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

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Introduction: Fossil fuel acquisition based on electrochemical or photoelectrochemical conversion represents one of the most promising means for the fast increase of global energy need, capable of offering a sustainable energy resource without unchecked accumulation of atmospheric CO_2. 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 polyethylene (PE), graphene, nickel or aluminum foam, which allow for subsequent folding, packing, and device integration. Our goal is to design and develop a protocol for deposition of metal on flexible electronic substrates for catalysis. We develop the metal deposition on flexible polyethylene substrates by sputtering for efficient CO_2 reduction.

Background for gold as CO_2 reduction catalyst

With the fast consumption of fossil fuels and gradual deterioration of global climate and environment situations due to carbon release, the research and progress of developing a scalable synthesis of carbon-containing fuels using renewable energy, H_2O, and CO is important. A key technological target for this goal is an efficient and robust electrochemical CO_2 reduction catalyst. However, the low efficiencies and high costs of current CO_2-to-fuels technologies have impeded widespread commercial use. A principle barrier to develop practical CO_2-to-fuels devices is the lack of efficient and selective catalysts for the multielectron, multi-proton reduction of CO_2. CO_2 reduction is most practically carried out in aqueous electrolytes, in which the reduction of protons to H_2 often outcompetes CO_2-to-fuels conversion, eroding reaction selectivity. Thus, a key prerequisite for any viable catalyst is the ability to preferentially activate CO_2 over H^+, despite the relative kinetic difficulty of the former process. Gold is targeted as an electrode material because it is reported to exhibit the highest activity and selectivity for CO_2 reduction to CO.

Background for PE as substrate

For the substrate, polyethylene (PE) is utilized due to its potential use in flexible conductive substrate in battery (Fig 1a). The commercial nanoPE has pores of 50 to 1000 nm in size and some aligned fiber like structure of a few micrometers wide (Fig 1b). In battery application, a PE separator is a permeable membrane that is placed between a battery's anode and cathode. The main function of a separator in battery is to keep the two electrodes apart to prevent electrical short circuits while also allowing the transport of ionic charge carriers that are needed to close the circuit during the passage of current in an electrochemical cell. But the PE membrane also has versatile use like radiative human body cooling by nanoporous polyethylene textile. Thus, we hope to sputter gold on PE membrane for CO_2 reduction.

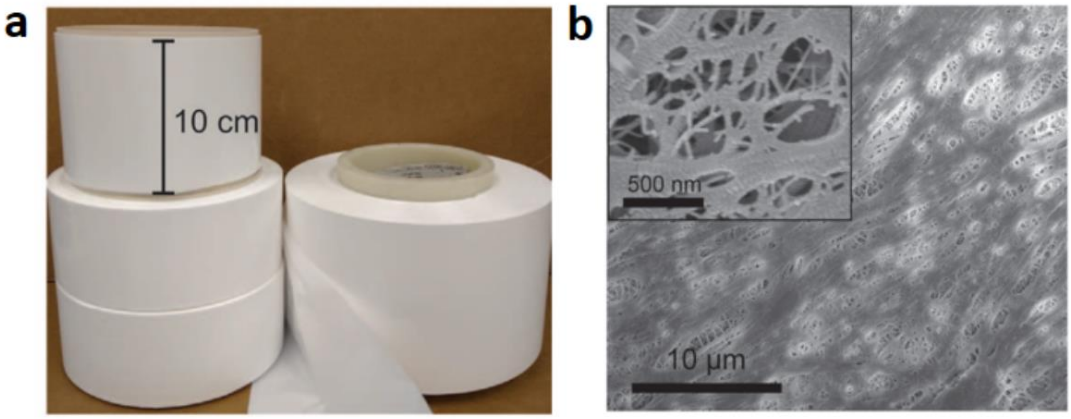

Figure 1. (a) Photo of commercial nanoPE. (b) High-resolution SEM images of nanoPE.

The nanopores are only 50 to 1000 nm in diameter

As shown in the scheme (Fig 2), there are quite a few advantages for this project. (1) Au is well- distributed by sputtering on PE, making it low resistance and good conductivity. (2) In this case, extra addition of carbon is not needed, leading to increased CO_2 reduction selectivity. (3) Au deposited to fibers, nano- and mirco-structure resulting in more CO_2 reduction catalytic sites. (4) The flexibility of substrate enables tuning of CO_2 diffusion by well-designed electrode configuration. (5) This fabrication is fast, making scale-up production possible.

Figure 2. Scheme of gold sputtered to polyethylene

Fabrication process

1. Firstly, Au is sputtered on PE with thickness control varying from 5nm to 50nm. The sputter parameter is listed below (Fig 3a). With increase of thickness, the color become deeper (Fig 3b). From SEM image, the thickest 50nm sample has much larger particles deposited on the PE fibers, whereas the 20nm sample has more pores (Fig 4a, b).

a

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

b

Thickness 5 nm 10 nm 20 nm 50 nm

Figure 3. (a) Parameter for Au sputtered on PE and (b) optical images of different size.

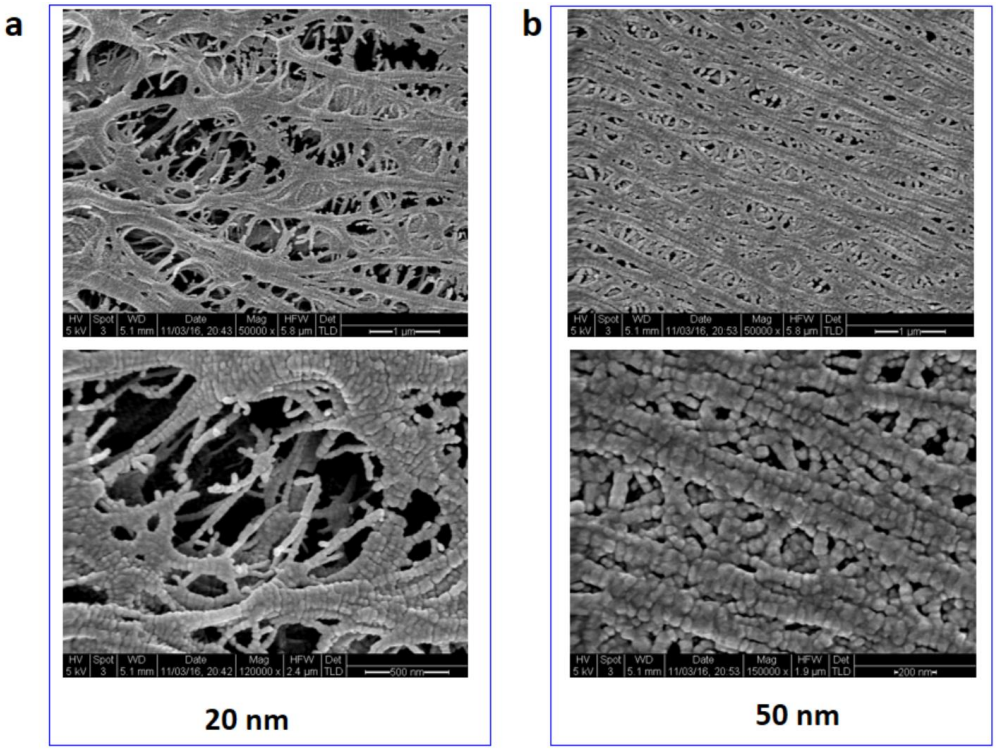

Figure 4. SEM image for (a) Au 20nm and (b) Au 50nm

2. Multi-layer Au/PE confined device is made by first punching pores with needle to allow gas and electrolyte flow (Fig 5a). Then top and bottom is sealed to push CO_2 flow through the multi-layer Au/PE (Fig 5b). This new configuration makes use of flexibility of PE and enables high surface area by PE nanostructure. Since CO_2 is forced to flow from inside to outside, there are increased reactive sites. Diffusional limitations are also imposed by multilayer gas/electrolyte confined device (Fig 5c).

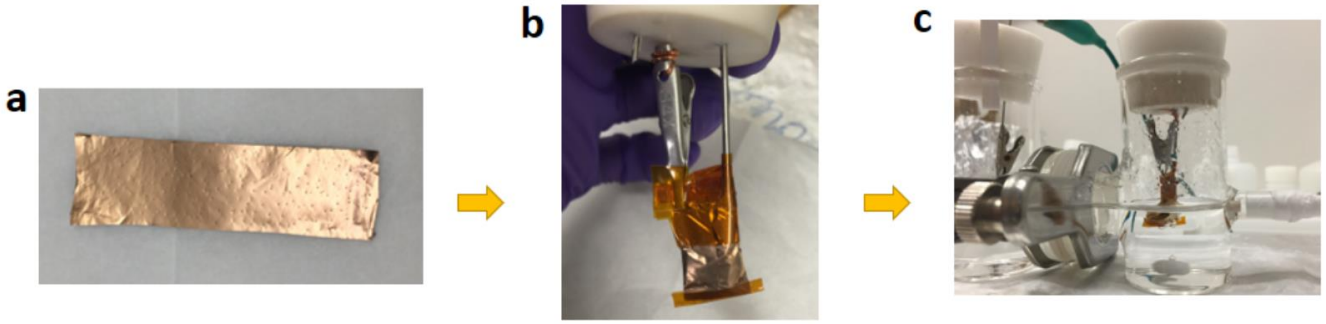

Figure 5. Process for fabricate multi-layer Au/PE confined device

CO_2 reduction performance is evaluated by 3-electrode cell with counter electrode, reference electrode and working electrode (Fig 6). Gas chromatography is used to collect CO and H_2 produced. And Biologic is used to know electron flow in the circuit. Then faradaic efficiency is calculated.

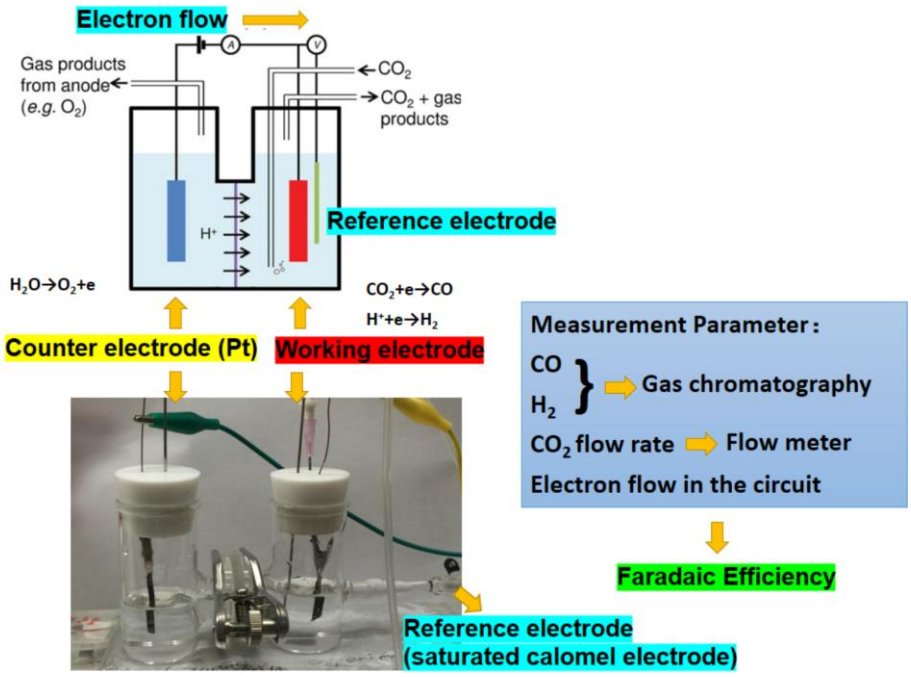

Figure 6. 3-electrode Cell for CO2 reduction measurement

Result

We test multi-layer Au/PE confined device (Fig 7b) and mono-layer Au sputtered on PE (Fig 7c) and mono-layer Au sputtered on Silicon wafer (Fig 7d) as comparison. From linear polarization curves, multi-layer Au/PE confined device has larger current density. At -1.5 V vs SCE, the current density is -9 mA cm^{-2} (Fig 7a). At -1.3 V, the faradaic efficiency for CO_2 is 86±3%, which is much larger than mono-layer Au/PE and mono-layer Au/Si wafer at the same potential for ~55% and ~15%, respectively.

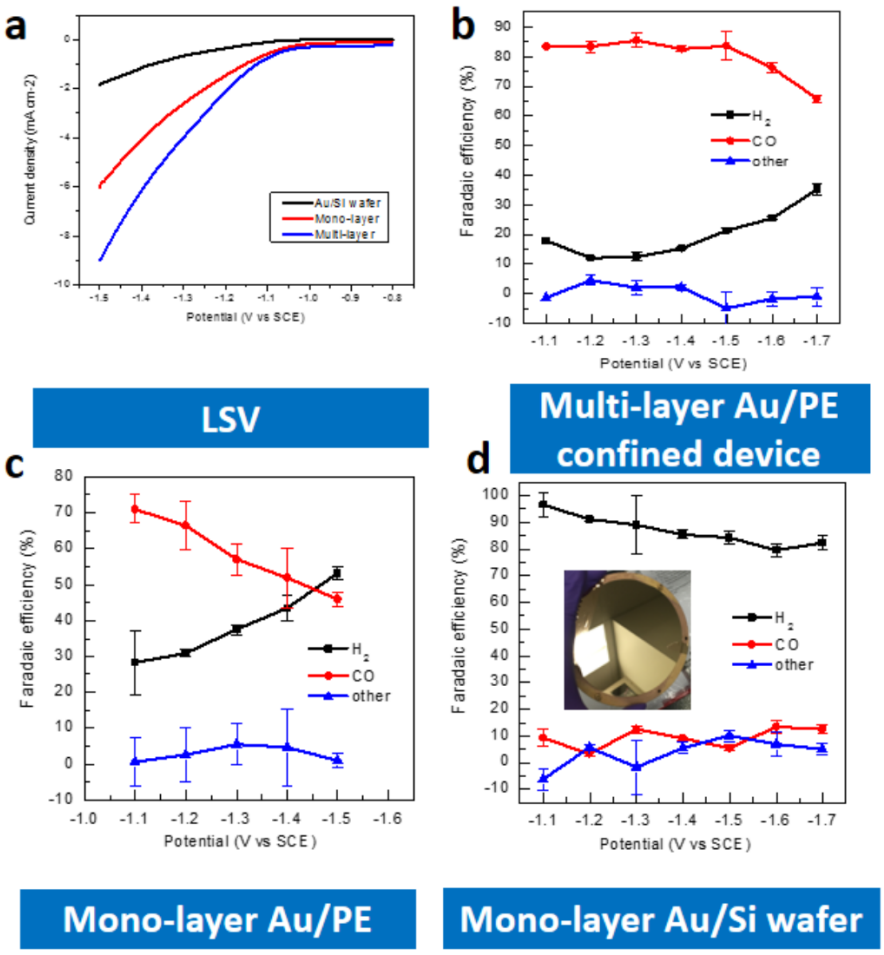

Figure 7. (a) Linear polarization curves from 3 conditions. FE for CO for (b) multi-layer Au/PE confined device and (c) mono-layer Au sputtered on PE and (d) mono-layer Au sputtered on Silicon wafer

Future work

We would like to combine Cu and Au for tandem reaction for further project (Fig 8). 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 product.

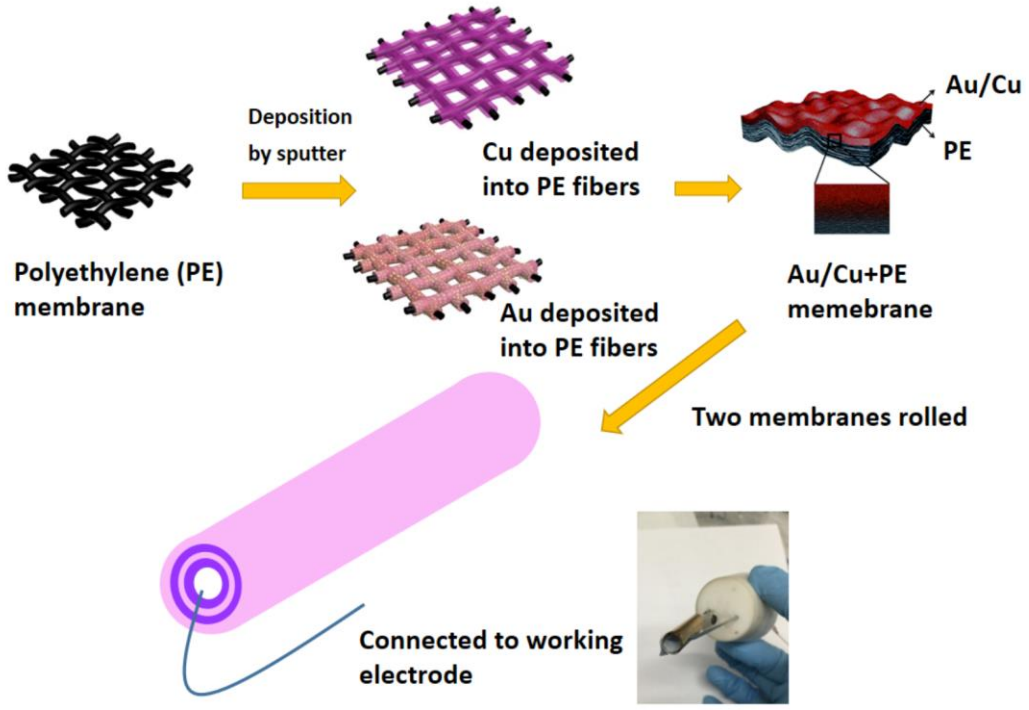

Figure 8. Scheme for Au/Cu tandem reaction device

Since Cu has a different optimized voltage for successive tandem reaction to convert CO to CH_4 and liquid product, we think up two solution:

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

The result of same voltage for both Au/Cu is shown below (Fig 9). Future work should be done to improve the faradaic efficiency.

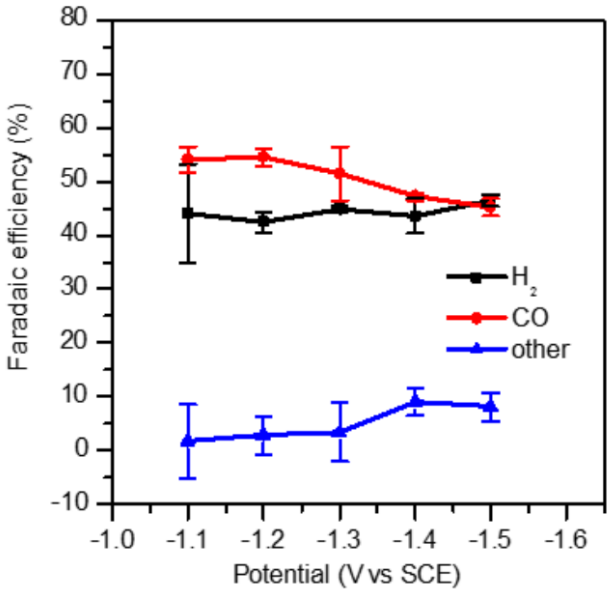

Figure 8. FE in applying same voltage for both Au/Cu

Conclusion: In this project, Au for efficient CO_2 reduction is achieved with control over particle size, substrate tuning and configuration change. The FE for CO is nearly 90%. Further tandem cell is demonstrated.

Reference:

1. Three-dimensional porous hollow fibre copper electrodes for efficient and high-rate electrochemical carbon dioxide reduction. NATURE COMMUNICATIONS, 2016. DOI:10.1038/ncomms10748
2. Radiative human body cooling by nanoporous polyethylene textile. Science, 2016, 353,1019.

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