하이드로카본 반응 시스템 및 관련소재
Hydrocarbon Reaction system and related materials

Uk Sim, Ph. D.

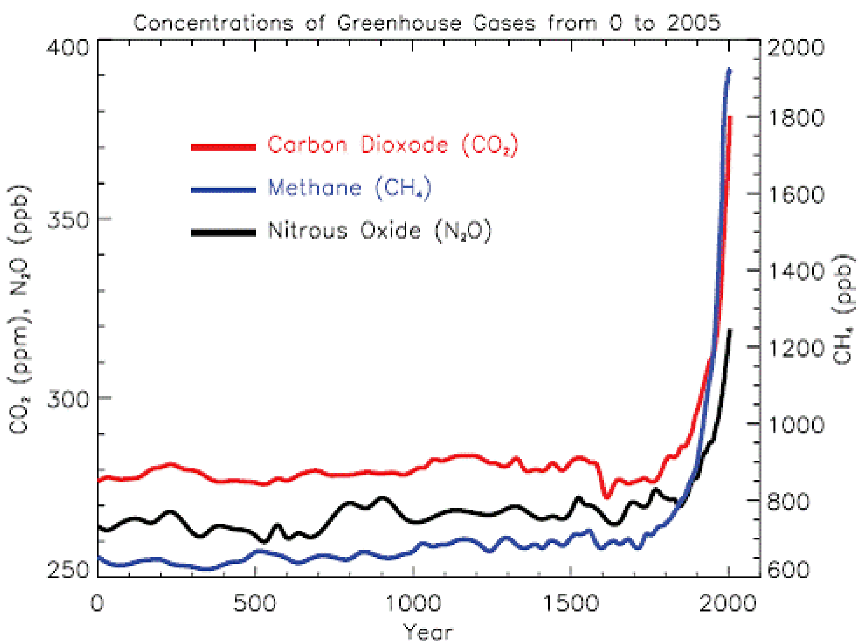
Nanomaterials for Energy & Environment Laboratory
www.uksim.org

Why should We Cut Down CO_2?

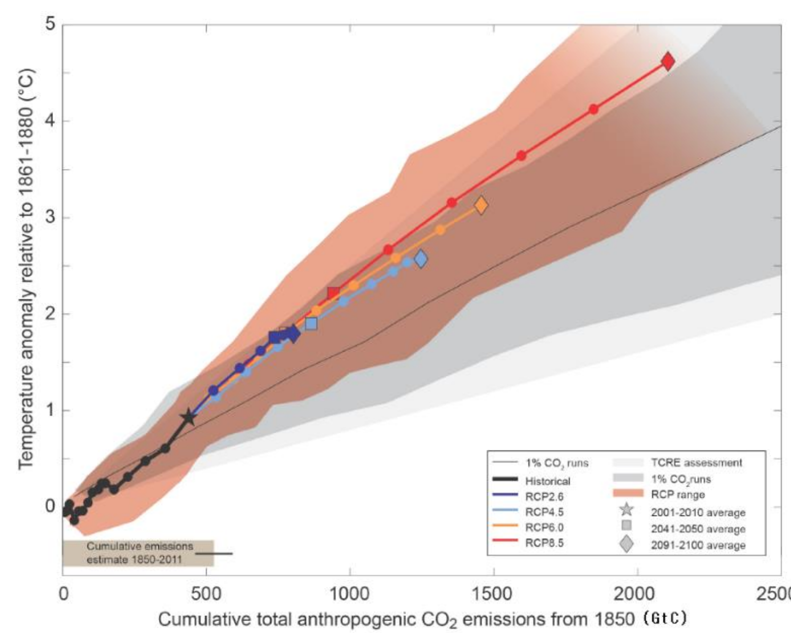
Possible impact of CO_2 on Global Warming

- CO_2 shows rapid increment since 19th century
- Intergovernmental Panel on Climate Change(IPPC) reported that increasing concentration of CO_2 is one of the main reasons of global warming(~1.5°C/500GtC)

Trends of Concentrations of Greenhouse Gases



Relation between concentration of CO_2 and Temperature Anomaly



IPCC AR5

Energy Policies on Reducing CO_2

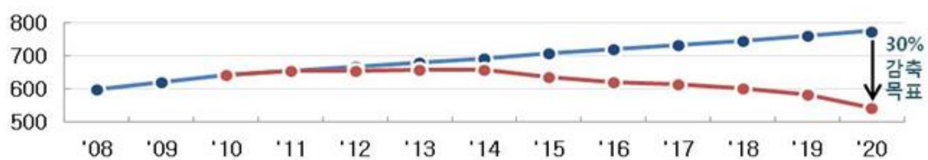
Policies proposed by Government of South Korea

Current policies are mainly focused on how to cut-down CO_2 emission rate

국가 온실가스 감축, 2020년 로드맵 마련

◇ 2020년 온실가스 배출전망치 7억7,600만톤CO_2e 대비 30% 2억3300톤 감축 목표로 설정

◇ 산업•건물•수송 등 7대 부문별 감축량을 설정하고 산업계 부담을 고려한 세부 이행 수단 마련



배출전망치[BAU] (백만톤CO_2e)	-	-	694.5	709.0	720.8	733.4	747.1	761.4	776.1
목표배출량 (백만톤CO_2e)	-	-	659.1	637.8	621.2	614.3	604.4	585.4	543.0
국가 감축률	1.6%	3.3%	5.1%	10.0%	13.8%	16.2%	19.1%	23.1%	30.0%

① 산업
친환경 연료대체 등 **81.3백만톤(18.5%) 감축**
▸연료대체 : 중유→LNG ('20, 25%) · 폐열회수설비 발전량 증대('20, 524천 TOE)

② 수송
스마트 교통시스템(ITS) 구축 등 **34.2백만톤(34.3%) 감축**
▸친환경차 보급 확대 : '20년까지 전기차 20만대, 수소연료 전지차 500대 보급 등

③ 건물
고효율 냉 · 난방기기 보급 확대 등 **45백만톤(27.0%) 감축**
▸에너지총량제(500㎡ 이상) 도입 · 20세대 이상 공동주택 고효율보일러 설치 확대

④ 공공/기타
공공부문 목표관리제 운영 등 **4.46백만톤(25.0%) 감축**
▸LED 보급률('20, 70%) · 사무용 전자제품 효율개선('20, 100%)

⑤ 농어업
가축분뇨 에너지화 시설 확충 등 **1.48백만톤(5.2%) 감축**
▸가축분뇨 에너지시설 (개): ('13)8→('20)30, 공동자원화시설(개) : ('13)95→('20)180

⑥ 폐기물
폐기물 에너지화 등 **1.71백만톤(12.3%) 감축**
▸유기성폐기물 에너지화(%) : ('15)26→('20)44, 매립가스 회수 · 발전(%) : ('20) 90

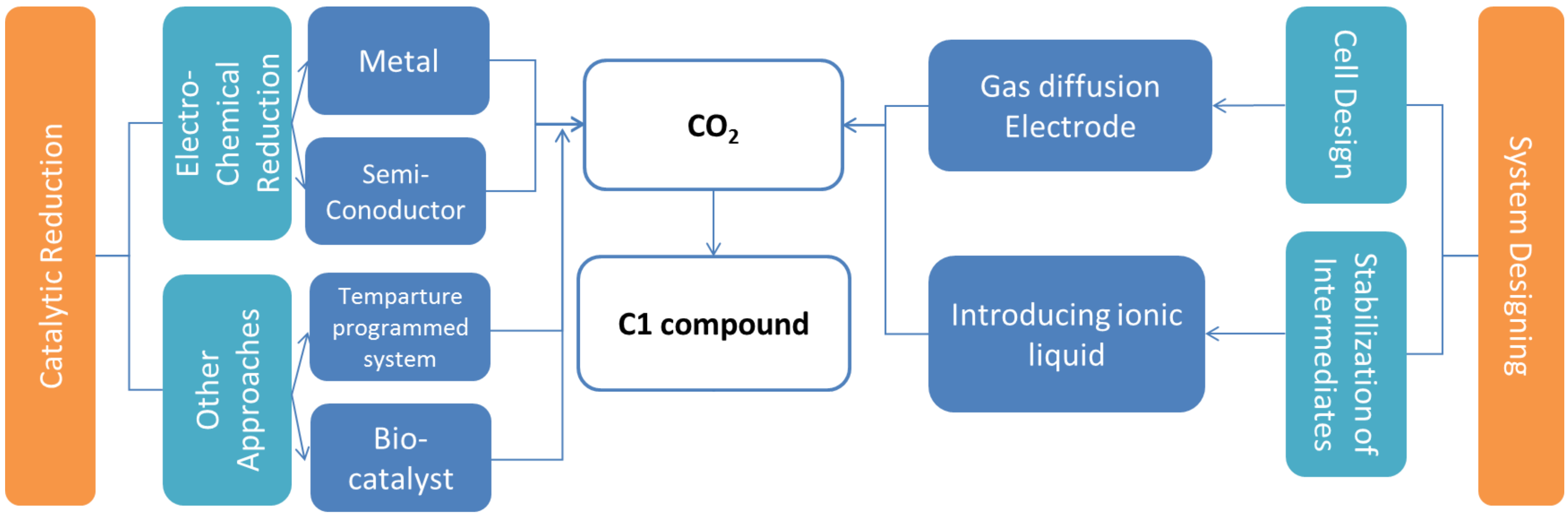
⑦ 전환/발전
신재생에너지 보급 확대 등 **64.9백만톤(26.7%) 감축**
▸탄소 포집 · 저장(CCS) 도입(2백만톤), 신재생에너지 비율 7.2% 확대 등

Other Countries

- Swiss, declaring climate law (2013~)
- France, paying carbon tax (2014~)
- Honkong, running zero-carbon emission bus(2014~)

Technologies directly transforming CO_2 is more important!!

Current technologies for Reducing CO_2



C1 compound production Methods

- ***Electrochemical CO_2 reduction (using renewable energy)***
  (i)metal itself or (ii)photoelectrode decorated with other catalyst are mainly used.
- ***Other Approaches***
  (iii) Temperature programmed system and (iv)using Bio-molecule also able to reduced CO_2

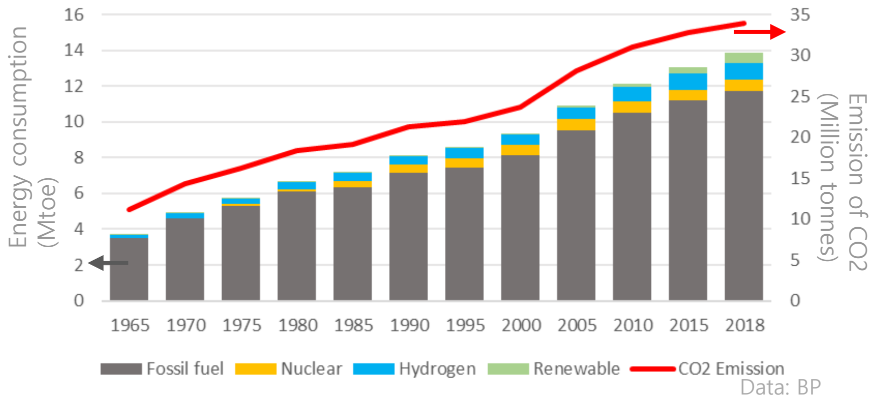
Potential of CO2 Reduction

- The only way to synthesizing natural gas without using petroleum
- Overcoming implementation of carbon-neutral energy source
- People hope to get **fuels(CH_4, CH_3OH)** from CO_2 reduction

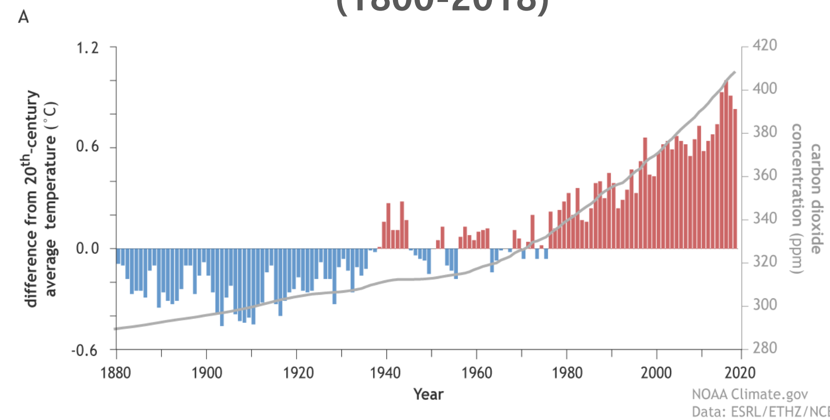
Introduction

Global issue according to CO_2

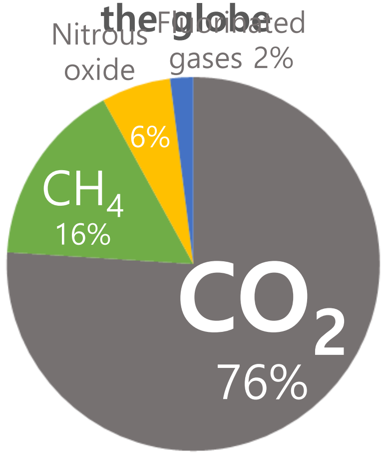
Energy consumption and CO_2 emission (1956-2018)



Atmospheric CO_2 and Earth's surface temperature (1800-2018)



Contribution ratio of human-caused greenhouse gas to total emissions around the globe



Source: IPCC (2014)

COP21 - 2015 United Nations Climate Change Conference

COP21 · CMP11
PARIS 2015
UN CLIMATE CHANGE CONFERENCE

Goal
: Limiting global warming to well below 2℃ compared to pre-industrial levels

INDC of Korea
: 37% reduction compared to Business As Usual

Introduction

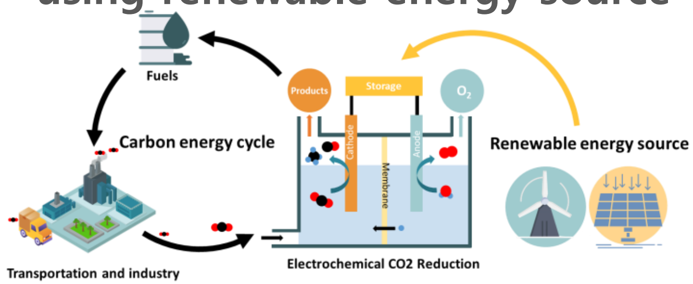
Electrochemical CO_2 reduction reaction

CO_2 reduction Strategy

- CO_2 Capture
- CO_2 Storage
- CO_2 Conversion
  - Photocatalyst
  - Biocatalyst
  - **Electrocatalyst***

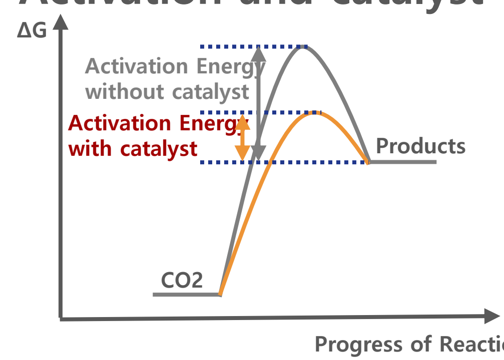
*Conversion of CO_2 to reduced chemical species using electrical energy

New carbon energy cycle using renewable energy source



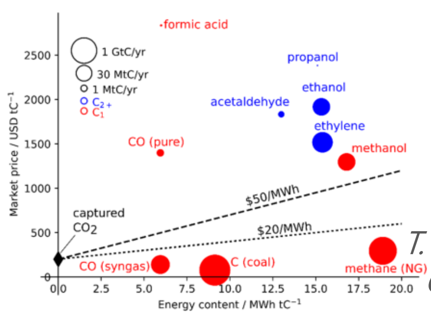
- In order to reduce actual carbon dioxide concentration, electrochemical CO_2 reduction system using renewable energy source is suggested. But renewable energy source is limited.

Activation and catalyst



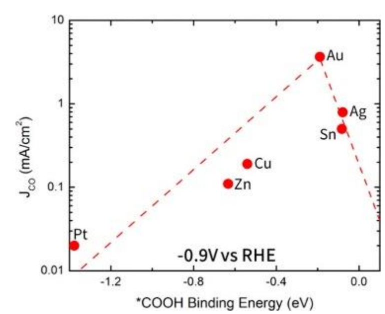
- It is essential to develop catalyst to utilize limited ene

Market price of select CO_2RR product

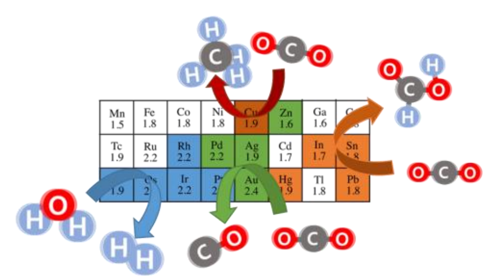


T. F. Jaramillo et al., Chem. Rev. (2018)

Cost problem



Selectivity problem



NEEL

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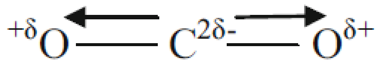
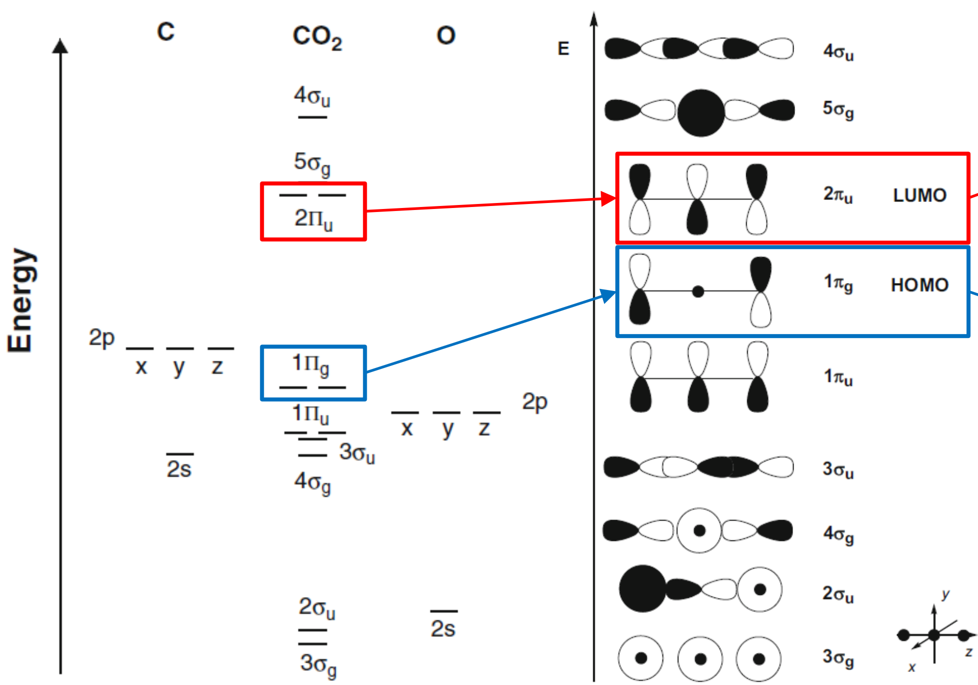
Mechanism of electrochemical CO_2RR

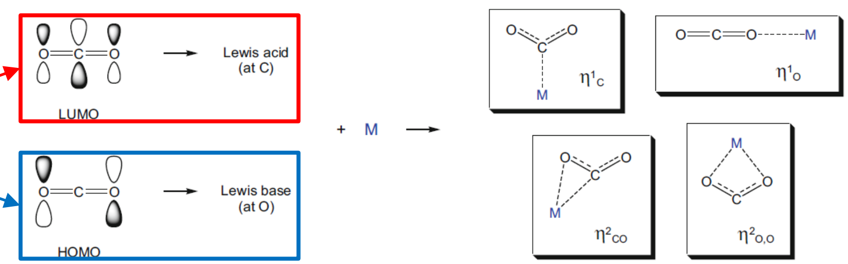
Characteristics of CO_2RR



- Binding energy = 750kJ mol -1
- Distance = 1.1600Å
- Linear and belong to the point group $D_{\infty h}$



Electrons and electron-rich species
(nucleophiles such as metals in a low oxidation state, bases, hydride ions, etc.)

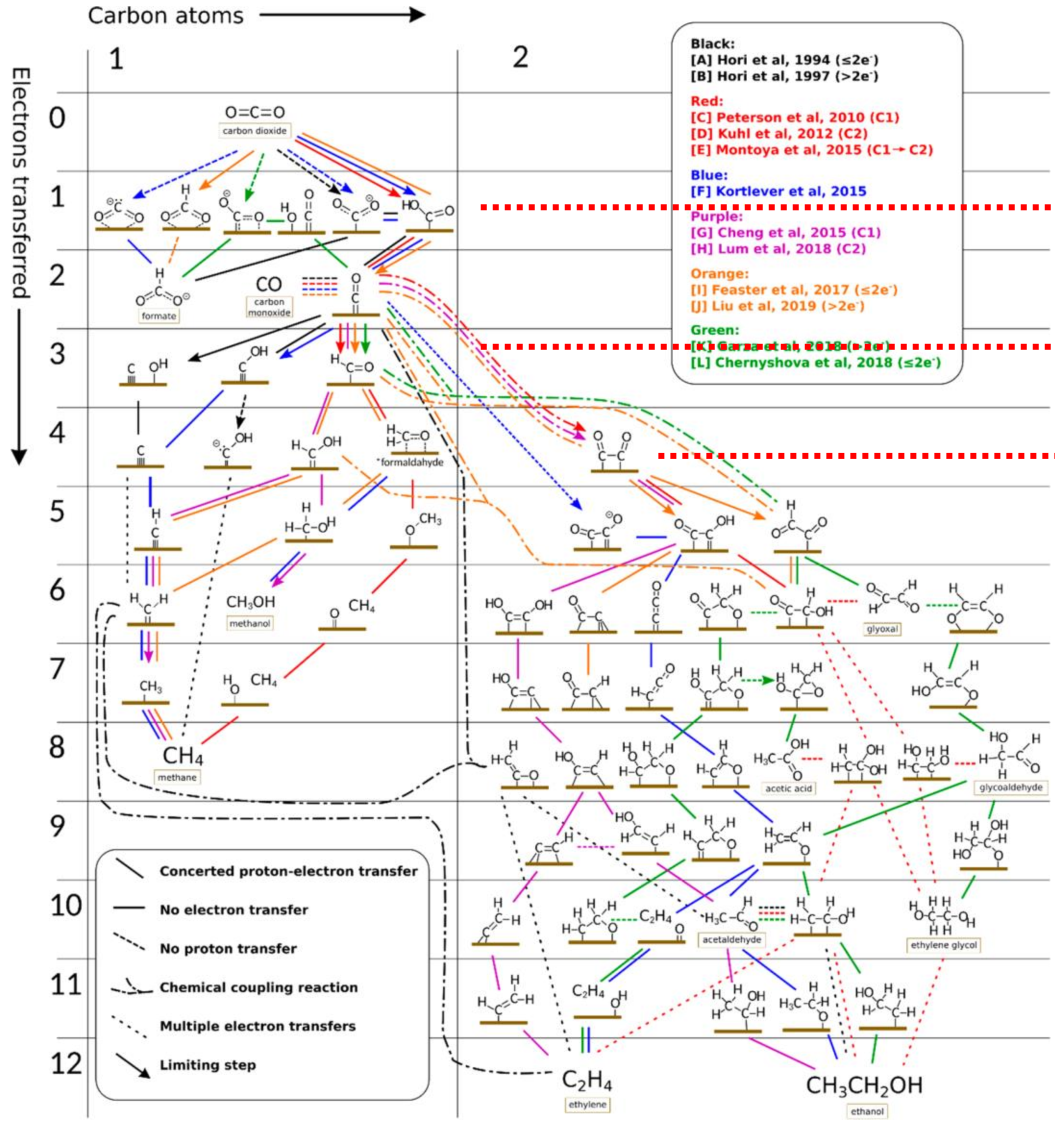


Electron-poor centers
(electrophiles such as the proton, metal centers in high oxidation states, electron deficient molecules, etc.)

M. Aresta et al., Springer. (2016)

Mechanism of electrochemical CO_2RR

Mechanism of electrochemical CO_2RR



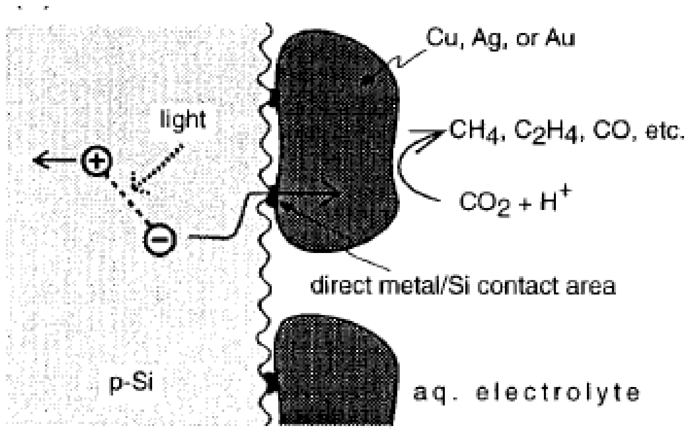
Characteristics of CO_2RR mechanism

1. Various bonding is generated depending on relationship between CO_2 and surface of catalyst
2. If the binding energy of *CO intermediate is strong, deep reduction is progressed.
3. If *CO intermediates are easily formed and each active site is close to the other active site, dimerization occur resulting C≥2 product.

T. F. Jaramillo et al., Chem. Rev. (2018)

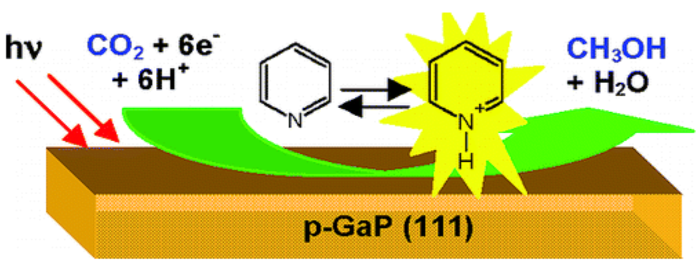
Problems in Current technologies

Electrochemical Reduction



Chem. Letter.. 1994, 1725-1729

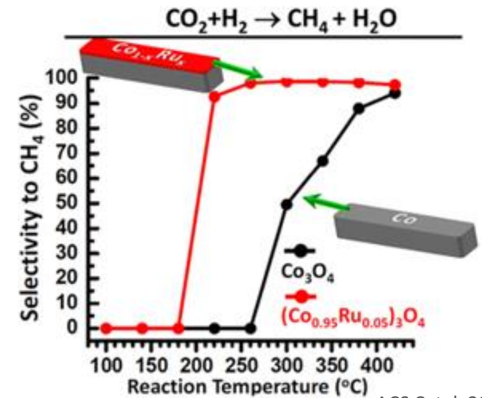
Not only CH_4 but also H_2, CO, C_2H_4 come out



J. AM. CHEM. SOC. 2010, 9, 132

GaP is too expensive to be used in industry

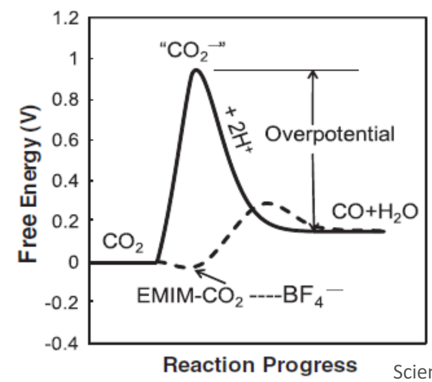
Temperature Programed System



ACS Catal. 2012, 2, 2403, 2008

Material shows activity only above 250°C

Using ionic liquid(IL)



Science, 2011, 334, 643-644

IL is expensive and hard to handle in air

Two main issues in CO_2 Reduction

Low Chemical Selectivity

- ✓ Thermodynamically, all values are close to the H_2 evolution potential
- ✓ Including HER, CO_2 can be reduced into various chemical form

$2H^+ + 2e^-$	$\leftrightarrow$	H_2	0.00 V
$CO_2 + 2H^+ + 2e^-$	$\leftrightarrow$	$CO + H_2O$	- 0.11 V
$CO_2 + 6H^+ + 6e^-$	$\leftrightarrow$	$CH_3OH + H_2O$	+ 0.02 V
$CO_2 + 8H^+ + 8e^-$	$\leftrightarrow$	$CH_4 + 2H_2O$	+ 0.16 V
$2CO_2 + 12H^+ + 12e^-$	$\leftrightarrow$	$C_2H_4 + 4H_2O$	+ 0.07 V
$2CO_2 + 12H^+ + 12e^-$	$\leftrightarrow$	$C_2H_5OH + 3H_2O$	+ 0.08 V
$3CO_2 + 18H^+ + 18e^-$	$\leftrightarrow$	$C_3H_7OH + 5H_2O$	+ 0.09 V

(V vs. RHE)

What about this reaction?

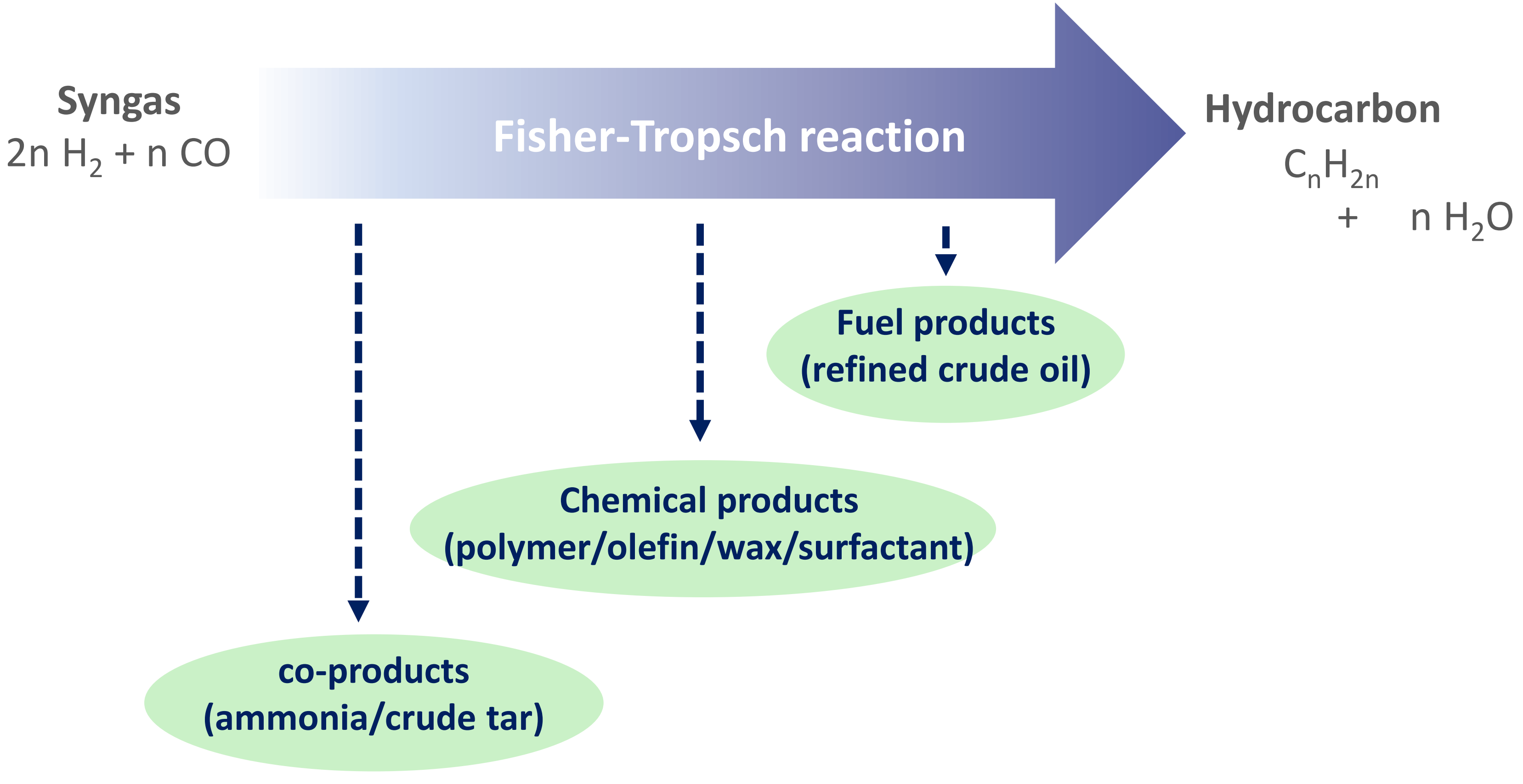
- ✓ CO_2 reduction is multi-electron and multi- proton involved reaction (kinetically limited, overpotential ~1.5V)

High Overpotential

Potential of CO_2 Reduction into CO

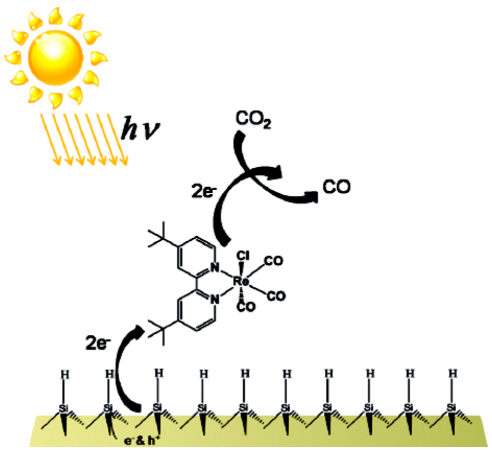
CO as an added-value C_1 product

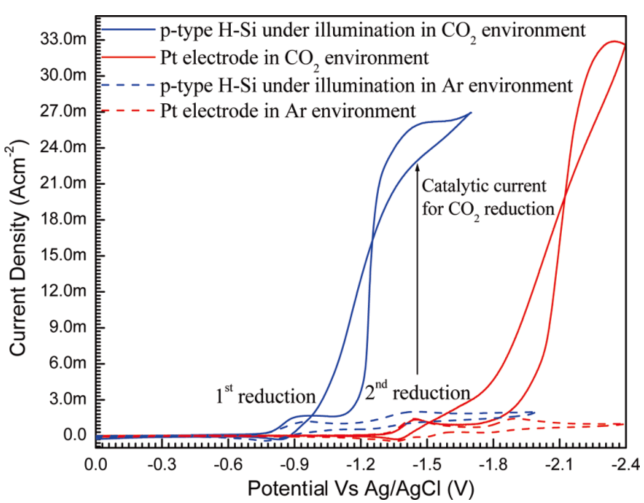
- CO and H_2 are called 'syngas' which can be used into production of hydrocarbon
- Through Fisher-Tropsch reaction, CO can be transformed into high C compound



Recent researches of CO_2 reduction into CO

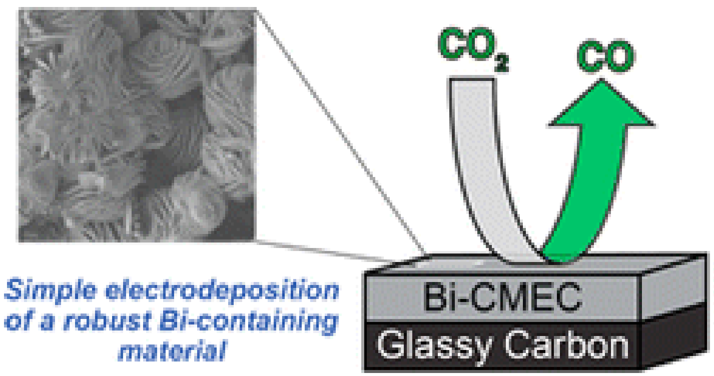
Homogenous catalyst : Re(bpy)(CO)3Cl

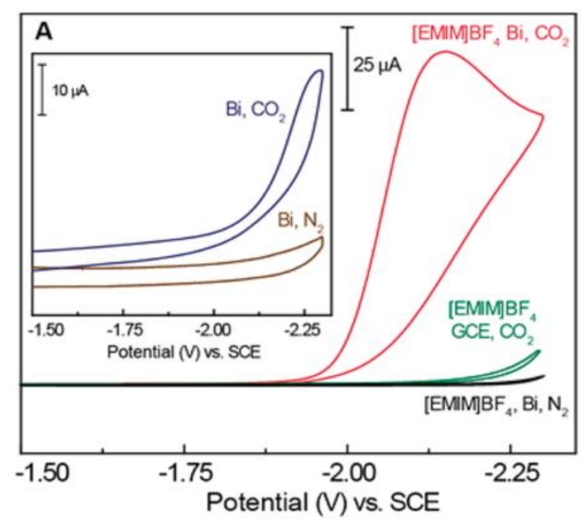




J. Phys. Chem. C **2010,** *114,* 14220–14223

Bi coated heterogeneous electrode





J. Am. Chem. Soc. 2013, 135, 8798–8801

Our Idea : p-Si based PEC CO_2 reduction

Limitations of Previous Researches

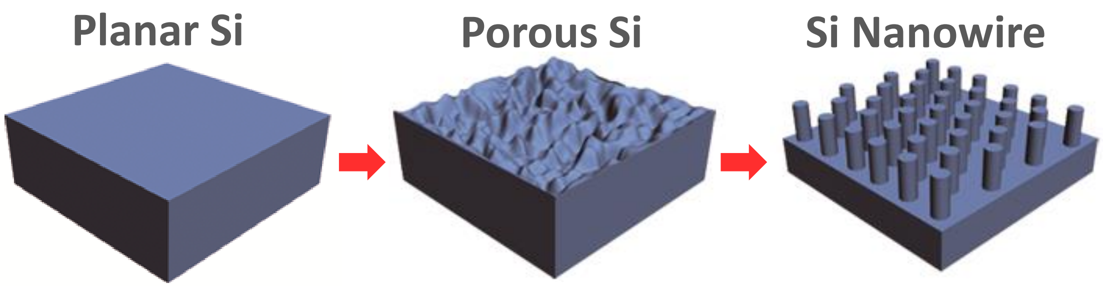
- Researches which decorate Si with molecular catalysts, they used rare metal
  ; $Re_2(CO)_{10}$ is 50,000won/1g
- Tradisionnally, 3-5 familiy semiconductor mainly used in PEC CO_2 reduction research
  ; Si has poor chemical selectivity(~70% CO in ACN) and relatively worthless C1 compounds (~30% HCOOH in aqoues solution)
- Totally metal-free Si based heteogeneous catalyst with high performance can be used as a first material for industrial scale CO production.

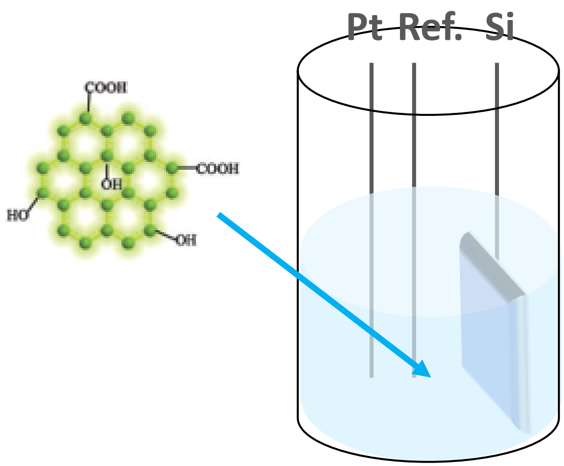
Our Goal

- Photoreduction of CO_2 on **Silicon based PEC cell**
- Highly **Selective photoreduction of CO_2 to CO**
- Catalytic reduction of CO_2 using **metal free catalyst**

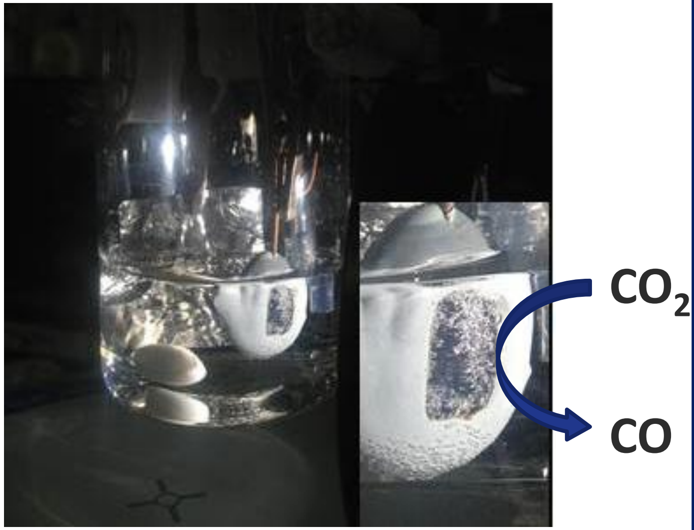
Decoration Nitrogen doped Carbon Quantum Dot on p-Si

Process of nanostructuring p-Si





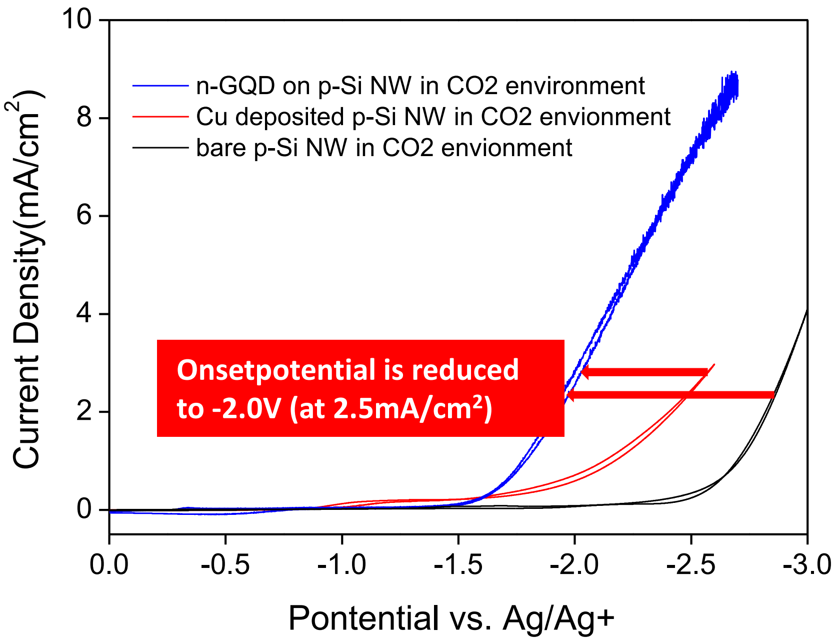
Electrophoretic deposition of CQD on p-Si Nanowire



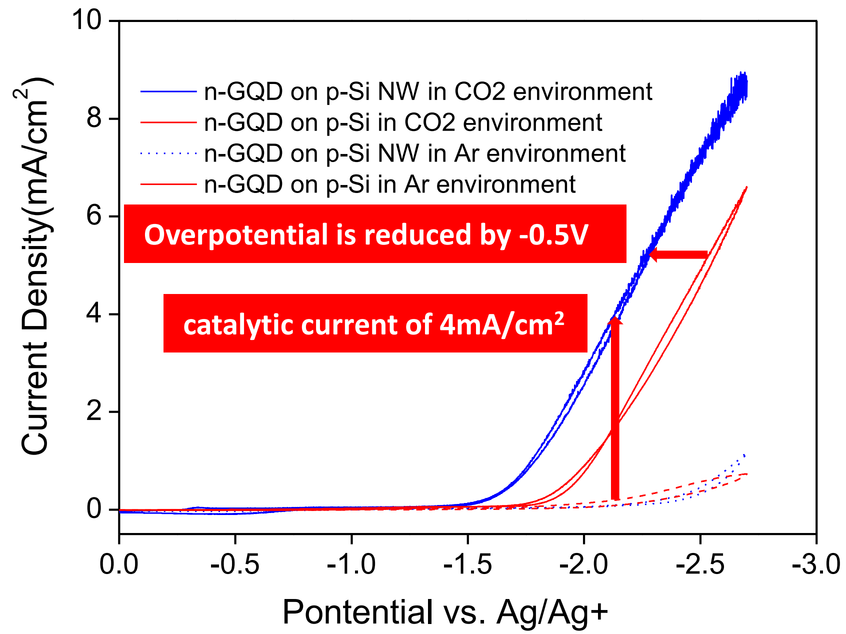
Electrochemical Cell for CO_2 reduction

Effect of N-GQD p-Si on CO2 reduction

N-doped graphene p-Si / bare p- Si / Cu p-Si in CO_2

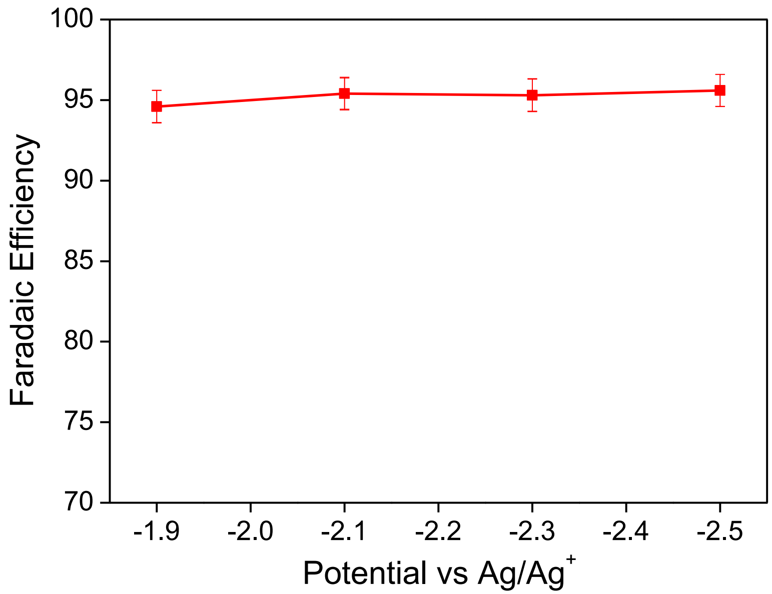


Nonstructural effect of p-Si



Gas Chromatography Analysis

CO selectivity depending on applied potential

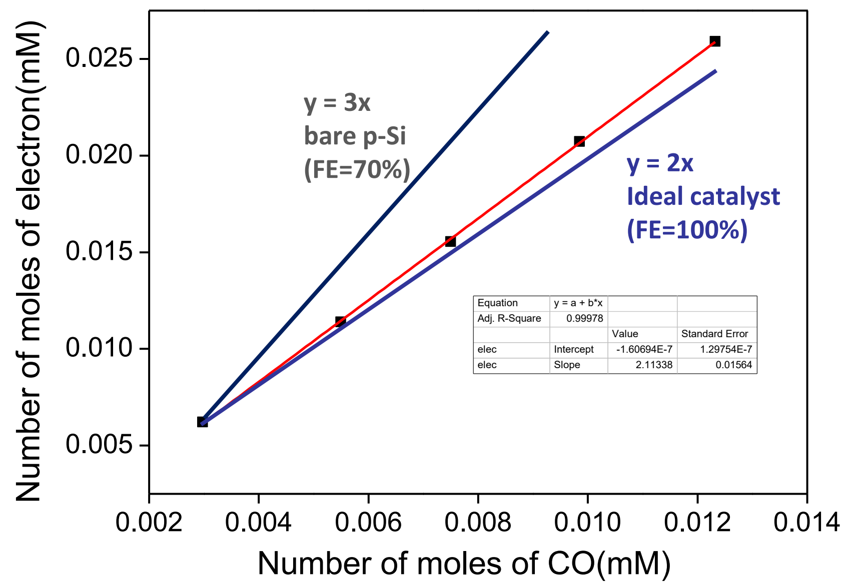


→ **Faradaic Efficiency(FE)**

= ~ 95%

(dependency of applied potential)

Relation btw charge & produced CO



Equation	y = a + b*x		
Adj. R-Square	0.99978		
		Value	Standard Error
elec	Intercept	-1.60694E-7	1.29754E-7
elec	Slope	2.11338	0.01564

→ **Faradaic Efficiency(FE)**

= (1/2. 11) x 2 x 100 = 95%

(94.78%)