Controlled metal Deposition on Flexible Polyethylene Substrates by Sputtering for CO_2 reduction

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Project Overview

- **Goal:** **To design and develop a protocol for deposition of metal on flexible electronic substrates for catalysis**
- **Rationale:** **High-efficient electrical devices like electrocatalysis need high surface area and highly conductive electrode arrays. One of the promising device architectures is the multi-layered metal thin films deposited on flexible electronic materials such as PE (polyethylene), graphene, nickel or aluminum foam, which allow for subsequent folding, packing, and device integration.**

Lesker sputter

Lesker is a load locked single wafer metal sputter providing flexible processing options for non-CMOS compatible materials.

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Mesostructure-Induced Selectivity in CO_2 Reduction Catalysis

Anthony Shoji Hall,[†] Youngmin Yoon,[†] Anna Wuttig,[†] and Yogesh Surendranath*[,†]

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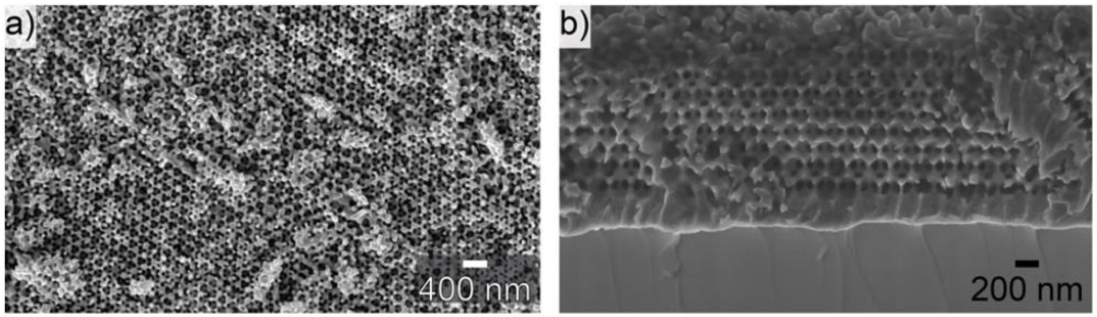
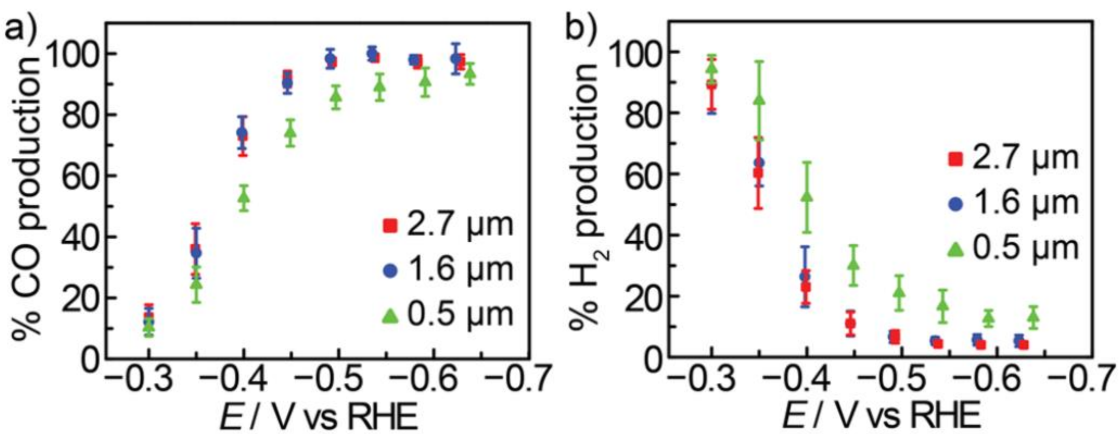
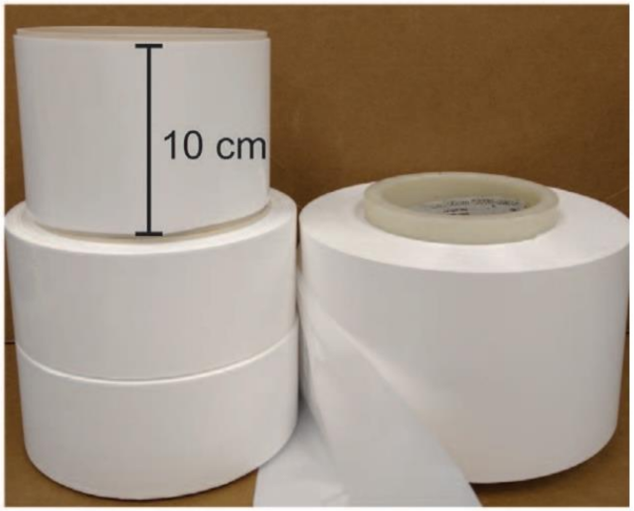


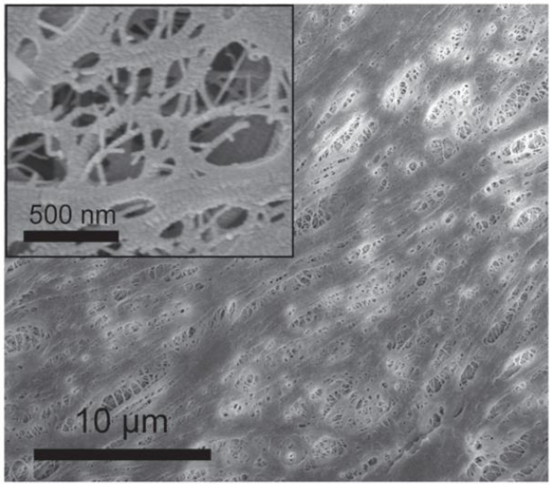


- Ordered Au inverse opal (Au-IO) thin films of varying thickness
- Forming mesostructure to modulate CO_2 reduction selectivity
- Increased electrode porosity improve selectivity for CO_2 reduction relative to HER

Polyethylene: Battery Separator for Versatile Usage

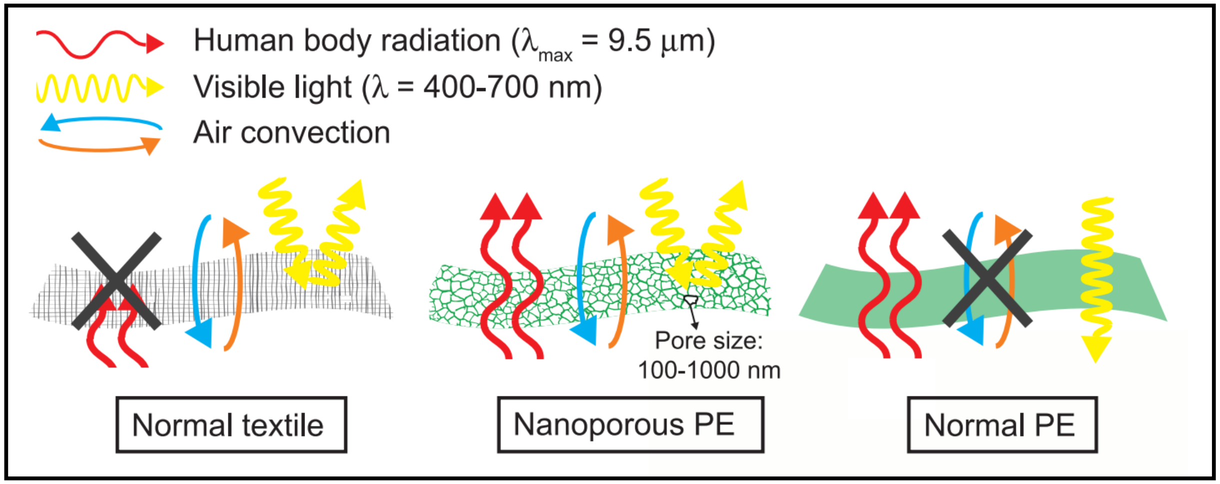


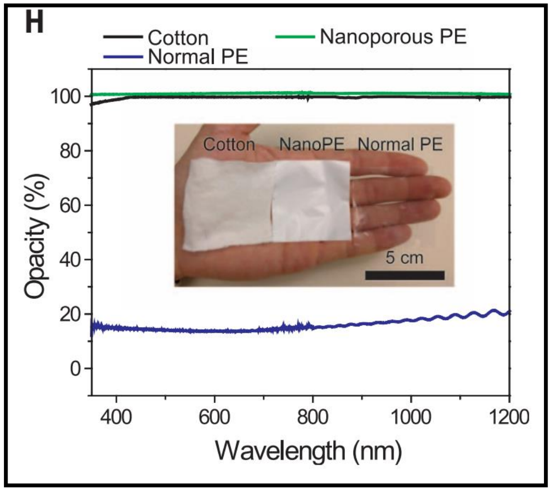
Commercial PE



SEM: The nanopores are 50 to 1000 nm in diameter

Nanoporous polyethylene textile for radiative human body cooling





Po-Chun Hsu, …, Yi Cui, ***Science.*** 2016, 353, 1019.

Background: device to control gas diffusion

nature COMMUNICATIONS

ARTICLE

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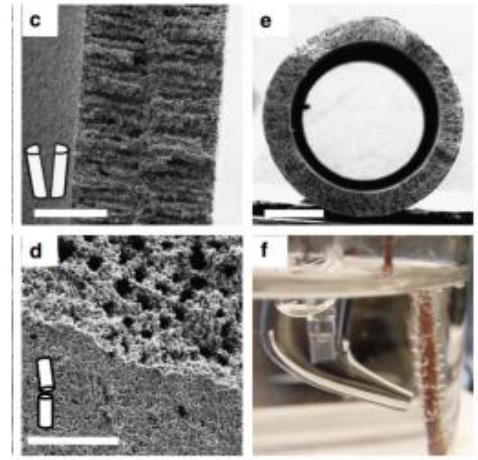
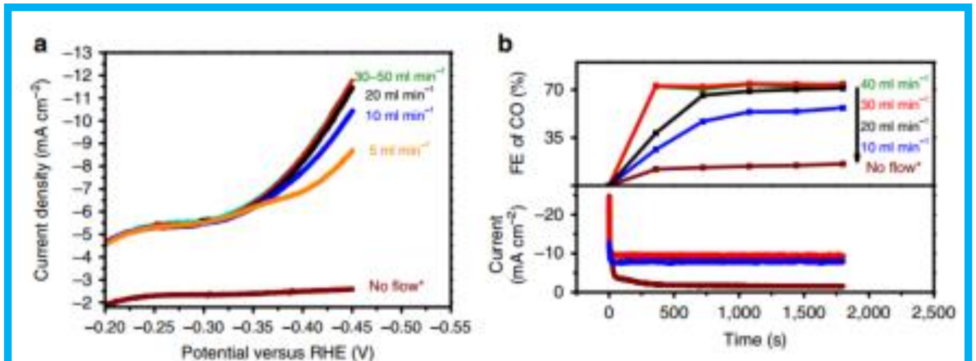
Three-dimensional porous hollow fibre copper electrodes for efficient and high-rate electrochemical carbon dioxide reduction

Recep Kas[1], Khalid Khazzal Hummadi[1,2], Ruud Kortlever[3], Patrick de Wit[4], Alexander Milbrat[1,5], Mieke W.J. Luiten-Olieman[4], Nieck E. Benes[4], Marc T.M. Koper[3] & Guido Mul[1]



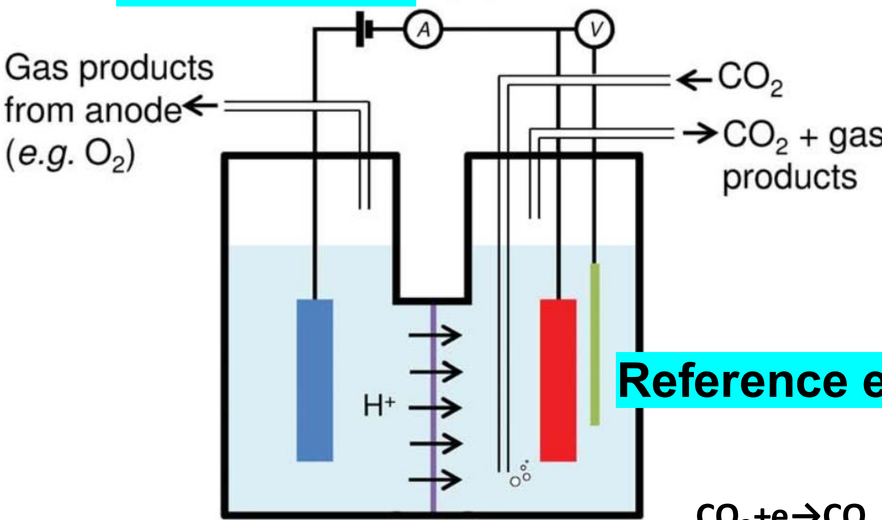
outer diameter 1.55±0.1 mm
inner diameter1.3±0.05 mm



- CO_2 was purged from the inside out of the fiber with pressure
- The FE of CO depends on the efficiency of mass transfer of CO_2 to the electrode surface
- Slow desorption rate of CO inhibits the hydrogen evolution reaction

How to evaluate CO_2 reduction performance： 3-electrode Cell

Electron flow



Reference electrode

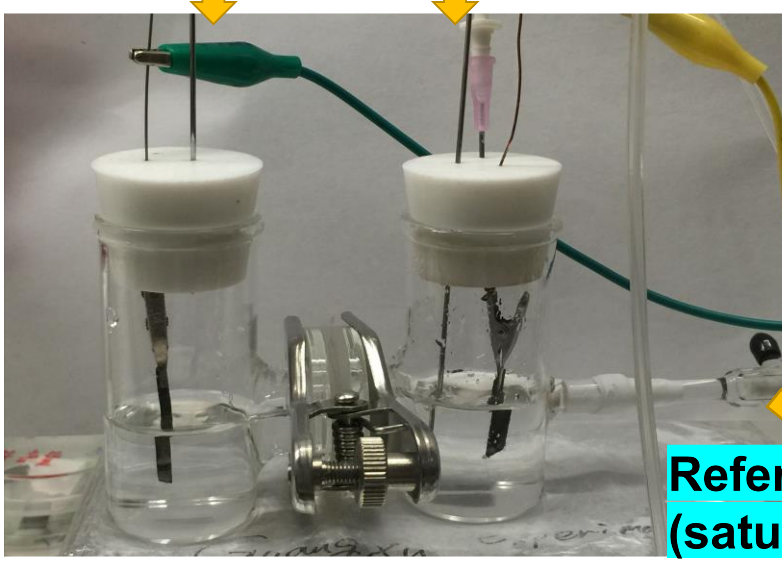
CO_2+e→CO

H^++e→H_2

H_2O→O_2+e

Counter electrode (Pt)

Working electrode



Reference electrode
(saturated calomel electrode)

Measurement Parameter：

CO, H_2 } → Gas chromatography

CO_2 flow rate → Flow meter

Electron flow in the circuit

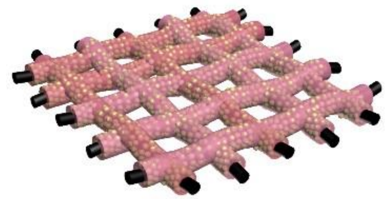
↓

Faradaic Efficiency

Scheme for Au/PE membrane

Polyethylene (PE) membrane

Deposition →



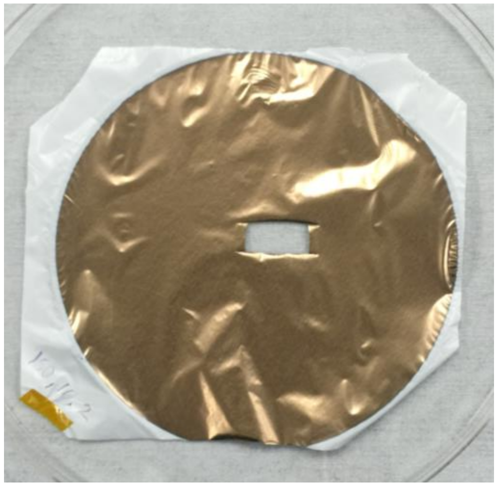
Au deposited on PE fibers

Advantages for Au sputtered on PE

- Well-distributed Au → Low resistance, good conductivity
- Without extra addition of carbon → Increased CO_2 reduction selectivity
- Au deposited to fibers, nano- and mirco-structure → More CO_2 reduction catalytic sites
- Fast fabrication → Scale-up production
- Flexibility → Tuning of CO_2 diffusion

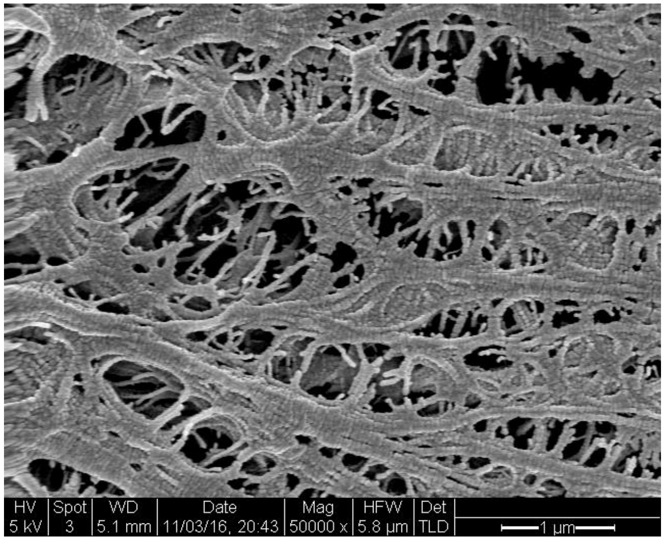
Sputtered Au on PE with thickness control

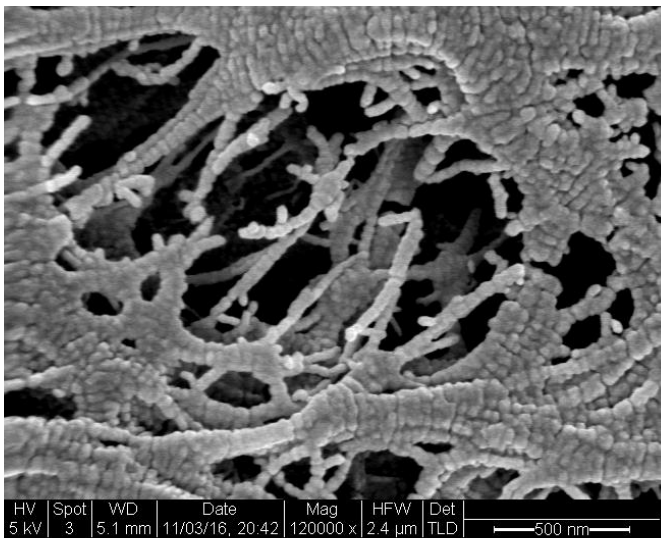
Group	Target	Power (W)	Pressure (mTorr)	Time (min)	Thickness calibration (nm)	Resistance (Ω)
1	**Au**	150	10	**5**	**50**	**1~2**
2	**Au**	150	10	**2**	**20**	**4~5**
3	**Au**	150	10	**1**	**10**	**100~200**
4	**Au**	150	10	**0.5**	**5**	**too large**



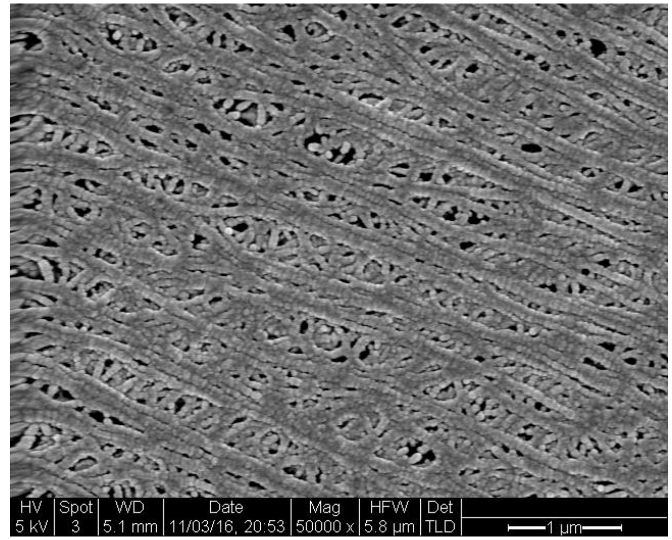
Thickness **5 nm** **10 nm** **20 nm** **50 nm**

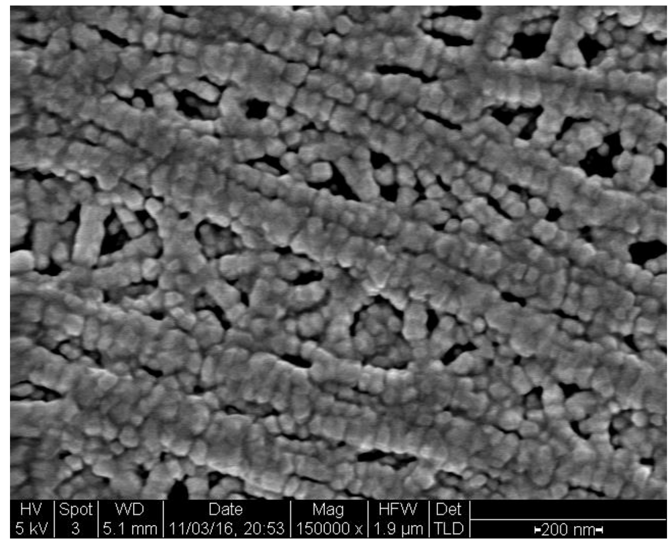
SEM image for Sputtered Au on PE





20 nm

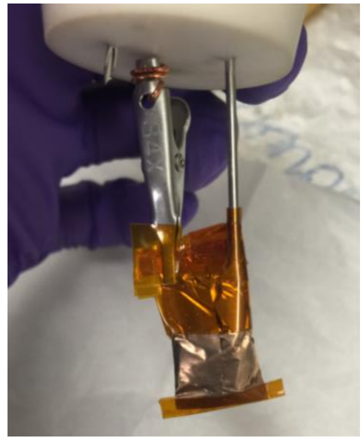




50 nm

Multi-layer Au/PE confined device

Punch pores with needle to allow gas and electrolyte flow



Sealed top and bottom to push CO_2 flow through the multi-layer Au/PE

Device design

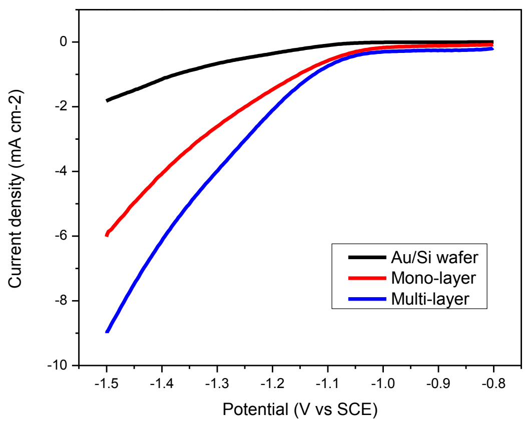
Au/PE CO_2 confined device

CO_2 bubble in

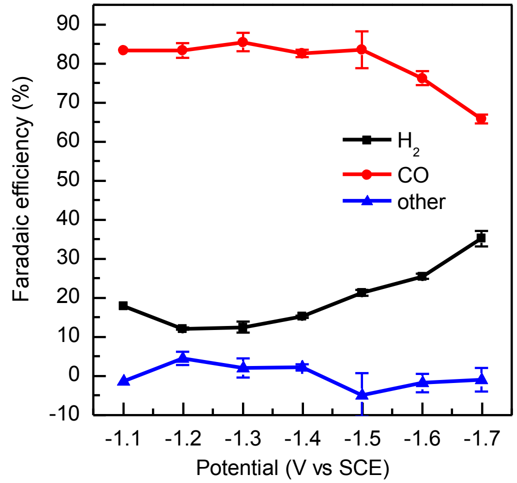
CO bubble out

- High surface area by PE nanostructure
- Increased reactive site from sealed device
- Diffusional limitations imposed by multilayer gas/electrolyte confined device

Results

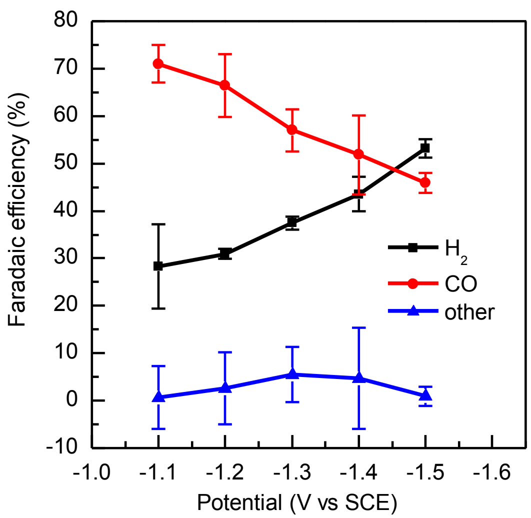


Linear polarization curves

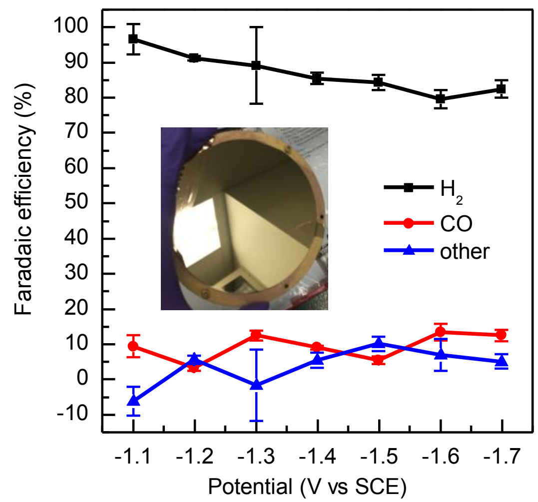


Multi-layer Au/PE confined device

At -1.3V, CO_2 FE=86±3%



Mono-layer Au/PE



Mono-layer Au/Si wafer

Control of thickness and particle size

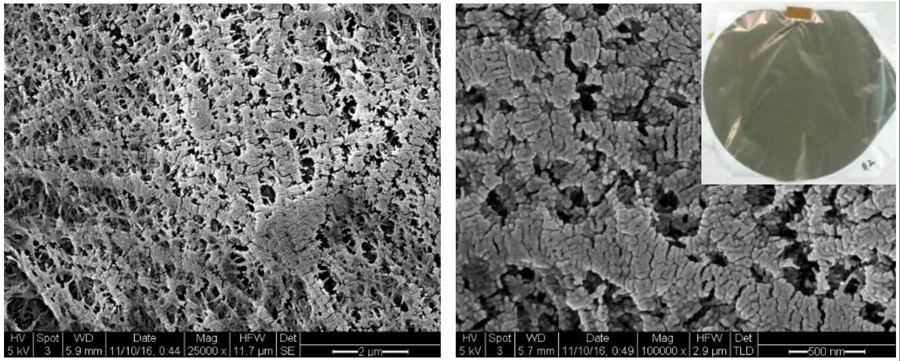
DOE

(Power, Pressure)

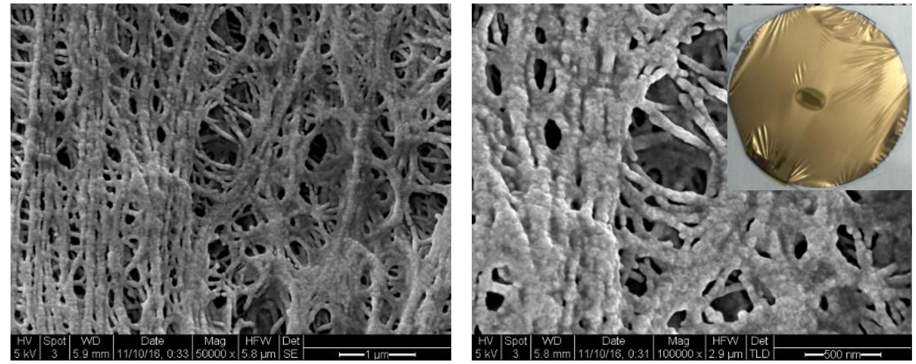
-- 50, 3		+- 250,3
	150 W, 10 mTorr	
-+ 50,50		++ 250,50

	Group	Target	Power (W)	Pressure (mTorr)	Time (min)
√	1	Au	150	10	2
√	2	Au	50	3	2
√	3	Au	250	3	2
	4	Au	50	50	2
	5	Au	250	250	2

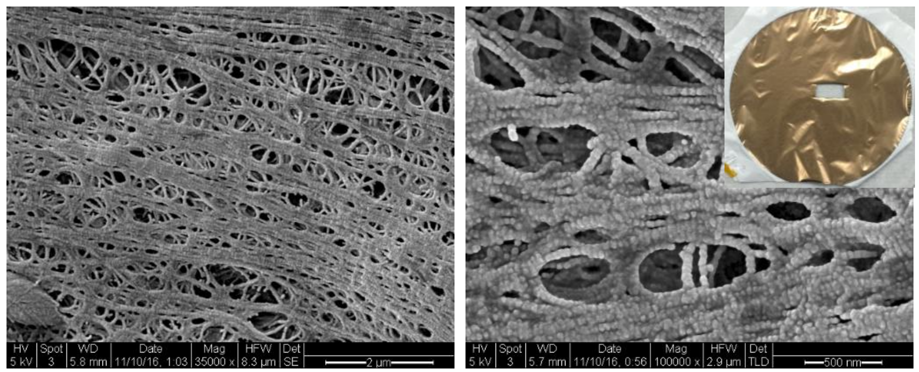
Control of thickness and particle size



50 W, 3 mTorr



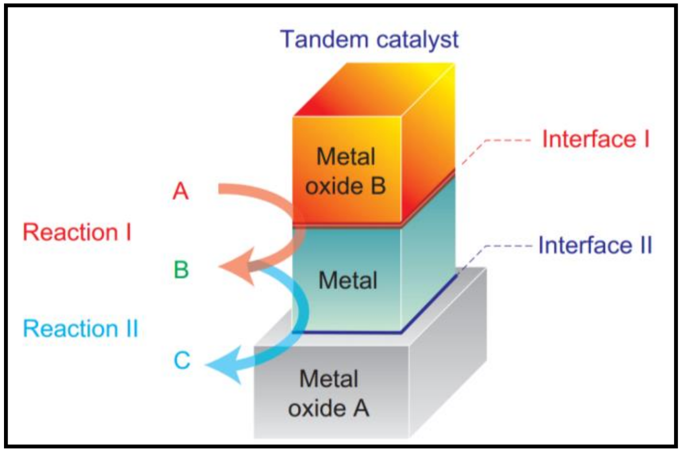
250 W, 3 mTorr



150 W, 10 mTorr

-- 50, 3		+- 250,3
	150 W, 10 mTorr, 20nm	
-+ 50,50		++ 250,50

Electrocatalysts in tandem may enable sequential reactions catalyzed by different interfaces in series towards final desired products selectively .

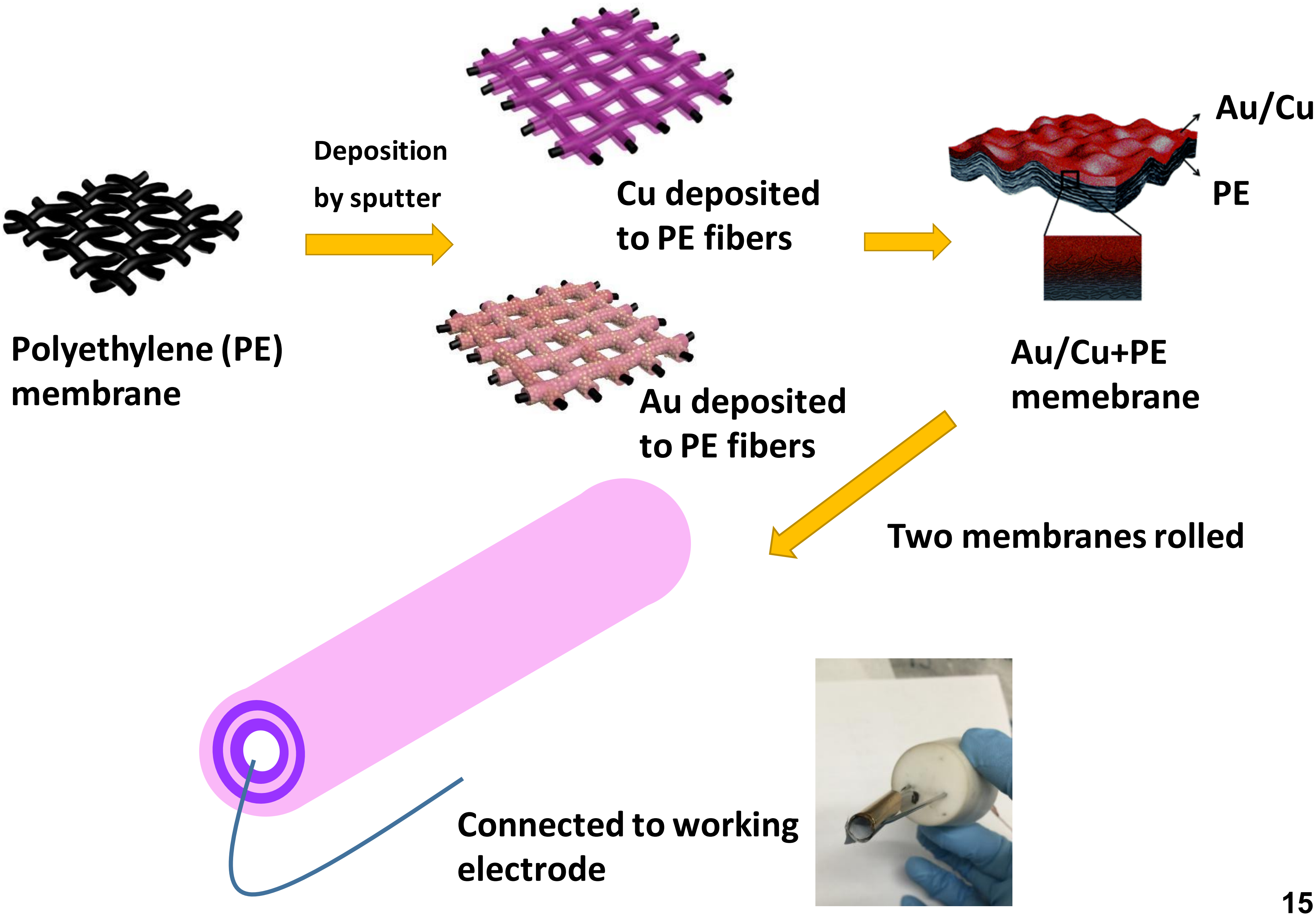


The electrocatalysis should take advantage of properties of both metals as to different selectivity.

Au for $CO_2 \rightarrow CO$

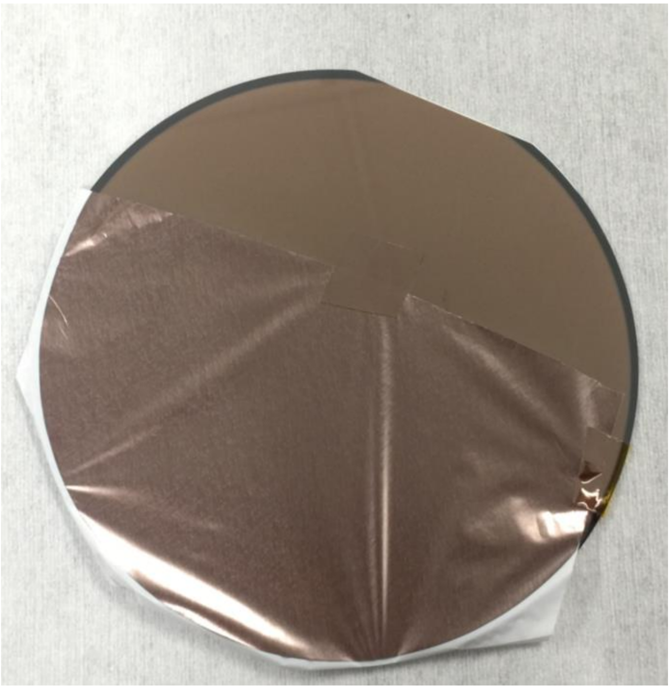
Cu for $CO \rightarrow$ subsequent hydrocarbon product

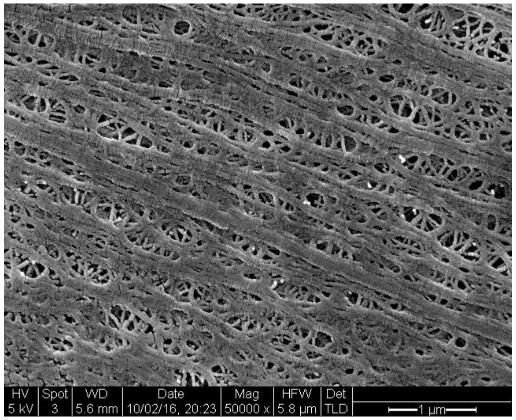
Scheme for tandem reaction

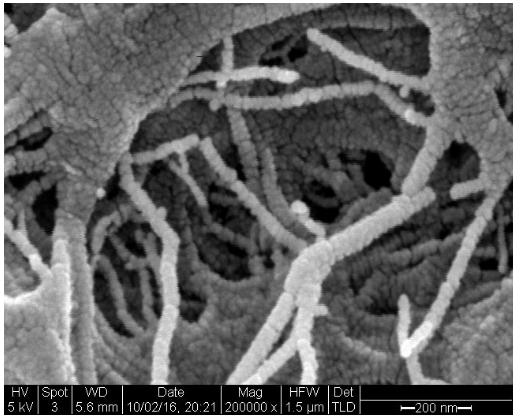


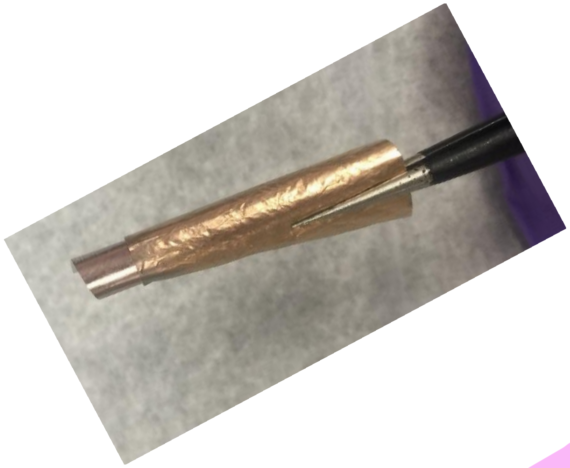
Sputtered Cu on PE and Si wafer

Cu	Power(W)	Pressure (mTorr)	Time(min)	Resistance(Ω)
#1	150	10	5	15
#2	150	10	2	200
#3	150	10	1	Too large







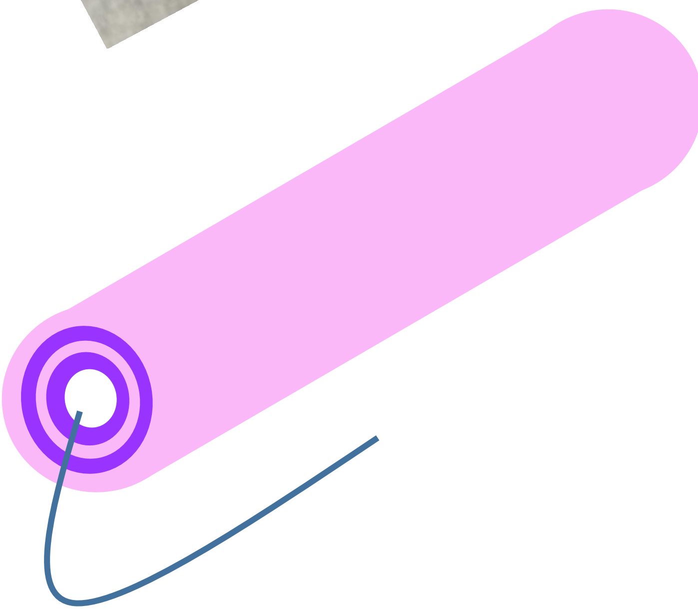


Challenges:

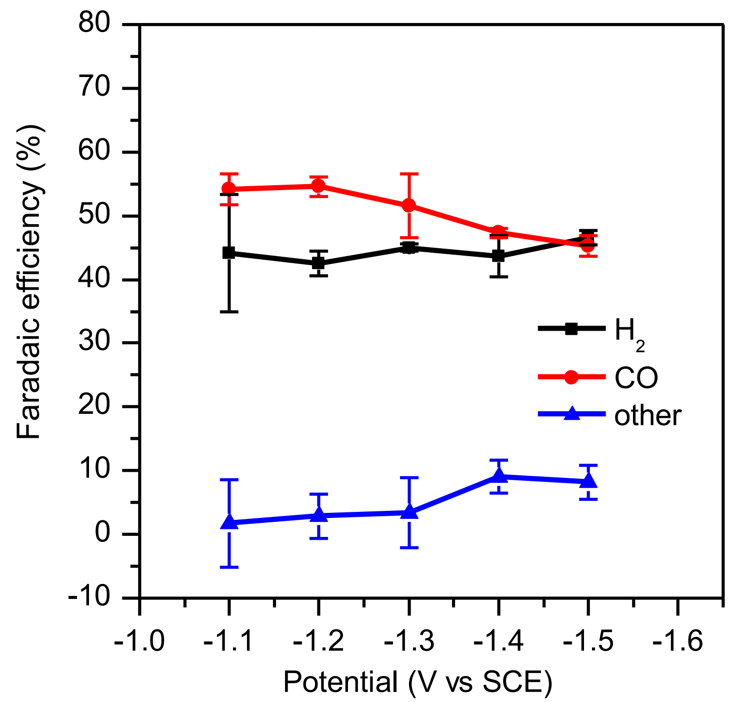
Cu has a different optimized voltage for successive tandem reaction to convert CO to CH4 and liquid product

Solution:

- **Optimized same voltage for both Au/Cu**
- **Two bias voltages**



Connected to working electrode



At -1.2 V vs SCE,
CO2 Faradaic Efficiency = ~ 55%

- **Cu, Cu_2O, CuO**
- **Particle size**

Acknowledgements

- Prof. Howe for making this course an excellent combination of theory and practice
- Mentors: Xiaoqing Xu, Antonio J Ricco, Hye Ryoung Lee
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