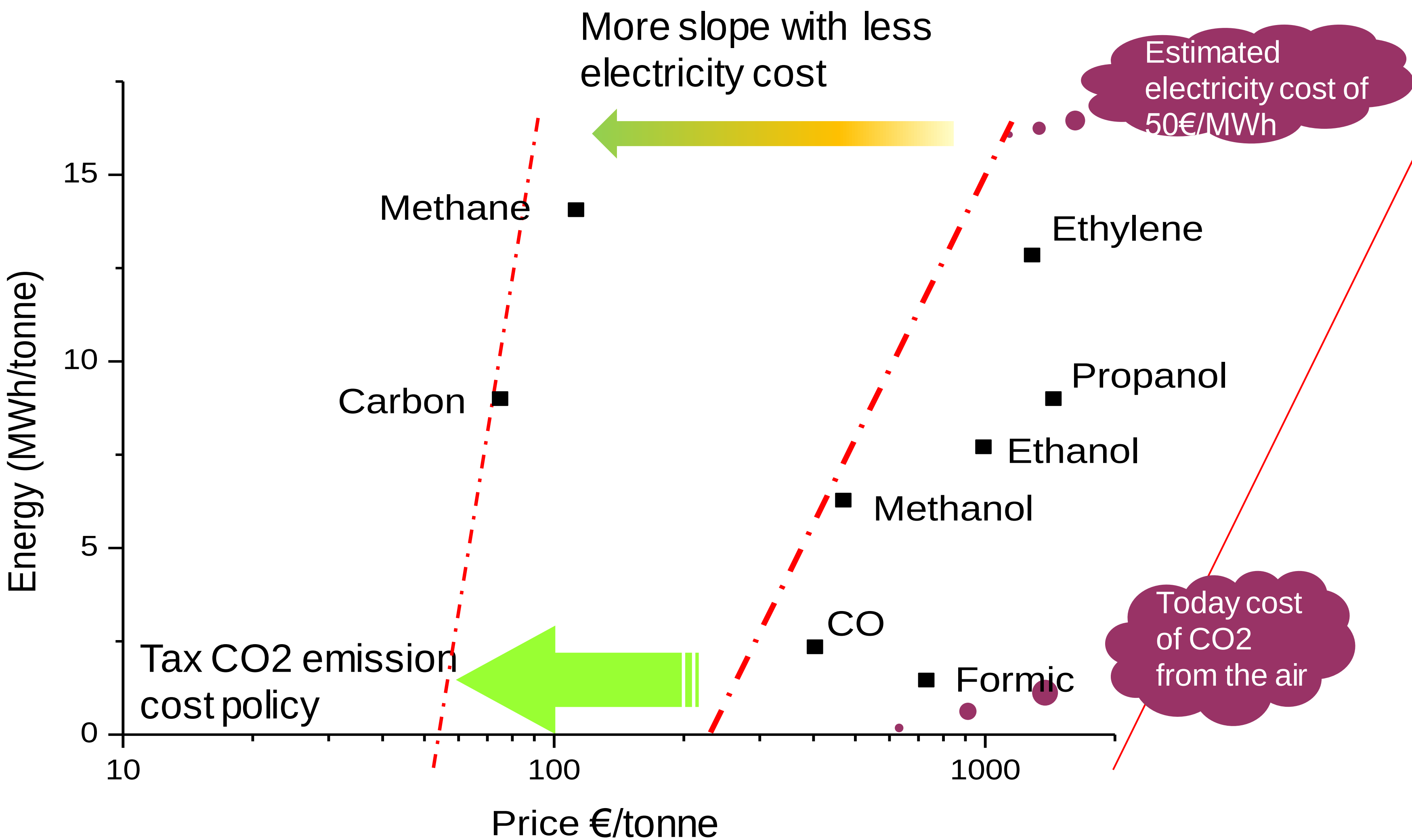

Renewable electroconversion must target first high value chemicals avoiding highly energy intensive thermochemical current routes.

In the next future, with the achieved technology maturity, new CO2 tax policies and contained electricity cost, it will replace shale gas applications too (renewable gases)

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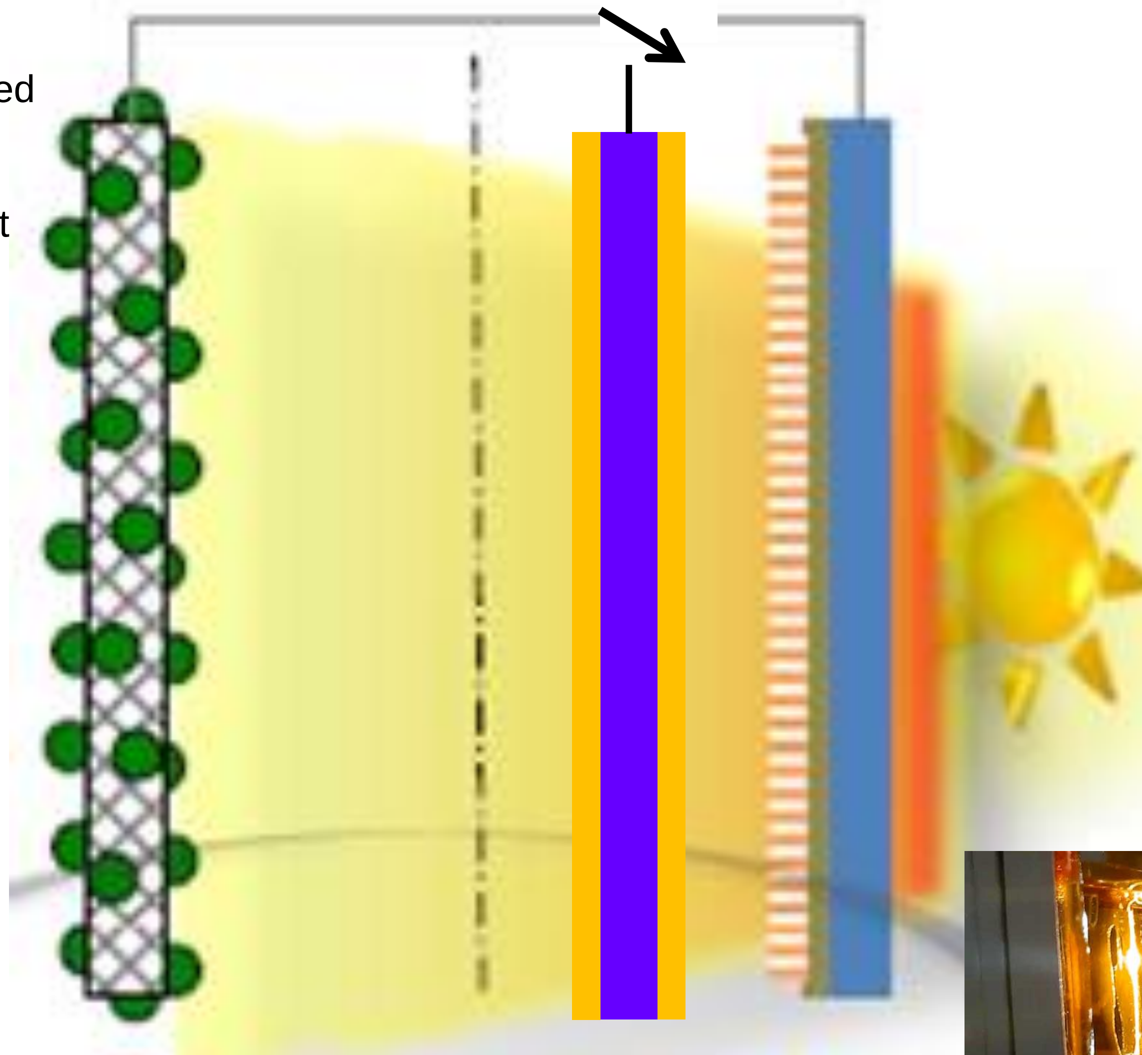
Many configurations on demand: dark or under illumination

3D
Nanostructured
Cathode
with Catalyst



EC CATHODE

PEC/EC ANODE

Strong interest in having back illumination especially for replacing electroreduction by photoelectroreduction of CO2.

PATENT:15382658.1

For CO_2R, NR or H_2: Cathode with appropriate catalyst
Anode with excellent OER.

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half-cell electrochemical reactions

$CO_{2(g)} + 2H^+ + 2e^- \leftrightarrow CO_{(g)} + H_2O_{(l)}$

$CO_{2(g)} + 2H^+ + 2e^- \leftrightarrow HCOOH_{(l)}$

$CO_{2(g)} + 6H^+ + 6e^- \leftrightarrow CH_3OH_{(l)} + H_2O_{(l)}$

$CO_{2(g)} + 8H^+ + 8e^- \leftrightarrow CH_{4(g)} + 2H_2O_{(l)}$

$2CO_{2(g)} + 12H^+ + 12e^- \leftrightarrow C_2H_{4(g)} + 4H_2O_{(l)}$

$2CO_{2(g)} + 12H^+ + 12e^- \leftrightarrow C_2H_5OH_{(l)} + 3H_2O_{(l)}$

$3CO_{2(g)} + 18H^+ + 18e^- \leftrightarrow C_3H_7OH_{(l)} + 5H_2O_{(l)}$

$2H^+ + 2e^- \leftrightarrow H_{2(g)}$

$$V_{cell} = V_o + \eta_{cat} + \eta_{ano} + \Delta V$$

Productivity I(V)

Product	Energy (eV)	Voltage cell *	Faraday efficiency	Energy efficiency**	PV+EC S to"X"
CO (Ag)	1,45	2,9*	87%	<44%	< 11%
Formic acid (Pb)	1,35	2,8*	95%	<46%	< 11%
Ethylene (Cu)	1,15	2,4*	<70%	<35%	< 8%
H2(Pt)	1,23	1,5 to 2,3	≈100%	< 80%	<19%

(*) representative value from references.
(**) these values depend on the working current density mA/cm2.
Requirements of low Tafel slopes mV/decade

Several sources: IREC

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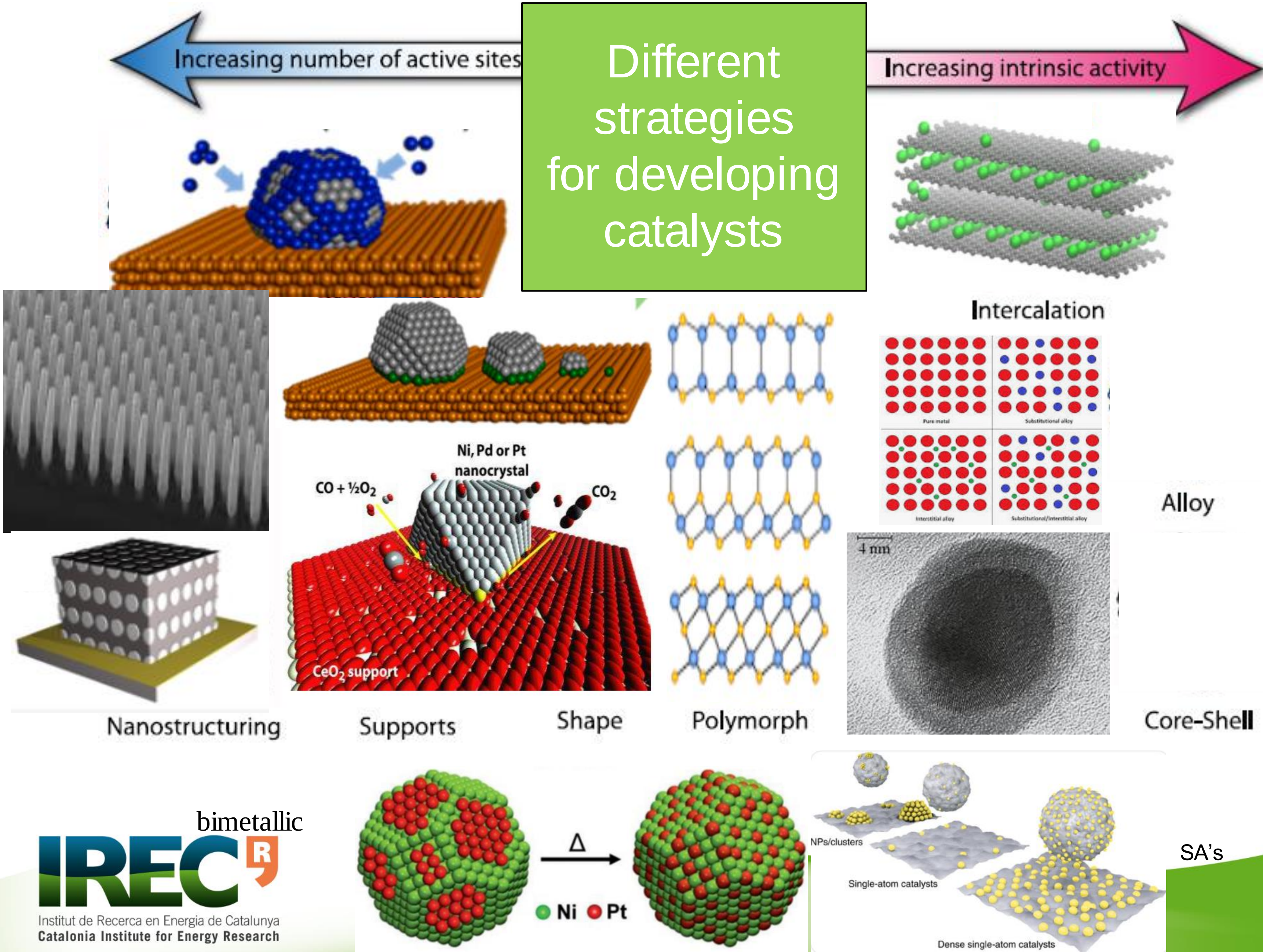
Different strategies for developing catalysts



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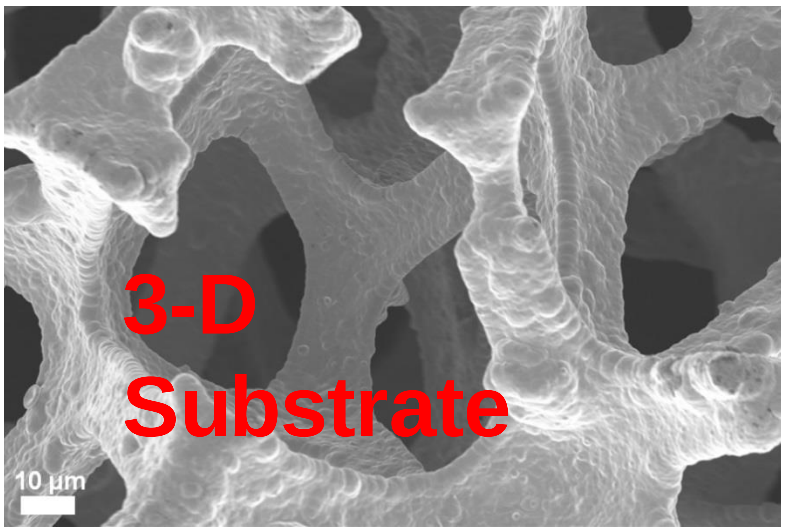
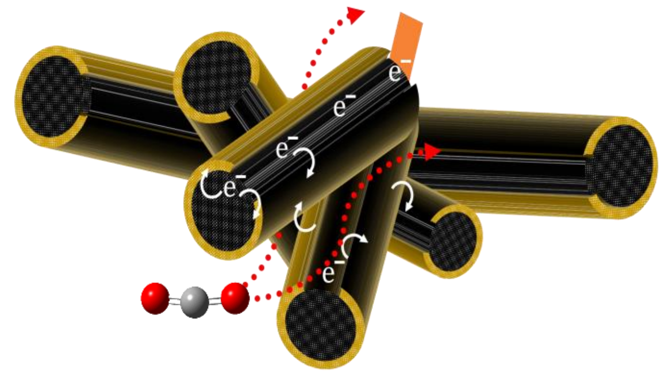
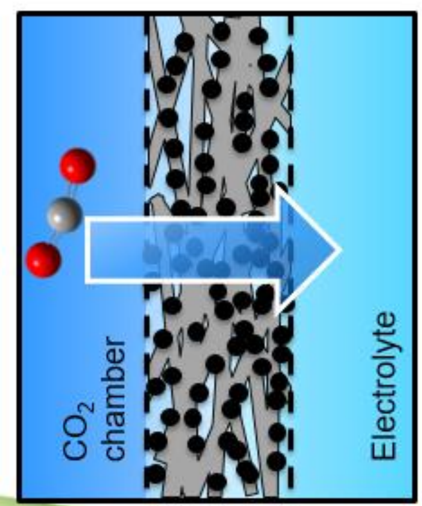
Catalyst Deposition ELECTRODE MICROSTRUCTURE

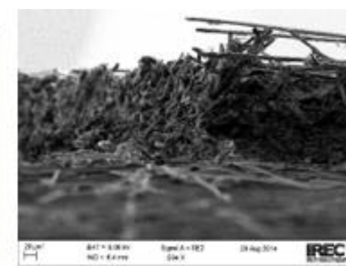
Requirements for catalyst substrate:

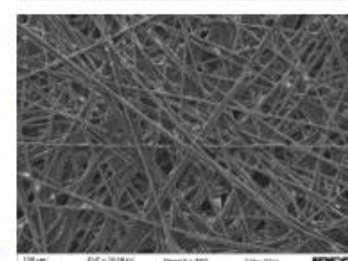
- High surface area >> geometric surface area
- High conductivity
- Improved mass transfer → circumvent CO_2 solubility problem
- Cost-effective and scalable to large areas → commercial applications











Challenge to solve:

- Perfect coverage with catalyst → avoid metallic substrate (Cu, Ni) to act as catalyst

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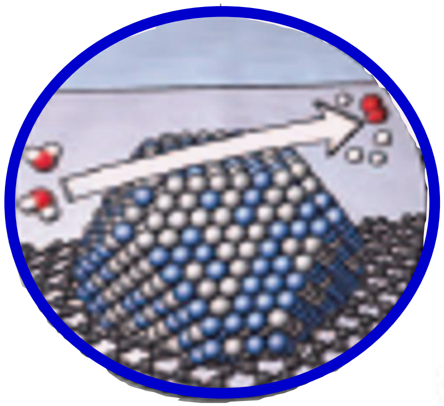
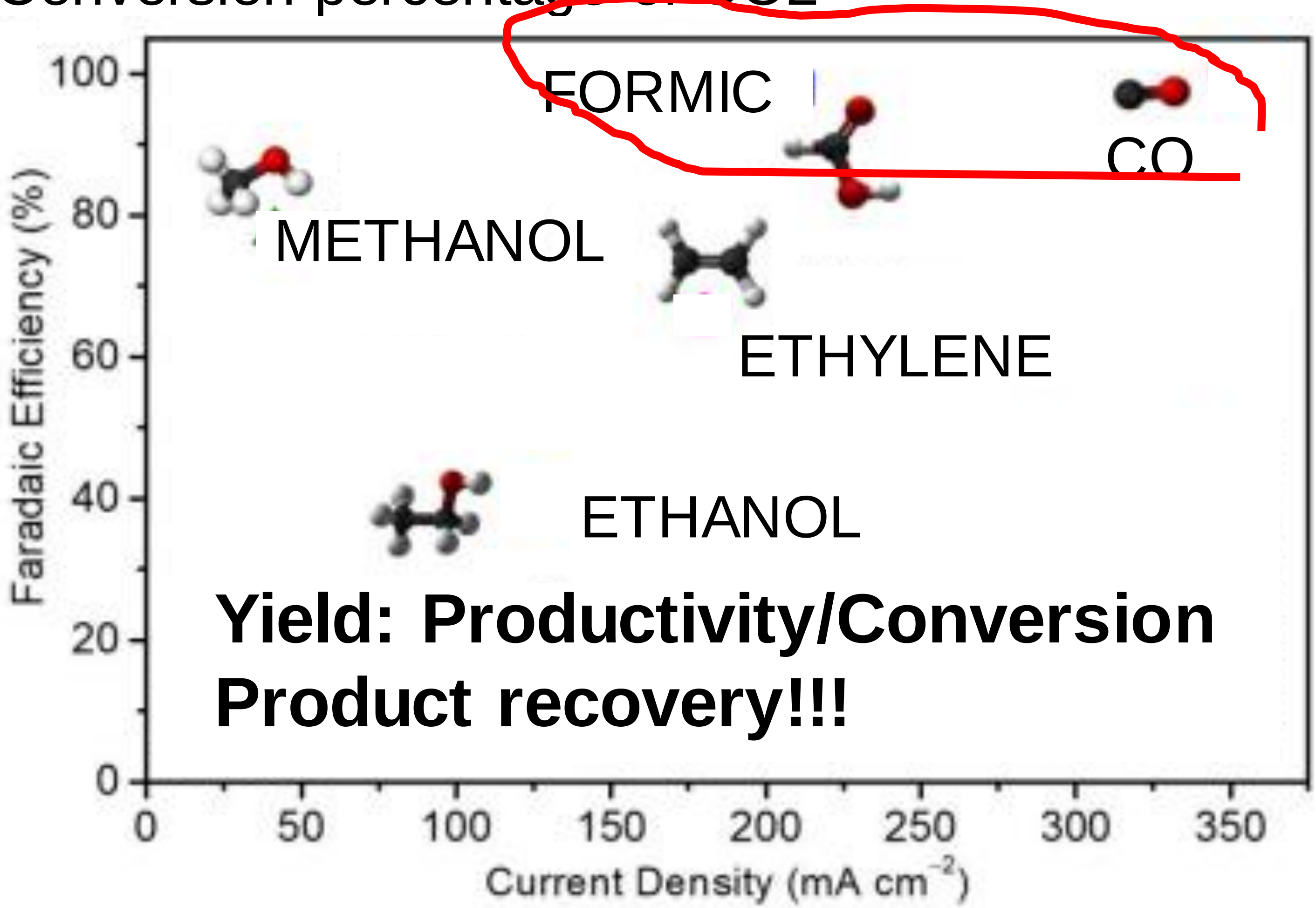
Challenges:

Catalyst: Yield (high current density) degradation.
Electrode: (Areas)
Electrolyte and membranes
Stack's of EC cells.
Product separation: gas/liquid; liquid /liquid
Conversion percentage of CO_2





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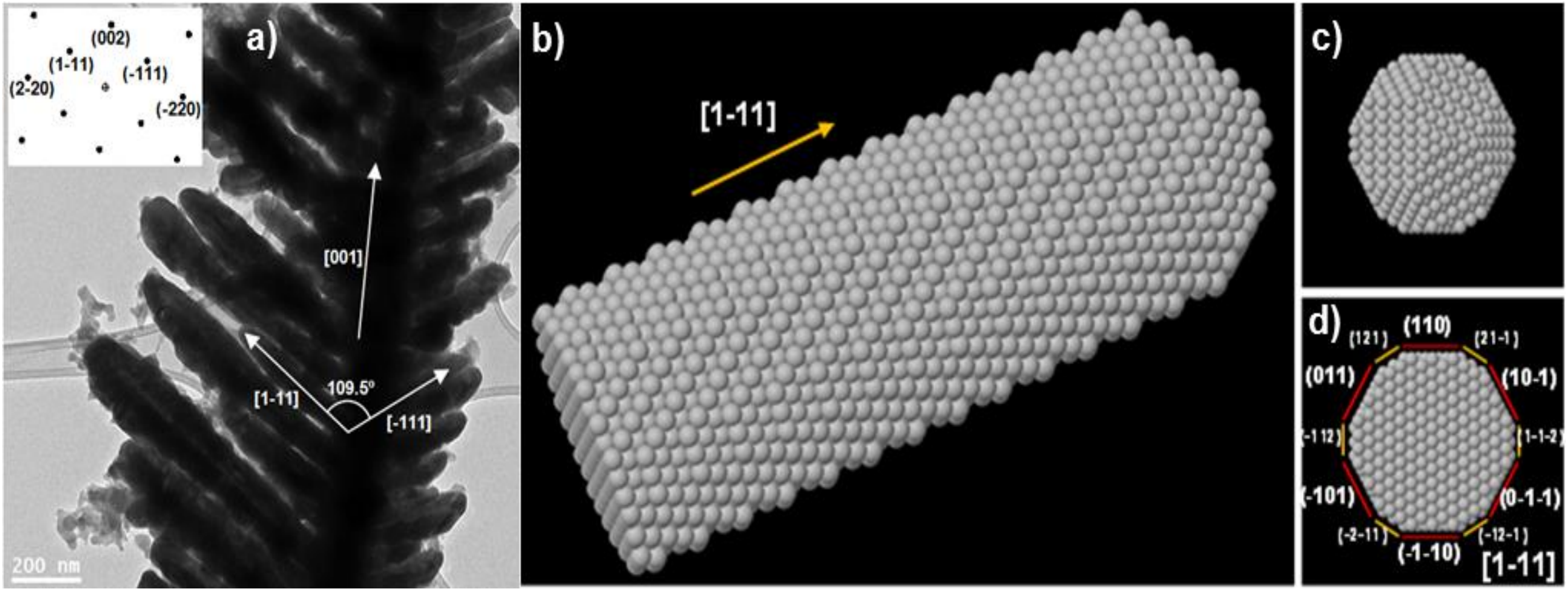
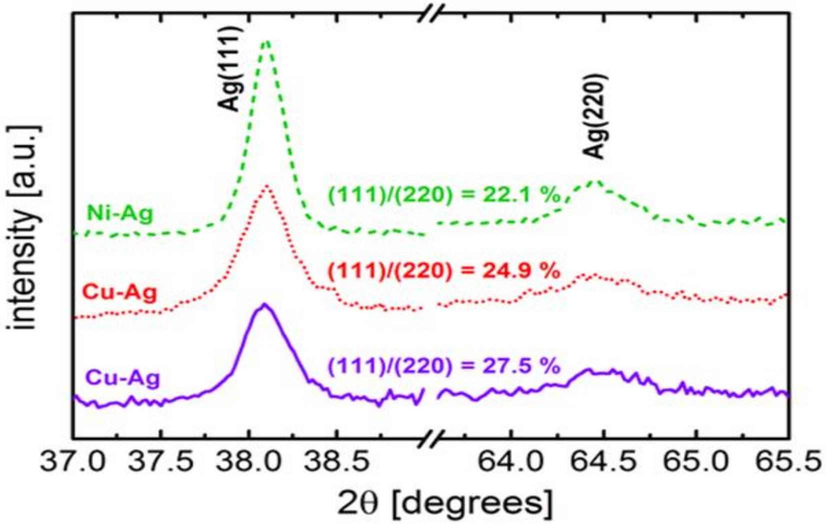


ACS applied materials and interfaces (2018)



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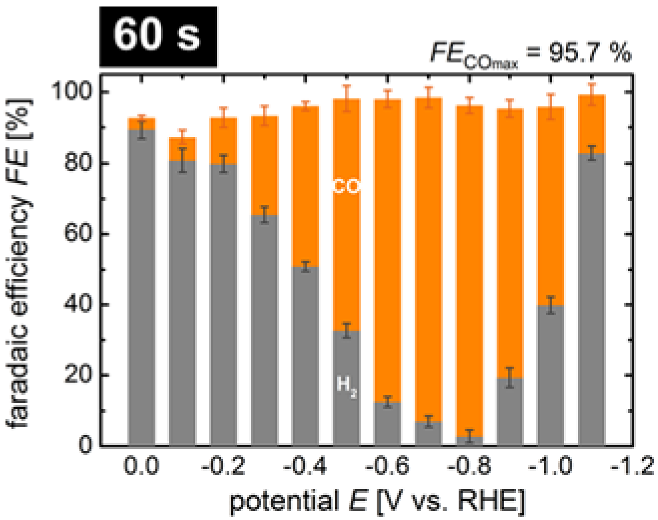

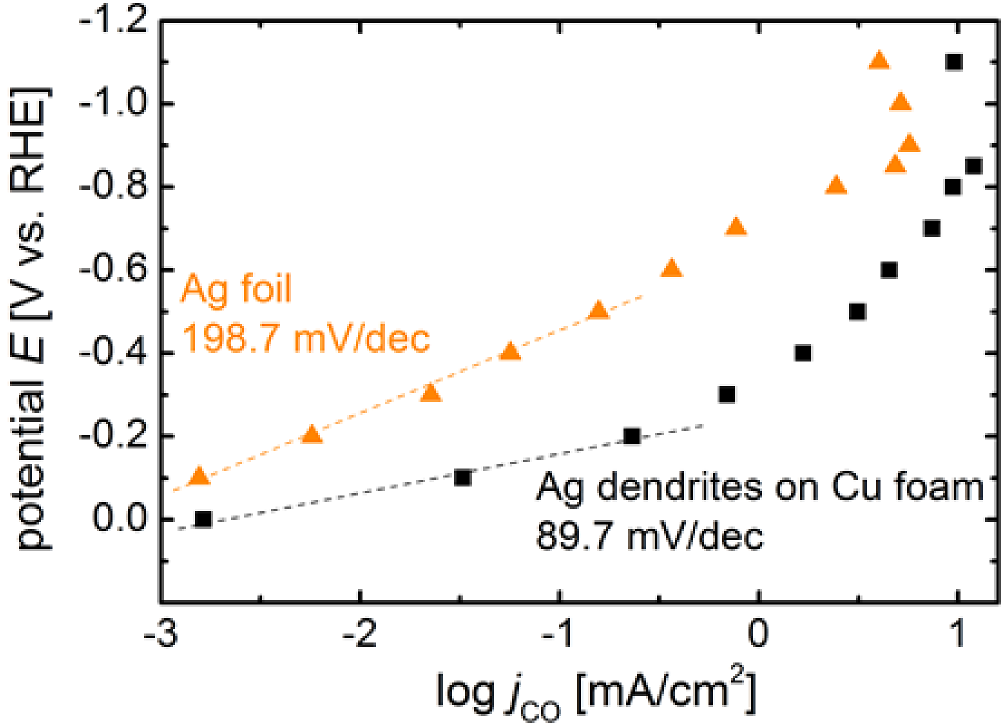

ACS applied materials and interfaces (2018)

ENERGY & ENVIRONMENTAL SCIENCE 10 , 10, 2256 (2017)

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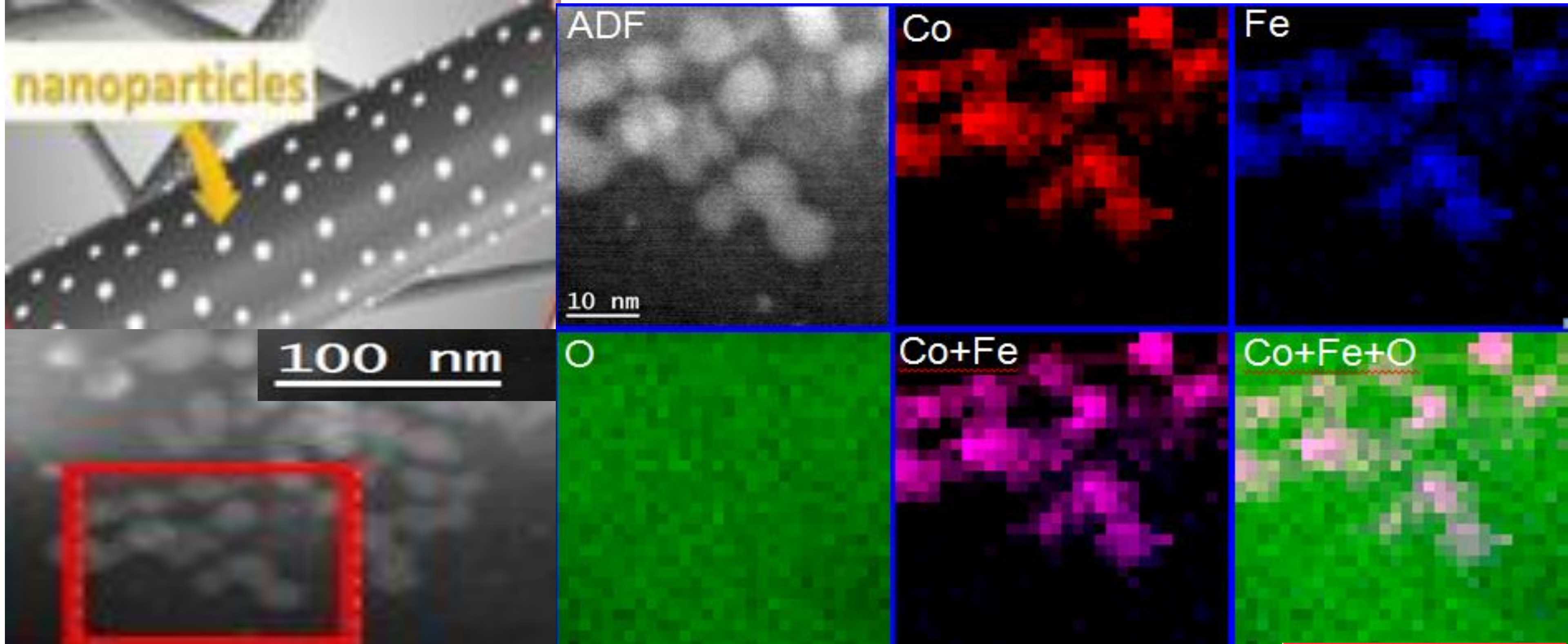

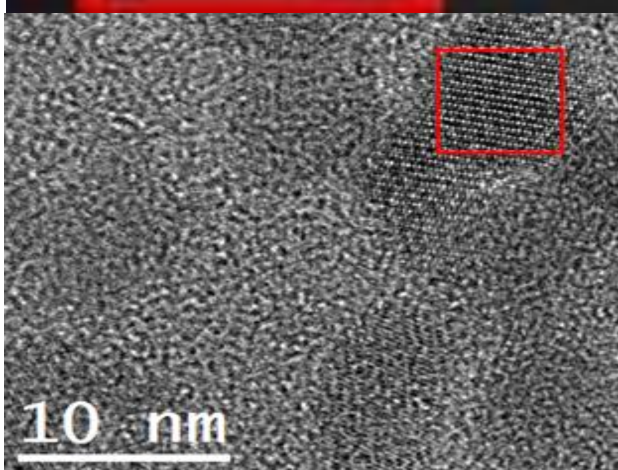

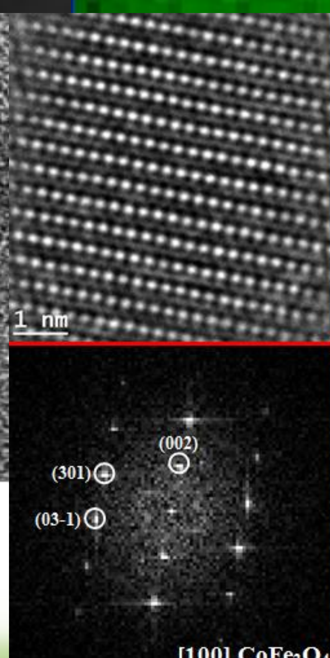

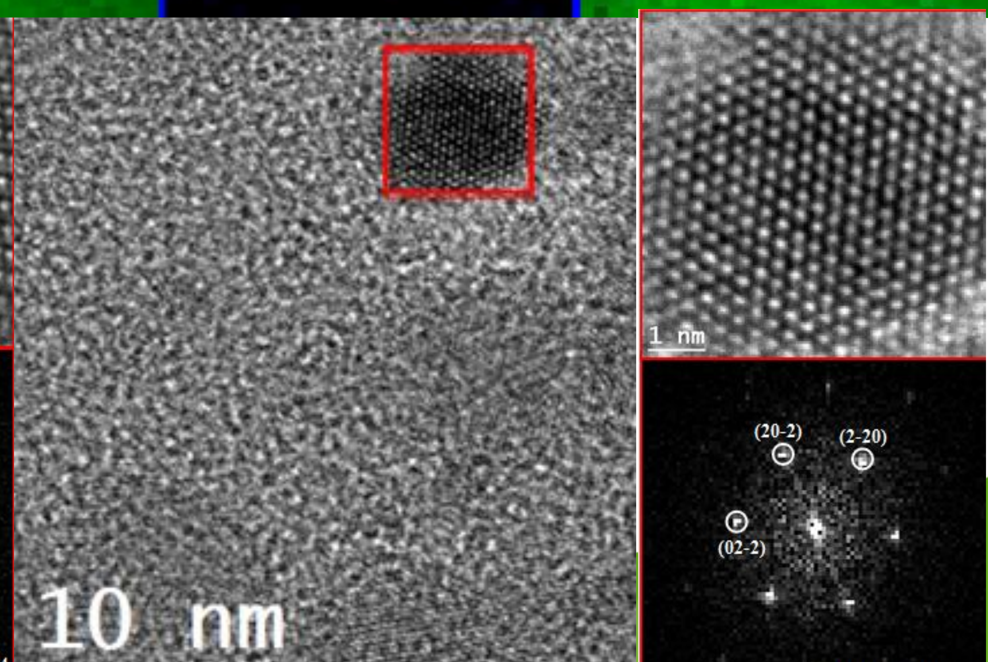

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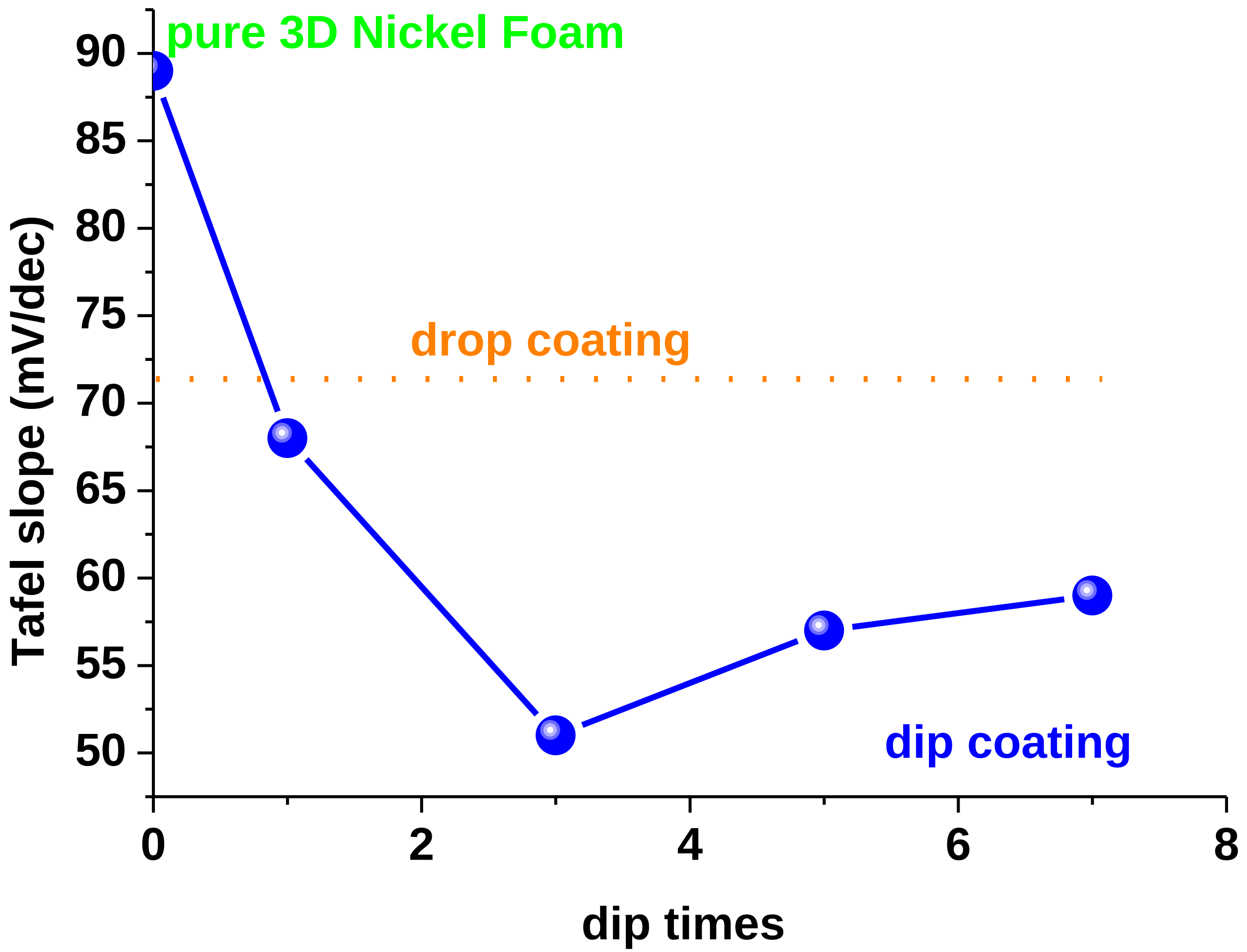

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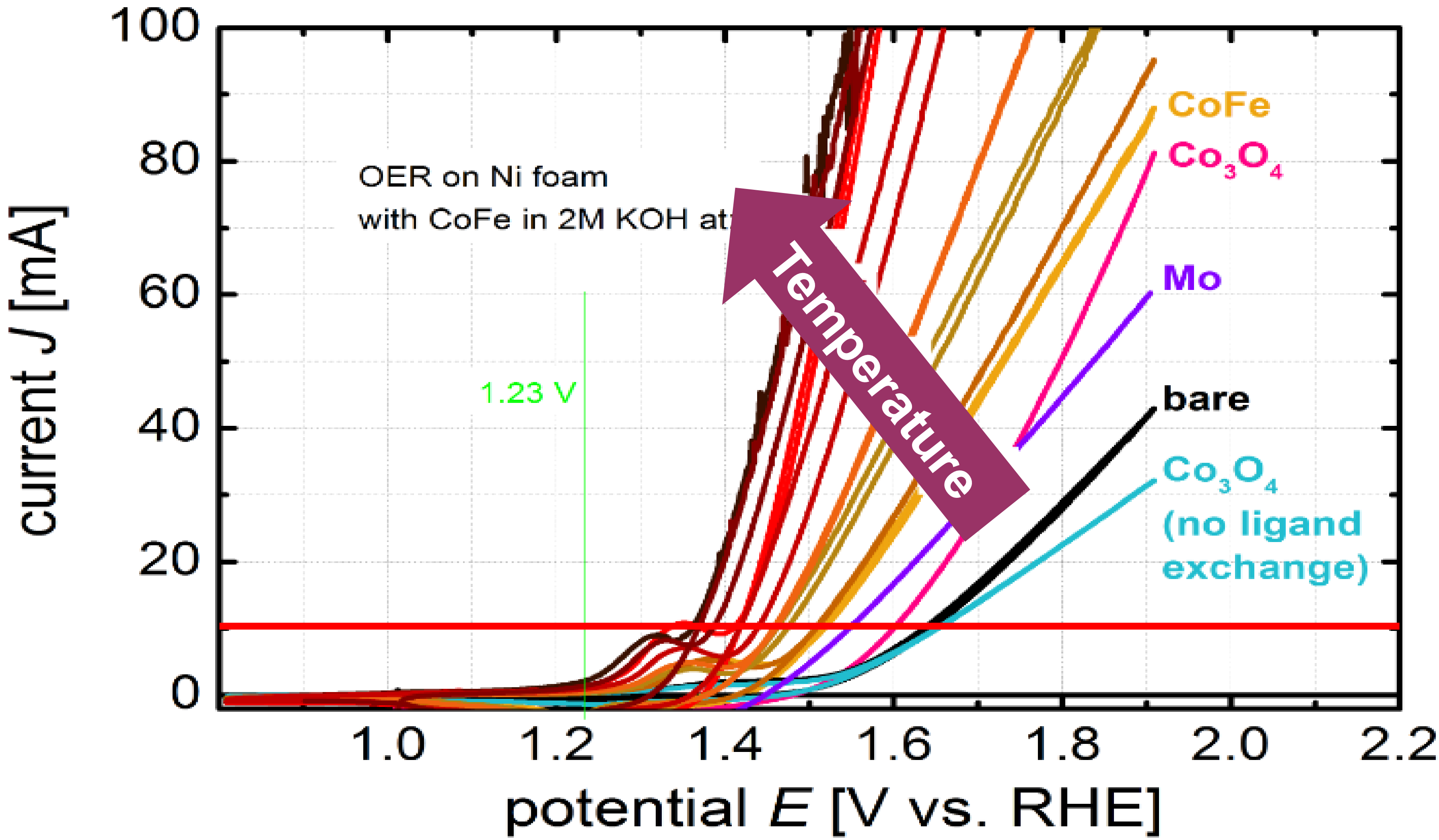

100
80
60
40
20
0
1.0
1.2
1.4
1.6
1.8
2.0
2.2
current J [mA]
potential E [V vs. RHE]
OER on Ni foam
with CoFe in 2M KOH at
1.23 V
Temperature
CoFe
Co3O4
Mo
bare
Co3O4
(no ligand
exchange)

Comparison among OER performances of electrodes with non-noble-metal electro catalysts in 1.0 M KOH.

LiCoBPO/NF	10	293	EnergyEnviron. Sci.DOI: 10.1039/c8ee01669k
RuB2/GCE	10	280	Adv. Energy Mater. 2018, 1803369
FeB2/NF	10	296	Adv. Energy Mater. 2017, **7**, 1700513
Co2B-500/NG	10	360	Adv. Energy Mater. 2016.**6**, 1502313
Ni3B-rGO	10	290	Electrochemistry Commun. 2017,**17**,30337
Co-Mo-B	10	320	Electrochimica Acta. 2017, **232**, 64–71
FeS2/CoS2 NSs	10	250	Small 2018, **14**, 1801070
Co-MoS2	10	260	Adv. Mater. 2018, **30**, 1801450
Fe-Ni@NC-CNTs	10	274	Angew. Chem. Int. Ed. 2018, **57**, 8921 –8926
Fe-Doped Ni2P	10	190	Adv. Funct. Mater. 2017, **27**, 1702513
MoP/ NF	10	280	Small Methods. 2018, **2**, 1700369
Ni11(HPO3)8(OH)6/NF	10	232	Energy Environ. Sci. 2018,**11**, 1287-1298
Pt-CoS2/CC	10	300	Adv. Energy Mater. 2018.**8**.1800935
Co-Ni/MoS2	10	235	Nat. Commun. 2017, **8**, 14430
Cu@CoSx/CF	10	169	Adv. Mater. 2017, **29**, 1606200
FeMnP	10	120	Nano Energy.2017, **39**, 444
Co-Ni/MoS2	10	235	Nat.Commun.2017, **8**, 15377
Co-Ni-B/NF	50	400	J. Mater. Chem. A, 2017, **5**, 12379-12384
Co-O@CoB/TM	50	290	Small.2017, **13**, 1700805
Ni-B/NF	100	360	Nanotechnology. 2016,**27**,12LT01
CoFe/NF	**10**	**190/140**	**Applied Catalysis B: Environ. 259 (2019) 118055 our results.**

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Comparison about the overall water splitting performance for electrodes with non-noble-metal electrocatalysts in 1.0 M KOH.

FeCoNi/NF	10	**1.43**	Nat. Commun. 2018. **9**.2452
N-Ni_3S_2/NF	10	1.48	Adv. Mater. 2017, **29**, 1701584
$Fe_{0.09}Co_{0.13}$-$NiSe_2$/CFC	10	1.52	Adv. Mater. 2018, 1802121
Ni_3N-NiMoN/CC	10	1.54	Nano Energy. 2018.**44**. 353–363
$CoSn_2$/NF	10	1.55	Angew. Chem. 2018, **130**, 15457 –15462
$Ni_{0.8}Fe_{0.2}$LDH/NF	10	1.55	Small 2018, **14**, 1800759
N-CoNiPS/C	10	1.56	Adv. Funct. Mater. 2018, 1805075
NC/NiCu/NiCuN	10	1.56	Adv. Funct. Mater. 2018, 1803278
G-Ni_4Fe/GF	10	1.58	Adv. Energy Mater. 2018, 1800403
Ni-Co-P HNBs	10	1.62	Energy Environ. Sci. 2018,**11**,872-880
NiFeSP/NF	10	1.58	ACS Nano 2017, **11**, 10303−10312
Pt-CoS_2/CC	10	1.55	Adv. Energy Mater. 2018, **8**, 1800935
$F_{0.25}C_1$CH/NF	10	**1.45**	Adv. Energy Mater. 2018, 1800175
FeS_2/CoS_2 NSs	10	1.47	Small . 2018, **14**, 1801070
Co-MoS_2	10	1.45	Adv. Mater. 2018, **30**, 1801450
MoP/Ni Foam (NF)	10	1.62	Small Methods .2018, **2**, 1700369
FCCH/NF	10	1.45	Adv. Energy Mater. 2018, 1800175
Co-Mn carbonate	10	1.68	J. Am. Chem. Soc. 2017.**139**, 8320-8328.
Se-(NiCo)Sx/(OH)x	10	1.6	Adv. Mater. 2018, **30**, 1705538
Pt/Ni/Ru nanocrystal	10	1.52	Adv. Mater. 2018, 1805546
$Ni_xCo_{3-x}S_4$/Ni_3S_2	10	1.53	Nano Energy, 2017, **35**, 161-170
FeCoNi HNTAs/NF	10	**1.43**	Nat.Commu2018.10.1038/s41467-018-4888-0
Ni-Mo-O nanorod/NF	10	**1.38**	Energy Environ. Sci., 2018, **11**, 1890-1897
$Fe_{0.09}Co_{0.13}$-$NiSe_2$	10	1.52	Adv. Mater. 2018, 1802121
Fe-Doped Ni_2P	10	1.49	Adv. Funct. Mater. 2017, **27**, 1702513
FeB_2/NF	10	1.57	Adv. Energy Mater. 2017, **7**, 1700513
$Ni_{11}(HPO_3)_8(OH)_6$/NF	10	1.60	Energy Environ. Sci. 2018,**11**, 1287-1298
Ni-BCD/NF	10	1.60	Energy Environ. Sci.10.1039/c8ee00934a
FeB_2/NF	10	1.57	Adv. Energy Mater. 2017, **7**, 1700513
N-Ni_3S_2/NF	10	1.48	Adv. Mater. 2017, **29**, 1701584.

It is feasible to obtain electrochemical cells for distributed PEC systems with worthy efficiency in front of the use of big centralized options depending on the photon absorption used approach:

Electrochemical efficiency >85% (1,23/1,43)

STH >18%

Electrochemical efficiency

- 80%

STF > 15%

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Thank you.

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