The 69th TIEC Research and Presentation

High efficient catalyst materials for electrochemical CO_2 reduction

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Outline

1. **Greenhouse effect and global warming problem**
2. **Strategies to reduce CO_2 emissions**
3. **Gold and silver as CO production catalyst**
4. **Catalyst morphology influence**

Mongolia. Capital city Ulaanbaatar

“Naadam” Festival Mid July

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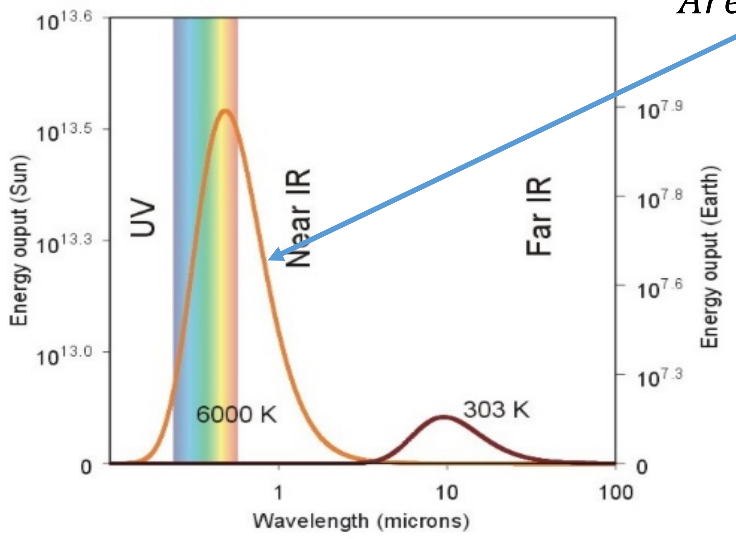
1. Greenhouse effect and global warming problem

2. Strategies to reduce CO2 emissions

3. Gold and silver as CO production catalyst

4. Catalyst morphology influence

Heat balance and greenhouse effect



$Area \sim T^4$

Stefan–Boltzmann Law

$$T_{earth} = 288K$$

$$\lambda_{max} \cdot T_{earth} = b \qquad \lambda_{max} = \frac{2.897 \cdot 10^{-3} m \cdot K}{288K} \approx 10 \cdot 10^{-6} m = 10 \mu m$$

Wien's displacement law

Earth's emission has maximum at 10μm which is absorbed and radiated back by **CO_2** molecules and other GHG

Thanks to the Greenhouse effect mean temperature of the Earth is higher

$$J_{sun} = (4\pi R_{sun}^2 \cdot \sigma T_{sun}^4)/(4\pi R_{e-s}^2) = 1.3 \frac{kW}{m^2}$$

$$E_{earth\ absorb} = \pi R_{earth}^2 J_{sun}$$

$$E_{radiate} = A \cdot J_{Earth} = 4\pi R_{earth}^2 \cdot \sigma T_{earth}^4$$

Heat Balance

$$T_{earth} = 275K$$

$$T_{earth} = 258K$$

If we assume that only 70% of Sun's radiation is reached to the earth's surface

$$J_{sun} = 1 \frac{kW}{m^2}$$

Global Carbon Fluxes

Anthropogenic Emissions by Sector (100% = 13 GtC/yr)	
Carbon Flux	Amount/[GtC/yr]
Electricity generation	3.3 (25%)
Agriculture and land-use change (deforestation)	3.2 (24%)
Industry (excluding electricity)	2.8 (21%)
Transportation	1.9 (14%)
Buildings	0.9 (6%)
Other	1.4 (10%)

Year 2010

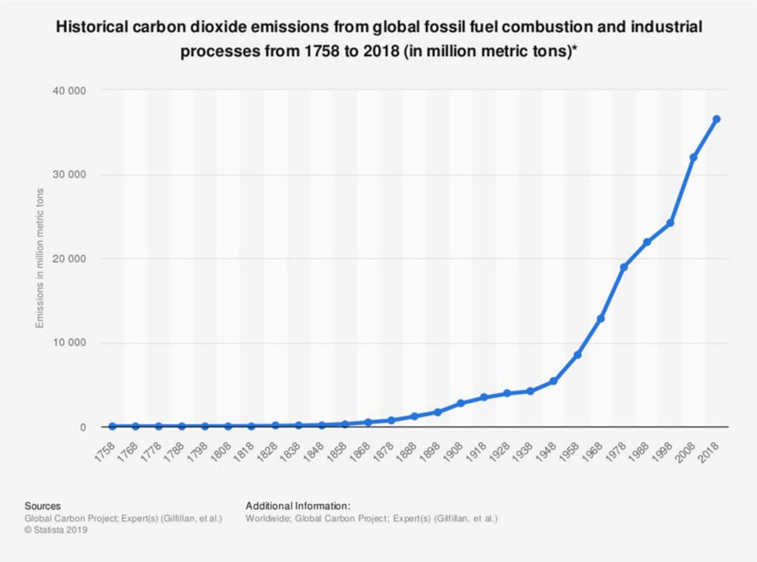
Intergovernmental Panel on Climate Change. Climate Change 2014: Synthesis Report; 2014.

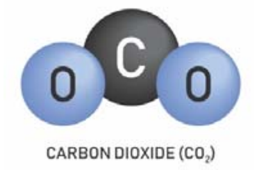
Global Carbon Fluxes

Carbon in Industrial Reactions, CO_2 as Ultimate Byproduct		
Carbon Flux	Amount/ [GtC/yr]	Year
Cement (calcination): $CaCO_3 \rightarrow CaO + CO_2$	0.59	2017
Steel (via CO): $2Fe_2O_3 + 6C + 3O_2 \rightarrow 4Fe + 6CO_2$	0.38	2017
Plastic (disposal): $(CH_2)_{2n} + 3nO_2 \rightarrow 2nH_2O + 2nCO_2$	0.26	2015
Ammonia (via H2): $3CH_4 + 6H_2O + 4N_2 \rightarrow 8NH_3 + 3CO_2$	0.045	2016
Aluminum (carbon anode): $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$	0.019	2016
Total nonfuel carbon as industrial reactant	1.28	

Intergovernmental Panel on Climate Change. Climate Change 2014: Synthesis Report; 2014.

Carbon dioxide emission and global warming





- ➢ As an essential resource of carbon for the photosynthesis of plants and main component in the life cycle of lives on earth, CO2 plays a significant role in Earth's carbon cycle.
- ➢ But from other side CO2 is recognized as one of the GHG which dominates among other gases.
- ➢ Before industrial revolution the CO2 release by human activity and natural process was at a good balance with photosynthesis process.

- ➢ The accumulation of the GHG CO2 in the atmosphere is the primary driver of today's climate change.
- ➢ The problem is urgent: net CO2 emissions needs to be decrease rapidly and cross zero around year 2050 if global warming is to be limited to relatively safe level of 1.5^{O}C above preindustrial level.

Can we preserve our planet?

Outline

1. **Greenhouse effect and global warming problem**
2. **Strategies to reduce CO_2 emissions**
3. **Gold and silver as CO production catalyst**
4. **Catalyst morphology influence**

1. Decarbonization

Carbon-free society

- In long term: exhaust of fossil fuel
- Short term: CO_2 accumulation which drives into climate change

This renewable energies are related to the natural resources that has similarity as infinite or constantly renewed resource

Solar

Wind

Hydropower

Geothermal

Biomass

1. Decarbonization

Zero CO2 Emission!

- Electricity from renewable sources such as wind turbines and photovoltaics is increasing in volume and decreasing in price.
- Private investment in renewable energy is outpacing investment in fossil fuels.

Solar

Wind

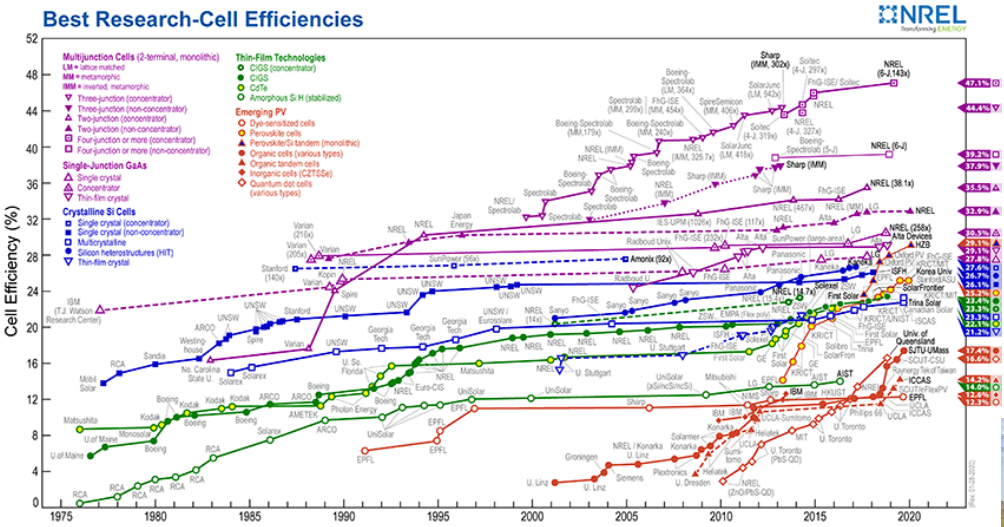
Hydropower

Geothermal

Biomass

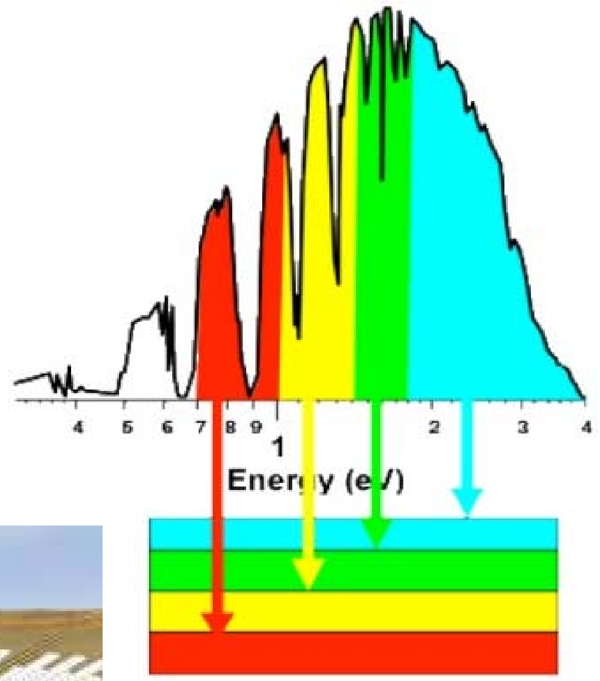
Solar cell technology

Historical efficiency record of the solar cell (record of the development in the laboratory level)



http://www.nrel.gov/ncpv/

Good efficiency. III-IV multi - junction solar cells



Decrease Thermal Loss

Concentrated Solar Power (CSP)

1. Decarbonization

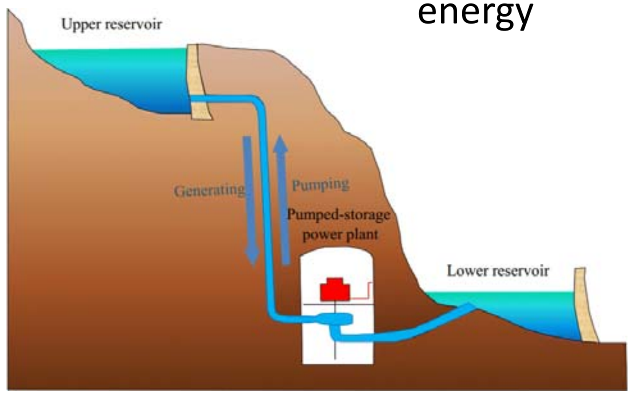
But to be fully decarbonized several challenges are remaining.

- Storage problem. Although there are several energy storing technologies such as H2, batteries, pumped hydro and so on. However there is no technology in use that could feasibly store enough renewable electricity to power the society through a cloudy on windless days.
- In transport there a clear advantages to energy in the form of liquid fuel.
- Even if we fully decarbonize the energy, CO_2 emission will still come from industry.

To store a high amount of energy H2 storage is more cheaper than battery storage

Electrical Energy → Mechanical Potential energy

Hydro pumped storate



2. Carbon Sequestration

Strategies to reduce CO2 emissions

This strategy is aims to prevent CO2 release into atmosphere. At present there a 18 large-scale “Carbon Capture and Storage” (CCS) project in operation worldwide, separating about 40 megatonnes of CO2 per year coming from industrial sources and storing it underground.
But this amount is below 0.1% of global carbon emissions.
In addition cost of the CO2 capture technologies from air is high (1500-2000$ per tonne of carbon removed from the atmosphere).

3. Carbon recycle

- Photosynthesis
- Direct CO_2 reduction
- Via Synthesis Gas

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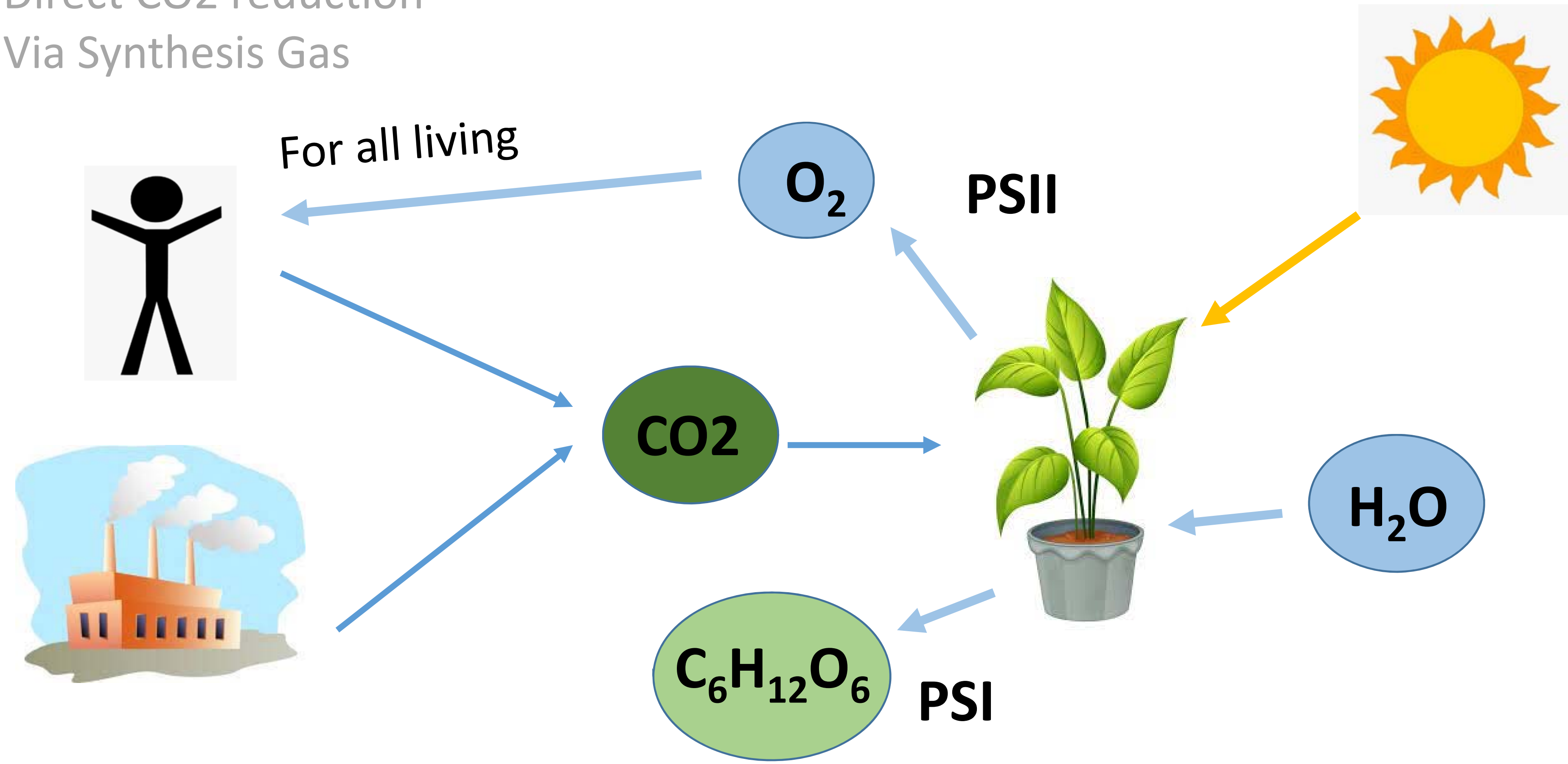
$$6CO_2+12H_2O \rightarrow (CH_2O)_6+6H_20+6O_2$$



3. Carbon recycle

- Photosynthesis
- Direct CO2 reduction
- Via Synthesis Gas

- Before industrial revolution CO_2 release by natural processes and human activities and the CO_2 uptake by photosynthesis was at good balance.
- Natural photosynthesis by plants and other phototrophs fixates a much larger amount of carbon globally.
- This is one way of carbon recycling.

3. Carbon recycle

- Photosynthesis
- Direct CO_2 reduction
- Via Synthesis Gas

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Faradaic efficiencies of products in CO_2 reduction at various metal electrodes

Electrode	Potential *vs* SHE, *V*	Current density, mA cm2	Faradaic Efficiency						
			CH_4	C_2H_2	Ethanol	CO	HCOOH	H_2	Total
Ni	-1.48	5	1.8	0.1			1.4	88.9	92.4
Fe	-0.91	5	0	0	0	0	0	94.8	94.8
Pt	-1.07	5	0	0	0	0	0.1	95.7	95.8
Cu	-1.44	5	33.3	25.5	5.7	1.3	9.4	20.5	100.5
Au	-1.14	5	0	0	0	87.1	0.7	10.2	98
Ag	-1.37	5	0	0	0	81.5	0.8	12.4	94.6
Zn	-1.54	5	0	0	0	79.4	6.1	9.9	95.4
Pb	-1.63	5	0	0	0	0	97.4	5	102.4
Hg	-1.51	0.5	0	0	0	0	99.5	0	99.5
In	-1.55	5	0	0	0	2.1	94.9	3.3	100.3

Electrolyte: 0.5M KHCO3, T=18.5°C
pH=6.8

Modern Aspects of Electrochemistry #42, edited by Vayenas et al., 2008 Electrochemical CO2 Reduction on Metal Electrodes, Pages 89-189, Hori, Yoshio

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3. Carbon recycle

- Photosynthesis
- Direct CO2 reduction
- Via Synthesis Gas

Cu is only unique metal that reduces CO_2 into various products

Advantages:

1. It combines the electrochemical water splitting and subsequent thermal hydrogenation into a single electrochemical process.
2. Enables products that can't easily be prepared by thermally driven processes.
3. Can often run at or near room temperature and ambient pressure.
4. Flexible energy input such as the use of electricity generated by renewable energies (solar, wind etc.)

Faradaic efficiencies of products in CO_2 reduction at various metal electrodes

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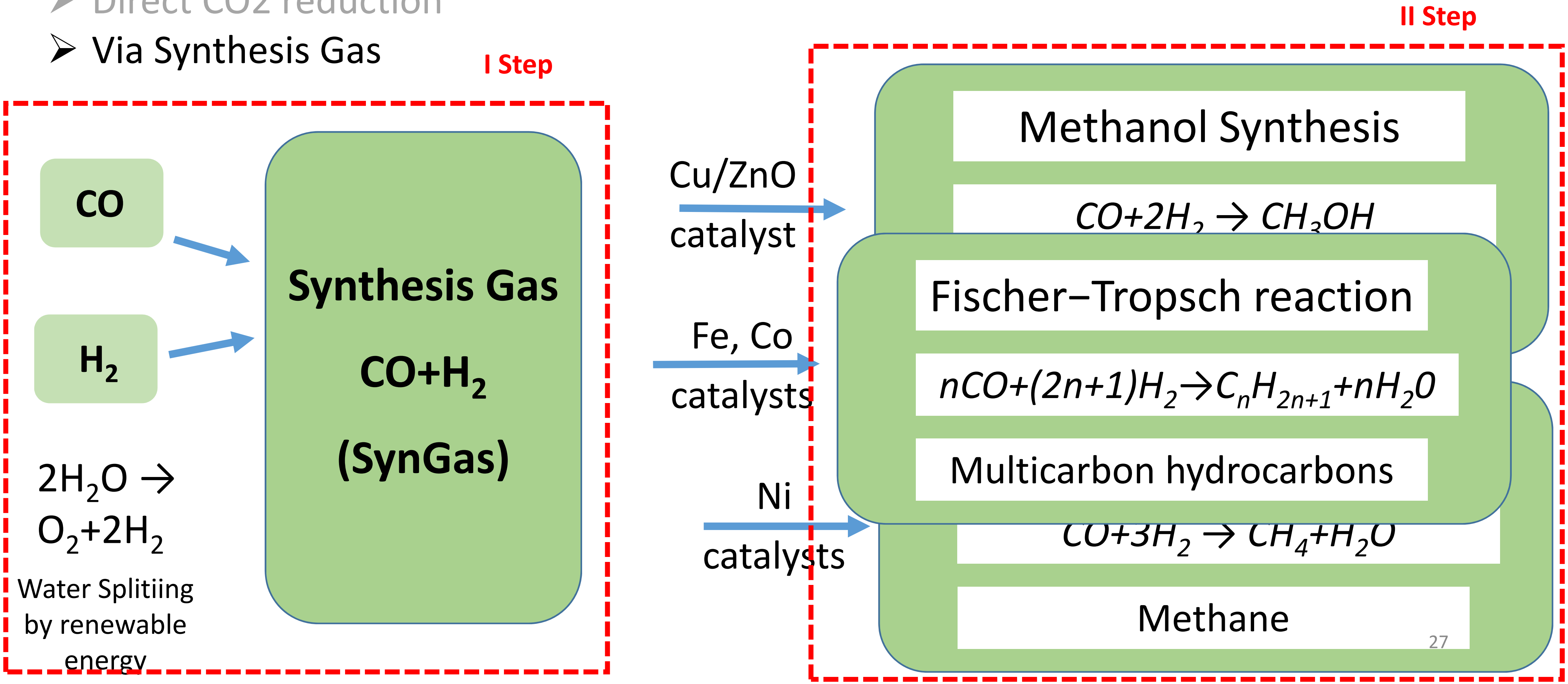


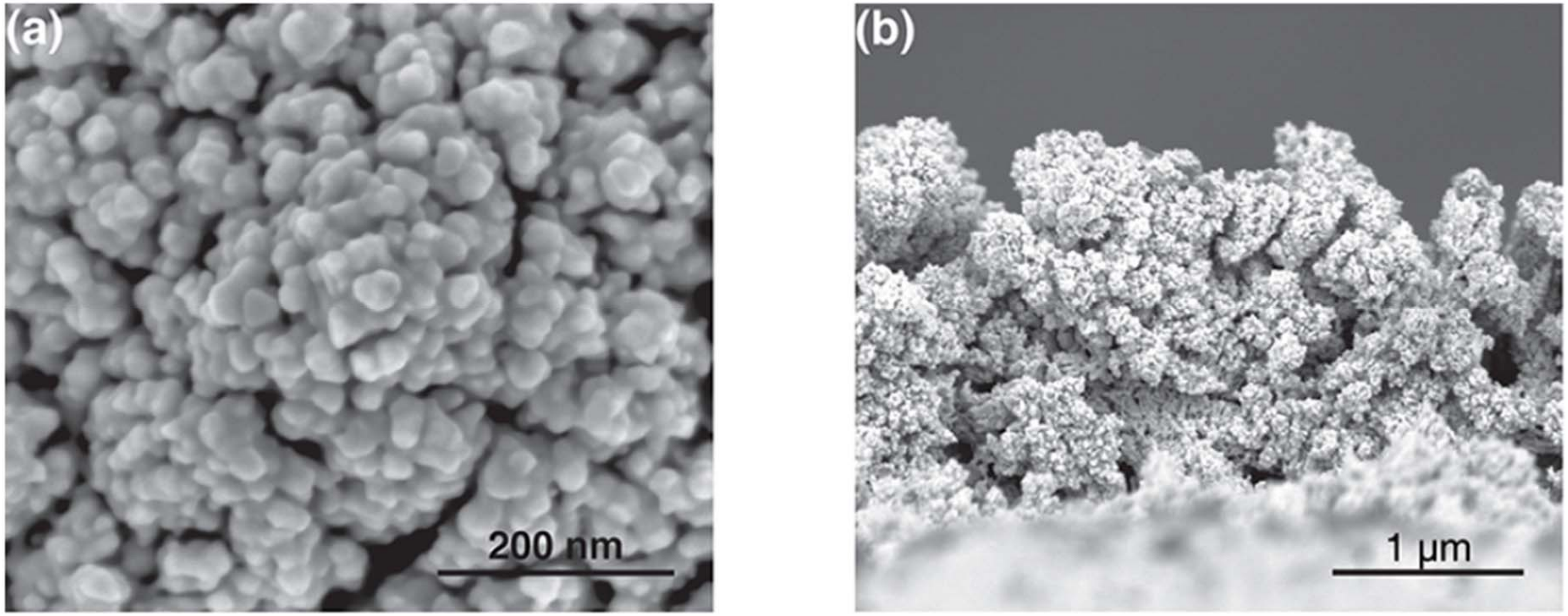
3. Carbon recycle

- Photosynthesis
- Via Synthesis Gas
- Direct CO2 reduction

Advantages:

1. The reaction can take place under relatively close conditions to the atm pressure and room temperature
2. The cost of CO produced is much lower (≈500$ per tonne of CO produced) than traditional synthesis of CO through the hydrogenation of CO2 at high temperature (≈1000$ per tonne of CO produced).
3. Flexible energy input such as the use of electricity generated by renewable energies (solar, wind etc.)

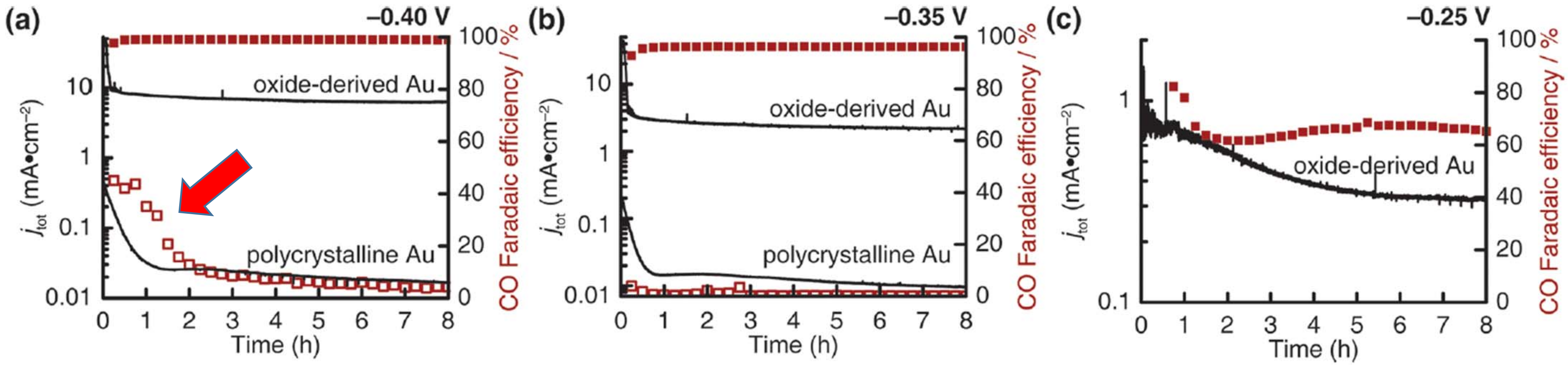
Oxide-derived gold as a catalyst in CO2 reduction



Characterization of oxide-derived Au NPs. (a) Top-down and
(b) cross-sectional SEM images

Chen Y. et al, J. Am. Chem. Soc. 2012

Faradaic Efficiency for CO formation



Comparison of CO2 reduction activity of polycrystalline Au with that of oxide-derived Au. Total current density vs time (—, left axis) and FE for CO production vs time (right axis) on oxide-derived Au (red,■) and polycrystalline Au (red,□) in electrolyses at (a) −0.4V, (b) −0.35V, and (c) −0.25 V vs RHE. Data were obtained in CO2-saturated 0.5 M NaHCO3, pH 7.2.

Chen Y. et al, J. Am. Chem. Soc. 2012

Silver as a catalyst in CO2 reduction

Silver is a promising material as a CO2 reduction catalysts

- It can reduce CO2 to CO with a good selectivity (≈87%). This selectivity is comparable to Au catalyst.
- It costs much less than other precious metal catalysts. (High cost of gold makes it unsuitable for large scale industrial applications).
- It is expected to more stable under harsh catalytic environment than homogenous catalysts

Tuning the Ag particle size and control of catalyst morphology has been widely recognized as one of strategies to increase the catalytic activity and selective ECR to CO of Ag catalyst

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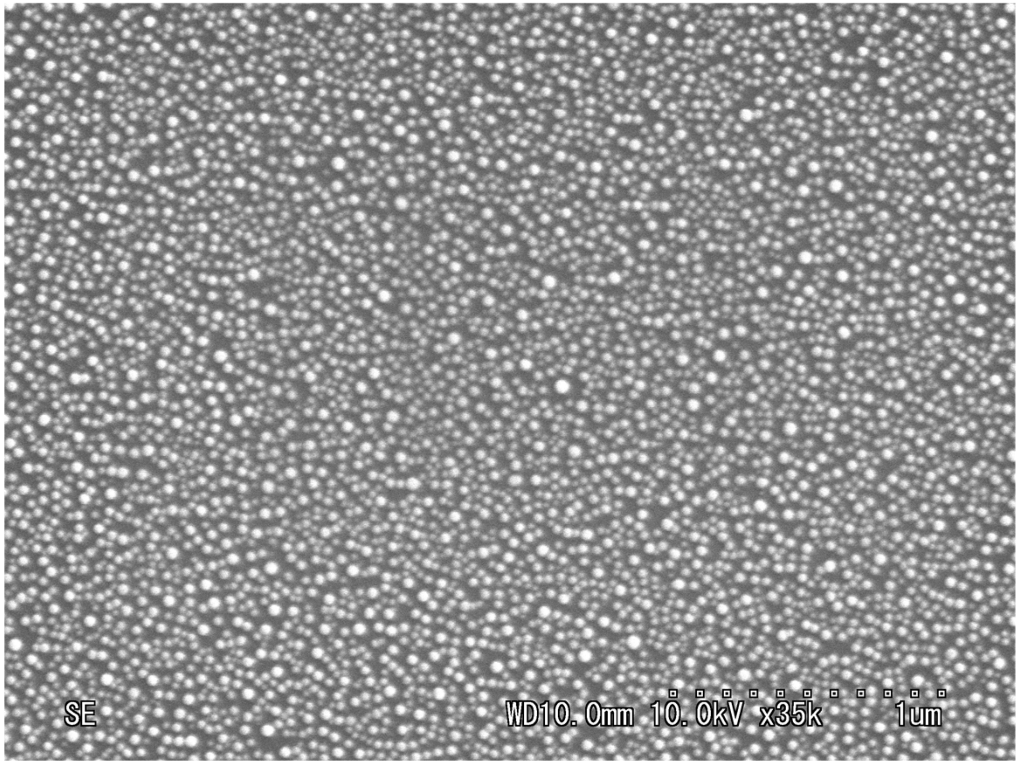
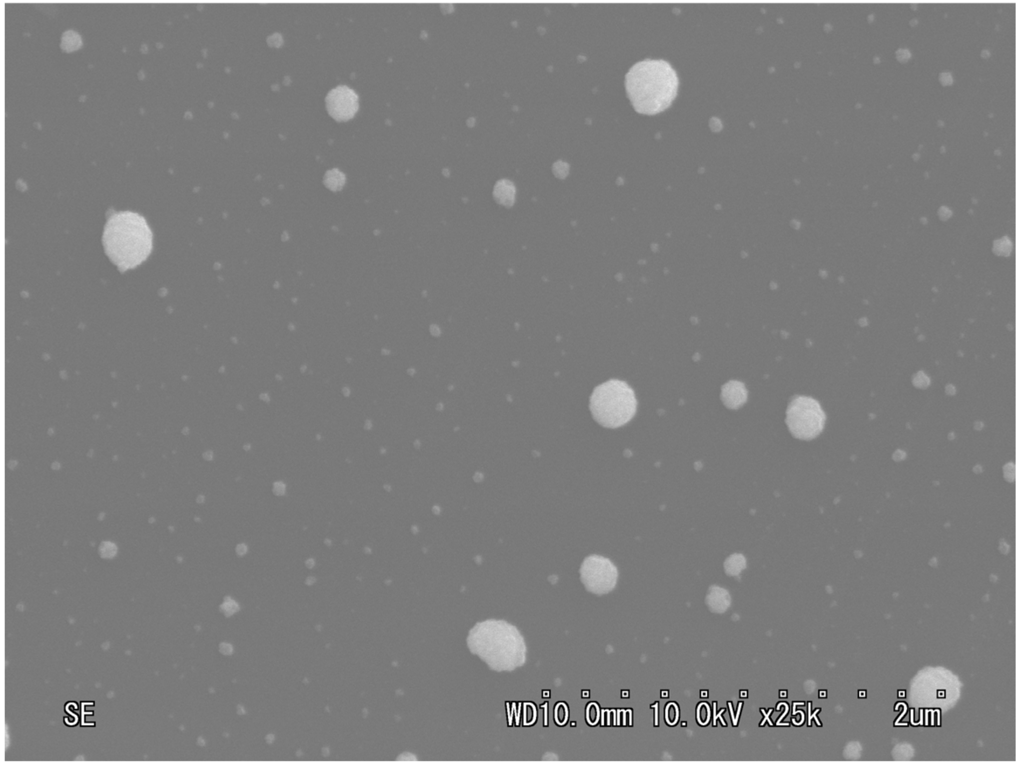
Spherical shaped nanoparticles

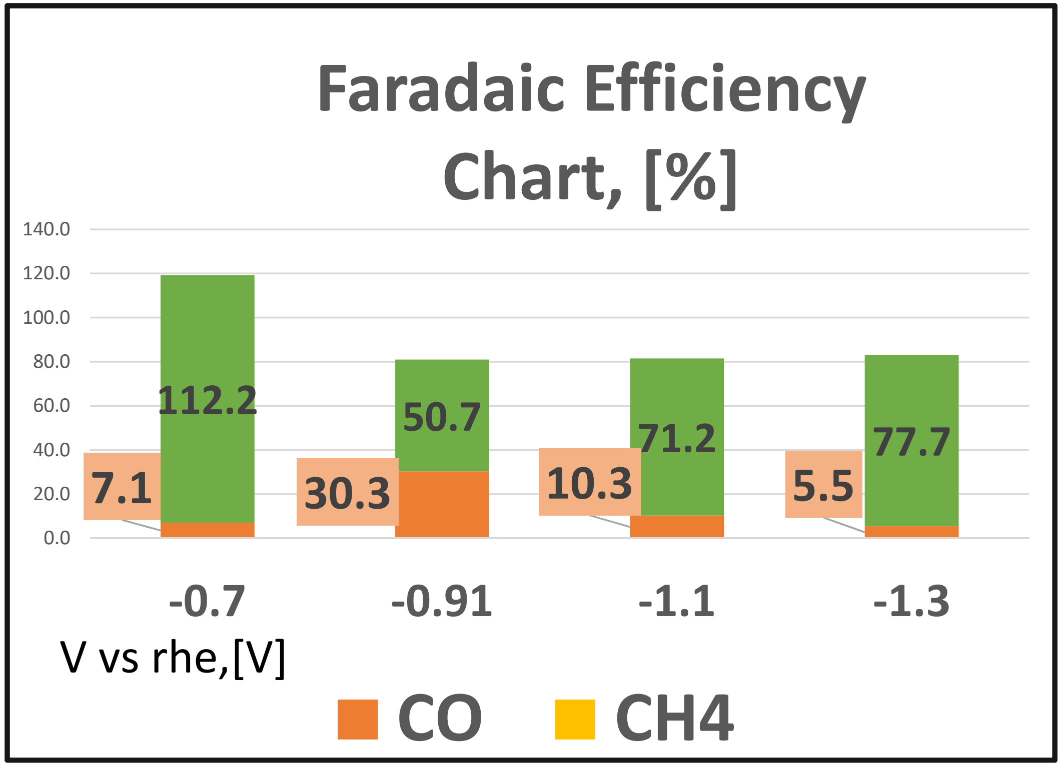


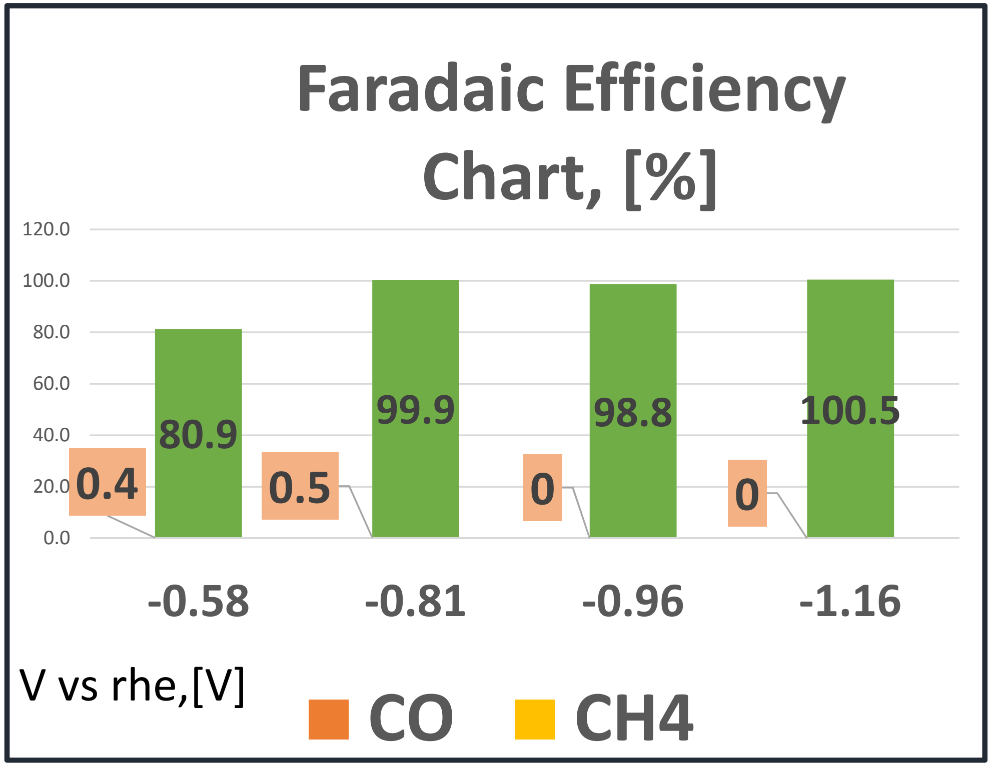
Working Electrode: TD6Ag24
Substrate: Glassy Carbon
Deposition: Ag 6nm thickness



Working Electrode: TD5.9Cu19
Substrate: Glassy Carbon
Deposition: Cu 5.9nm thickness

Spherical Shaped Structure

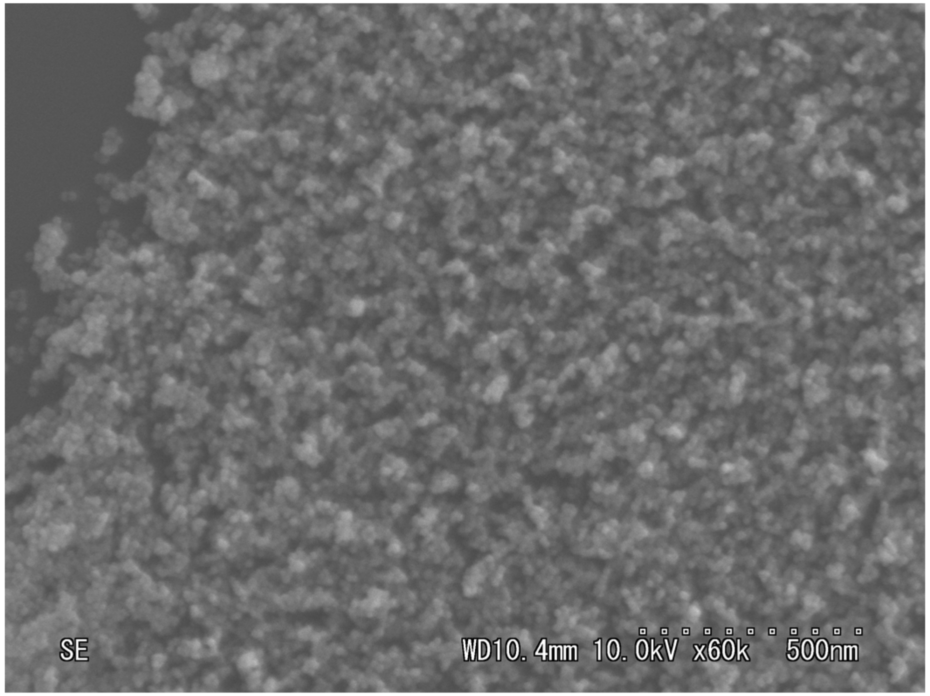




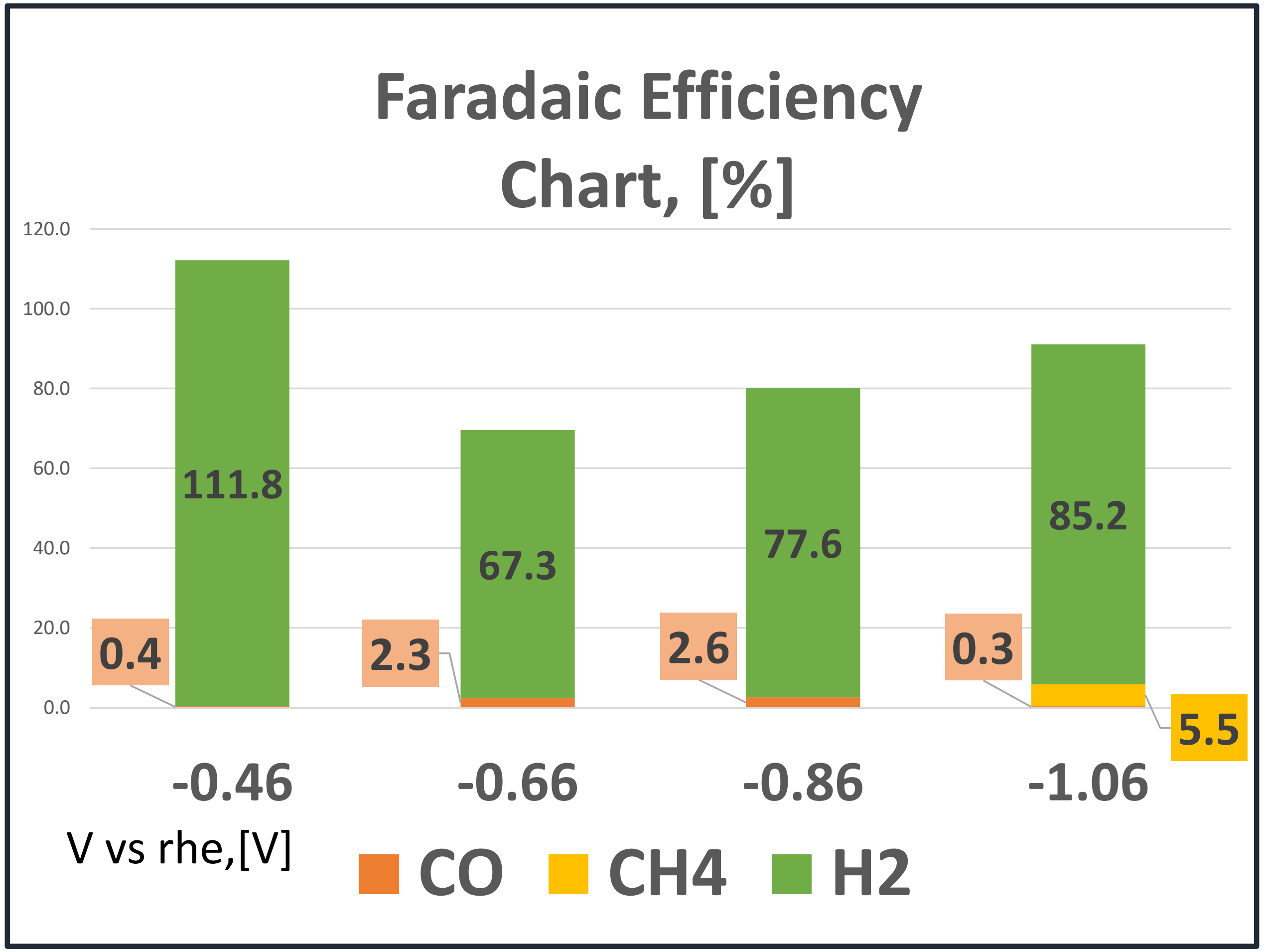
Working Electrode: TD6Ag24
Substrate: Glassy Carbon
Deposition: Ag 6nm thickness

Working Electrode: TD5.9Cu19
Substrate: Glassy Carbon
Deposition: Cu 5.9nm thickness

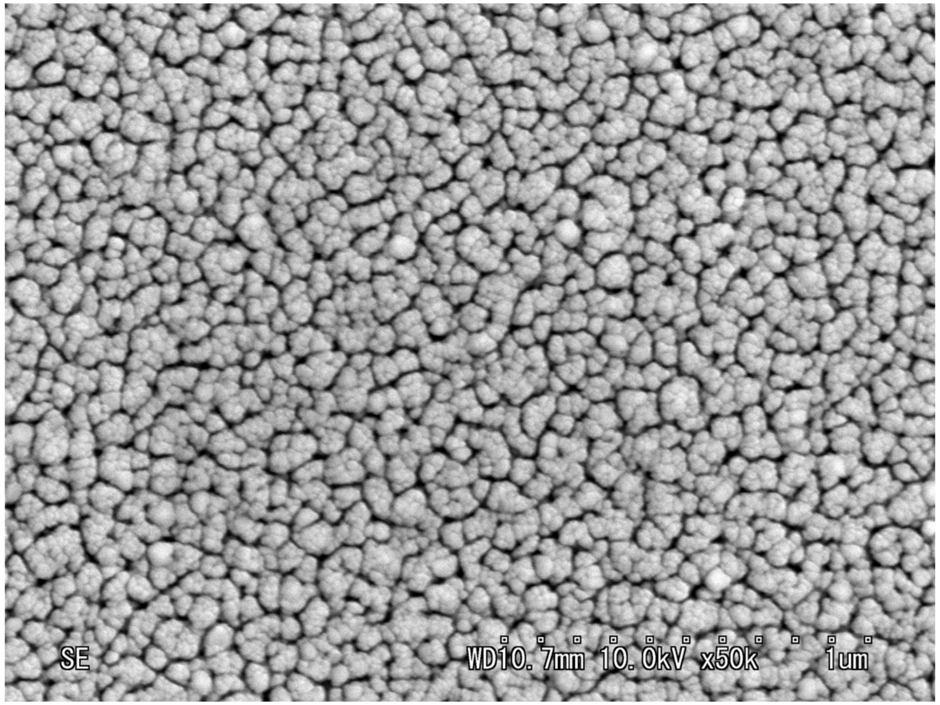
Granular Cu morphology on Glassy Carbon



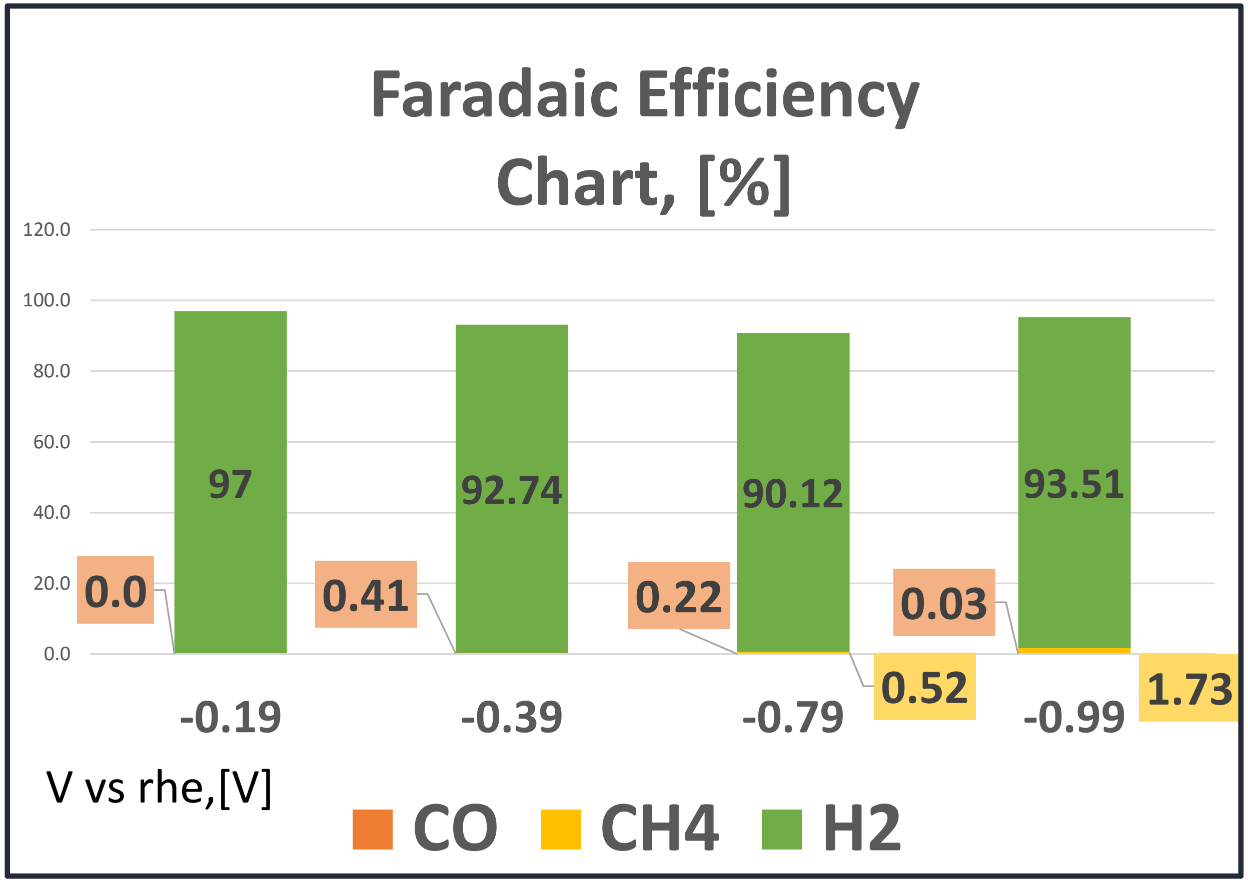
Working Electrode: Cu Jap 4
Substrate: Glassy Carbon
Deposition: Cu



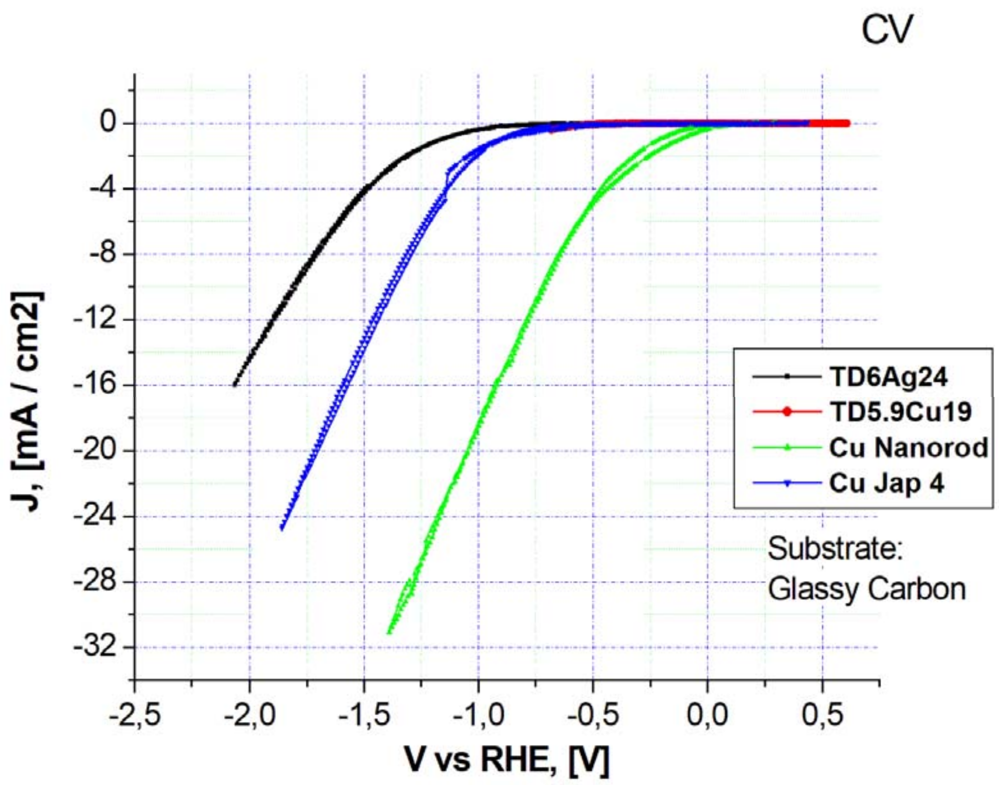
Nanorod shaped structure



Working Electrode: Cu Nanorods
Substrate: Glassy Carbon
Deposition: Cu



CV curves for comparison. Glassy Carbon Substrate



Substrate: Glassy Carbon

Sample Name	Metal deposition	Deposition thickness
TD6Ag24	Ag	6nm
Cu Nanorod	Cu	Unknown
TD5.9Cu19	Cu	5.9nm
Cu Jap 4	Cu	Unknown

Thank you for

your attention