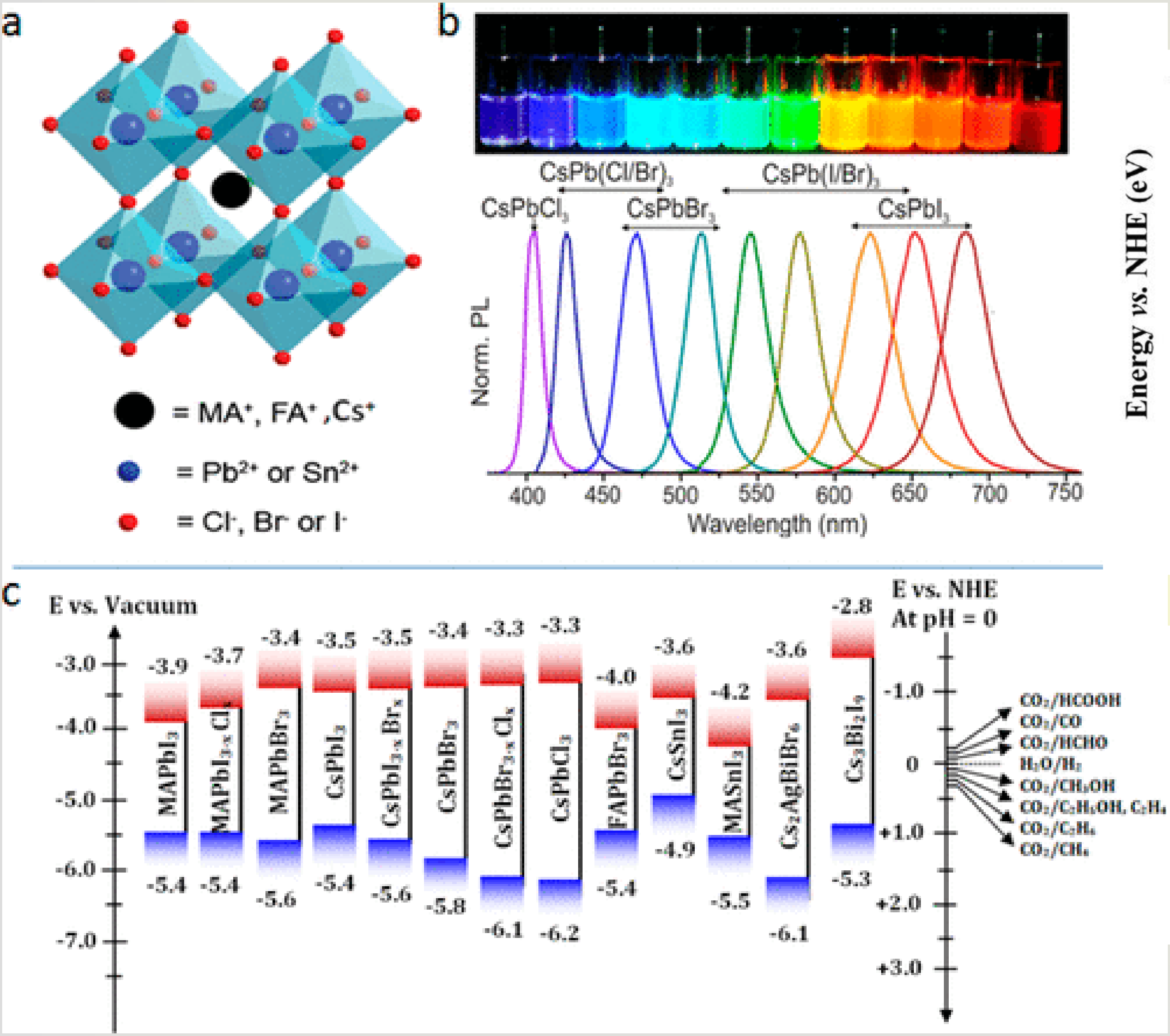
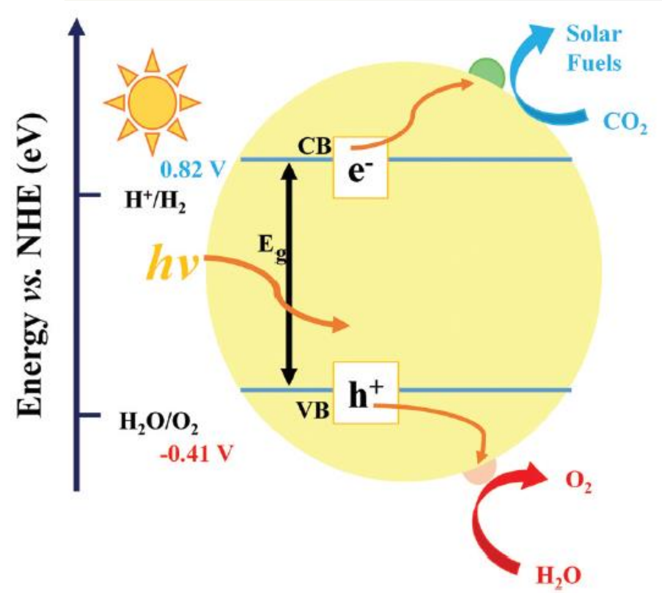
Halide Perovskites as Photocatalysts for CO_2 Reduction

Eric Wei-Guang Diau（刁維光）
Department of Applied Chemistry
Institute of Molecular Science
National Yang-Min Chiao-Tung University (NYCU)
Hsinchu, Taiwan

Why Halide Perovskites?





$CO_2 + 1e^- = CO_2^-$ -1.90 V

$CO_2 + 2H^+ + 2e^- = HCOOH(aq)$ -0.61 V

$CO_2 + 2H^+ + 2e^- = CO(g) + H_2O$ -0.53 V

$CO_2 + 4H^+ + 4e^- = HCOH(aq) + H_2O$ -0.48 V

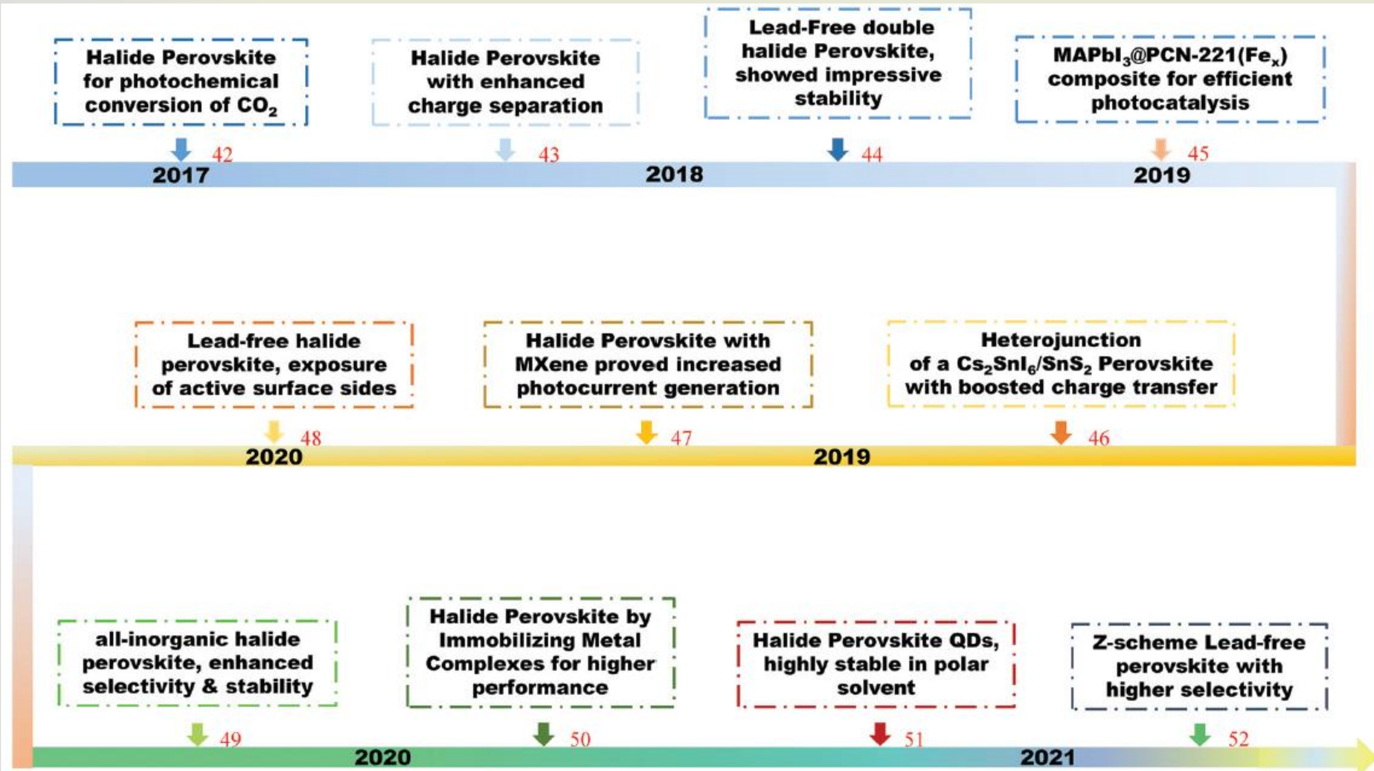
$CO_2 + 6H^+ + 6e^- = CH_3OH(aq) + H_2O$ -0.38 V

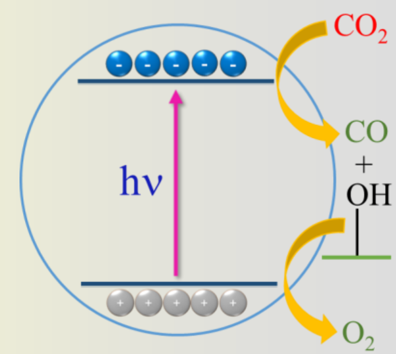
$CO_2 + 8H^+ + 8e^- = CH_4(g) + 2H_2O$ -0.24 V

Mater. Adv. **2021**, *2*, 7187-7209.

J. Phys. Chem. Lett. **2020**, *11*, 6921-6934.

Timeline for Development of Halide Perovskites for CO_2 Reduction





Water-free self-photocatalytic CO_2 splitting

2022

42 Y.-F. Xu, M.-Z. Yang, B.-X. Chen, X.-D. Wang, H.-Y. Chen, D.-B. Kuang and C.-Y. Su, *J. Am. Chem. Soc.*, 2017, **139**, 5660–5663.

43 Y. F. Xu, X. D. Wang, J. F. Liao, B. X. Chen, H. Y. Chen and D. B. Kuang, *Adv. Mater. Interfaces*, 2018, **5**, 1801015.

44 L. Zhou, Y. F. Xu, B. X. Chen, D. B. Kuang and C. Y. Su, *Small*, 2018, **14**, 1703762.

45 L. Y. Wu, Y. F. Mu, X. X. Guo, W. Zhang, Z. M. Zhang, M. Zhang and T. B. Lu, *Angew. Chem., Int. Ed.*, 2019, **58**, 9491–9495.

46 X.-D. Wang, Y.-H. Huang, J.-F. Liao, Y. Jiang, L. Zhou, X.-Y. Zhang, H.-Y. Chen and D.-B. Kuang, *J. Am. Chem. Soc.*, 2019, **141**, 13434–13441.

47 A. Pan, X. Ma, S. Huang, Y. Wu, M. Jia, Y. Shi, Y. Liu, P. Wangyang, L. He and Y. Liu, *J. Phys. Chem. Lett.*, 2019, **10**, 6590–6597.

48 C. Lu, D. S. Itanze, A. G. Aragon, X. Ma, H. Li, K. B. Ucer, C. Hewitt, D. L. Carroll, R. T. Williams and Y. Qiu, *Nanoscale*, 2020, **12**, 2987–2991.

49 S. Kumar, M. Regue, M. A. Isaacs, E. Freeman and S. Eslava, *ACS Appl. Energy Mater.*, 2020, **3**, 4509–4522.

50 Z. Chen, Y. Hu, J. Wang, Q. Shen, Y. Zhang, C. Ding, Y. Bai, G. Jiang, Z. Li and N. Gaponik, *Chem. Mater.*, 2020, **32**, 1517–1525.

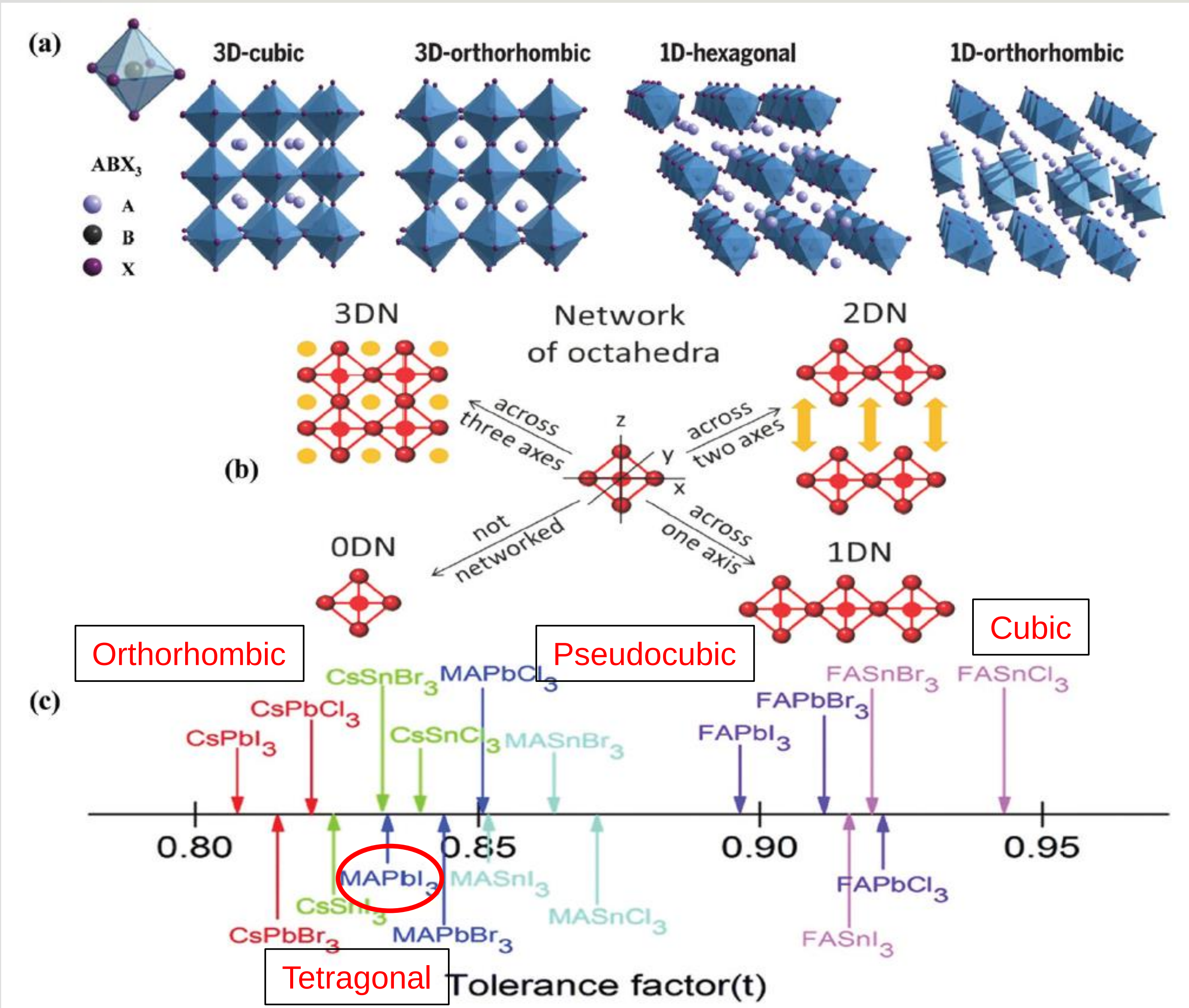
51 M. Que, Y. Zhao, L. Pan, Y. Yang, Z. He, H. Yuan, J. Chen and G. Zhu, *Mater. Lett.*, 2021, **282**, 128695.

52 Y. Wang, H. Huang, Z. Zhang, C. Wang, Y. Yang, Q. Li and D. Xu, *Appl. Catal., B*, 2021, **282**, 119570.

Mater. Adv. **2021**, *2*, 7187-7209.

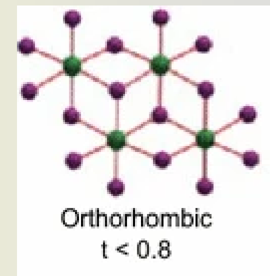
Halide Perovskite Crystal Structures

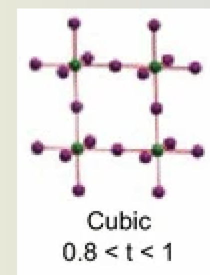
Crystal Structures of Halide Perovskites

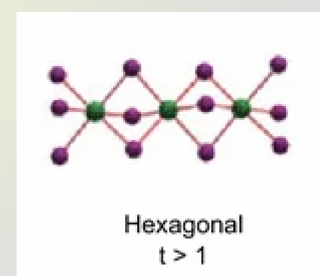


Tolerance factor (t)

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$







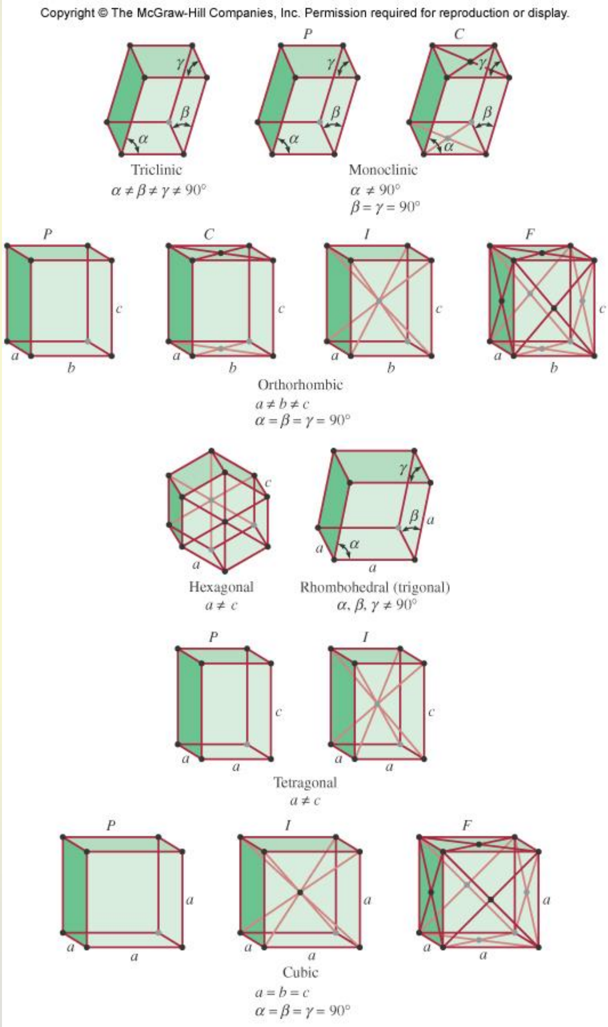
Mater. Adv. **2021**, *2*, 7187-7209.

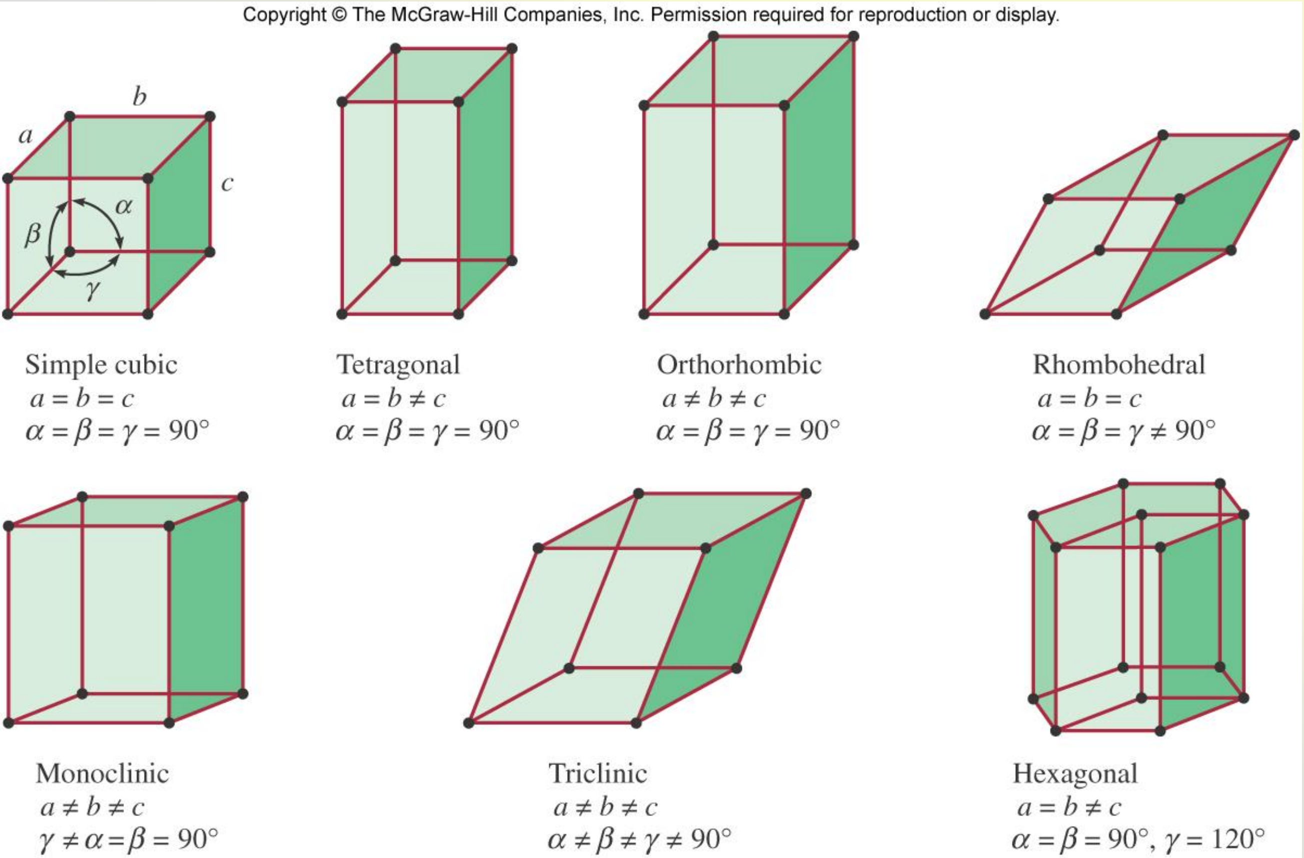
Unit Cells of 14 Bravais Lattices

A ***unit cell*** is the basic repeating structural unit of a crystalline solid.

There are 7 types of unit cells.

There are total 14 Bravais lattices in crystals.





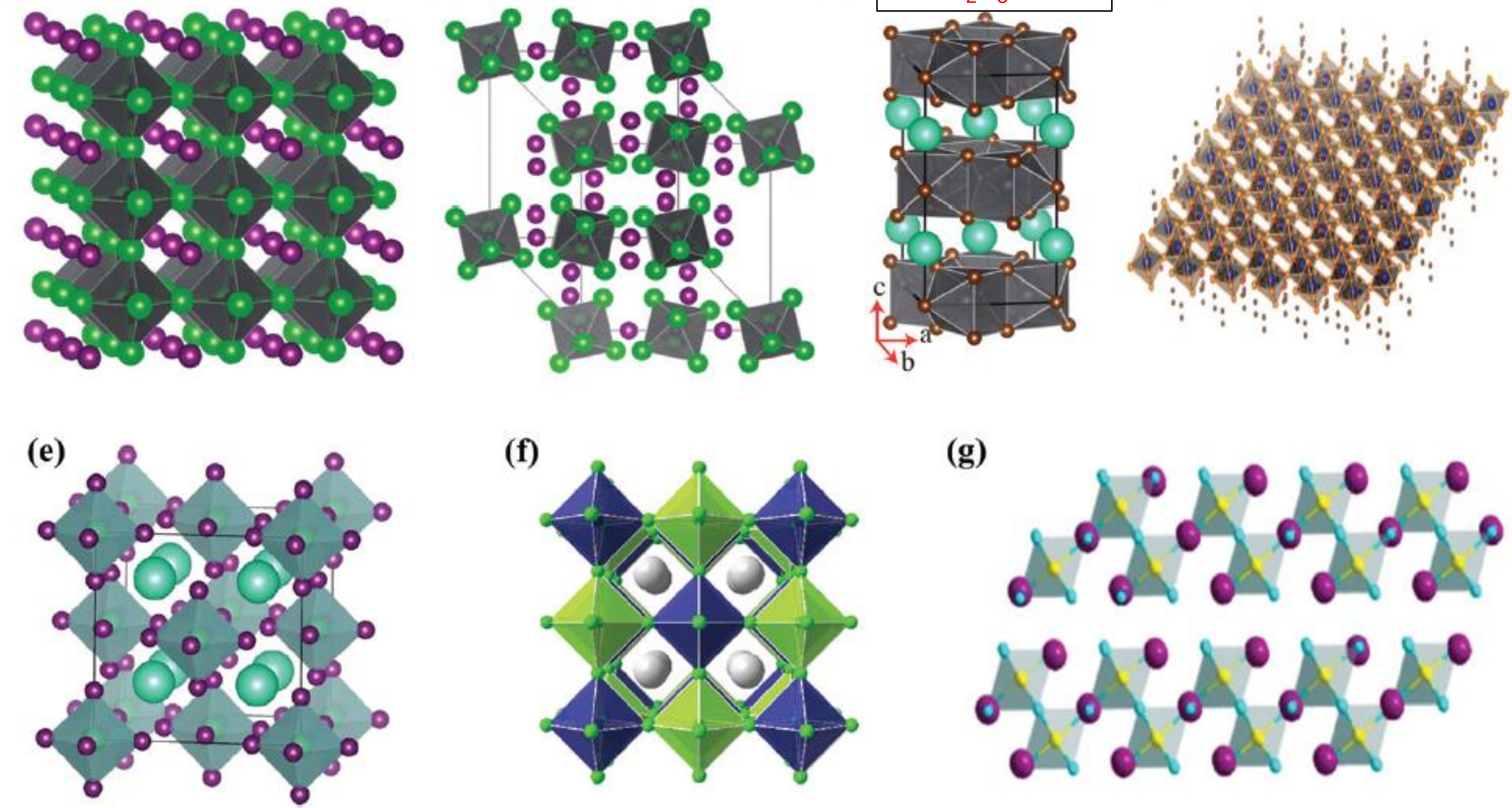
Perovskite-Related Crystal Structures

Pseudocubic 3D: $FAPbX_3$

0D: Cs_4PbX_6

Tetragonal 2D: $CsPb_2X_5$

Layered 2D: A_2PbX_4



Double perovskite: Cs_2SnX_6

Double perovskite: Cs_2AgBiX_6

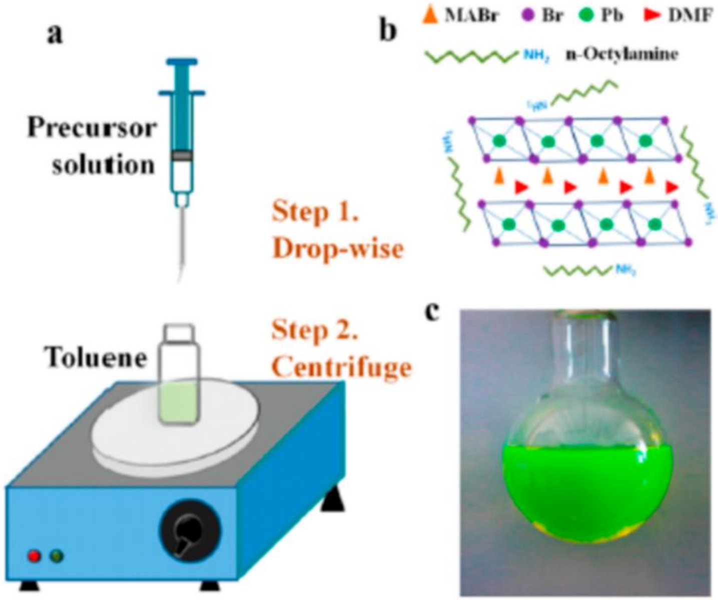
Triple perovskite, layered 2D: $Cs_3Bi_2X_9$

Mater. Adv. **2021**, *2*, 7187-7209.

Preparations of Halide Perovskite Nanostructures

Preparation of Perovskite Nanocrystals

Ligand assisted reprecipitation (LARP)

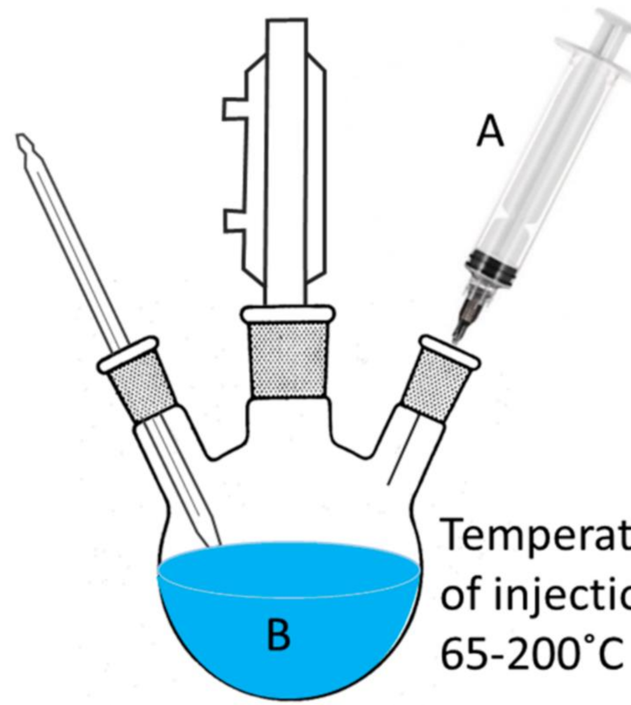


Precursor solution:

PbX_2 + MAX + capping ligands in DMF

Bad Solvent: Toluene

Hot injection



Temperature of injection: 65-200˚C

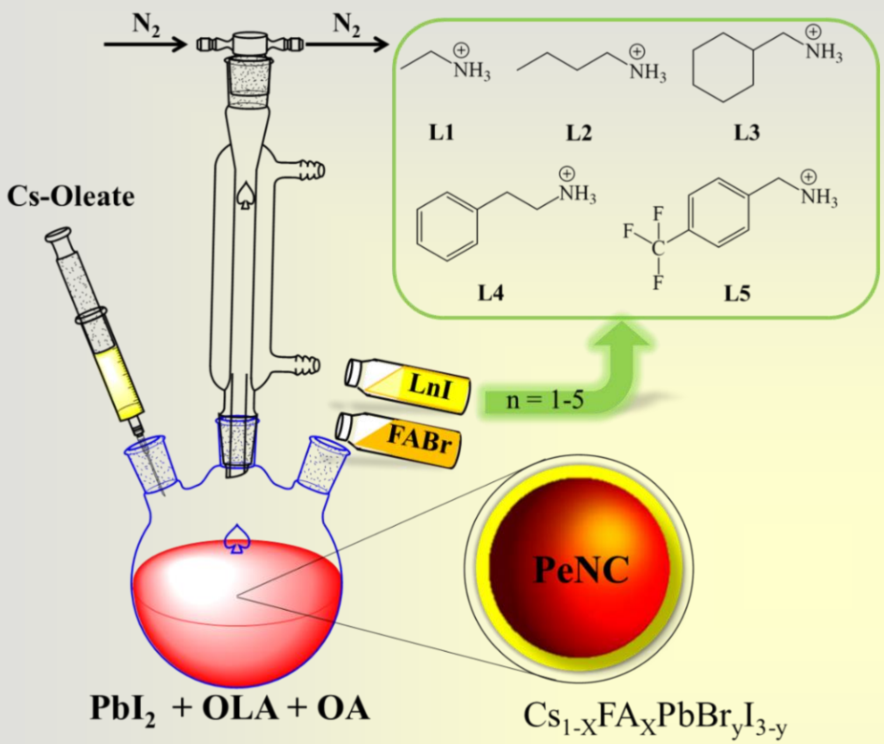
A: A cation-oleate / Halide precursor

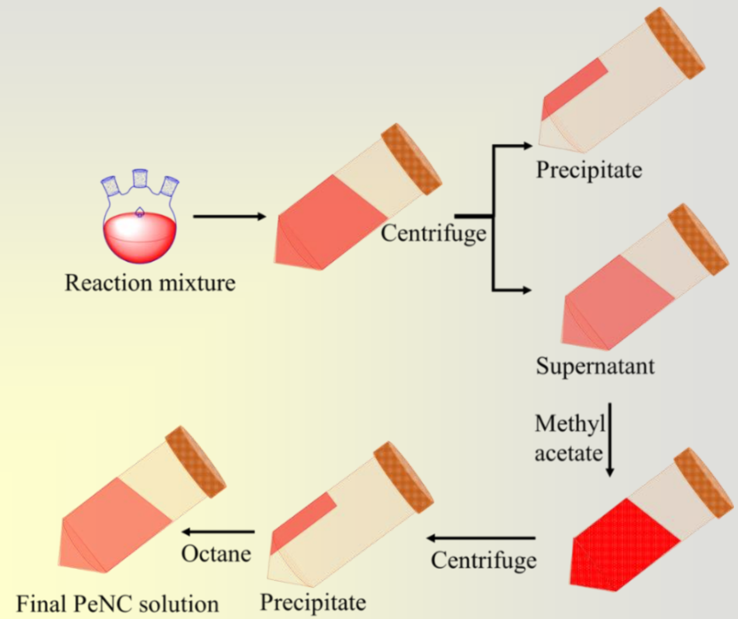
B: PbX_2 in ODE with ligands /Solution of A cations and Pb^{2+} with ligands

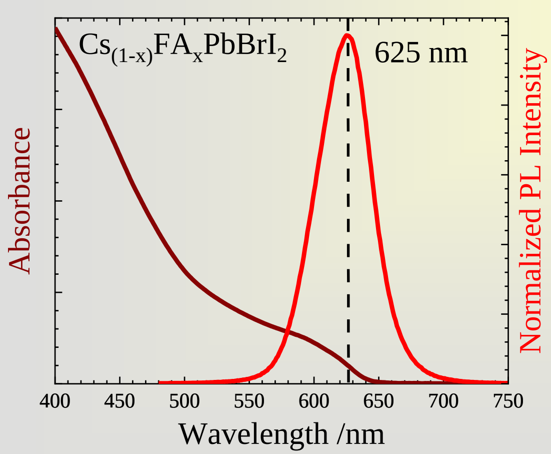
$$Cs{-}oleate + 3PbBr_2 \rightarrow 2CsPbBr_3 + Pb(oleate)_2$$

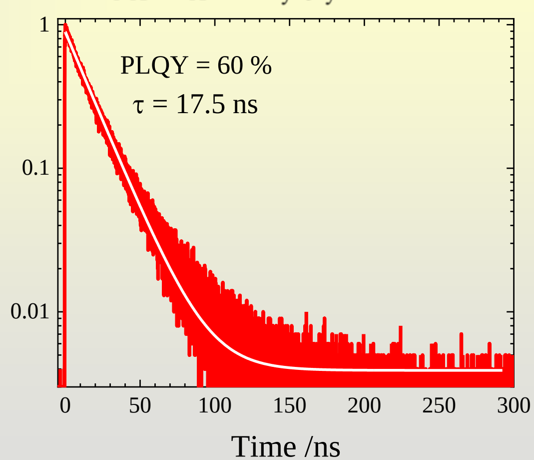
Crystal **2018**, *8*, 182.

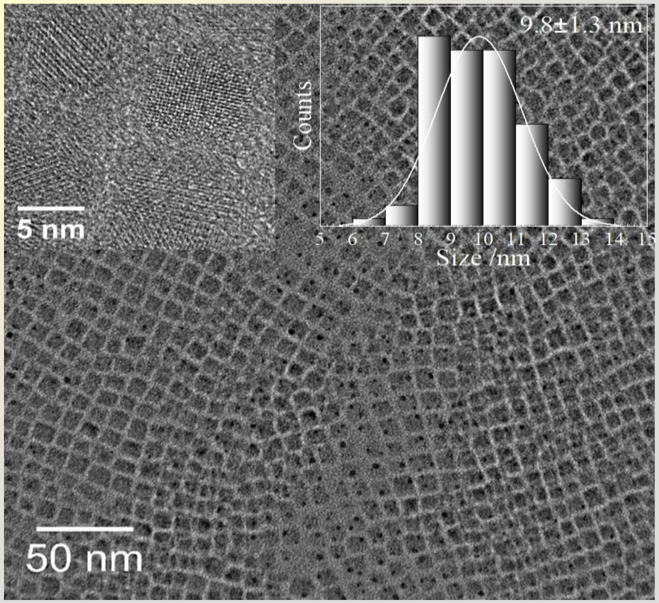
Hot-Addition Method to Prepare PeNC





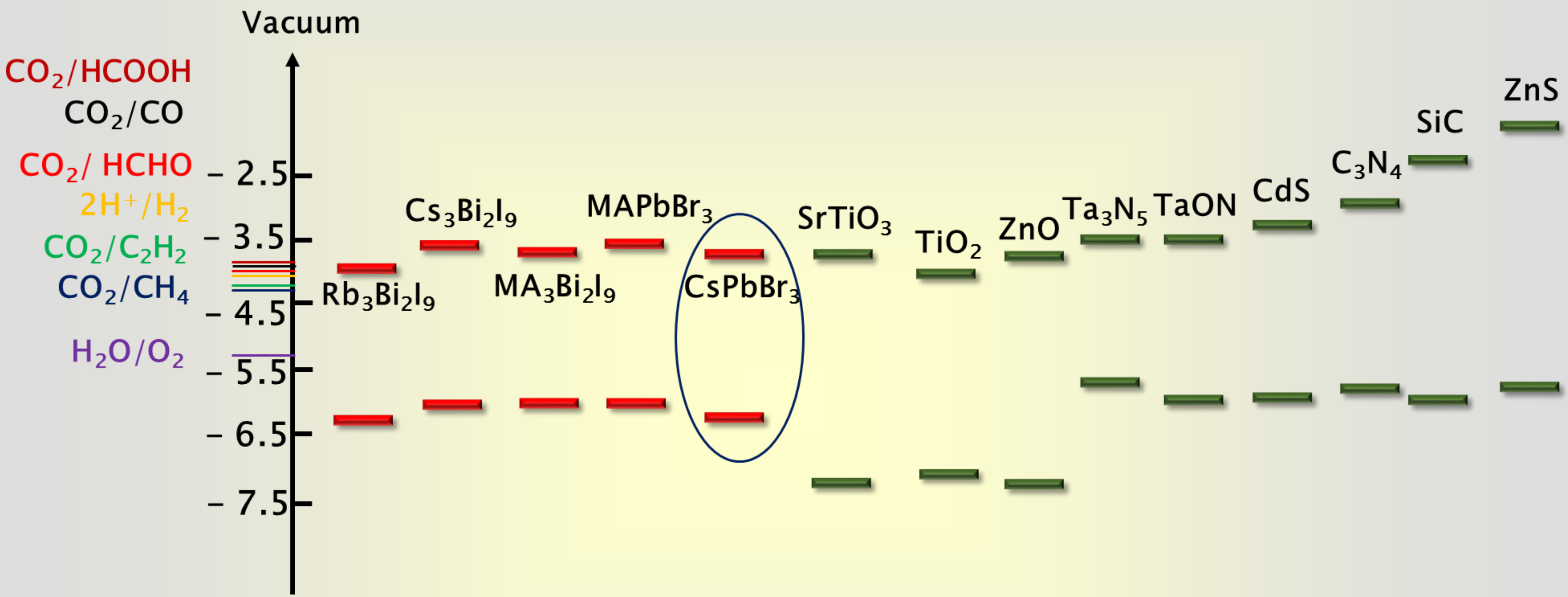






J. Mater. Chem. C **2021**, *9*, 17341–17348

Potential Energy Levels



$CO_2 + e^- \rightarrow CO_2^{\bullet-}$, $E^0 = -1.90$ V (1)

$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$, $E^0 = -0.53$V (2)

$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$, $E^0 = -0.61$V (3)

$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$, $E^0 = -0.48$ V (4)

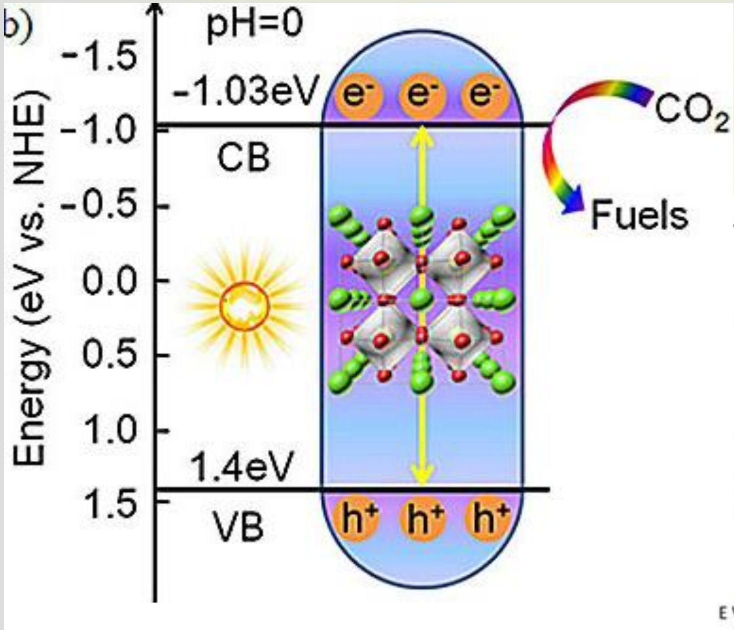
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$, $E^0 = -0.38$ V (5)

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$, $E^0 = -0.24$V (6)

PeNC as Photocatalyst for CO_2 Reduction

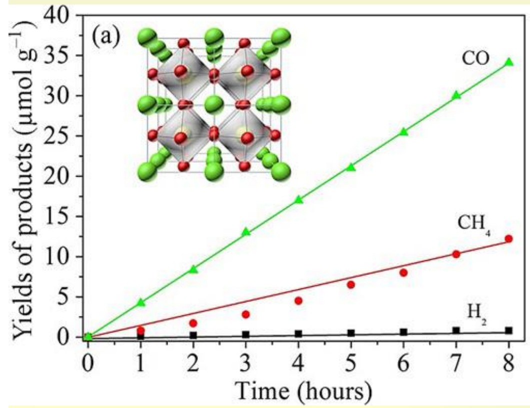
The First CO_2 Reduction using $CsPbBr_3$ PeNC

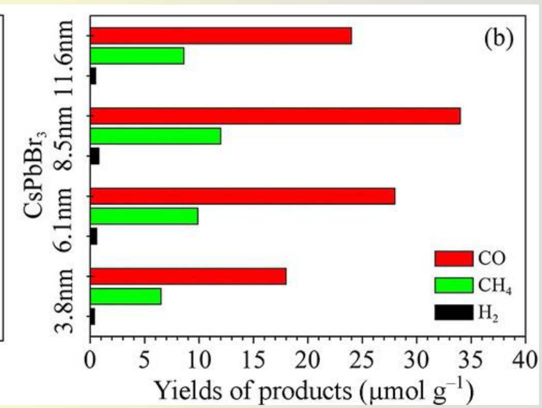
Using $CsPbBr_3$ Nanocrystal (PeNC) for CO_2 Reduction



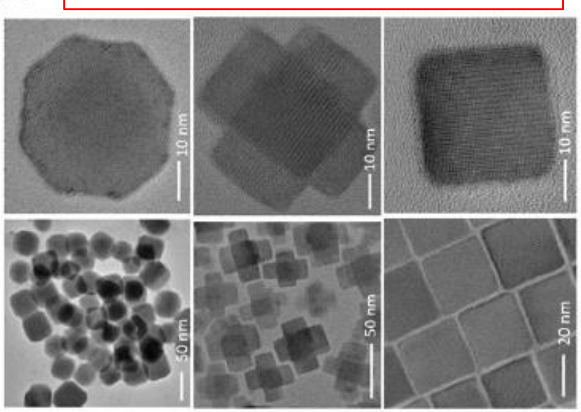
Gas-solvent interface
Solvent: 15 mL ethyl acetate and 50 µL water
Light power: 300 W

The crystal size effect

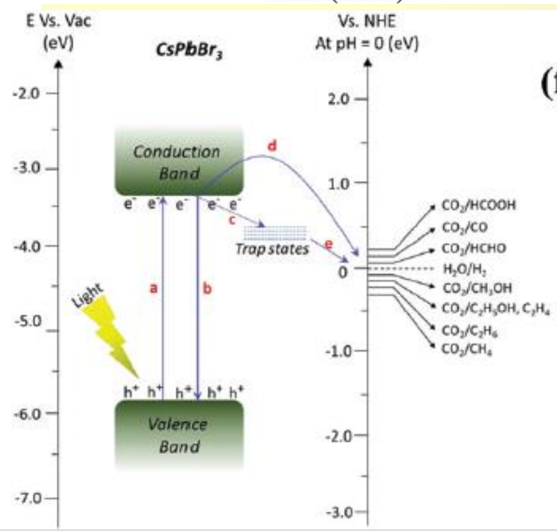




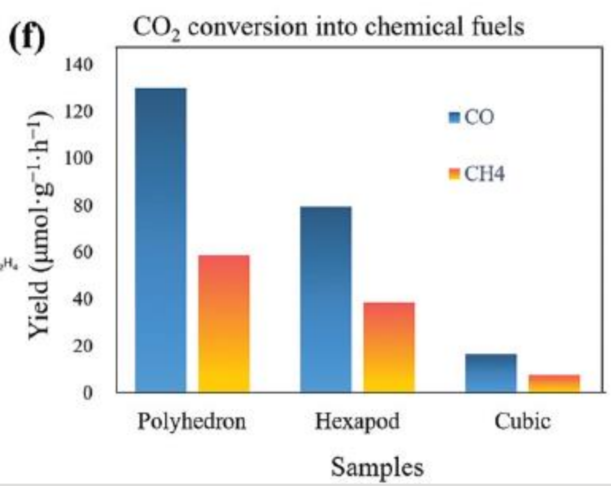
(d) The crystal shape effect



(e)



(f)



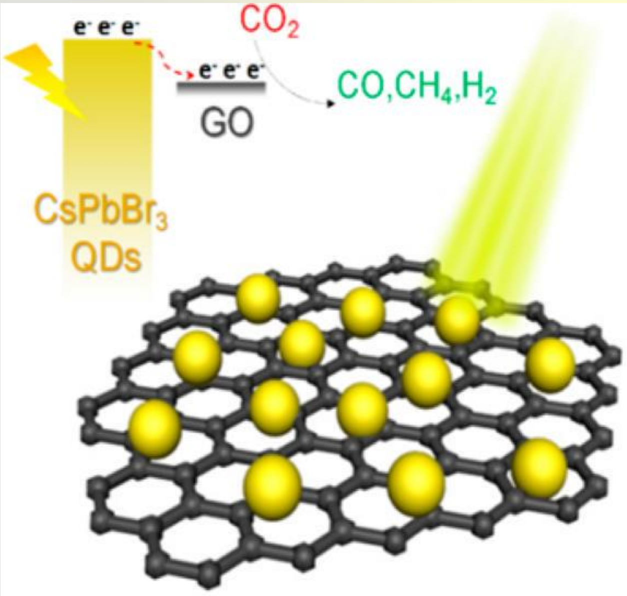
J. Phys. Chem. Lett. **2020**, *11*, 3608-3614.

Sun et al., Chem. Eur. J. **2017**, *23*, 9481-9485.

The First $CsPbBr_3$ PeNC/GO Heterojunction

Using $CsPbBr_3$ PeNC/GO composite for CO_2 Reduction

Gas-solvent interface
Solvent – ethyl acetate
Light power: 100 W



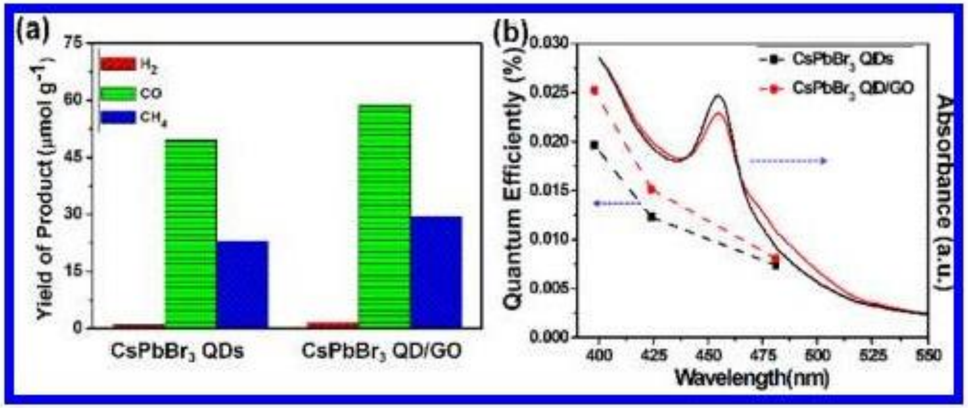


Figure 3. (a) Photocatalytic performance: yield of the CO_2 reduction products after 12 h of photochemical reaction. (b) UV−vis absorption spectra and the external quantum efficiency plots.

Table 1. Summary of the Photocatalytic CO_2 Reduction Performances after 12 h of Constant Illumination

Sample	R(CO)/ μmol g^{-1}	R(CH_4)/ μmol g^{-1}	R(H_2)/ μmol g^{-1}	$R_{electron}$ [a]/ μmol g^{-1}	select. for CO_2 red.[b]/%
$CsPbBr_3$ QDs	49.5	22.9	1.07	284.7	99.3
$CsPbBr_3$ QD/GO	58.7	29.6	1.58	357.4	99.1

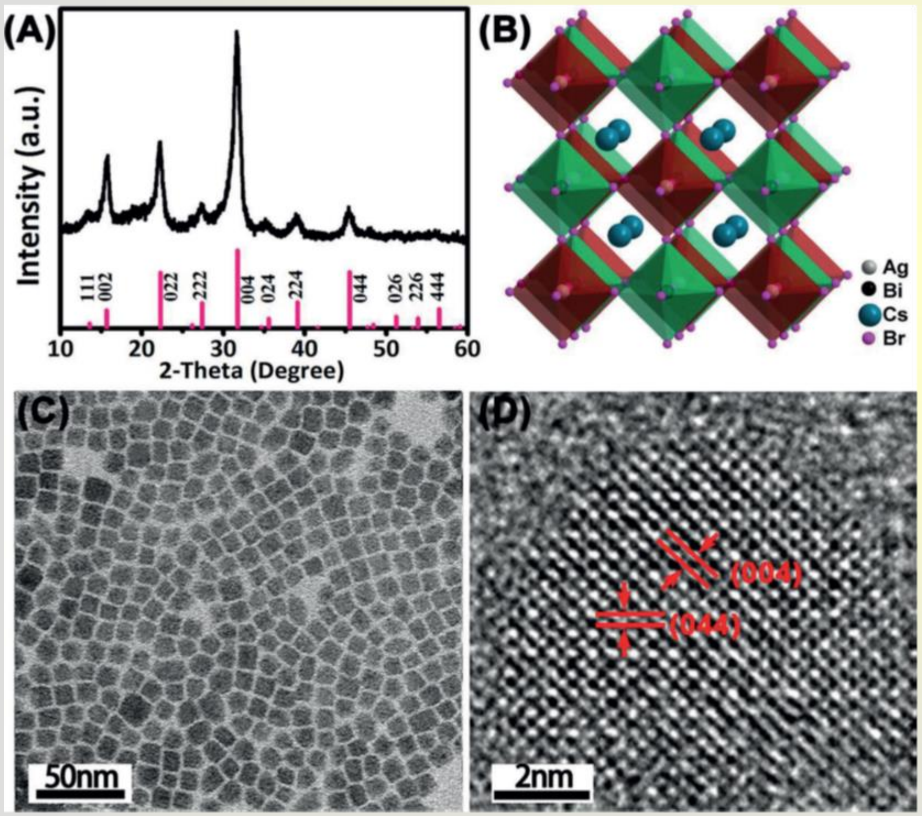
[a] $R_{electron}$ is the rate of electron consumption for the reduced product; $R_{electron} = 2R(CO) + 8R(CH_4) + 2R(H_2)$. [b] Selectivity for CO_2 reduction = $[2R(CO) + 8R(CH_4)]/R_{electron} \times 100\%$.

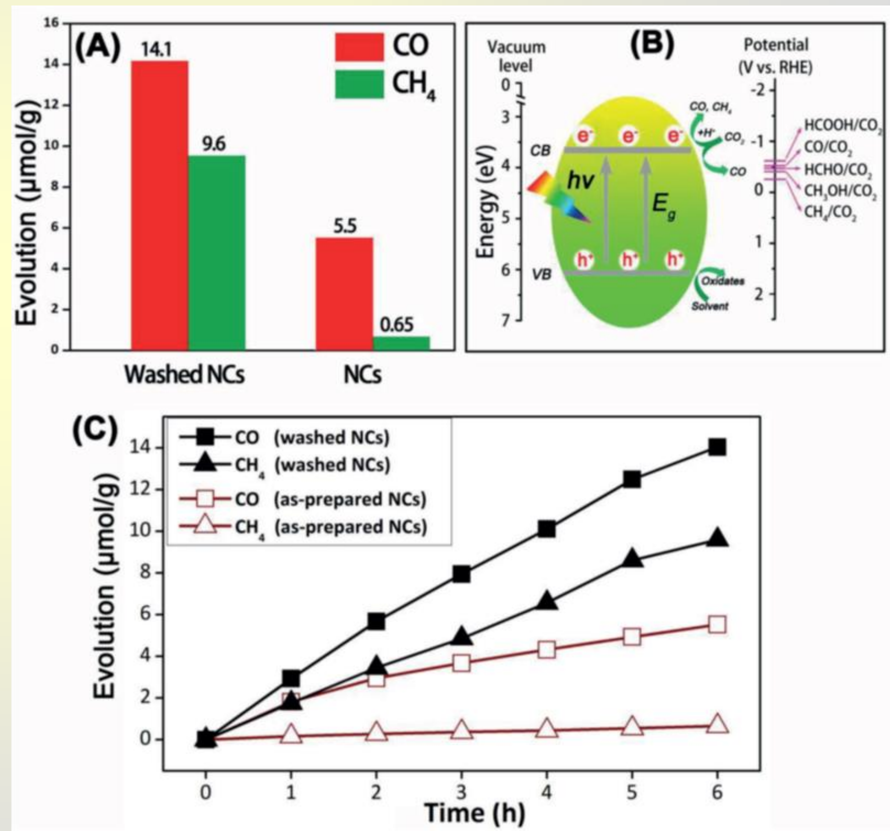
Kuang et al., J. Am. Chem. Soc. **2017**, *139*, 5660−5663.

The First Double Perovskite Catalyst

$Cs_2AgBiBr_6$ PeNC was used for CO_2 Reduction in liquid media

Gas-solvent interface
Solvent – ethyl acetate



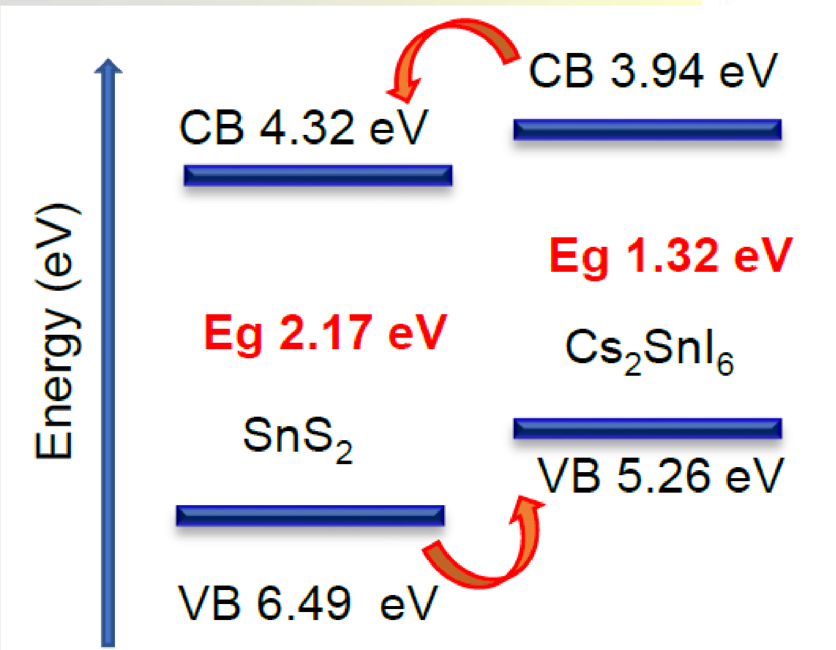


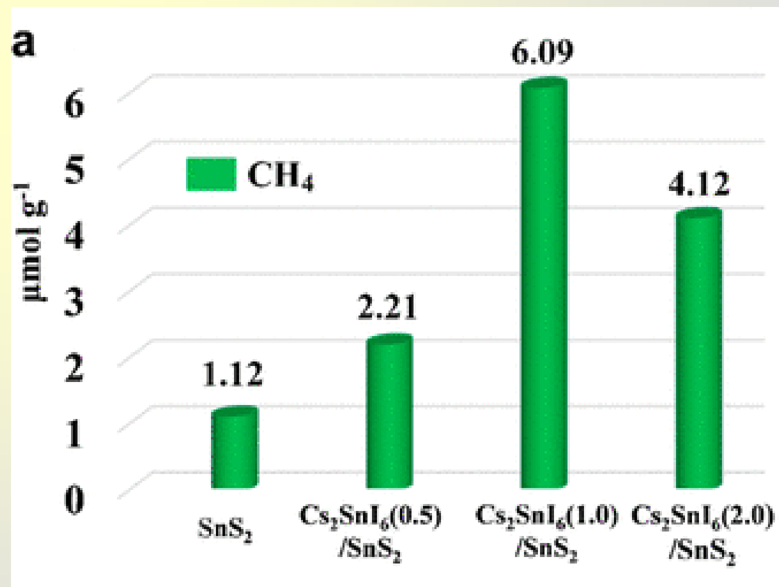
Kuang *et al.*, *Small* **2018**, *14*, 1703762.

Double Perovskite QD/SnS_2 Heterojunction

Cs_2SnI_6 PeNC/SnS_2 nanosheet composite was used for CO_2 Reduction.

Gas-solvent interface
Solvent – H_2O/MeOH

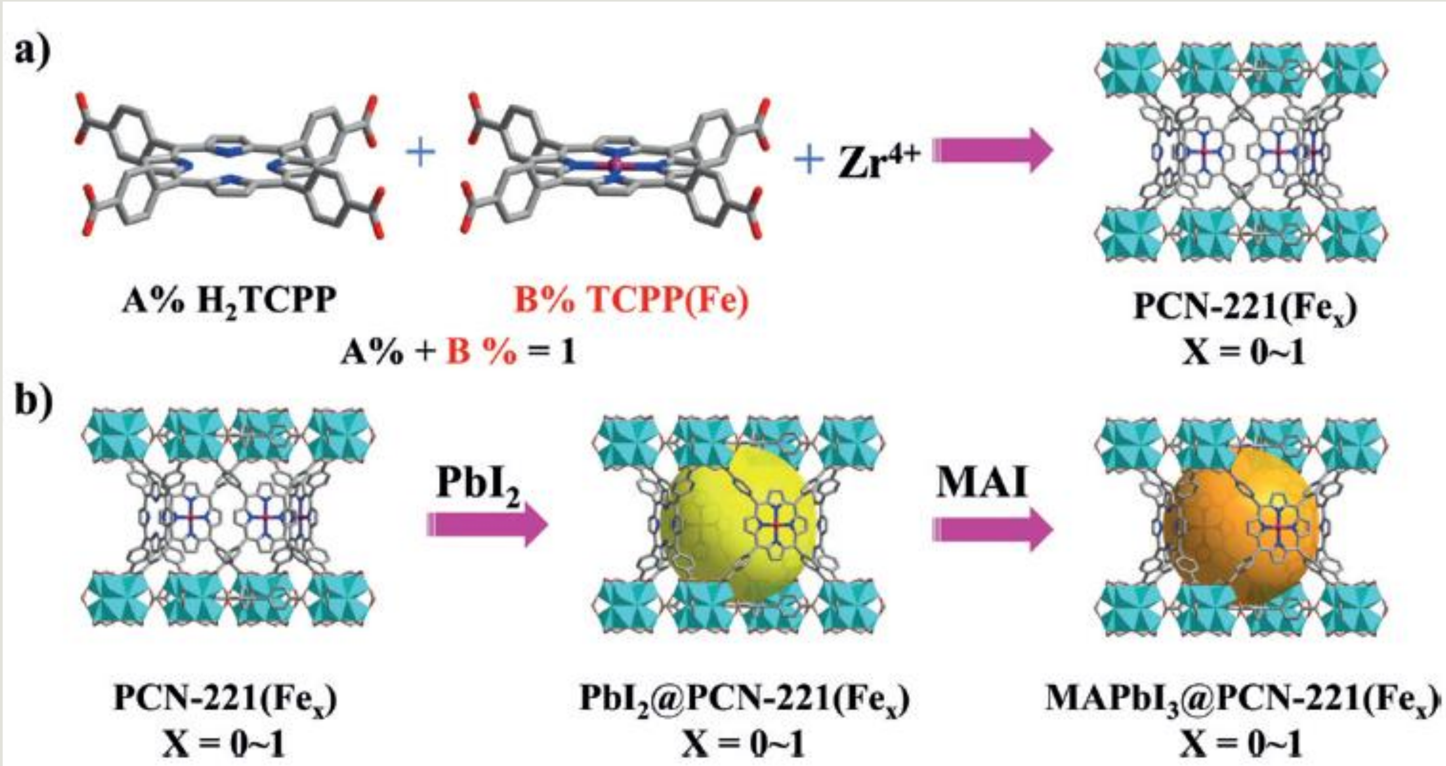


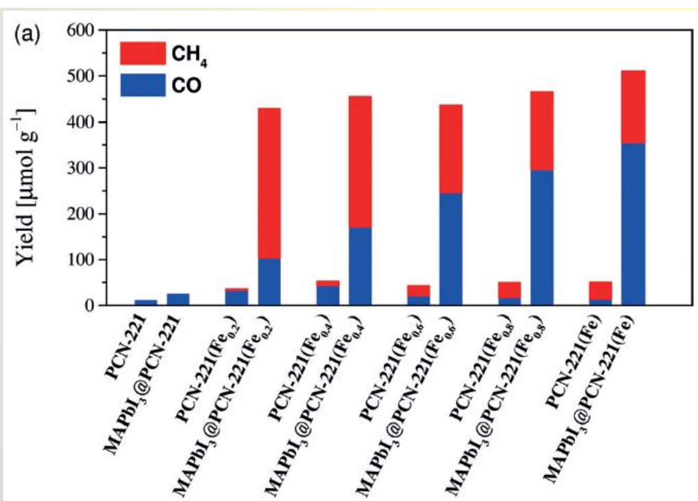


An example of Type-II heterojunction photocatalyst

Kuang et al., J. Am. Chem. Soc. **2019**, *141*, 13434−13441.

The First PeNC/MOF Composite Catalyst

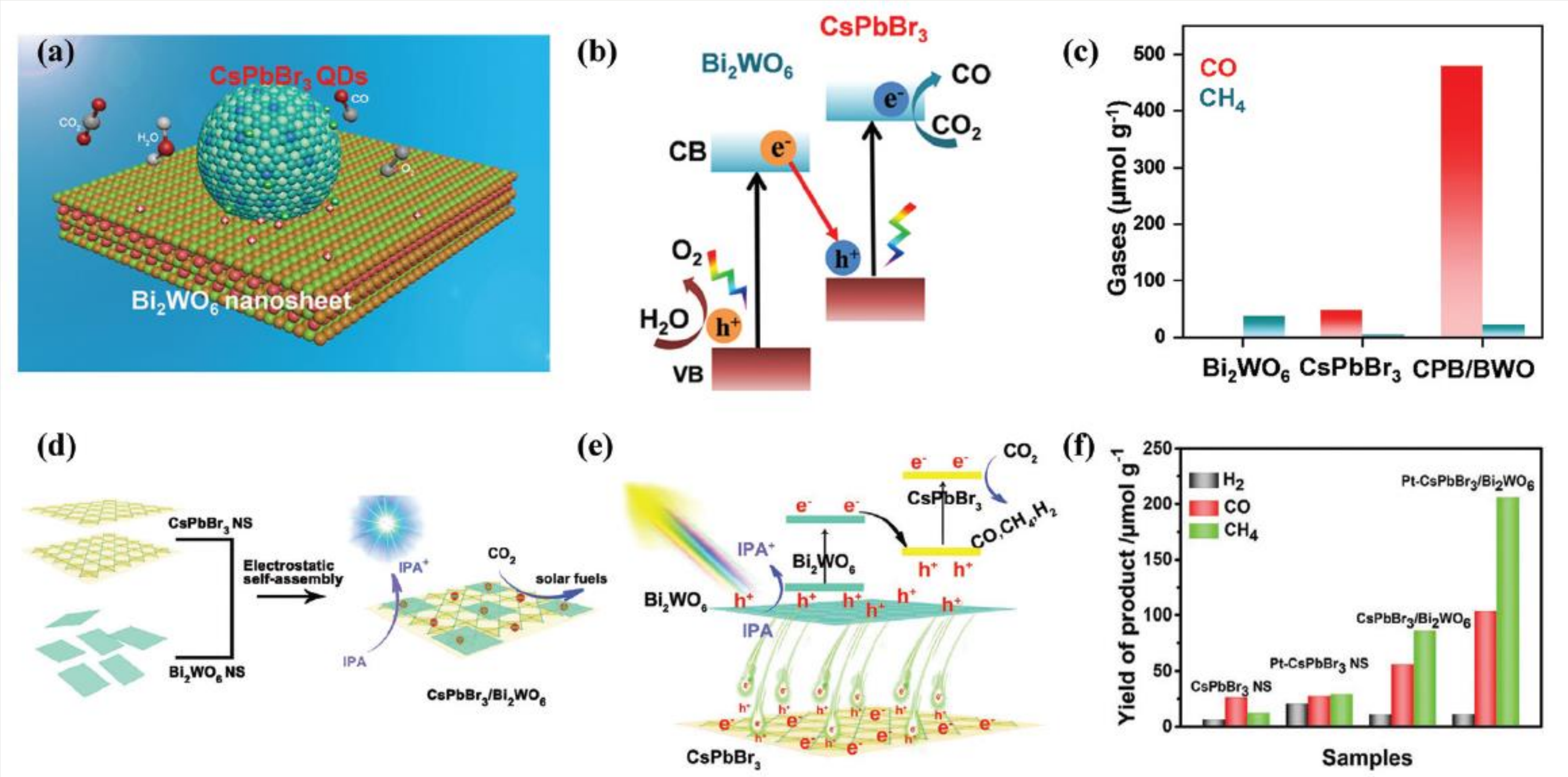




Gas-solvent interface
Solvent – ethyl acetate/water
Irradiation time – 25 h

Wu et al., Angew. Chem. Int. Ed. **2019**, *58*, 9491-9495.

Z-Scheme 0D/2D and 2D/2D Heterojunction



Gas-solvent interface

Solvent – ethyl acetate/IPA mixture

(i) Strong interaction with $CsPbBr_3$

(ii) Visible light response

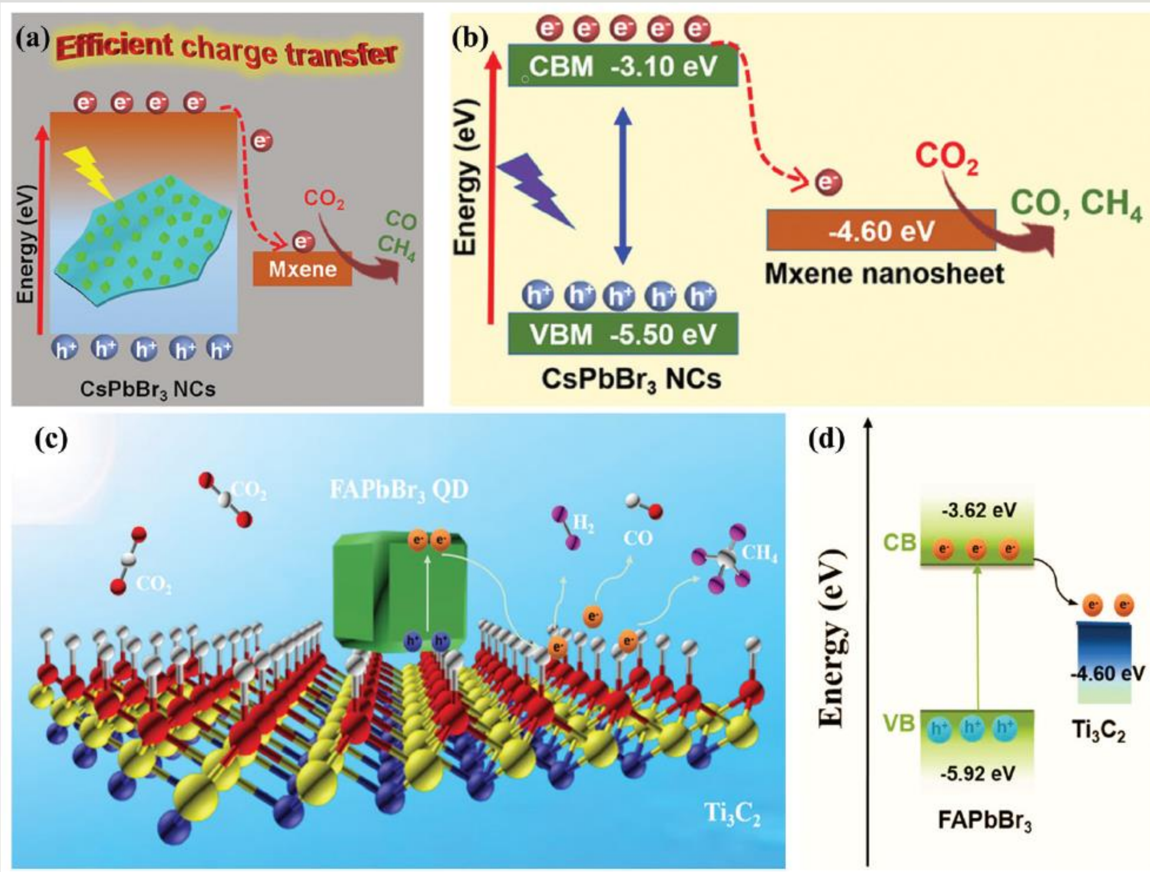
(iii) High catalytic activity for oxidation

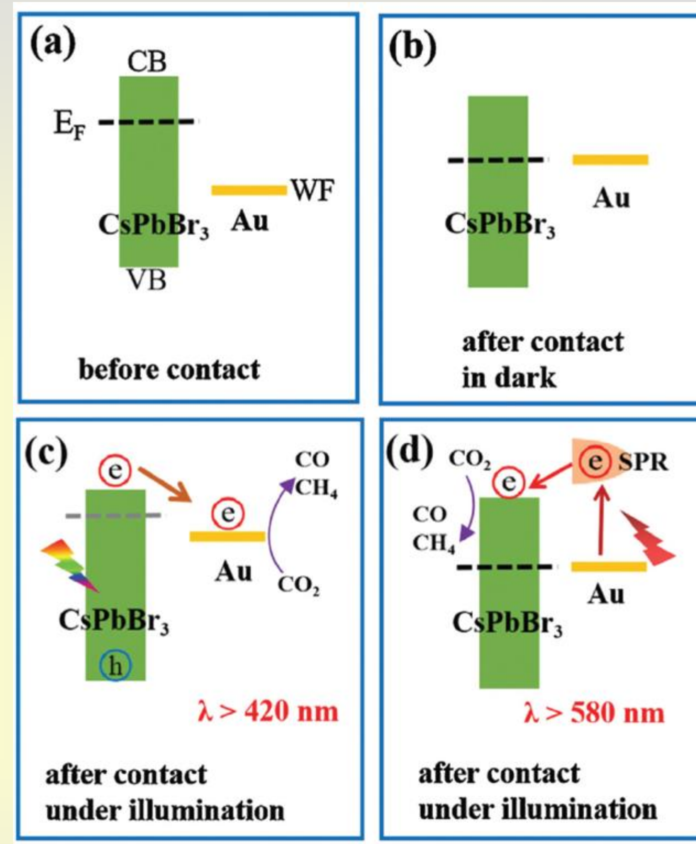
(iv) Comparable band structure with $CsPbBr_3$

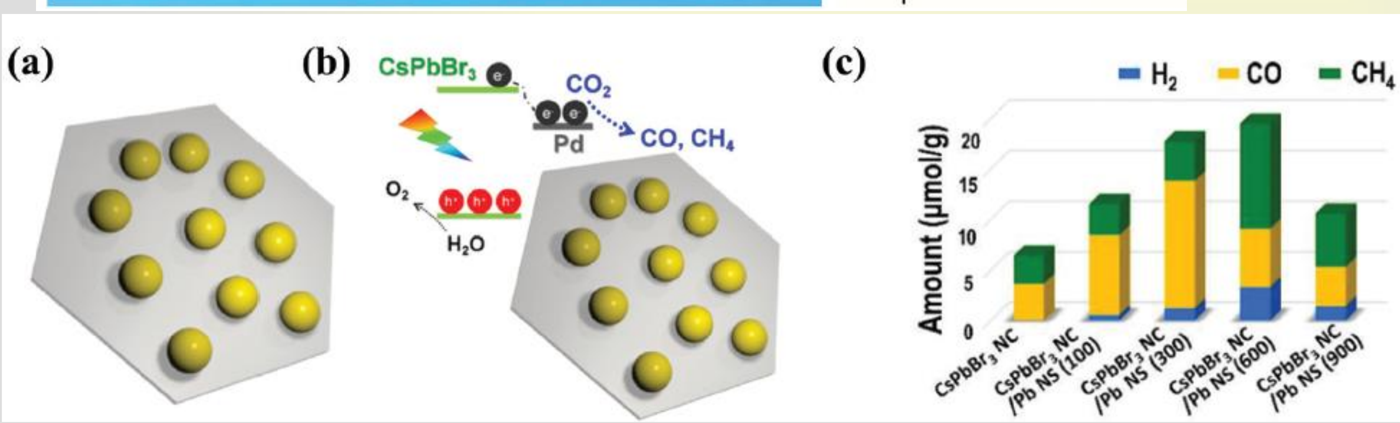
Wang et al., ACS AMI **2020**, *12*, 31477.

Kuang et al., Adv. Funct. Mater. **2020**, *30*, 2004293.

PeNC QD/MXene or Metal Heterojunction







1. Energy-level alignment
2. Localized surface plasmon resonance (LSPR) effect
3. Hot-electron transfer

Mater. Adv. **2021**, *2*, 7187-7209.

Effect of Solvents as Media for CO_2 Reduction

Photocatalytic Performance of CO_2 Reduction

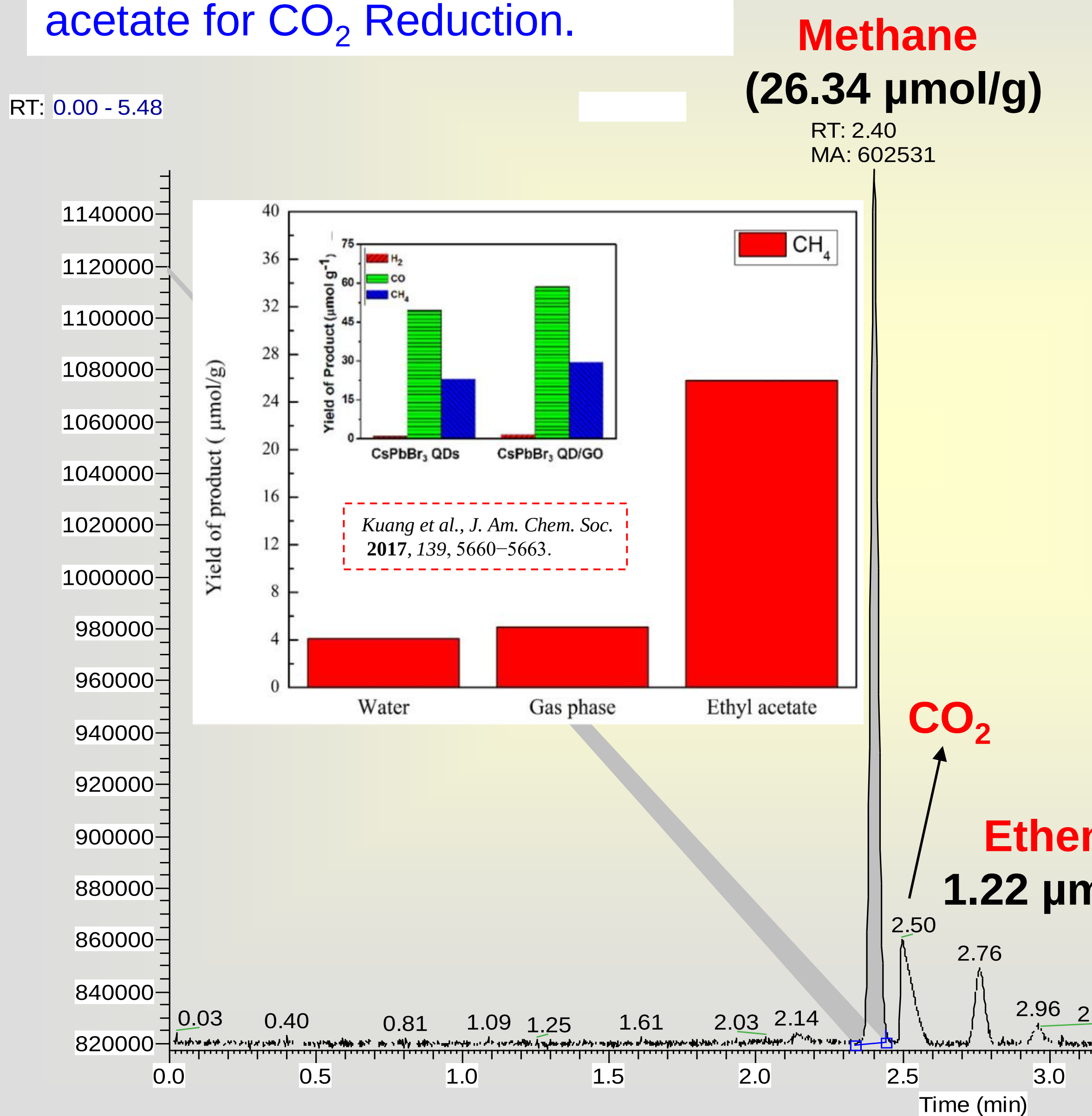
Photocatalyst	Medium	Light source	Products	Yield (μmol g^{-1} h^{-1})
$CsPbBr_3$ QDs	Ethyl acetate/water	300 W Xe lamp (AM 1.5G)	$CO + CH_4 + H_2$	4.3 + 1.5 + 0.1
$CsPbBr_3@g\text{-}C_3N_4$	Ethyl acetate	450 W Xe lamp AM 1.5G	$CO + CH_4$	2.1 + 22.8
$CsPb(Br_{0.5}/Cl_{0.5})_3$ NCs	Ethyl acetate	300 W Xe lamp (AM 1.5G)	$CO + CH_4$	85.2 + 12.0
$CsPbBr_3$ QD/GO	Ethyl acetate	150 mW cm^{-2} (AM 1.5G)	$CO + CH_4 + H_2$	4.9 + 2.5 + 0.1
$CsPbBr_3$@TiO-CN	Ethyl acetate/water	300 W Xe lamp ($\geq$400 nm)	CO	12.9
$CsPbBr_3$ NCs/MXene	Ethyl acetate	300 W Xe lamp ($\geq$420 nm)	$CO + CH_4$	26.3 + 7.3
$CsPbBr_3$ NCs/BZNW/MRGO	(CO_2 + water vapor)	150 W Xe lamp (AM 1.5G)	$CO + CH_4$	0.9 + 6.3
$CsPbBr_3$ NCs/Pd NS	(CO_2 + water vapor)	150 W Xe lamp ($\geq$420 nm)	$CO + CH_4 + H_2$	1.9 + 3.5 + 1.1
$CsPbBr_3$-Re(600)	Toluene/isopropanol	150 W Xe lamp ($\geq$420 nm)	$CO + H_2$	104.4 + 5.6
$CsPbBr_3$ NCs/a-TiO_2	Ethyl acetate/ isopropanol	150 W Xe lamp (AM 1.5G)	$CO + CH_4 + H_2$	3.9 + 6.7 + 1.5
$CsPbBr_3$ NCs@ZIF-67	(CO_2 + water vapor)	150 mW cm^{-2} (AM 1.5G)	$CO + CH_4$	2.1 + 3.5
$CsPbBr_3$ NCs@ZIF-8	(CO_2 + water vapor)	100 W Xe lamp (AM 1.5G)	$CO + CH_4$	0.7 + 2.0
$CsPbBr_3$ QDs/ UiO66(NH_2)	Ethyl acetate/water	300 W Xe lamp ($\geq$420 nm)	$CO + CH_4$	8.2 + 0.3
$MAPbI_3$@PCN221(Fe_x)	Ethyl acetate/water	300 W Xe lamp ($\geq$400 nm) 100 mW cm^{-2}	$CO + CH_4$	4.2 + 13.0
Fe: $CsPbBr_3$ NCs	Ethyl acetate/water	450 W Xe lamp 150 mW cm^{-2}	$CO + CH_4$	3.2 + 6.1
$FAPbBr_3/Bi_2WO_6$	Benzyl alcohol	150 W Xe lamp AM 1.5G 100 mW cm^{-2}	CO + Benzaldehyde	170.0 + 250.0
$FAPbBr_3$ QDs	Ethyl acetate/water	300 W Xe lamp 100 mW cm^{-2}	$CO + CH_4 + H_2$	181.3 + 16.9 + 2.37
$CsPbBr_3$ QDs/Bi_2WO_6	Ethyl acetate/water	100 mW cm^{-2} > 400 nm	$CO + CH_4$	Totally 50.3
Cs_2SnI_6/SnS_2 NCs	($CH_3OH + CO_2$ + water vapor)	150 mW cm^{-2} ($\geq$400 nm)	CH_4	6.1
$Cs_3Sb_2Br_9$	Octadecene	300 W Xe lamp 100 mW cm^{-2}	CO	127.2
α-Fe_2O_3/Amine-RGO/ $CsPbBr_3$	(CO_2 + water vapor)	150 W Xe lamp AM 1.5G, >420 nm	$CO + CH_4 + H_2$	2.4 + 9.5 + 0.3
$CsPbBr_3$-Ni(tpy)	Ethyl acetate/water	300 W Xe lamp >400 nm 100 mW cm^{-2}	$CO + CH_4$	431.0 + 48.8
$Cs_2AgBiBr_6$ NCs	Ethyl acetate	150 mW cm^{-2} (AM 1.5G)	$CO + CH_4$	2.4 + 1.6
$Cs_3Bi_2I_9$	(CO_2 + water vapor)	80.38 μW cm^{-2} (AM 1.5G)	$CO + CH_4$	7.7 + 1.5
$Co_{2\%}@CsPbBr_3/Cs_4PbBr_6$	Water	300 W Xe lamp 100 mW cm^{-2}	$CO + CH_4$	12.0 + 1.8
Mn/CsPb(Br/Cl)$_3$	Ethyl acetate	300 W Xe-lamp with AM 1.5 filter	CO, CH_4	213, 9.1
Co-$CsPbBr_3/Cs_4PbBr_6$	Acetonitrile/water/ Methanol	300 W Xe lamp 100 mW cm^{-2}	CO	122
Pt/$CsPbBr_3$	Ethyl acetate	150 W Xe-lamp with 380 nm cut o filter	CO	5.6
Ni and Mn-doped $CsPbCl_3$ NCs	(CO_2 + water vapor)	300 W Xe-lamp with AM 1.5 filter	Ni—CO Mn—CO	169.37, 152.49
Cs_4PbBr_6/rGO	Ethyl acetate/water	300 W Xe-lamp with 420 nm filter (light intensity, 100 mW cm^{-2})	CO	11.4
Cu-RGO-$CsPbBr_3$	(CO_2/water vapor)	Xe-lamp irradiation with a 400 nm filter	CH_4	12.7
$TiO_2/CsPbBr_3$	Acetonitrile/water	300 W Xe-arc lamp	CO	9.02
$Cs_2AgBiBr_6@g\text{-}C_3N_4$	Ethyl acetate/ Methanol	Xe-lamp (80 mW cm^{-2} light intensity)	CO, CH_4	2

Entry	O_2%	Mixed gas	CO	CH_4
1	100%	Pure oxygen	151	27
2	80%	Flow rate control O_2/N_2, ca 80:20	124	22
3	80%	Flow rate control O_2/CO_2, ca 80:20	123	24
4	80%	Flow rate control O_2/Ar, ca 80:20	126	24
5	50%	Flow rate control O_2/N_2, ca 50:50	78	18
6	50%	Flow rate control O_2/CO_2, ca 50:50	78	19
7	50%	Flow rate control O_2/Ar, ca 50:50	76	17
8	20%	Air, O_2/N_2, ca 20:80	24	4
9	20%	Flow rate control O_2/ CO_2, ca 20:80	24	5
10	20%	Flow rate control O_2/ CO_2, ca 20:80	26	5
11	0.1%	CO_2 gas sparging, O_2 residue read out from O_2 sensor	6	1
12	<1ppm	N_2 gas sparging, O_2 residue read out from O_2 sensor	<0.1	<0.1
13	<1ppm	Ar gas sparging, O_2 residue read out from O_2 sensor	<0.1	<0.1
14	<1ppm	Ultra-pure CO_2 gas sparging, O_2 residue read out from O_2 sensor	<0.1	<0.1

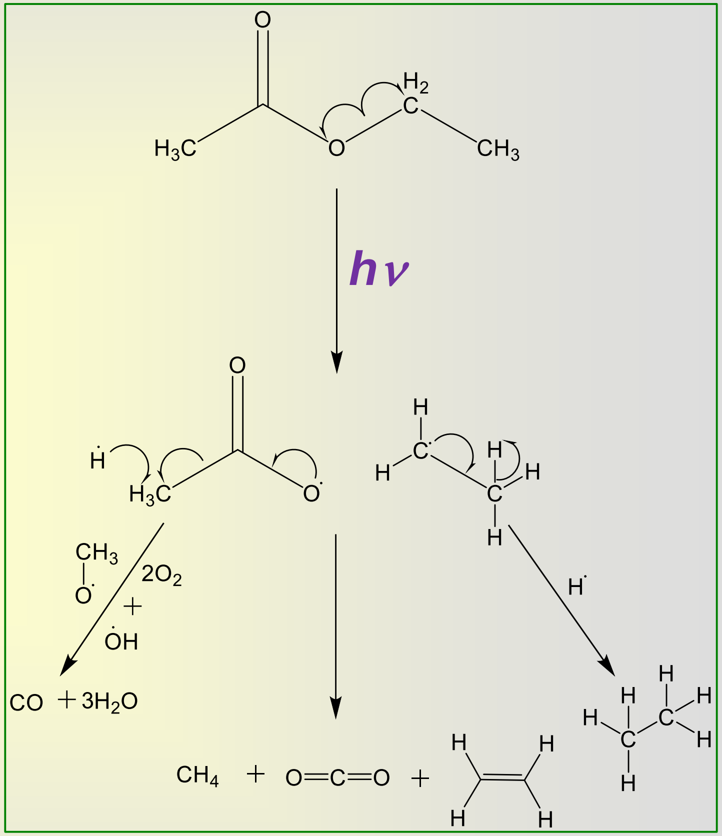
$$CH_3COOCH_2CH_3 + x\,O_2 \xrightarrow[\text{Blue LED}]{\text{perovskite } CsPbBr_3} y\,CO + z\,CH_4 \qquad y/z>5$$

The Problem of Photodissociation in Gas-Liquid Phase

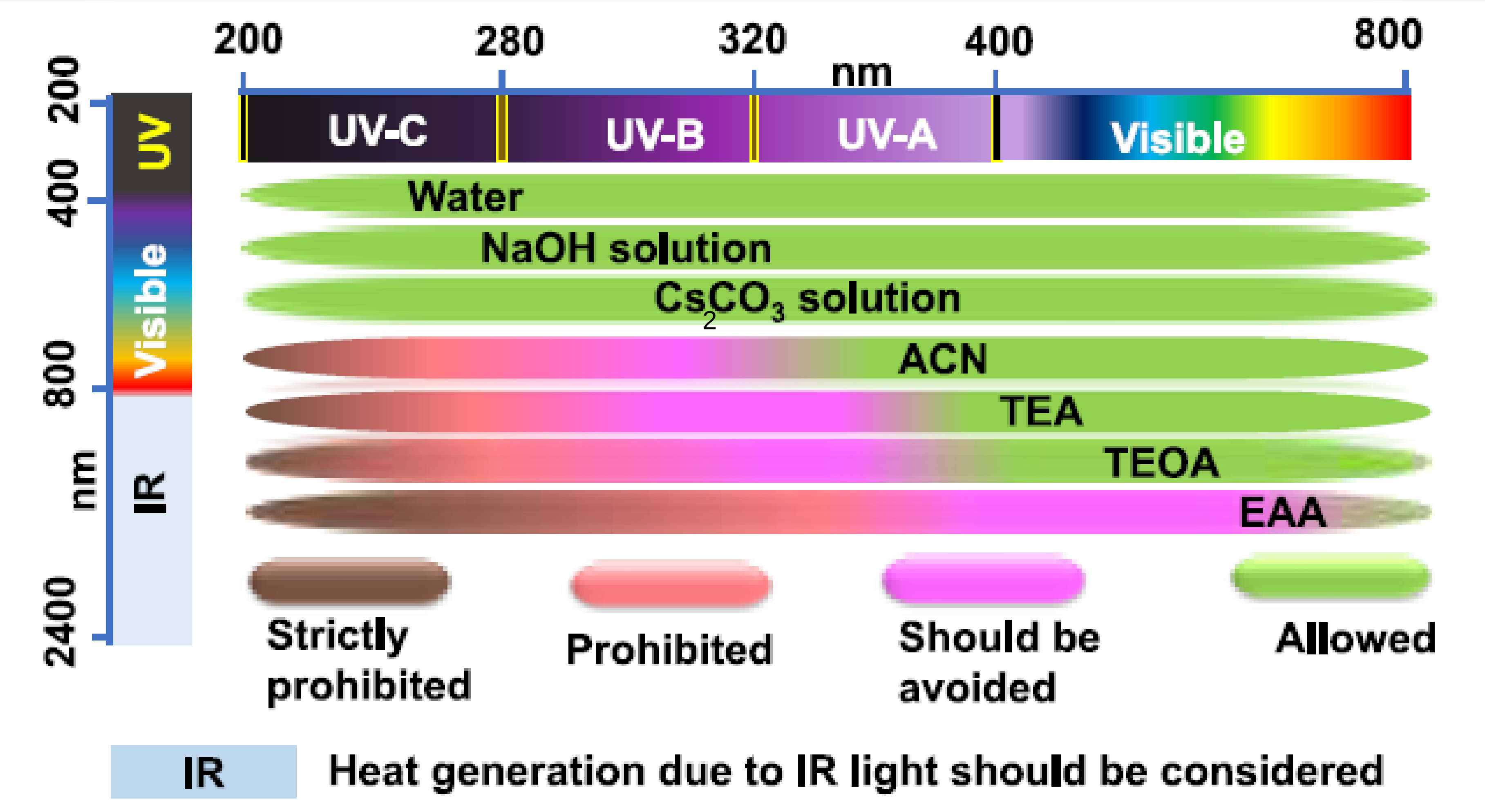
We used $MAPbBr_3$ PeNC in ethyl acetate for CO_2 Reduction.



Photoreactions of ethyl acetate



Guideline Flowchart for Choosing an Appropriate Solvent



ACN: Acetonitrile CH_3CN
TEA: Triethyl amine $(C_2H_5)_3N$
TEOA: Triethanol amine $(C_2H_4OH)_3N$
EAA: Ethyl acetate $CH_3COOC_2H_5$

H_2O is usually required for oxidation but

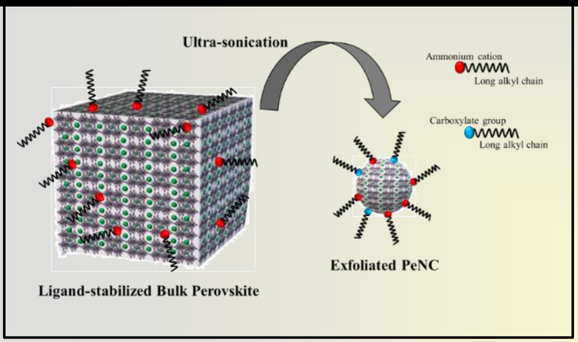
1. CO_2 has low solubility in water.
2. PeNC would be decomposed in water.

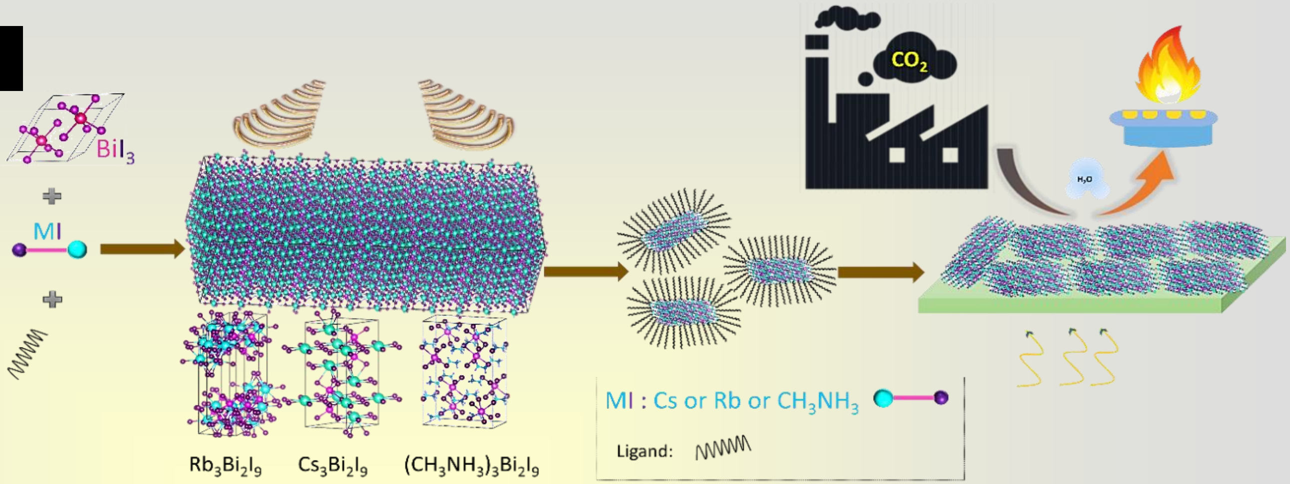
ACS Energy Lett. **2021**, *6*, 3270-3274.

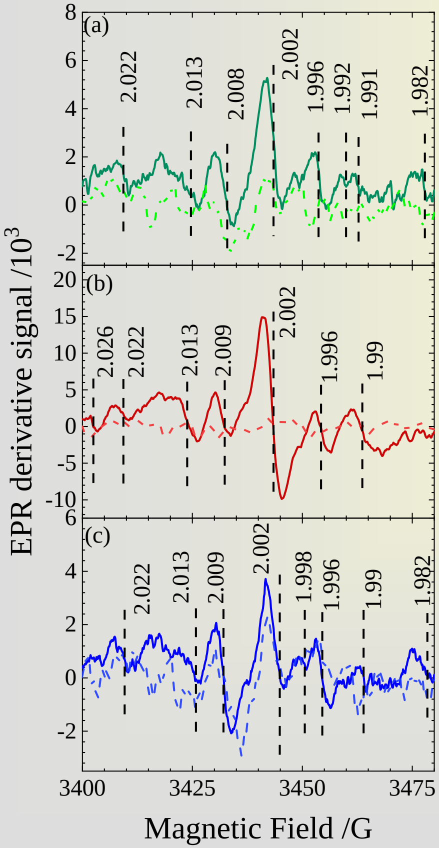
Photocatalytic CO_2 Reduction at Gas-Solid Interface

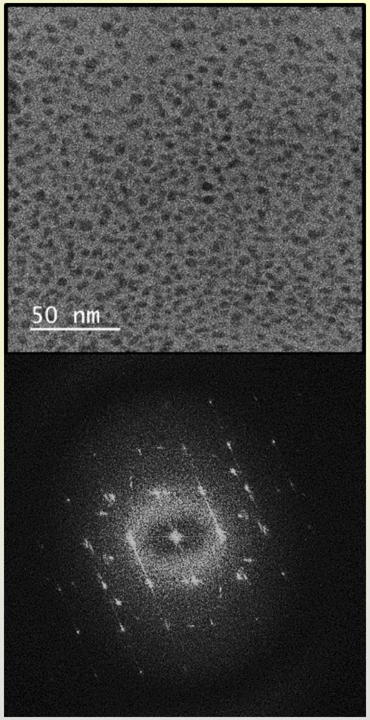
Triple Perovskites at the Gas-Solid Interface

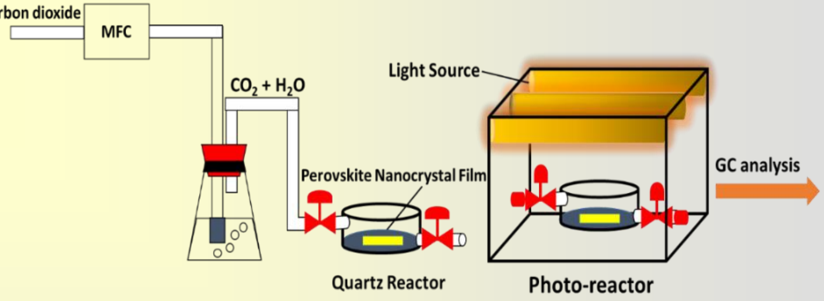
Top-down, ultra-sonication approach

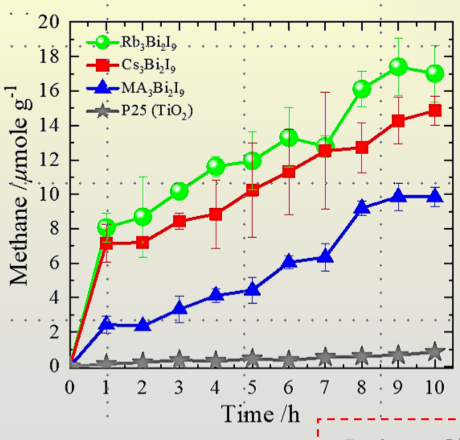


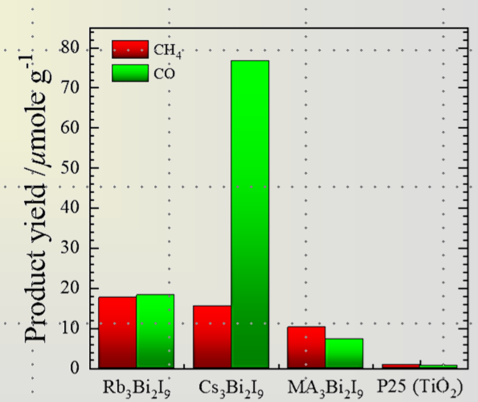






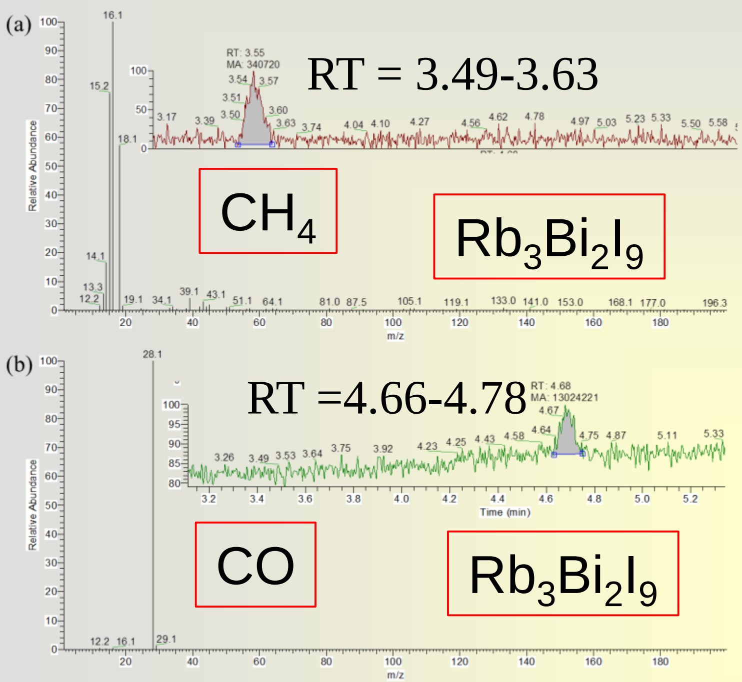


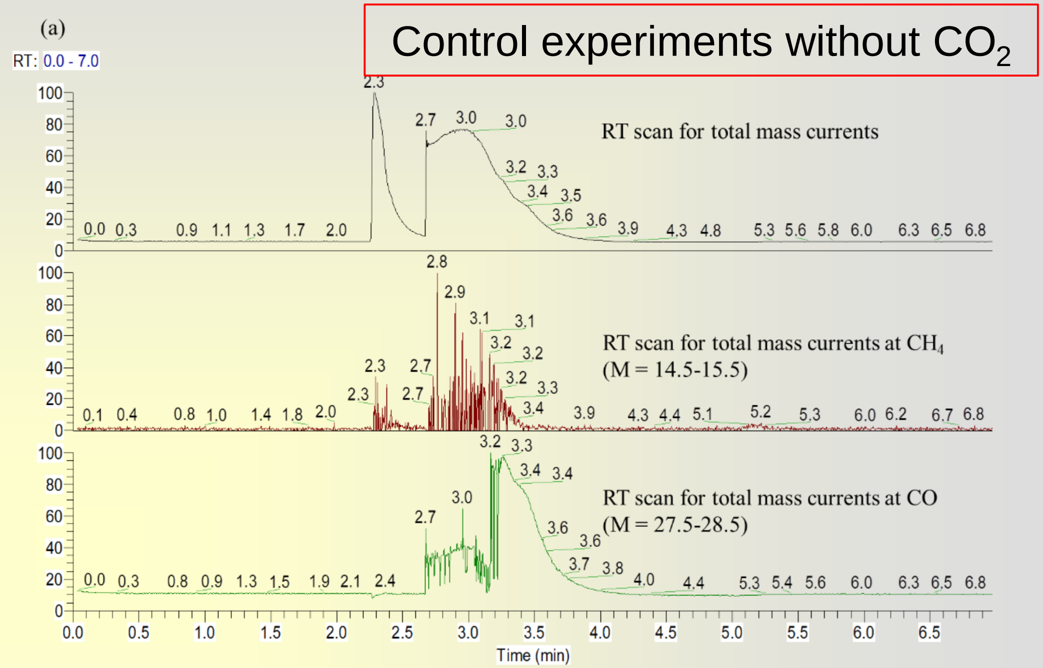


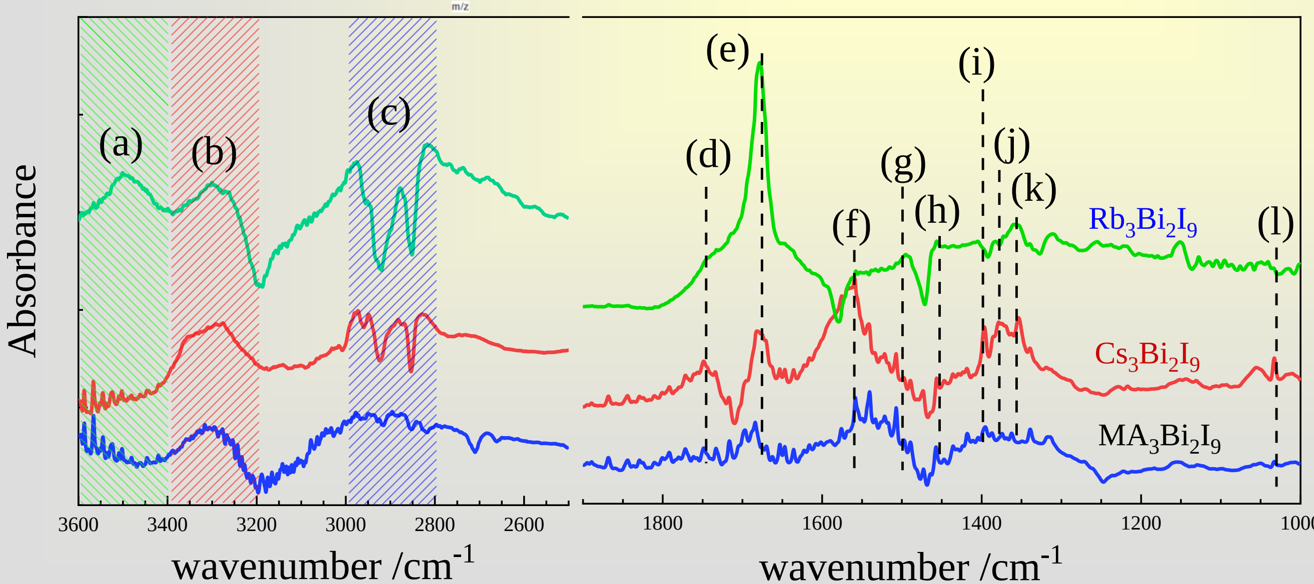


J. Am. Chem. Soc. **2019**, *141*, 20434-20442

Results of GC-Mass and FTIR



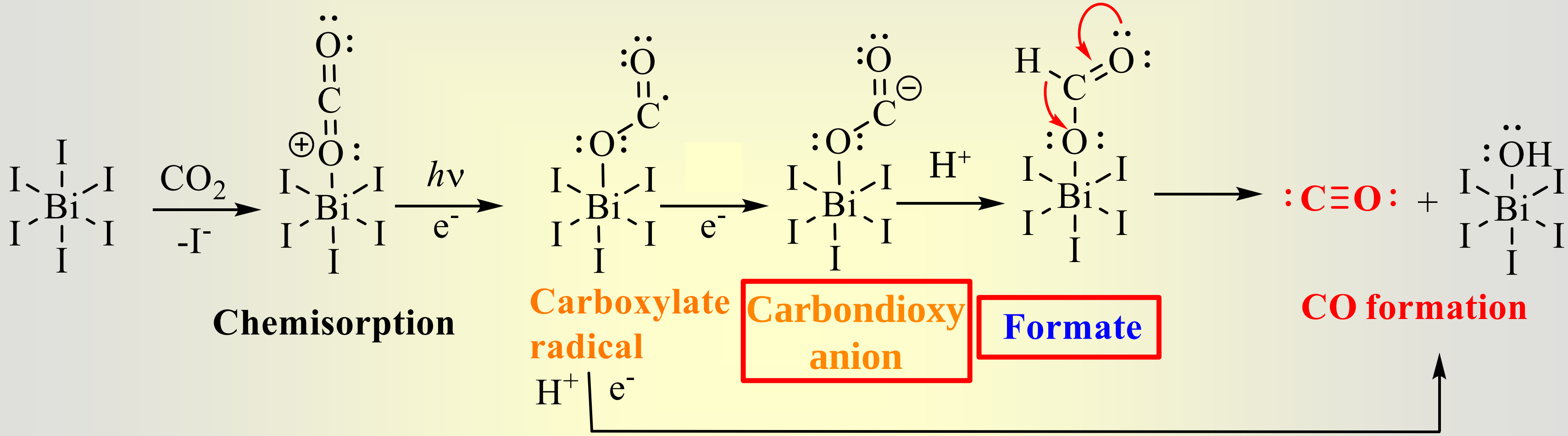




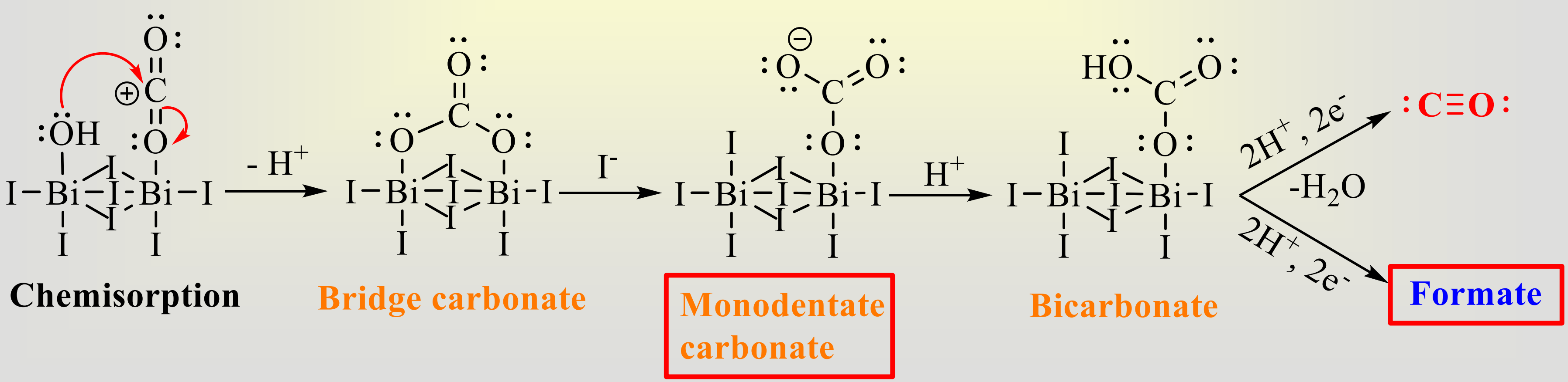
(a) Free –OH
(b) H bonded –OH
(c) OA and OLA liagnds
(d) Bridge carbonate
(e) Dioxycarbon anion $-OCO^-$
(f) and (i) Monodentate carbonate
(g) and (j) Bidentate carbonate
(h) Bicarbonate
(k) Formate
(l) Methoxy

Mechanism for CO_2 Reduction

(1) Monodentate Mechanism

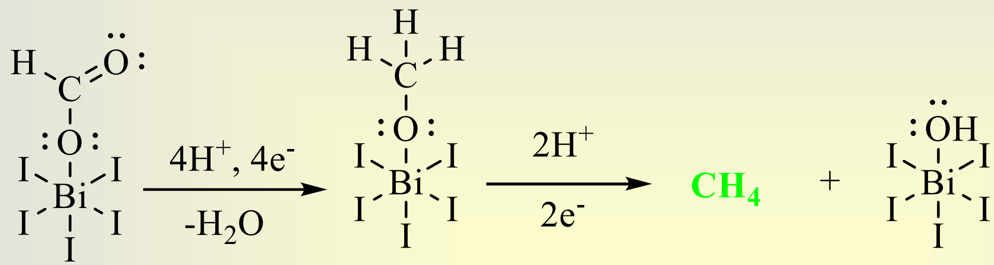


(2) Bidentate Mechanism



Mechanism for CO_2 Reduction

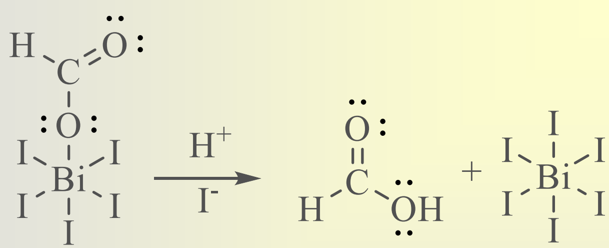
(3) Formation of methane from formate



Formate **Methoxy** **CH_4 formation**

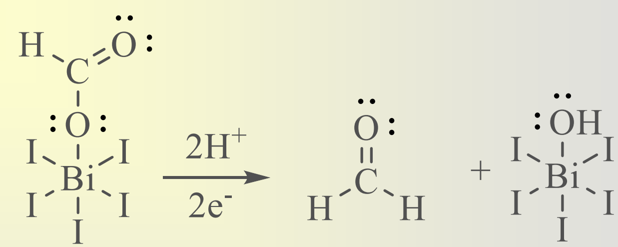
(4) Side reactions

(a)



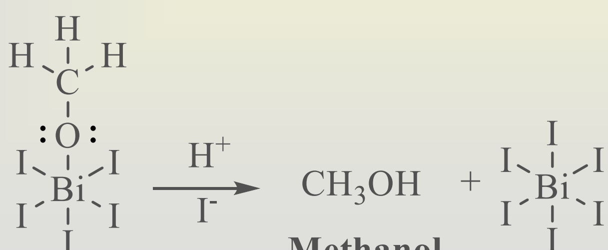
Formic acid

(b)



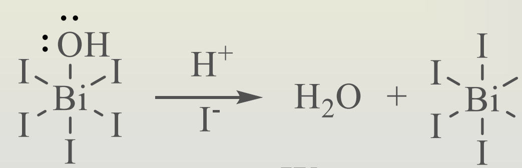
Formaldehyde

(c)



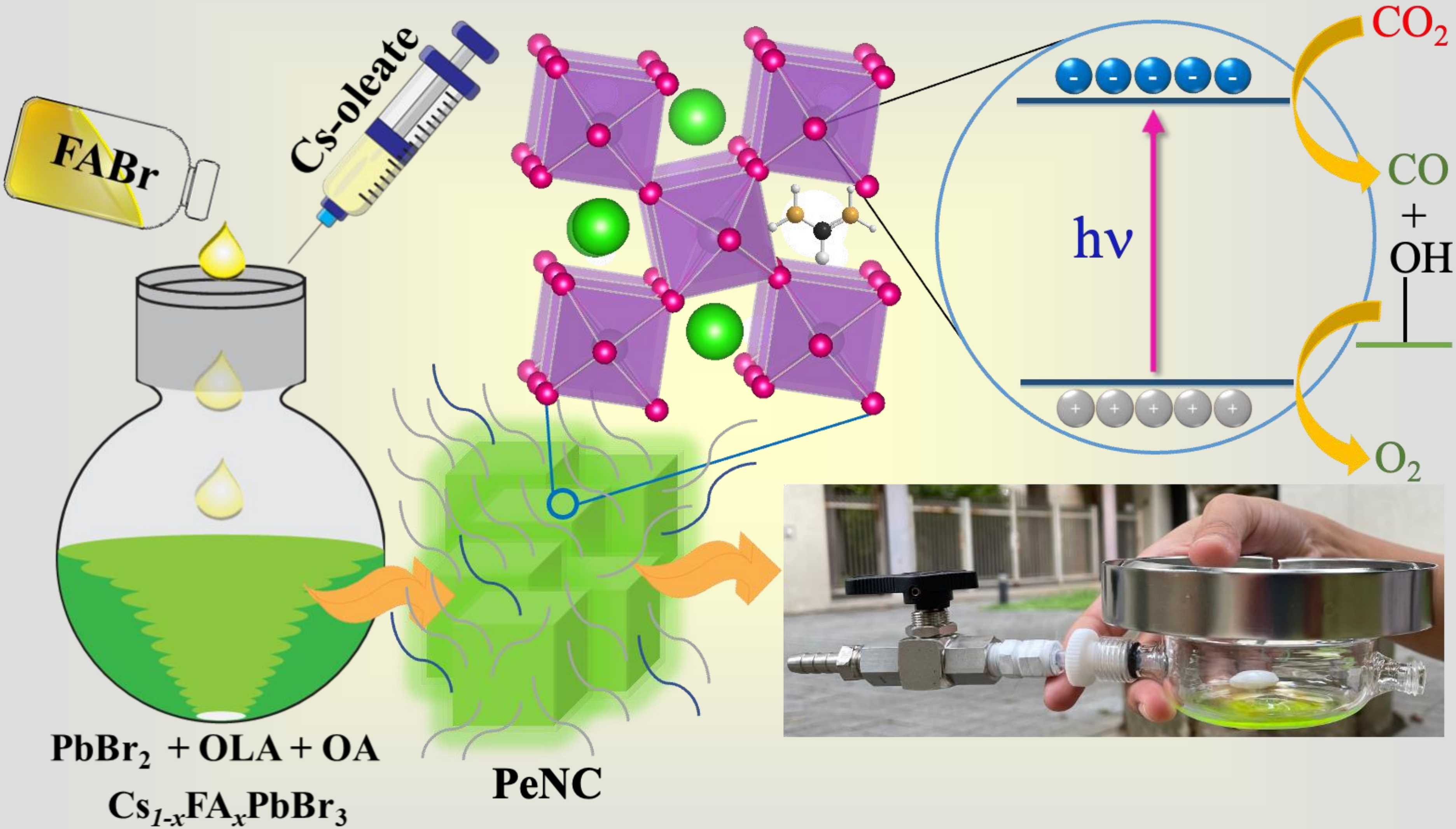
Methanol

(d)



Water

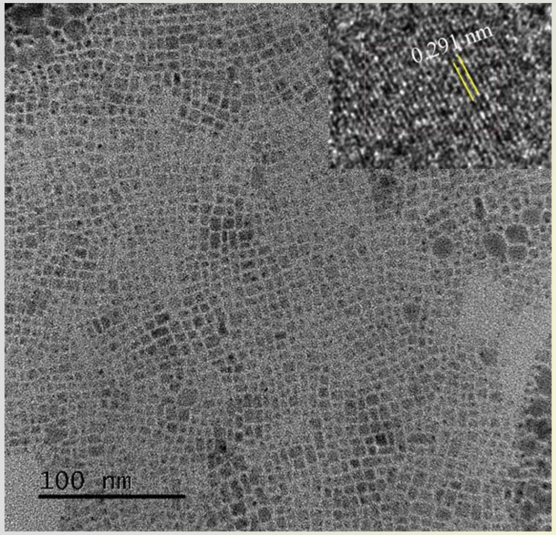
Water-Free Self-Photocatalytic CO_2 Splitting

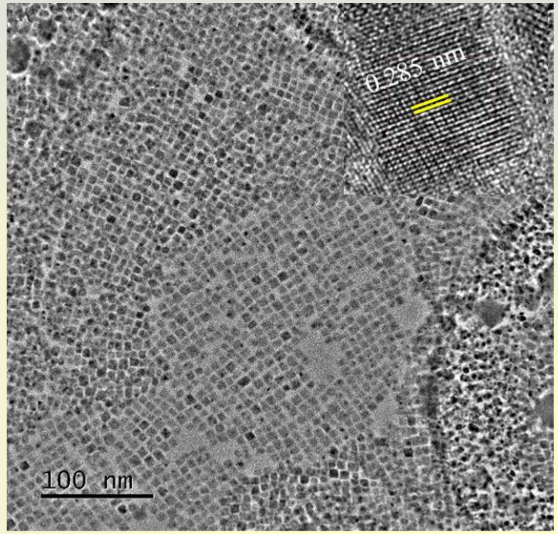


Reaction at gas-solid interface

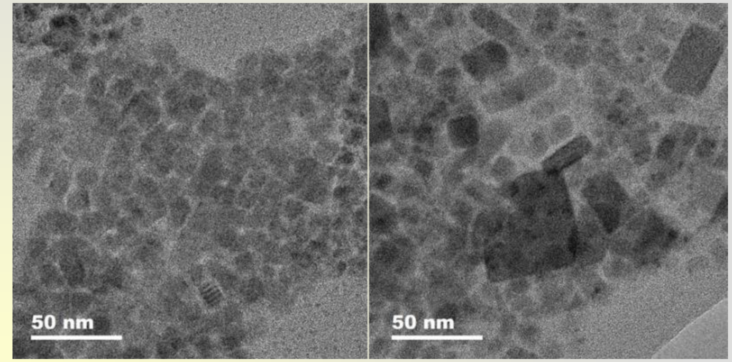
Unpublished Results

Morphology and Crystallinity

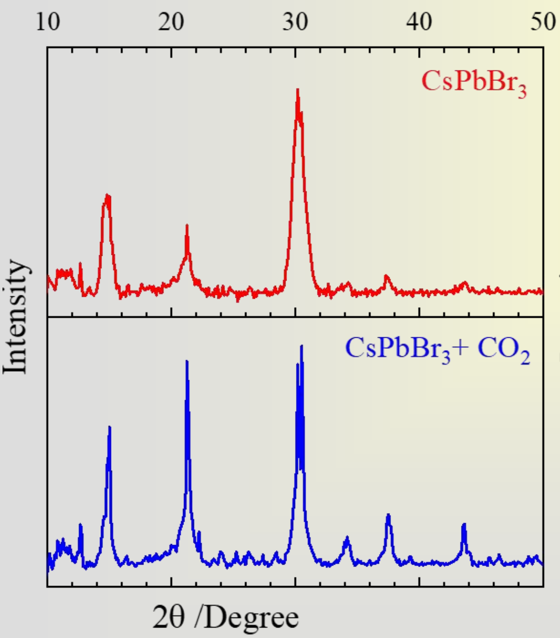


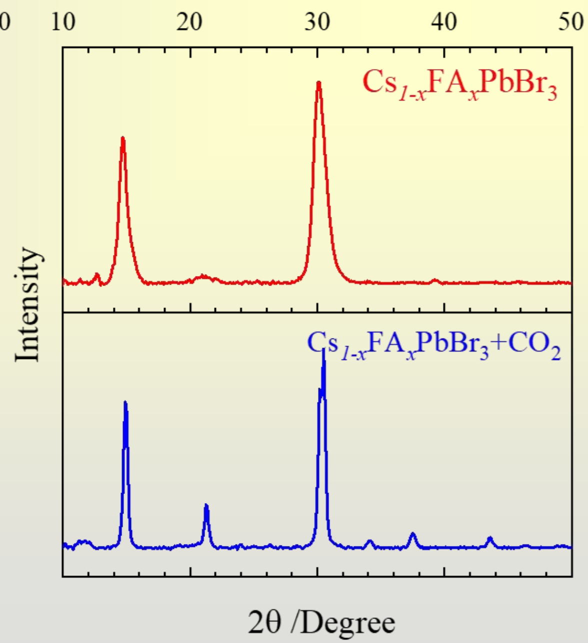


PeNC+CO_2 after irradiation for 12 h



Particle size: 8 nm → >15 nm





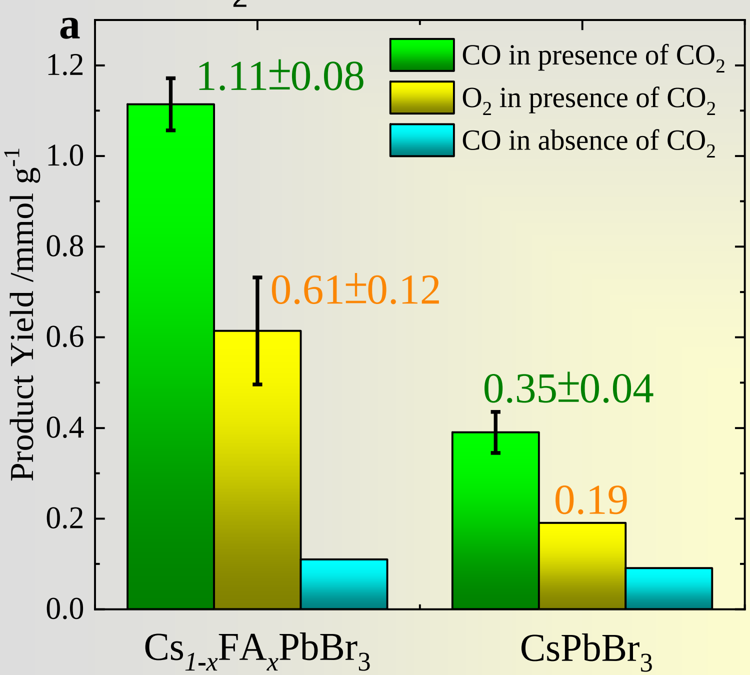
Original PeNC without irradiation
CS: Orthorhombic phase 62%
Cubic phase 38%
CF: Orthorhombic phase 93%
Cubic phase 7%

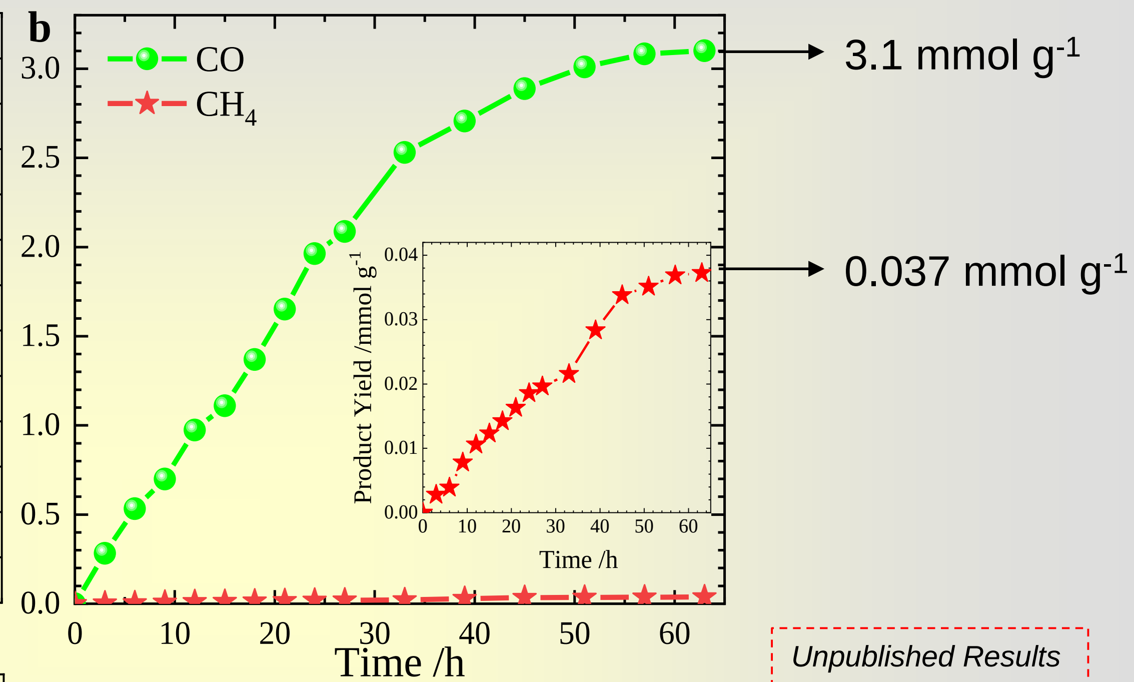
PeNC+CO_2 after irradiation for 12 h
CS: Orthorhombic phase 27%
Cubic phase 73%
CF: Orthorhombic phase 53%
Cubic phase 47%

Unpublished Results

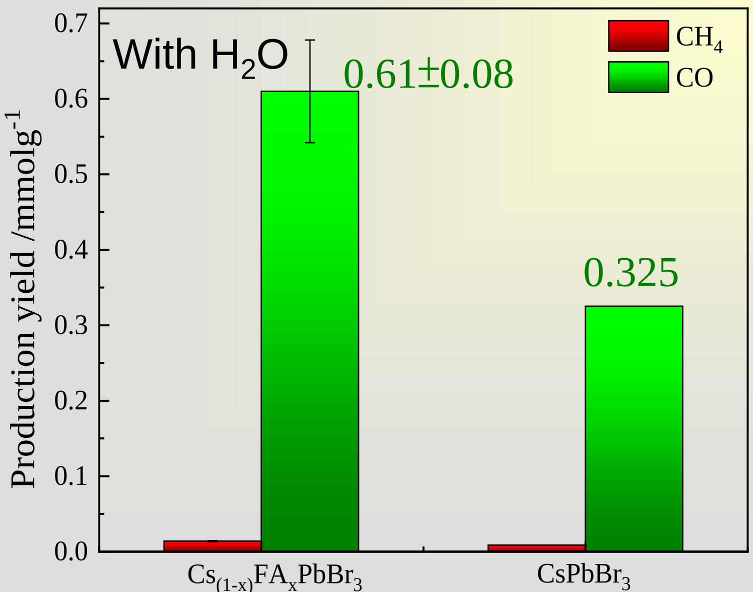
World-Record CO Production Yield (Rate)

Without H_2O





Unpublished Results



CF: 12 h irradiation without water
CO = 1.26 mmol $g^{-1} \rightarrow$ 105 μmol g^{-1} h^{-1}

CF: 12 h irradiation with water
CO = 0.70 mmol $g^{-1} \rightarrow$ 58 μmol g^{-1} h^{-1}

CS: 12 h irradiation without water
CO = 0.37 mmol $g^{-1} \rightarrow$ 31 μmol g^{-1} h^{-1}

CS: 12 h irradiation with water
CO = 0.325 mmol $g^{-1} \rightarrow$ 27 μmol g^{-1} h^{-1}

Redox Potentials for CO_2 Reduction

Overall Reaction

$$\mathrm{CO_2 \rightarrow CO + \frac{1}{2}O_2} \qquad \Delta G^0 = 257.2\ kJ\ mol^{-1}$$

$$E^0 = -1.335\ V$$

Half Reactions in the presence of water

$$Reduction:\ \mathrm{CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O} \qquad E^0_{red} = -0.106\ V$$

$$Oxidation:\ \mathrm{H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-} \qquad E^0_{ox} = -1.229\ V$$

Half Reactions in the absence of water

$$Reduction:\ \mathrm{CO_2 + H^+ + 2e^- \rightarrow CO + OH^-} \qquad E^0_{red} = ???$$

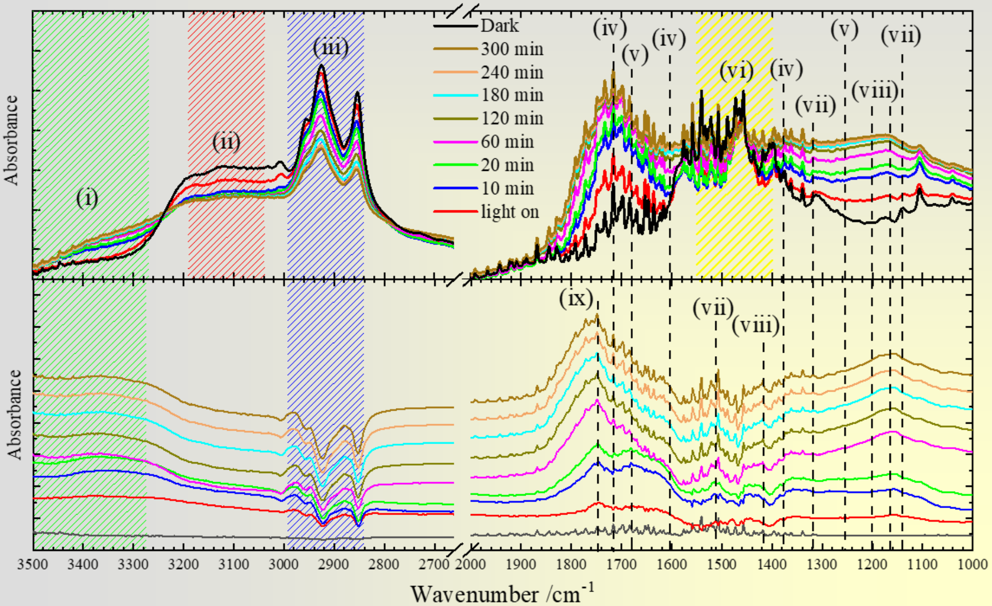
$$Oxidation:\ \mathrm{OH^- \rightarrow \frac{1}{2}O_2 + H^+ + 2e^-} \qquad E^0_{ox} = ???$$

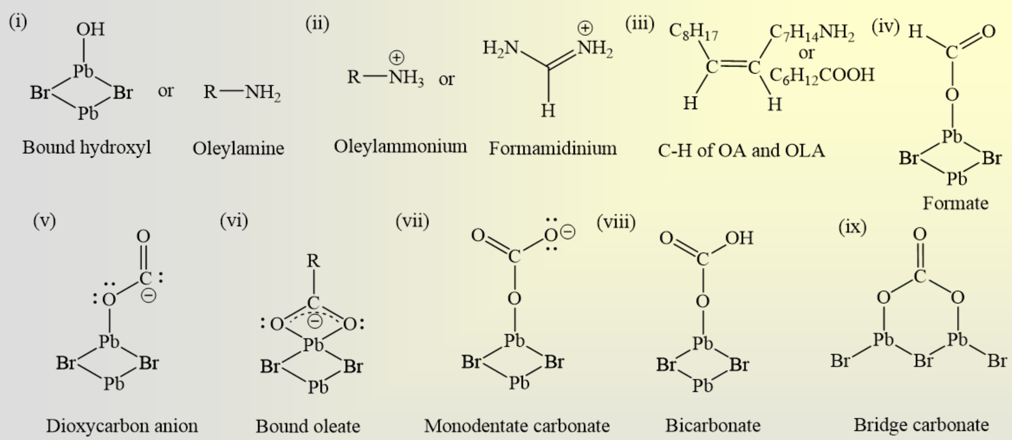
$$\mathrm{H_2O \rightarrow H^+ + OH^-} \qquad \mathrm{H^+ + OH^- \rightarrow H_2O}$$

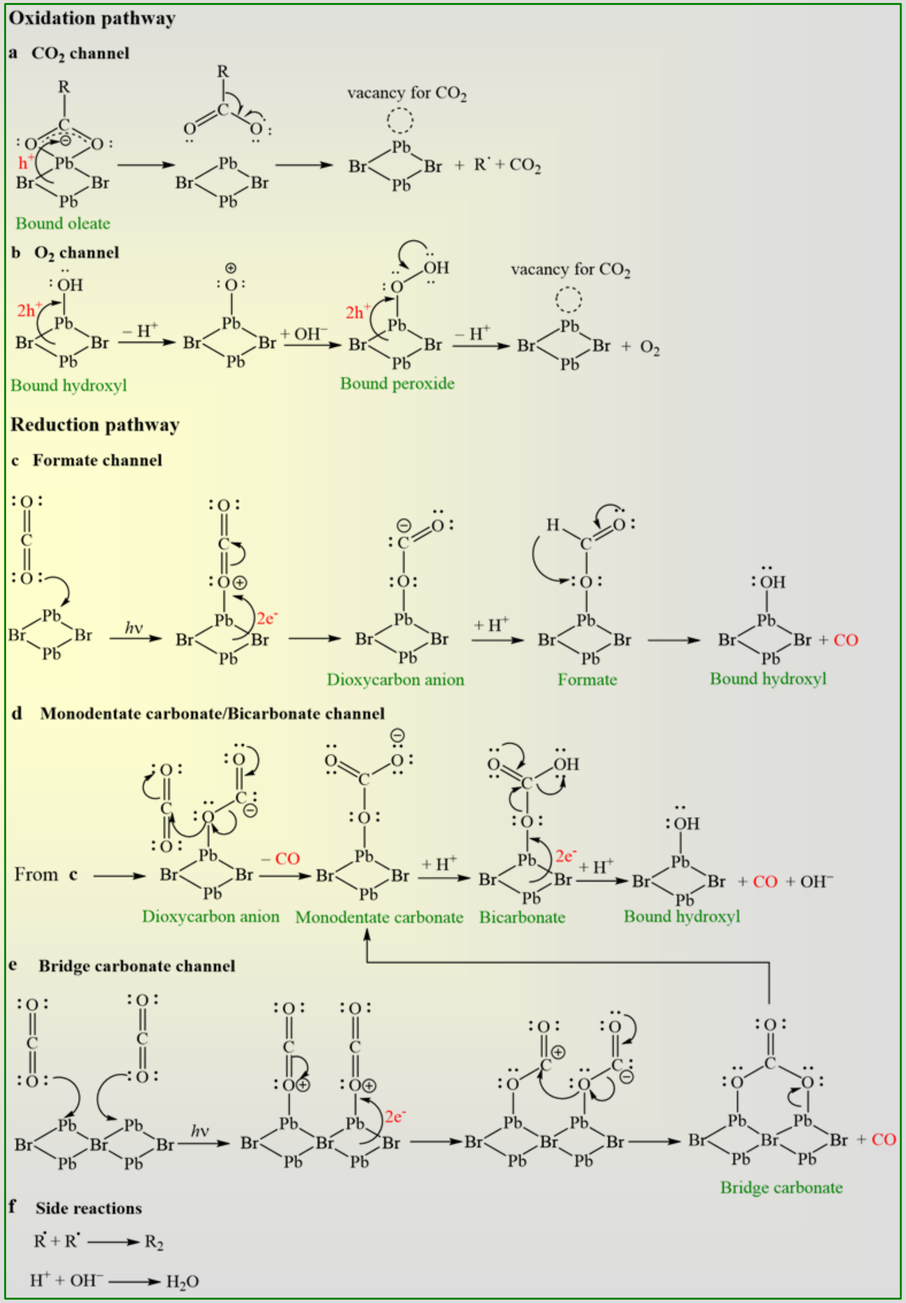
$$Reduction:\ \mathrm{CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^-} \qquad E^0_{red} = -0.934\ V$$

$$Oxidation:\ \mathrm{2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-} \qquad E^0_{ox} = -0.401\ V$$

DRIFT Spectra and Reaction Mechanism







$$\textit{Reduction}: \quad CO_2 + H^+ + 2e^- \rightarrow CO + OH^-$$

$$\textit{Oxidation}: \quad 2OH^- \rightarrow O_2 + 2H^+ + 4e^-$$

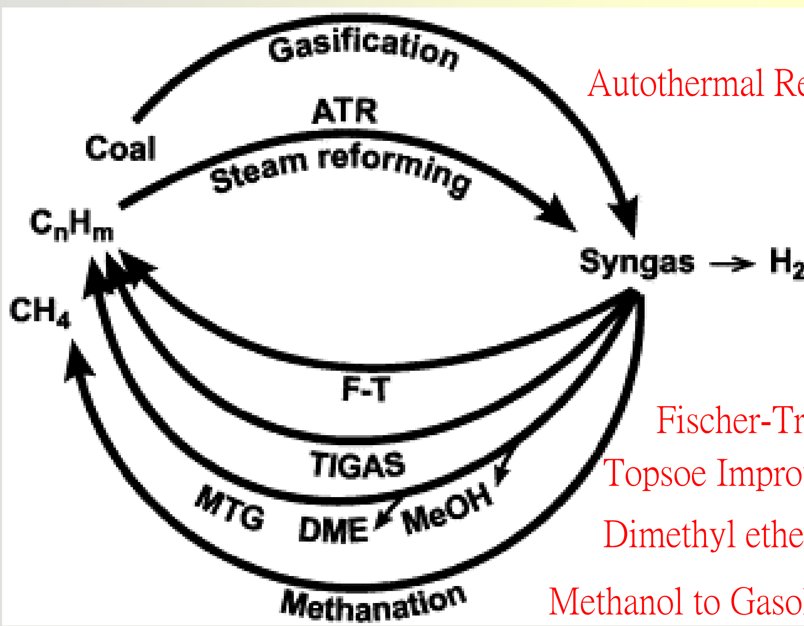
Summary of CO_2 Reduction Results

1. The first example of self-photocatalysis for CO_2 reduction.
2. The first CO_2 splitting using PeNC in the absence of water.
3. World record on CO production yield at gas-solid interface.

Potential Application for CO_2 Reduction to Form CO

Energy Storage Source: Syngas (CO + H_2)

- Syngas is also called as Synthesis gas.
- Syngas is a fuel gas mixture of H_2 + CO (carbon monoxide).
- Syngas is combustible.
- Syngas is an indispensable, critical C_1 feedstock for organic products.
- Demands of syngas is increasing for large scale chemicals.



Autothermal Reformer (ATR)

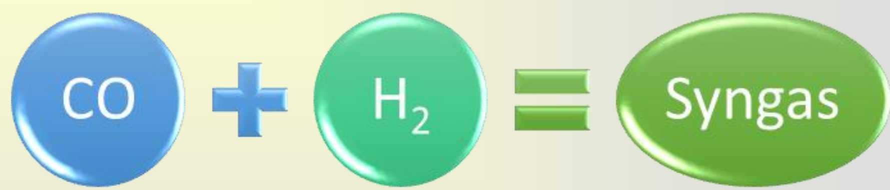
Fischer-Tropsch (F-T)

Topsoe Improved Gasoline Synthesis (TIGAS)

Dimethyl ether (DME)

Methanol to Gasoline (MTG) Process

The syngas cycle.



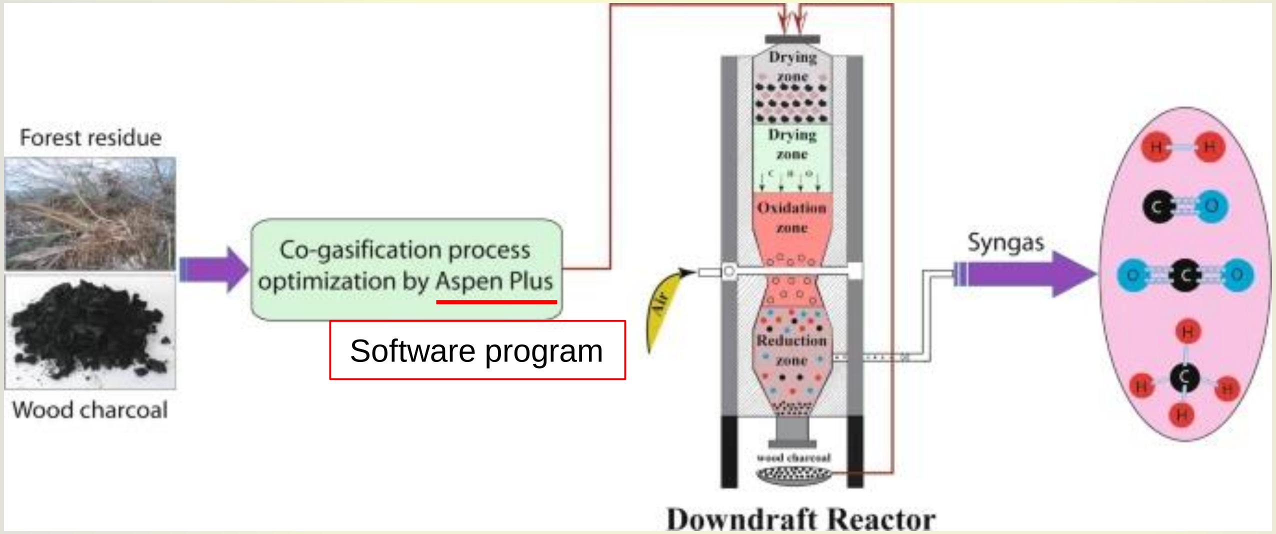
Catalysis Today 71 (2002) 243–247.

Production of Syngas

(1) Gasification of biomass/coal

(2) Methane steam reforming:

- High energy consumption
- Energy intensive process



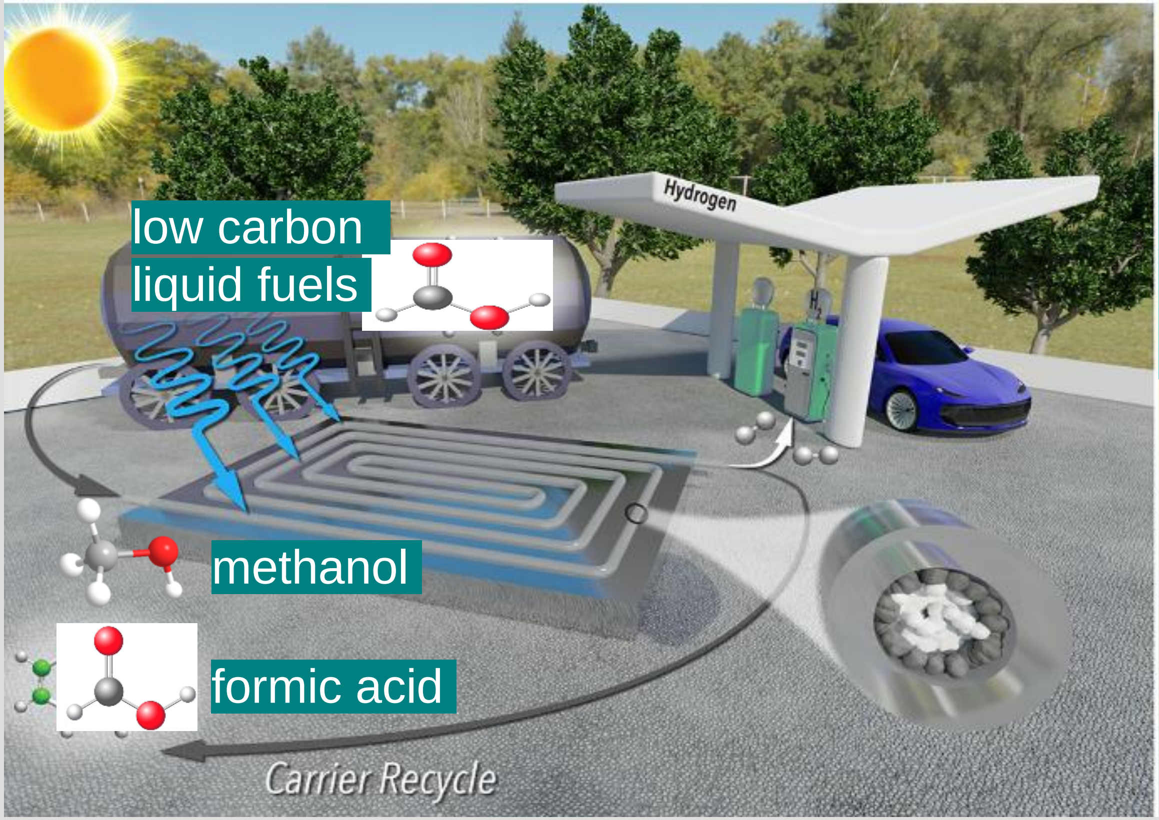
$$C_xH_y + xH_2O \rightarrow xCO + (x+\frac{y}{2})H_2$$
$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

Waste and Biomass Valorization (2020) 11:635–651

Syngas Conversion to Methanol

Methanol (CH_3OH)

1. Primary chemical product.
2. Directly used as a fuel or fuel supplement.
3. Important chemical feedstock for gasoline. ex., ExxonMobil
4. Syngas is major source to obtain methanol.



$$2H_2 + CO \rightarrow CH_3OH$$
$$3H_2 + CO_2 \rightarrow CH_3OH + H_2O$$
$$CO + H_2O \rightarrow CO_2 + H_2$$

(highly exothermic reaction)

Image from
North Carolina State University

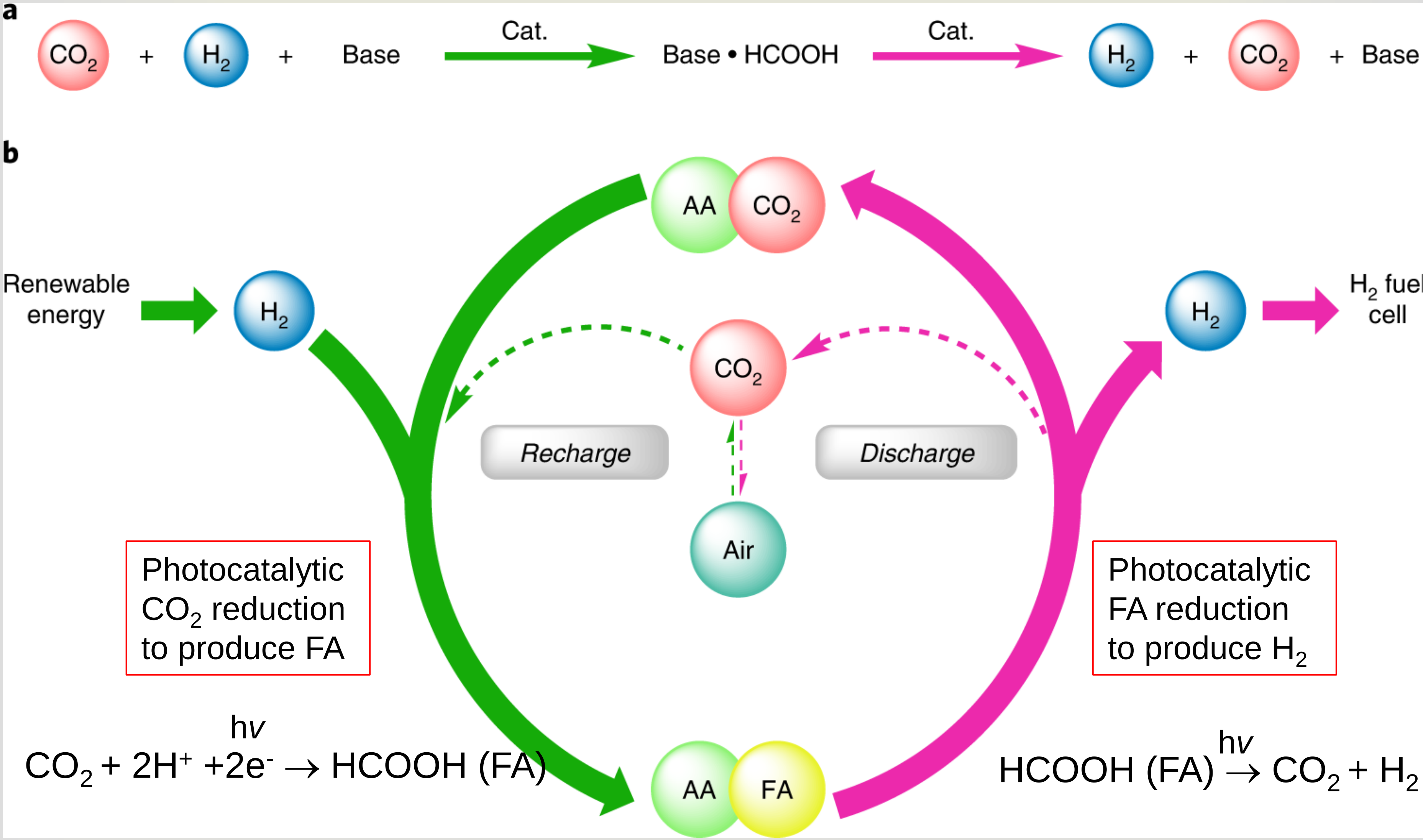
Fischer-Tropsch (F-T) Process

1. German inventors, Franz Fischer and Hans Tropsch -1920.
2. Converting syngas (CO and H_2) into liquid hydrocarbons.
3. Commercial process.
4. Highly exothermic.
5. Important for liquefaction technology.
6. End products controls by catalyst and reactor conditions such as feed, composition, internal temperature and pressure.

$$(2n+1)\ H_2 \quad + \quad n\ CO \quad \rightarrow$$
$$C_n\ H_{(2n+2)} \quad + \quad n\ H_2O$$

- Catalysts considered for Fischer-Tropsch synthesis are based on transition metals of iron, cobalt, nickel and ruthenium.

H_2 Production from Formic Acid Cycle



Nature Energy **2022**, *7*, 438-447.


(C)fuul
Thanks