Photocatalysts

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

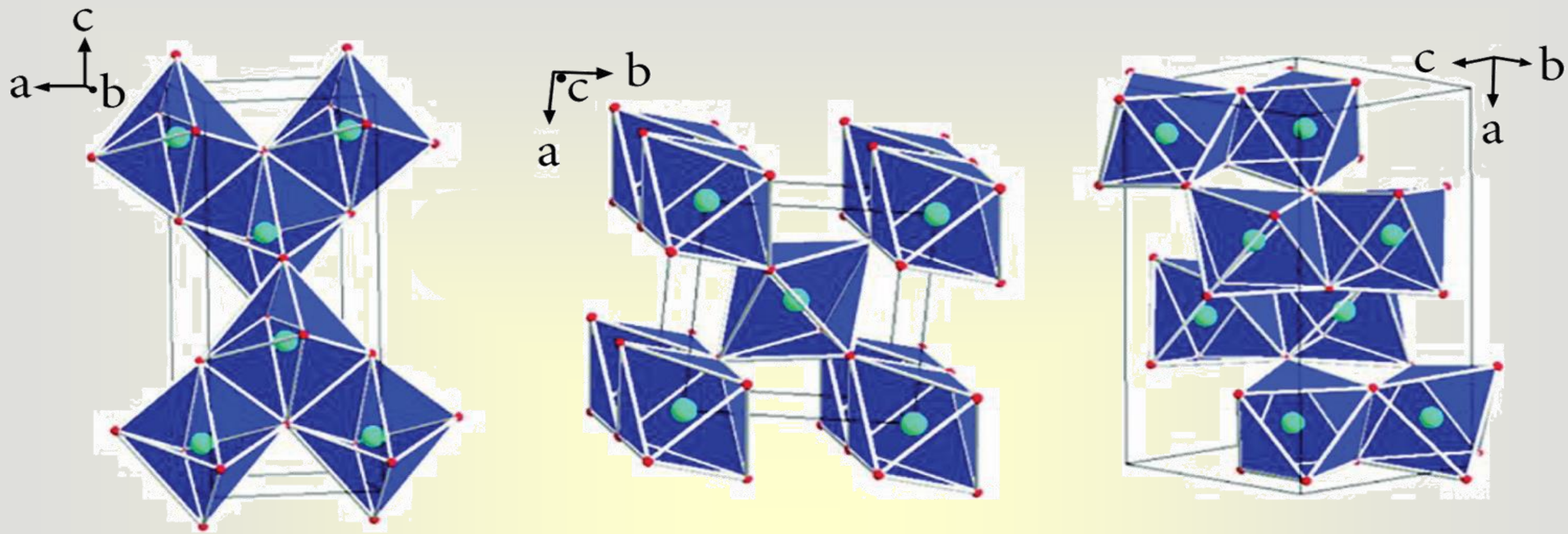
Types of Photocatalysts

Examples:

- Metal oxides (TiO_2, ZnO, $BiVO_4$, Fe_2O_3, CeO_2)
- Metal sulfides (CdS, SnS_2, MoS_2)
- Inorganic perovskite oxides ($CaTiO_3$, $SrTiO_3$, $BiWO_6$)
- Inorganic perovskite halides ($MAPbI_3$, $CsPbI_3$, Cs_2SnI_6, $Cs_3Bi_2I_9$)
- Metal-free 2D materials (g-C_3N_4, GO/rGO, Mxene, Black phosphorus)
- Metal-organic frameworks (MOFs)
- Covalent-organic frameworks (COFs)

Photocatalyst 1
TiO_2

Different Phase Structures of TiO_2



Anatase | Rutile | Brookite

O-2
Ti+4

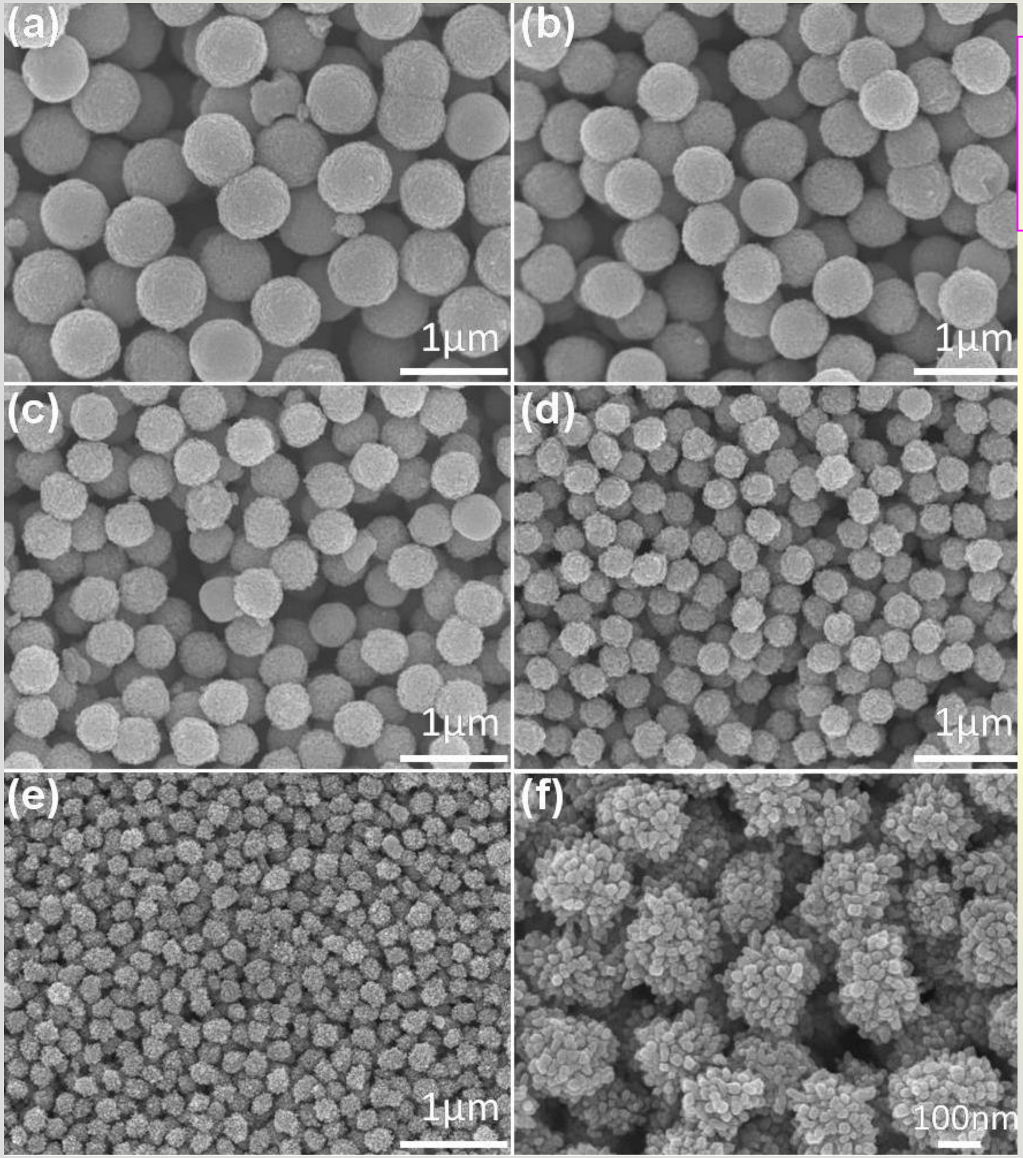
Particle size effect on phase stability of TiO_2.

	Phase	Conditions	Particle size (nm)	Techniques
	Brookite	—	11 to 35	Sol-gel
TiO_2	Anatase	Room temperature	Below 11	Sol-gel
	Rutile	Above 850°C	Higher than 35	Sol-gel

Brookite phase is metastable and difficult to synthesize, so it is seldom studied.

Journal of Nanomaterials, 2018, 2018, ID: 5953609

Sol-gel Synthesis of Rutile DHRS TiO_2



Non-hydrothermal low-T synthesis of Dandelion-like Hierarchical Rutile TiO_2 nano-Spheres (DHRS)

Sol-gel procedure in three simple steps:

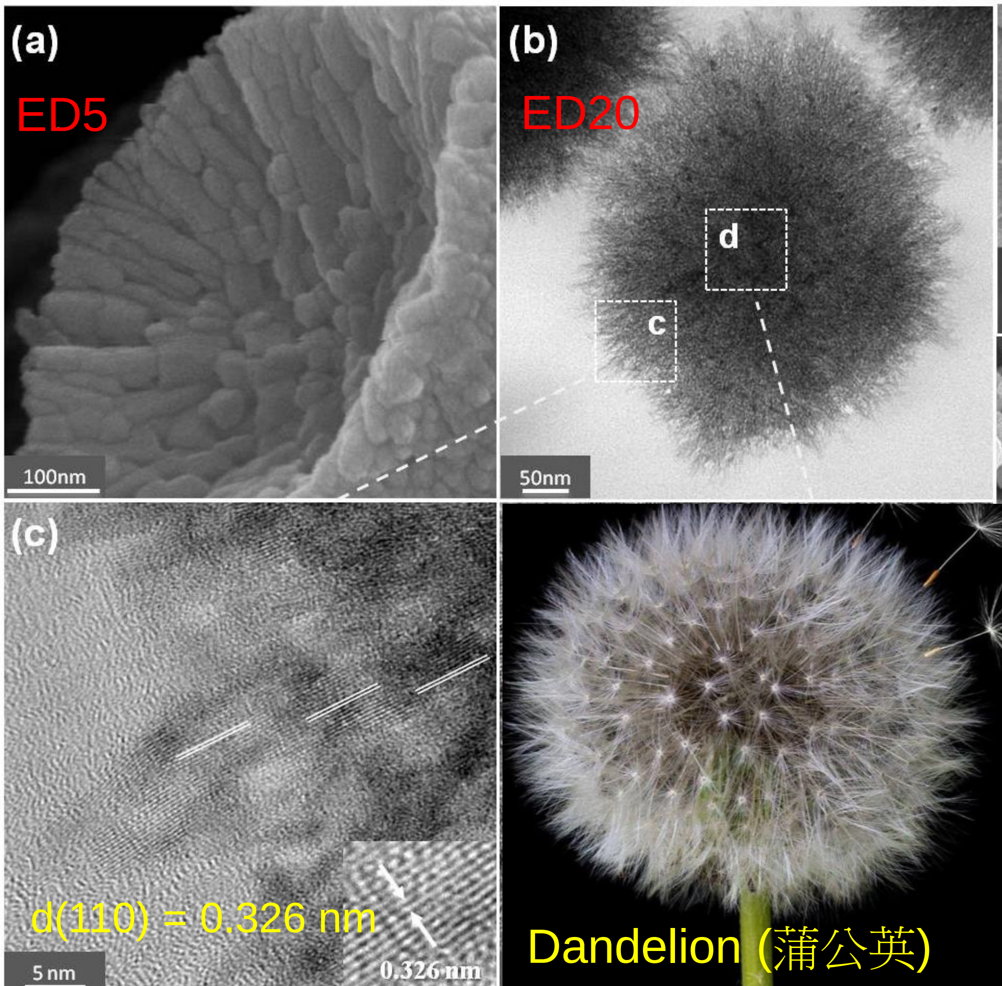
1. 5 ml $TiCl_4$ + 50 ml H_2O at 0 °C for 1h.
2. (1) + 50 ml ED/H_2O at 25 °C for 1h.
3. (2) was heated to 70 °C for 2h.

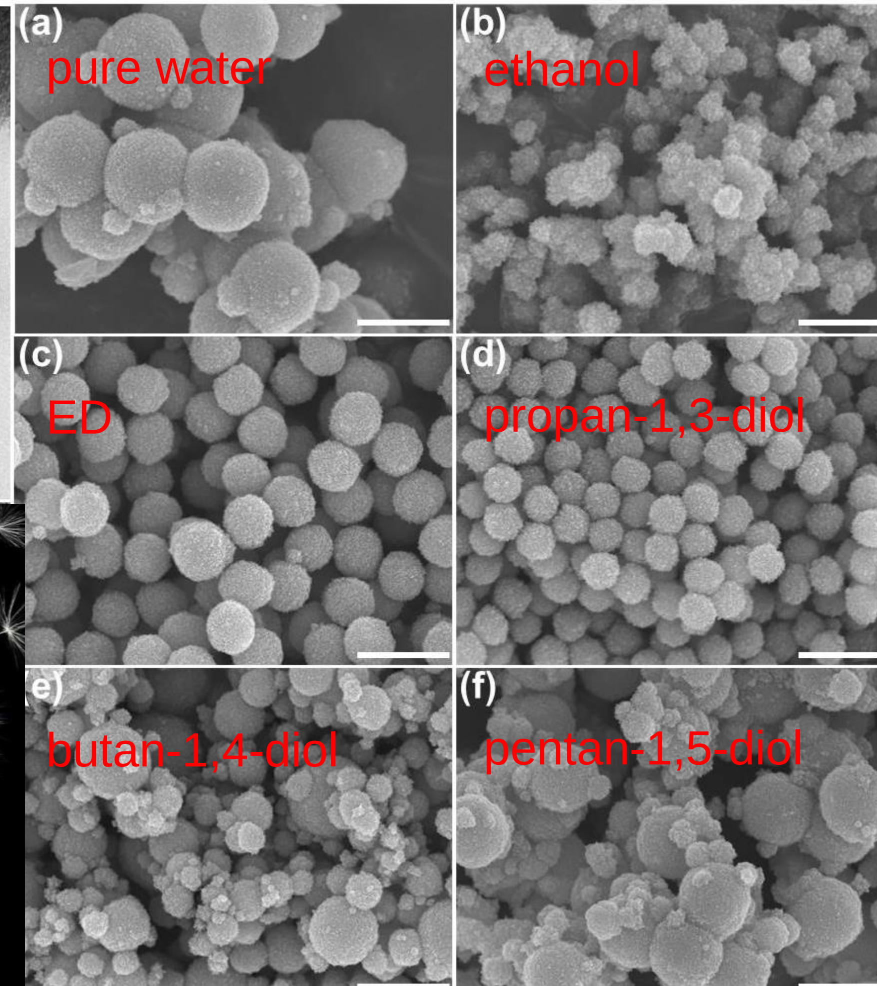
Particle sizes were controlled by the volume ratios of the ED/H_2O mixture:
(a) 5 % (ED5), diameter ~650 nm.
(b) 10 % (ED10), diameter ~550 nm.
(c) 15 % (ED15), diameter ~400 nm.
(d) 20 % (ED20), diameter ~300 nm.
(e) 25 % (ED25), diameter ~200 nm.

ED: 1,2-ethanediol (ethylene glycol)

Diau et al., RSC Adv. **2013**, *3*, 559-565.

Morphology , Crystallinity and Uniformity

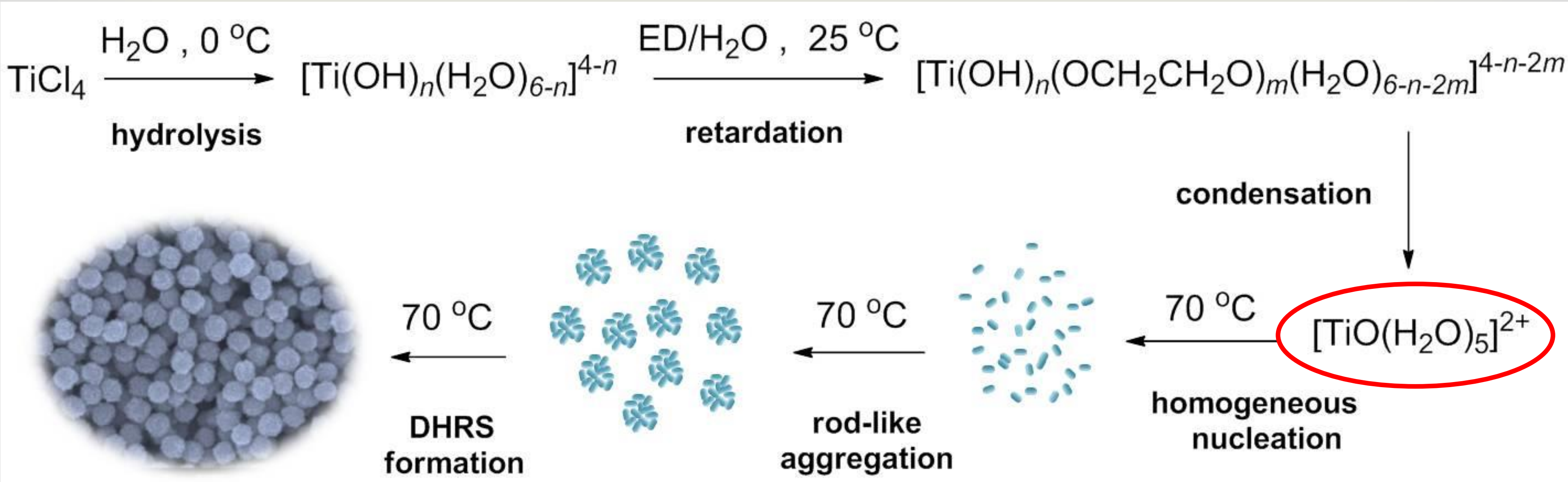


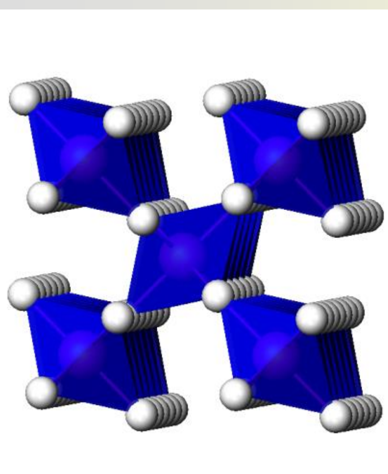


co-solvent/H_2O/$TiCl_4$ = 10/90/5

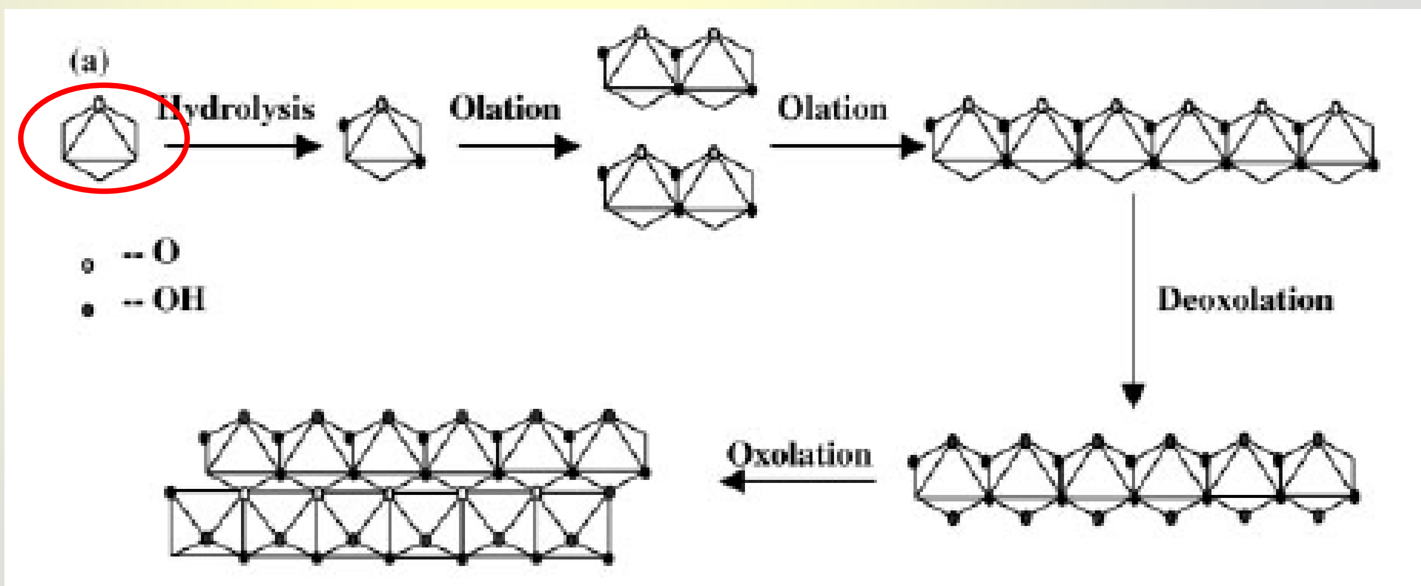
Diau et al., RSC Adv. **2013**, *3*, 559-565.

Mechanism for Formation of DHRS



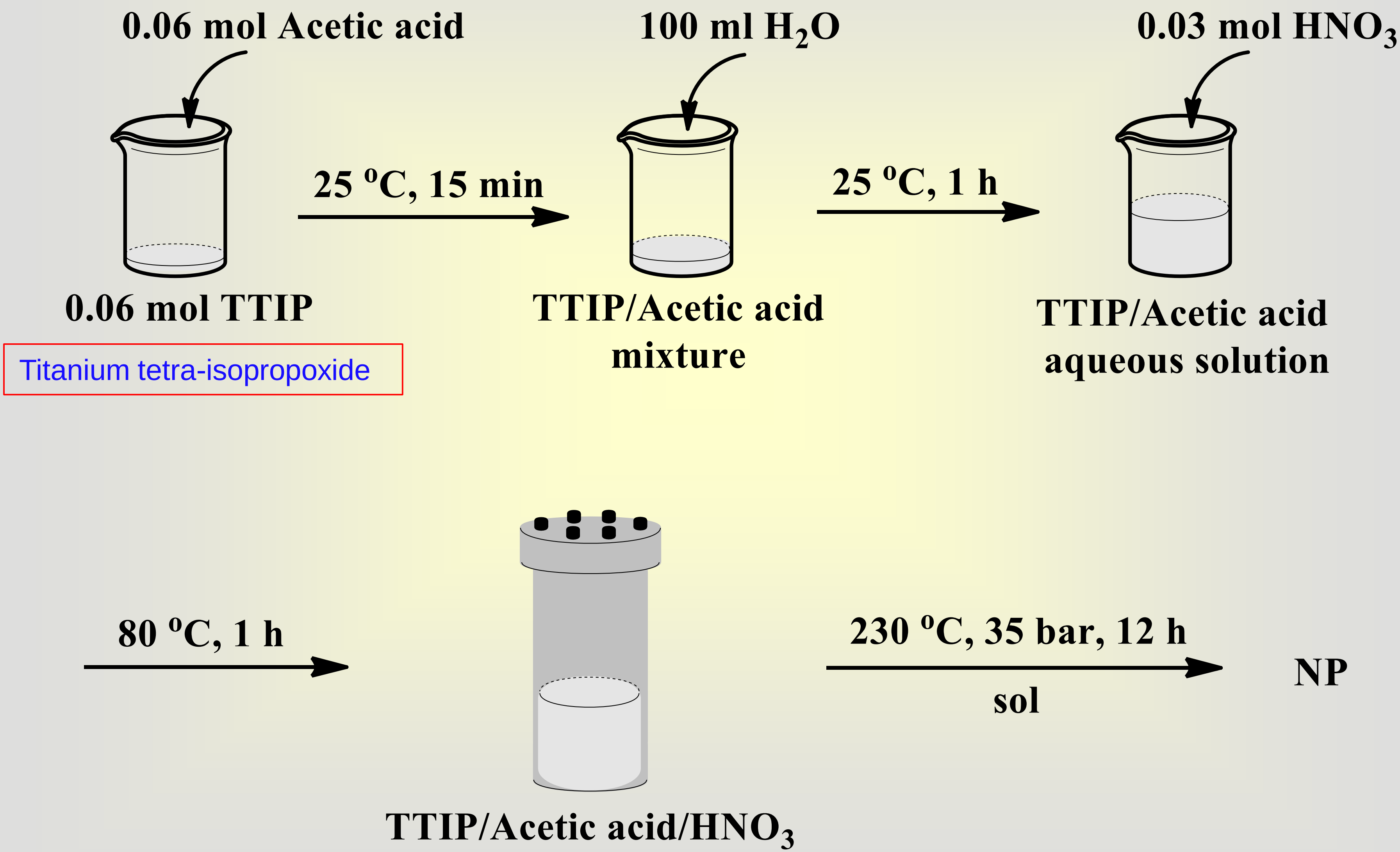


Rutile TiO_2



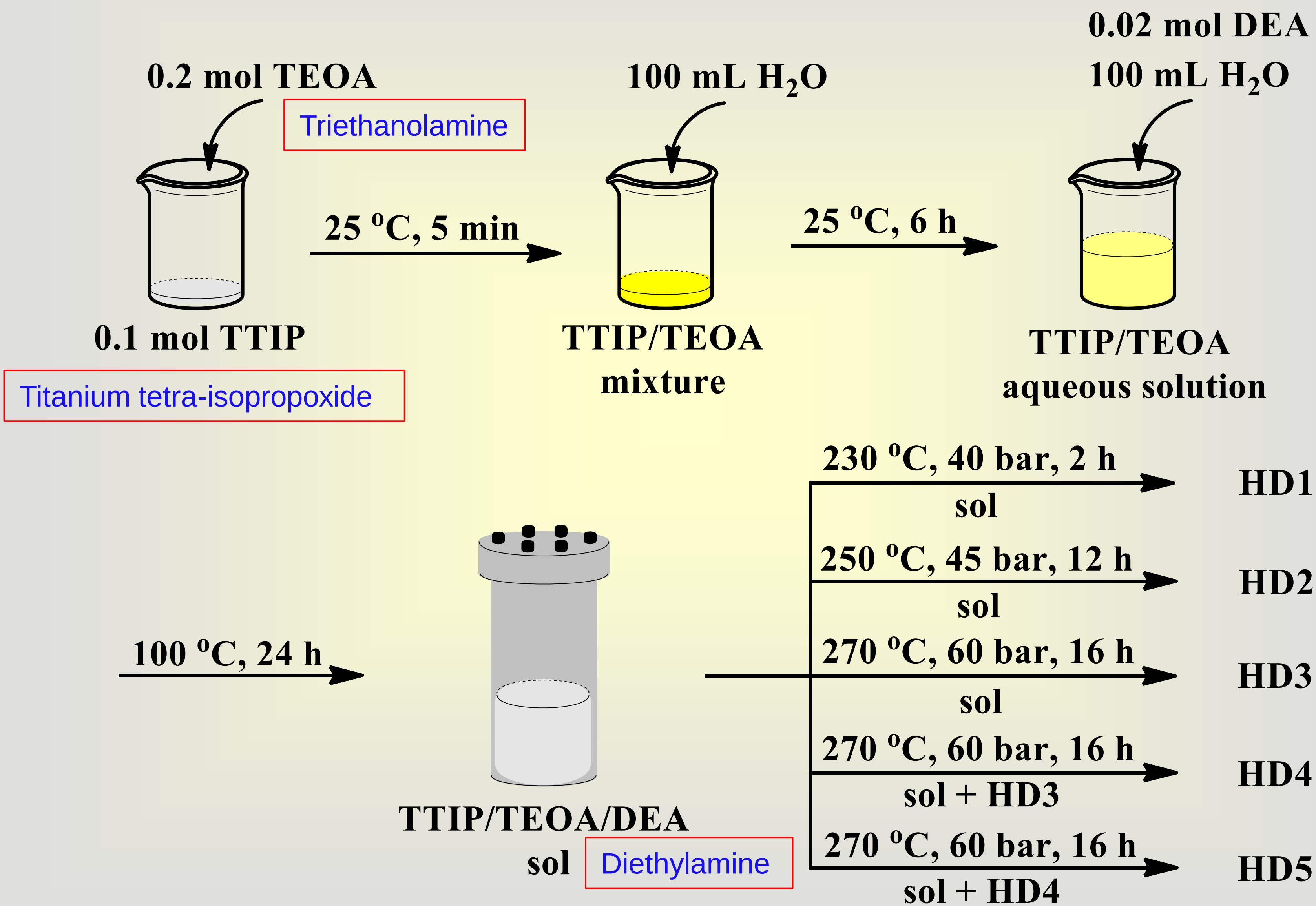
Zheng et al. *J. Mater. Chem.* **2001**, *11*, 1547.

Hydrothermal Synthesis of TiO_2 Nanoparticles (NP)



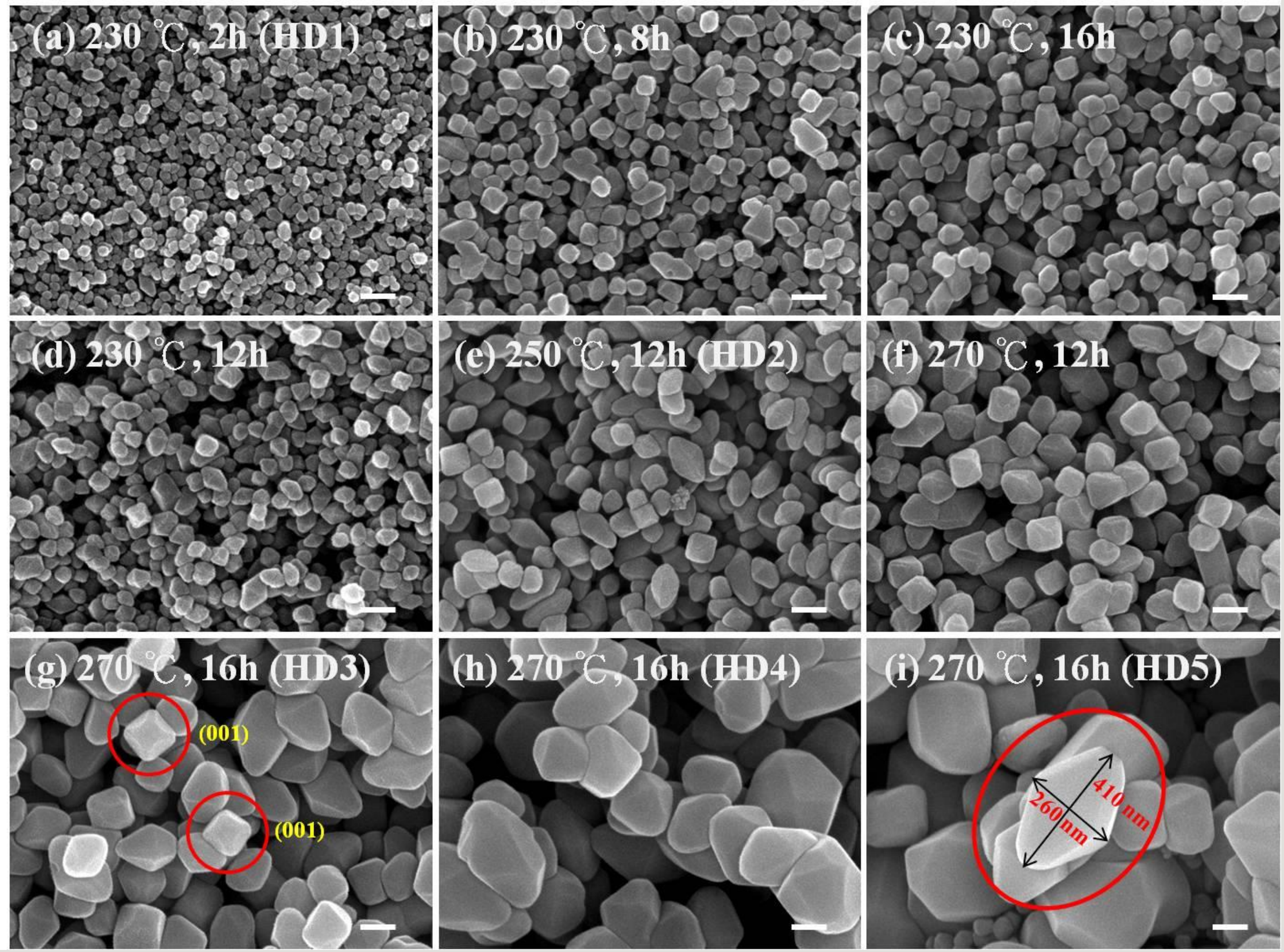
Grätzel et al., Thin Solid Films, **2008**, *516*, 4613.

Formation of Octahedral TiO_2 Nanocrystals



Diau et al., *ACS Nano* **2012**, *6*, 10862-10873.

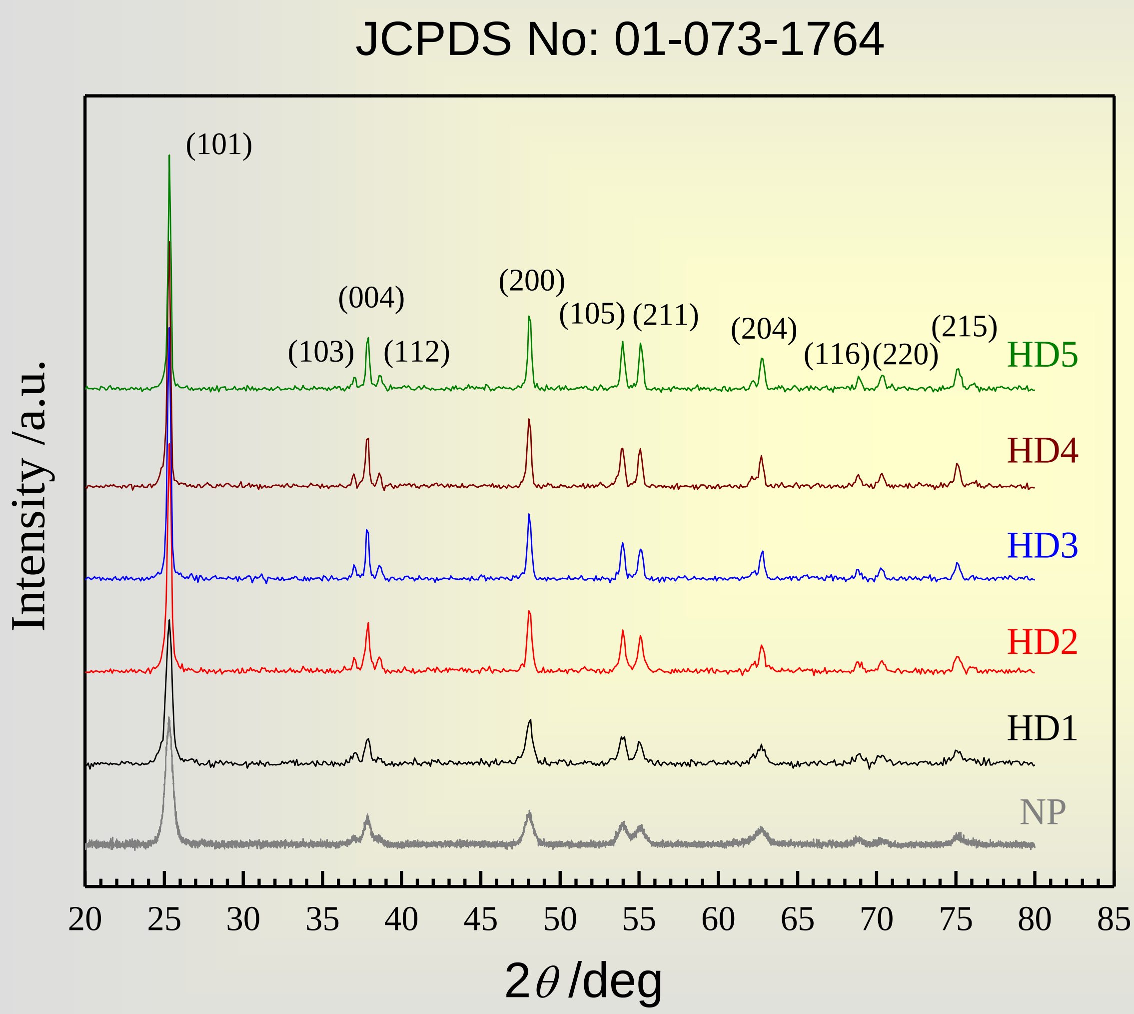
Size and Morphological Control

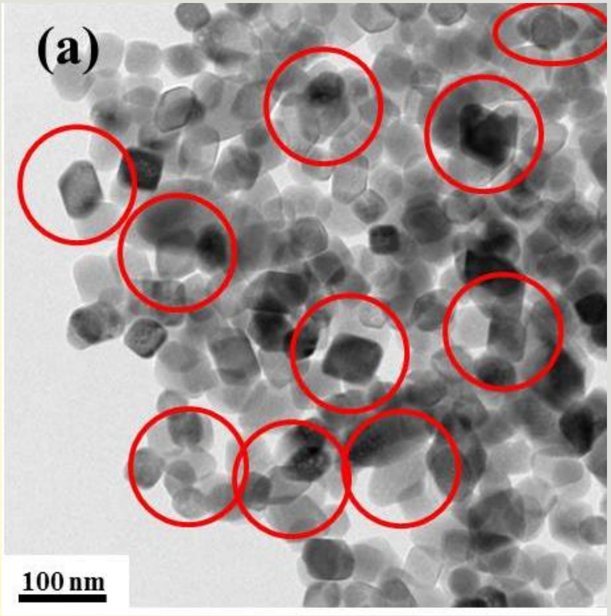


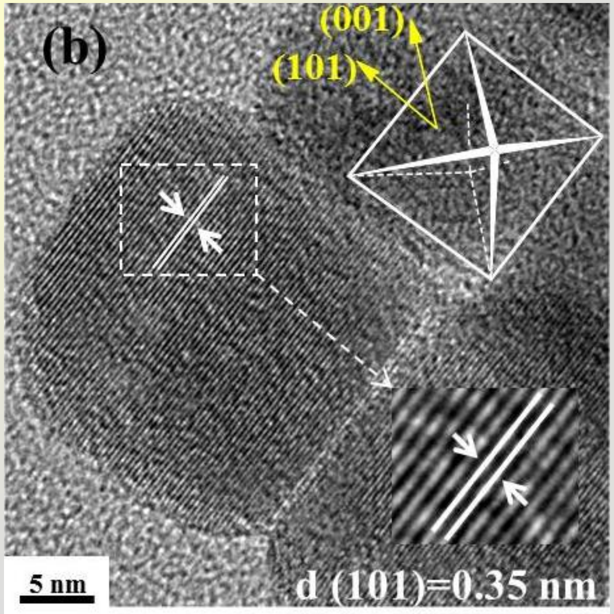
Diau et al., *ACS Nano* **2012**, *6*, 10862-10873.

scale bar = 100 nm

Crystallinity: XRD and TEM

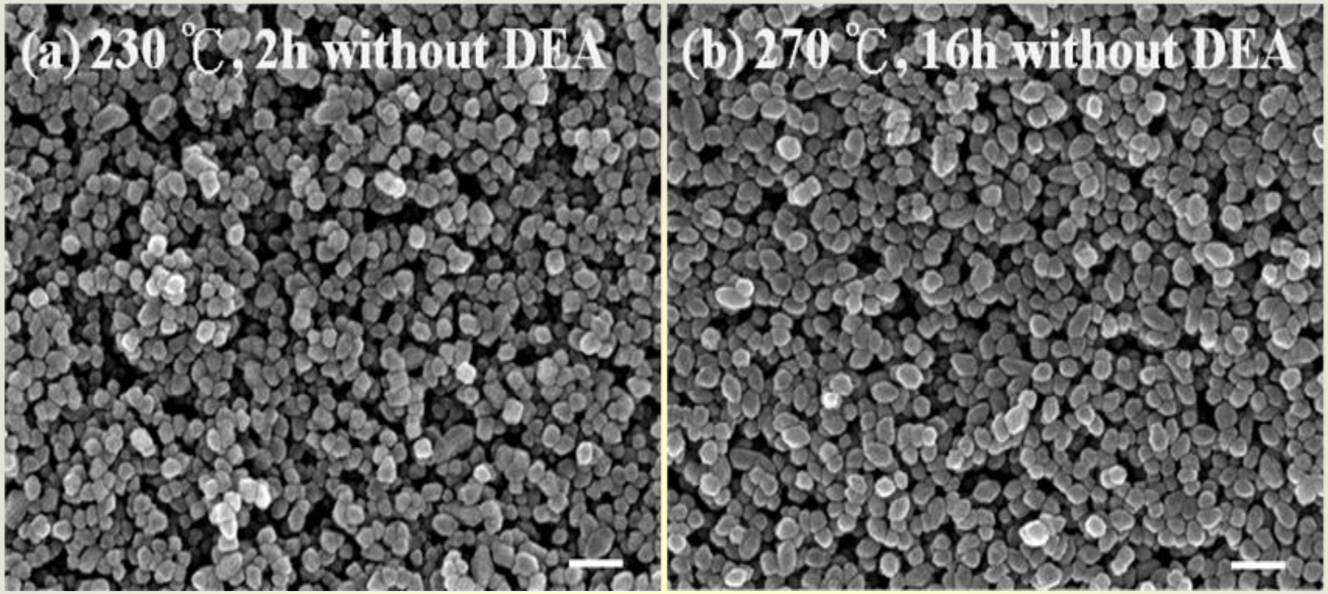


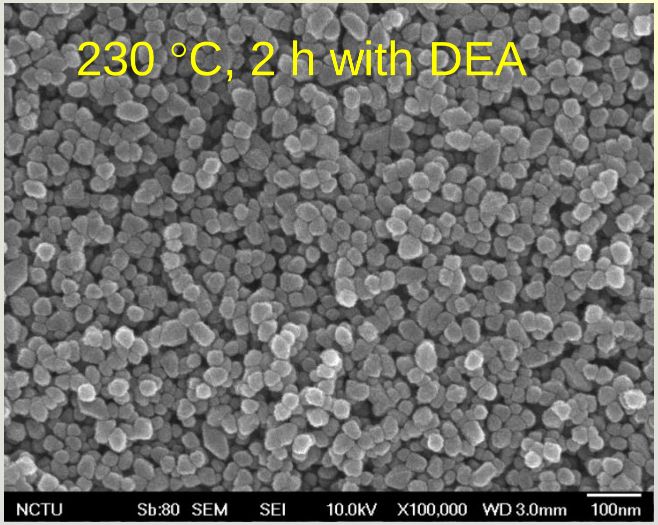


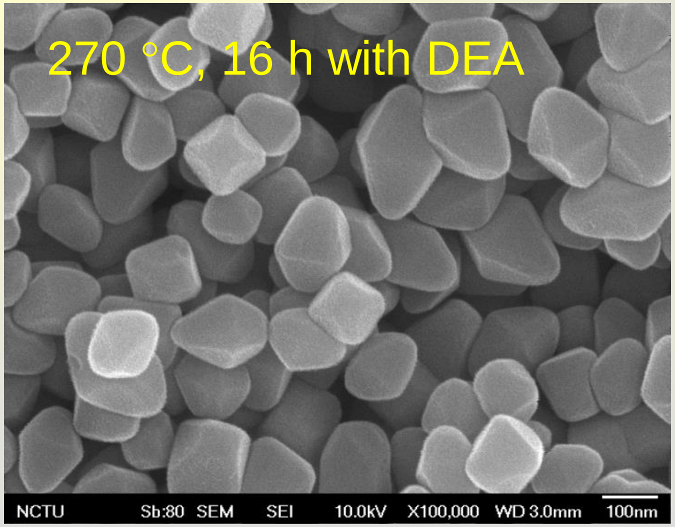


Diau et al., *ACS Nano* **2012**, *6*, 10862-10873.

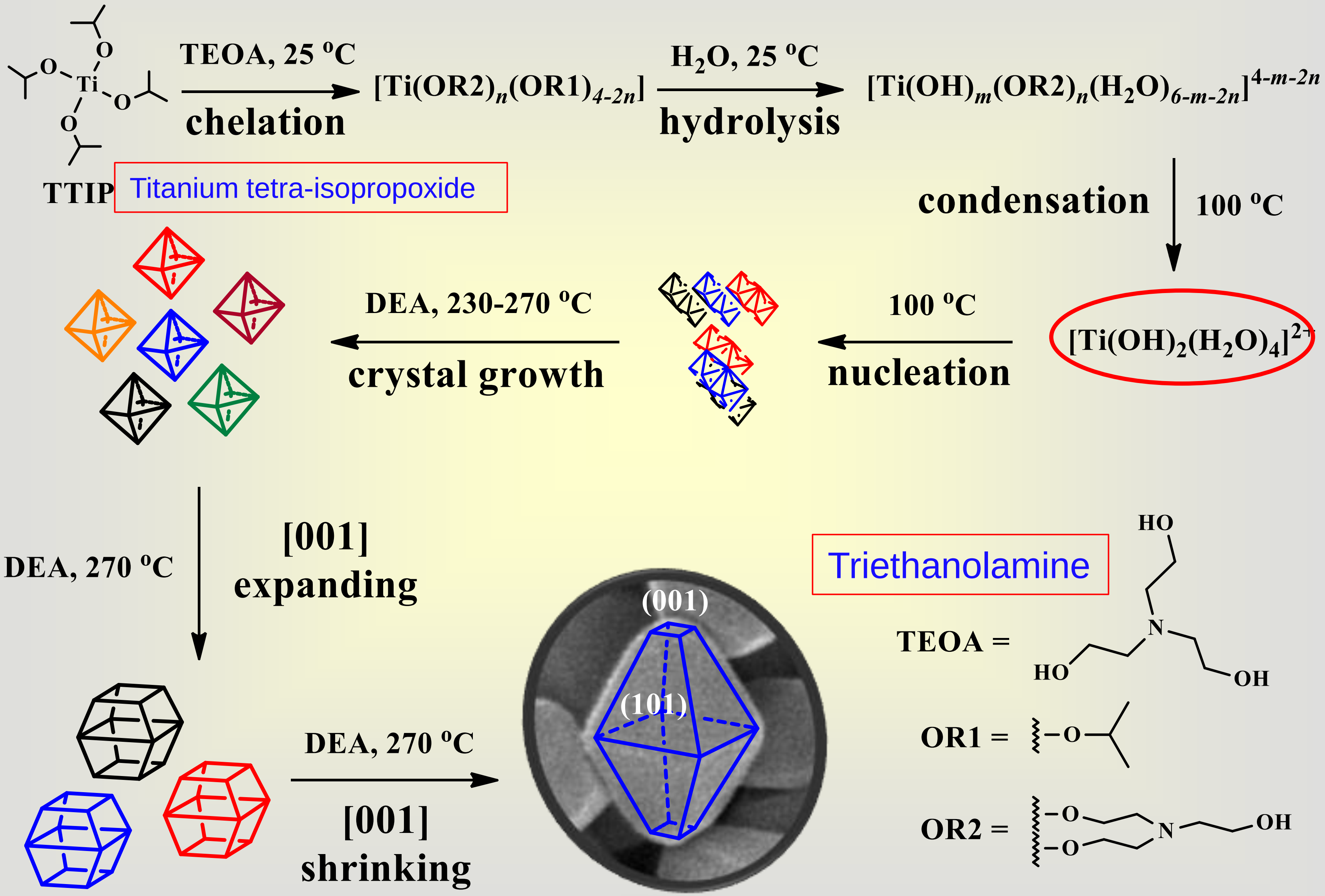
The Role of Diethylamine (DEA)





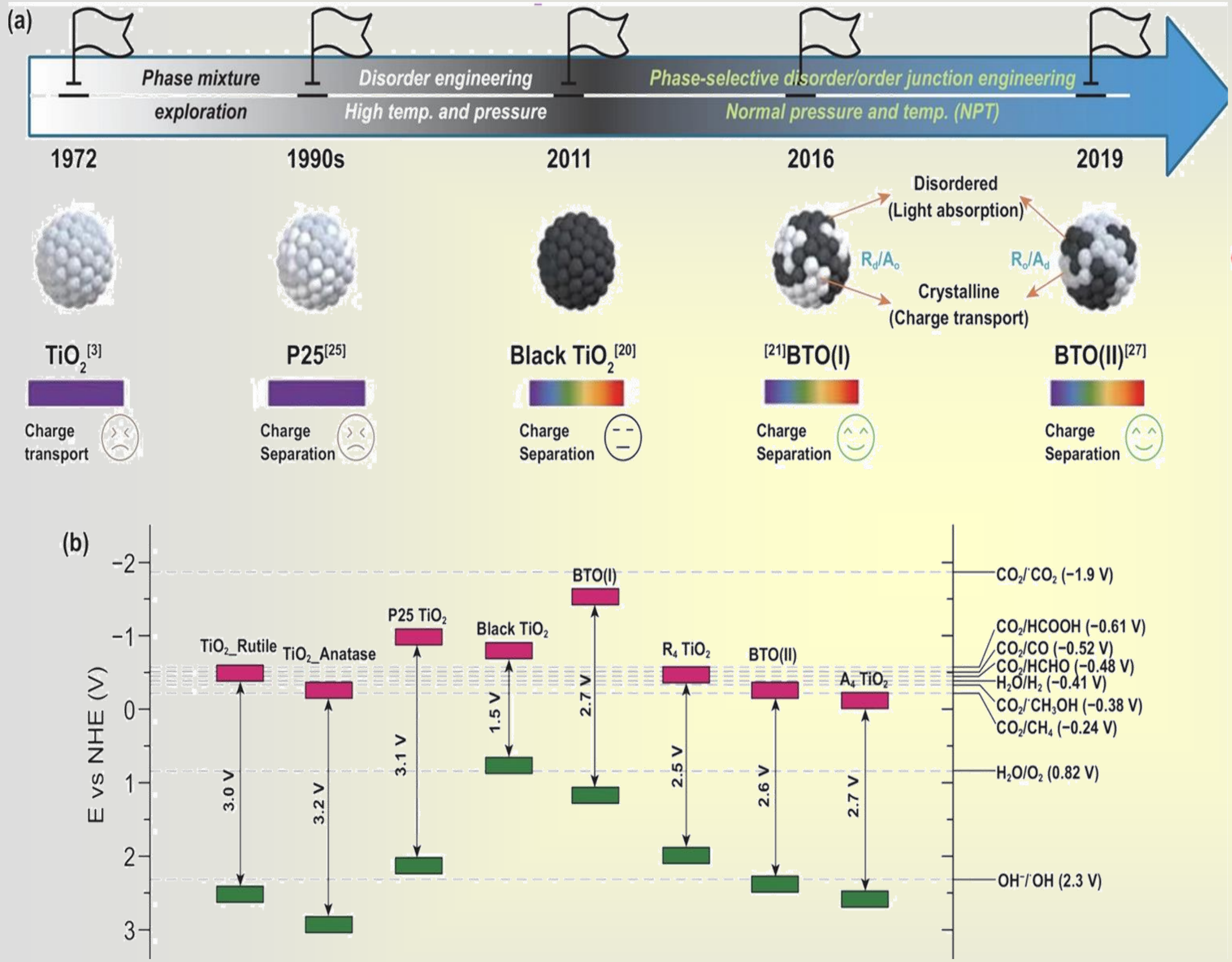


Mechanism for Formation of HD1-HD5

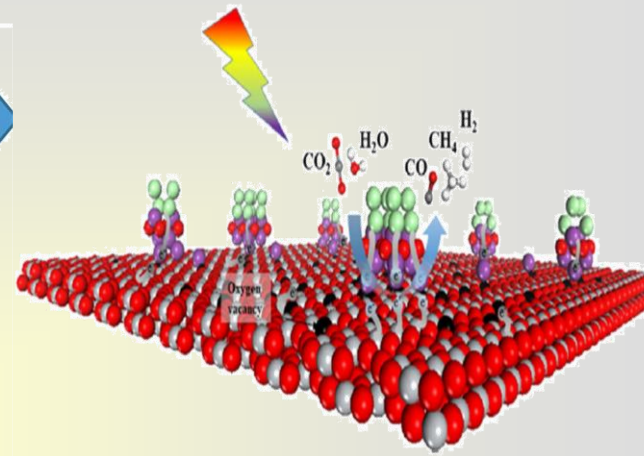


Diau et al., *ACS Nano* **2012**, *6*, 10862-10873.

Progress of TiO_2 NP Development



a) Milestones in TiO_2 material development, and b) the corresponding band structure of each typical TiO_2 configuration.



Advantages

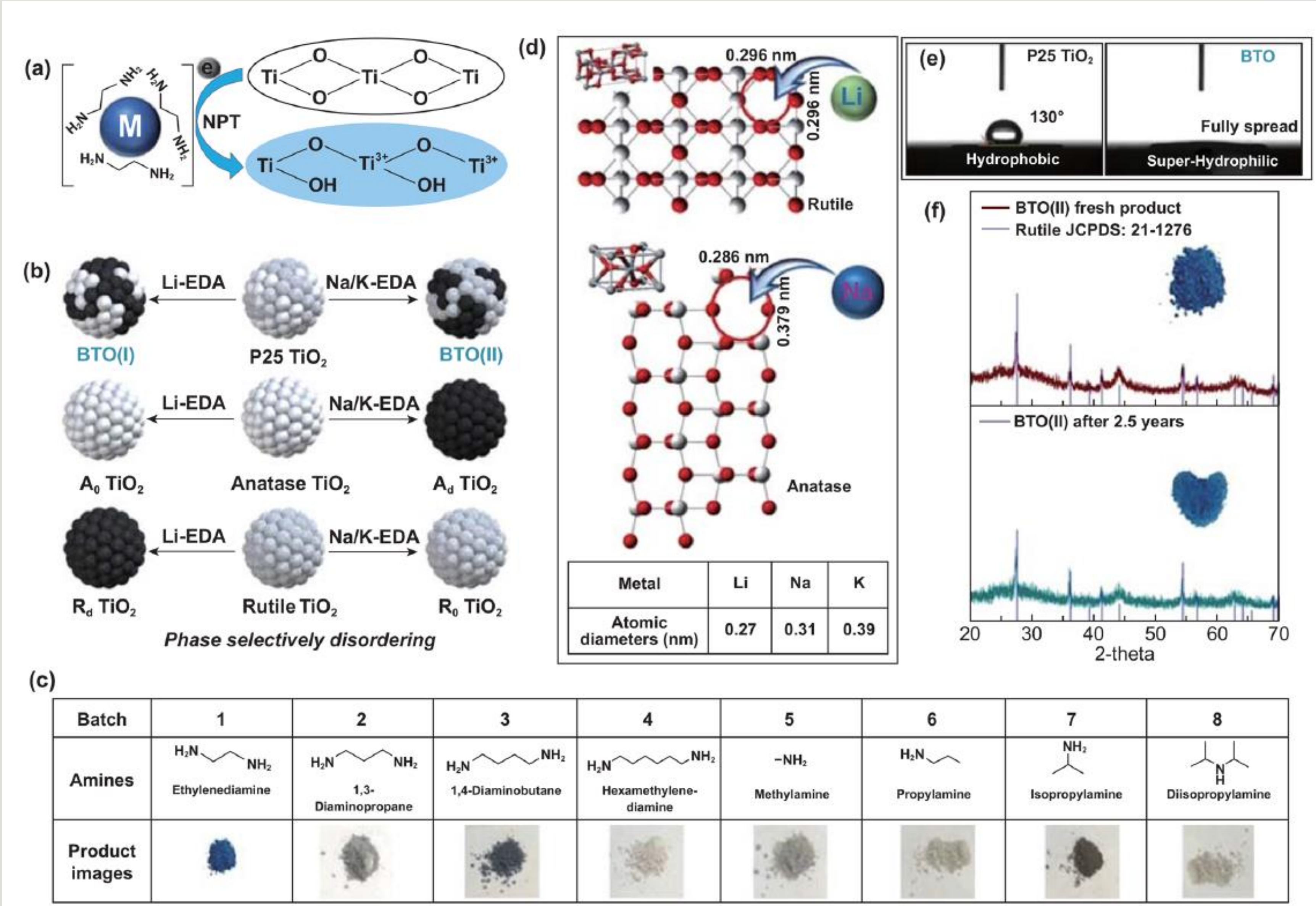
- Nontoxicity
- Low price
- High stability
- Extraordinary photocatalytic performance in ultraviolet region

Limitation

- Large band gap (around 3.2 eV)
- Low light absorption range

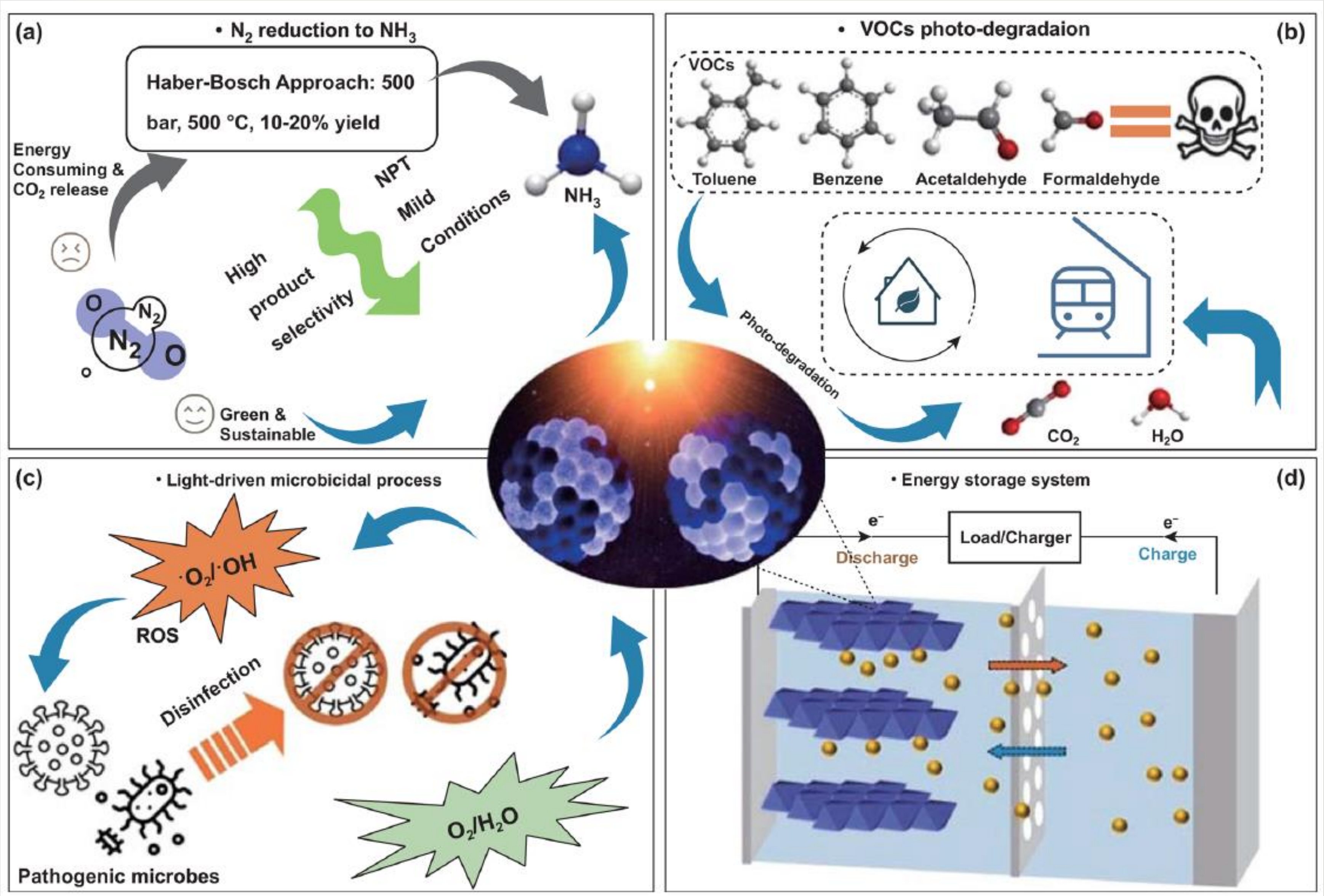
Nano-Micro Lett. 13 (1), 2021, 13-45

Synthesis of BTO using M-EDA



Nano-Micro Lett. 13 (1), 2021, 13-45

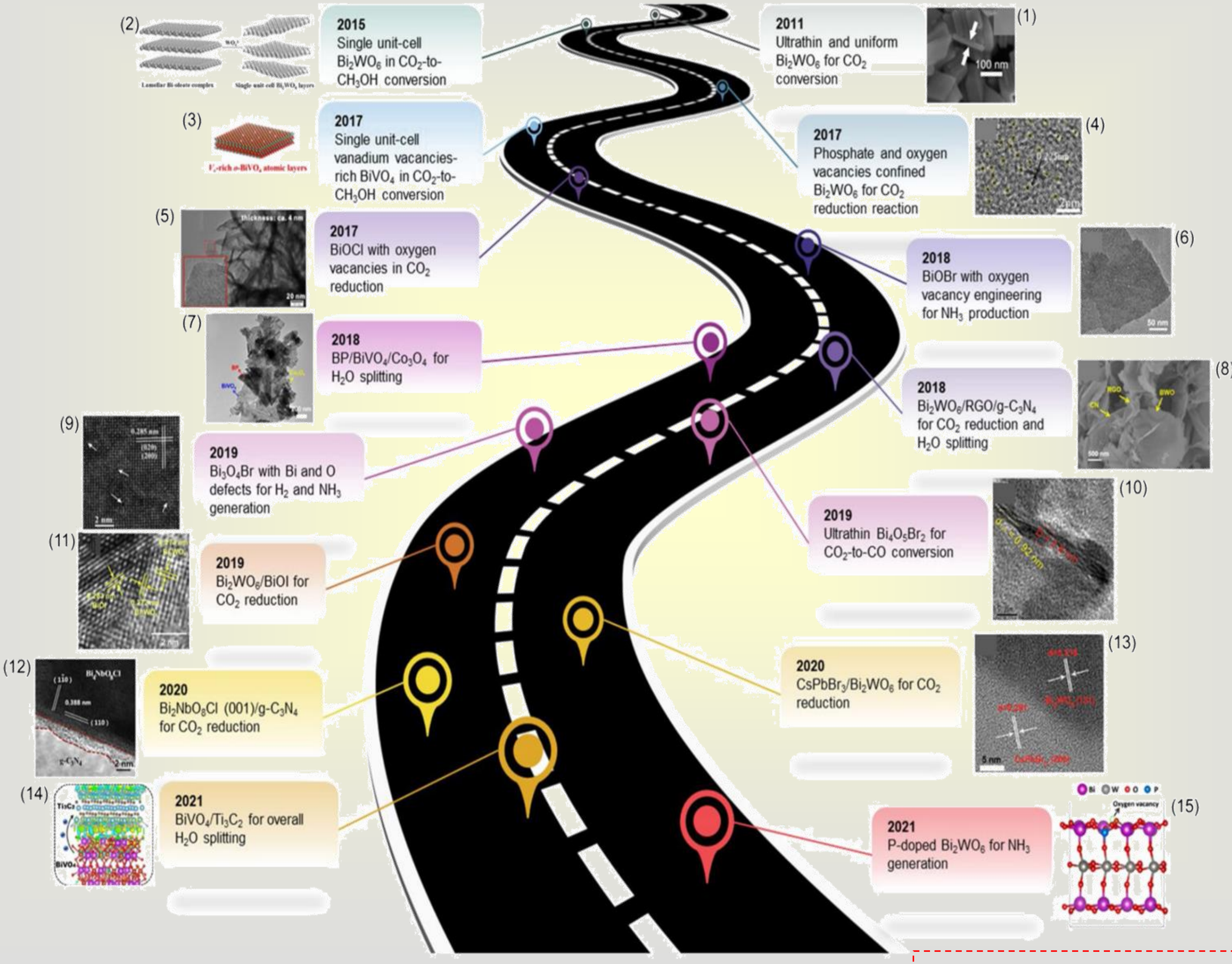
Potential Applications of BTO



Nano-Micro Lett. 13 (1), 2021, 13-45

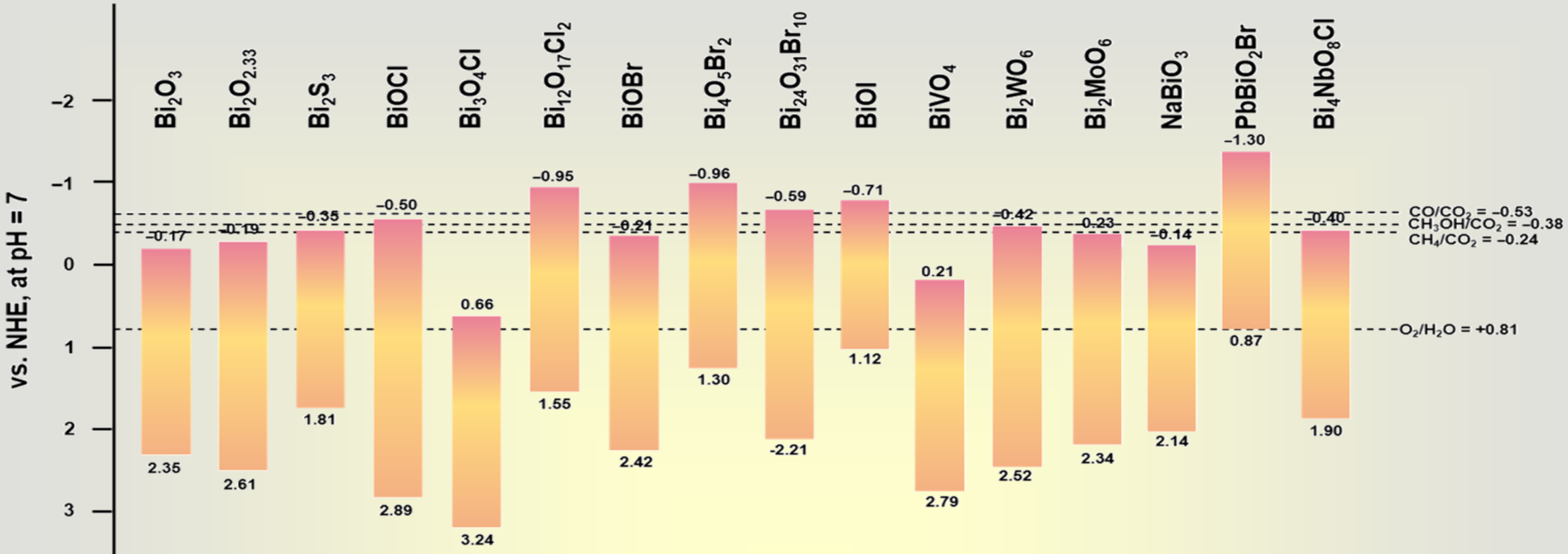
Photocatalyst 2
2D Bismuth Materials

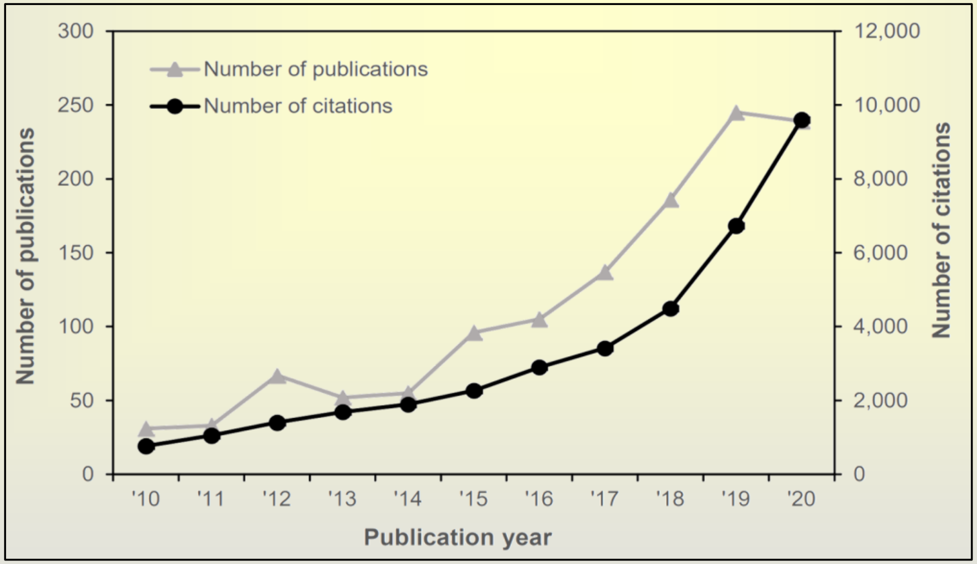
2D Bismuth-based Photocatalysts



Nano Research, 2022, 261

The Band position of the Bismuth-based Photocatalyst



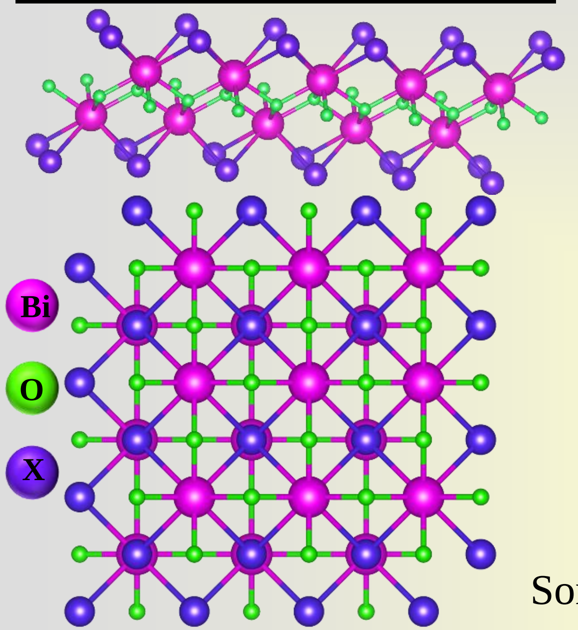


Number of publications reported from 2010 to 2020, sourced from Web of Science database with the topic keyword "2D Bismuth" on 19th October 2021.

Nano Research, 2022, 261

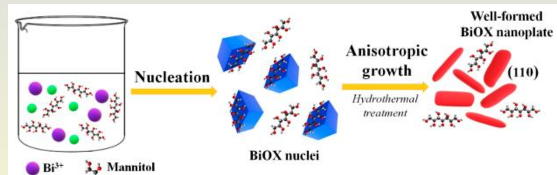
BiOX (X = Br, I) for CO_2 reduction

Crystal Structure

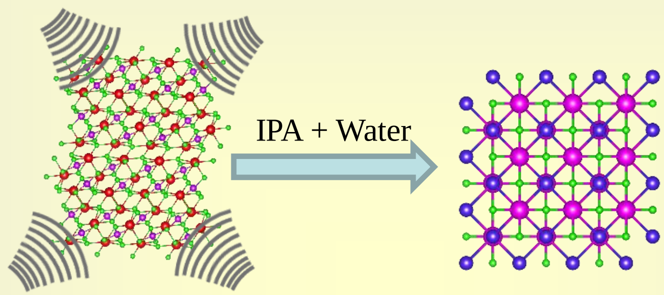


Tetragonal structure

Synthesis



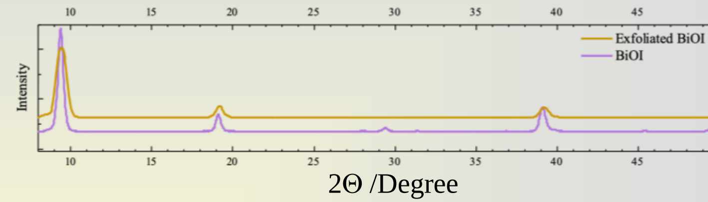
Catalysts **2021**, *11*(3), 312

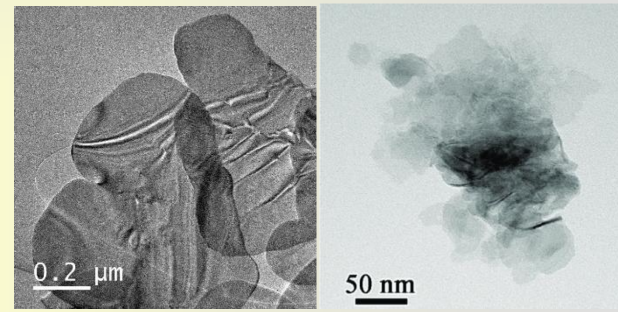


Sonicated $Rb_3Bi_2I_9$

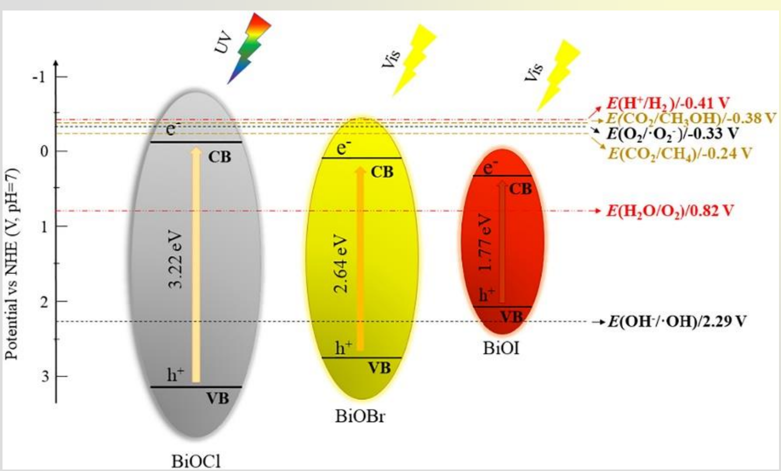
Our work

TEM and XRD

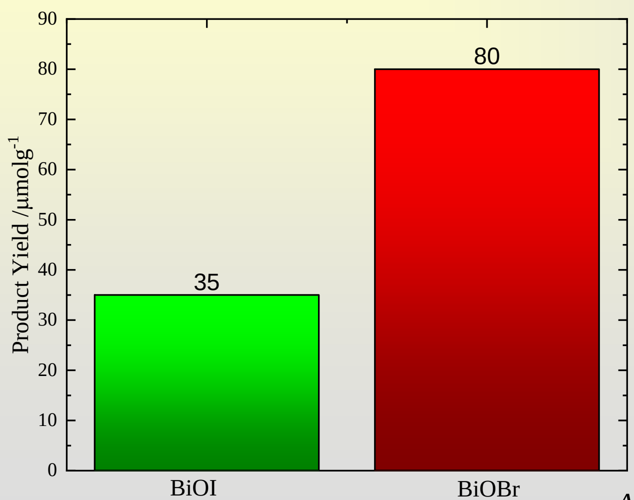


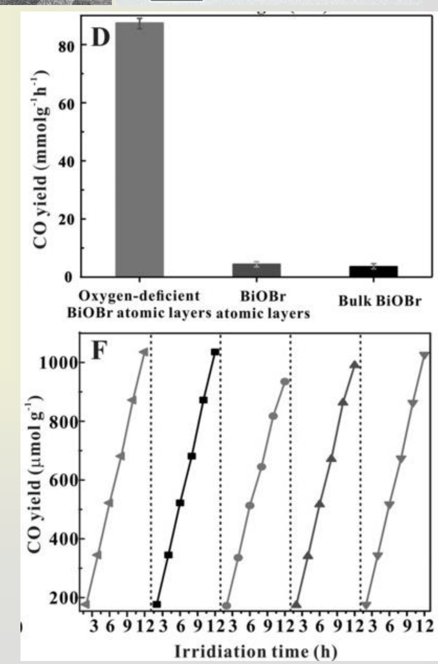


Photocatalytic CO2 reduction



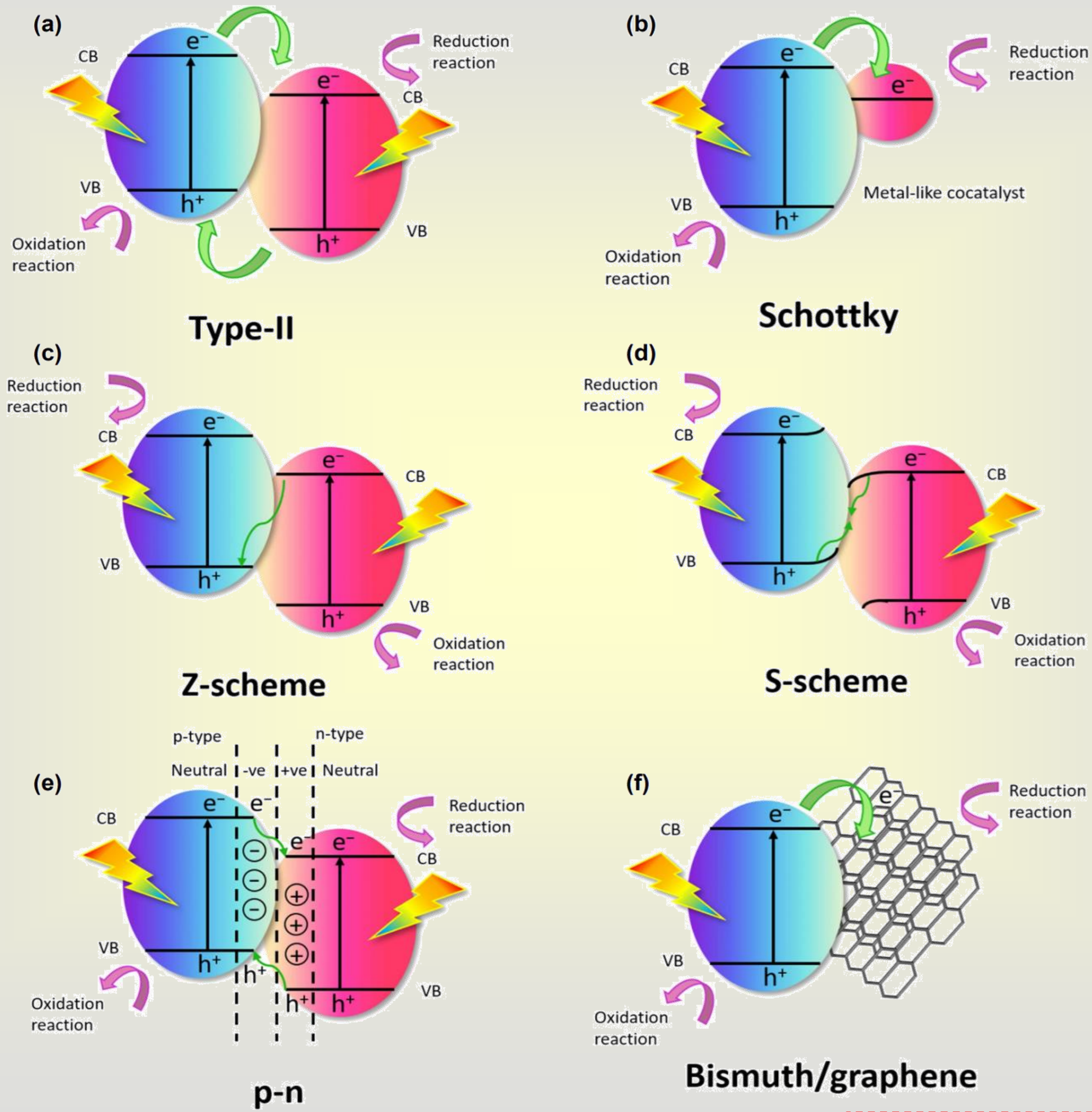
Advances in Colloid and Interface Science ***2018***, 254, 76–93





Angew.Chem.Int.Ed. **2018**,57,8719–8723

2D Bismuth-based Heterojunctions



Nano Research, 2022, 261.

Photocatalyst 3
Perovskite

What is Perovskite? – History

❑Introduction

- The mineral discovered in the Ural Mountains of Russia by Gustav Rose in 1839.
- Named after the Russian nobleman and mineralogist Lev Alekseyevich Perovski.
- Perovskite's crystal structure was first described by Victor Goldschmidt in 1926.
- Historically, oxide-based perovskites have been mostly studied.

Ex: $CaTiO_3$, $BaTiO_3$, $PbTiO_3$, $SrTiO_3$, $BiFeO_3$, etc.,.

Ex. Calcium titanate ($CaTiO_3$)

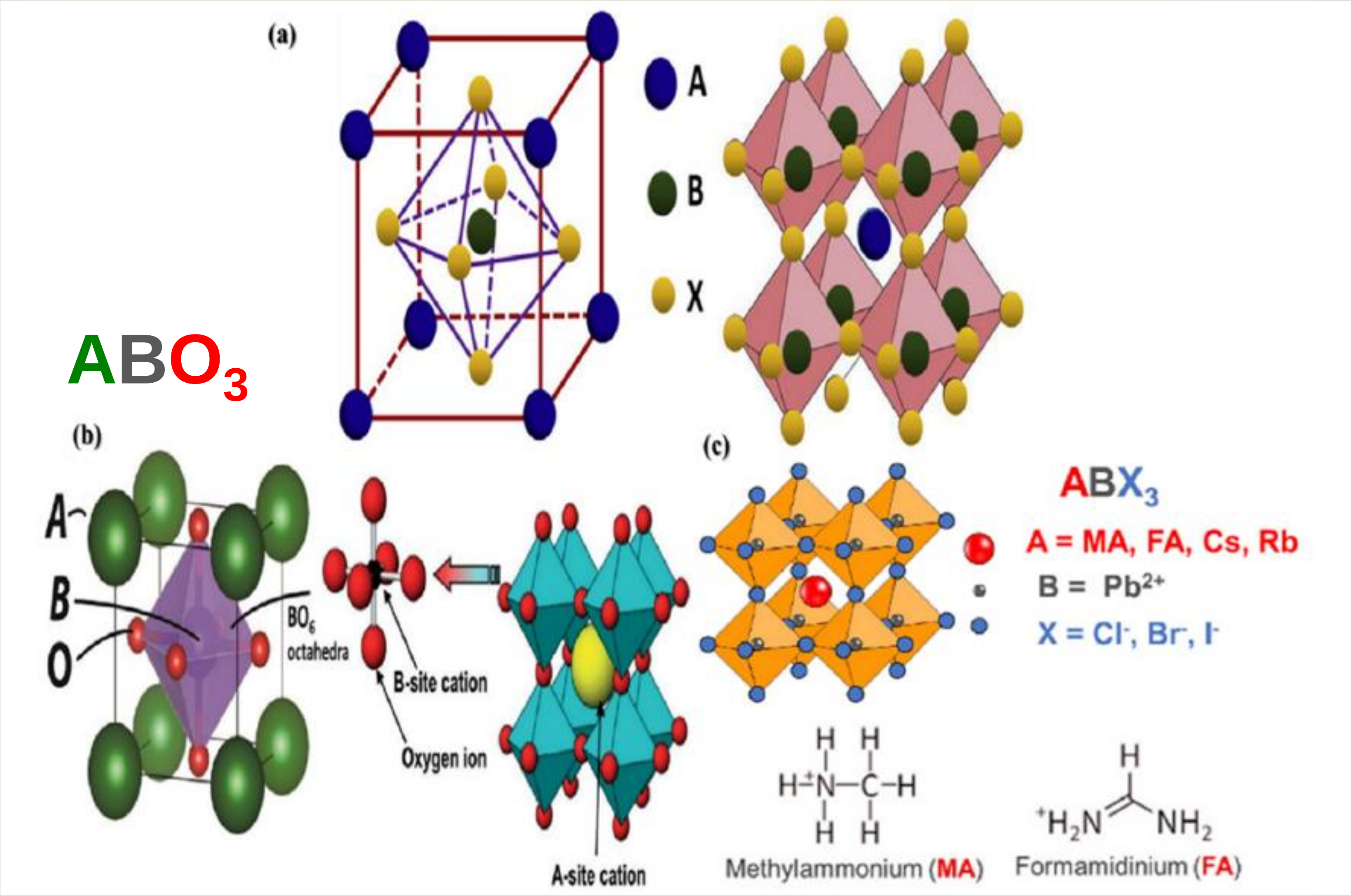
Gustav Rose (German mineralogist)

Lev Alekseyevich Perovski (Russian mineralogist)

Source: google image

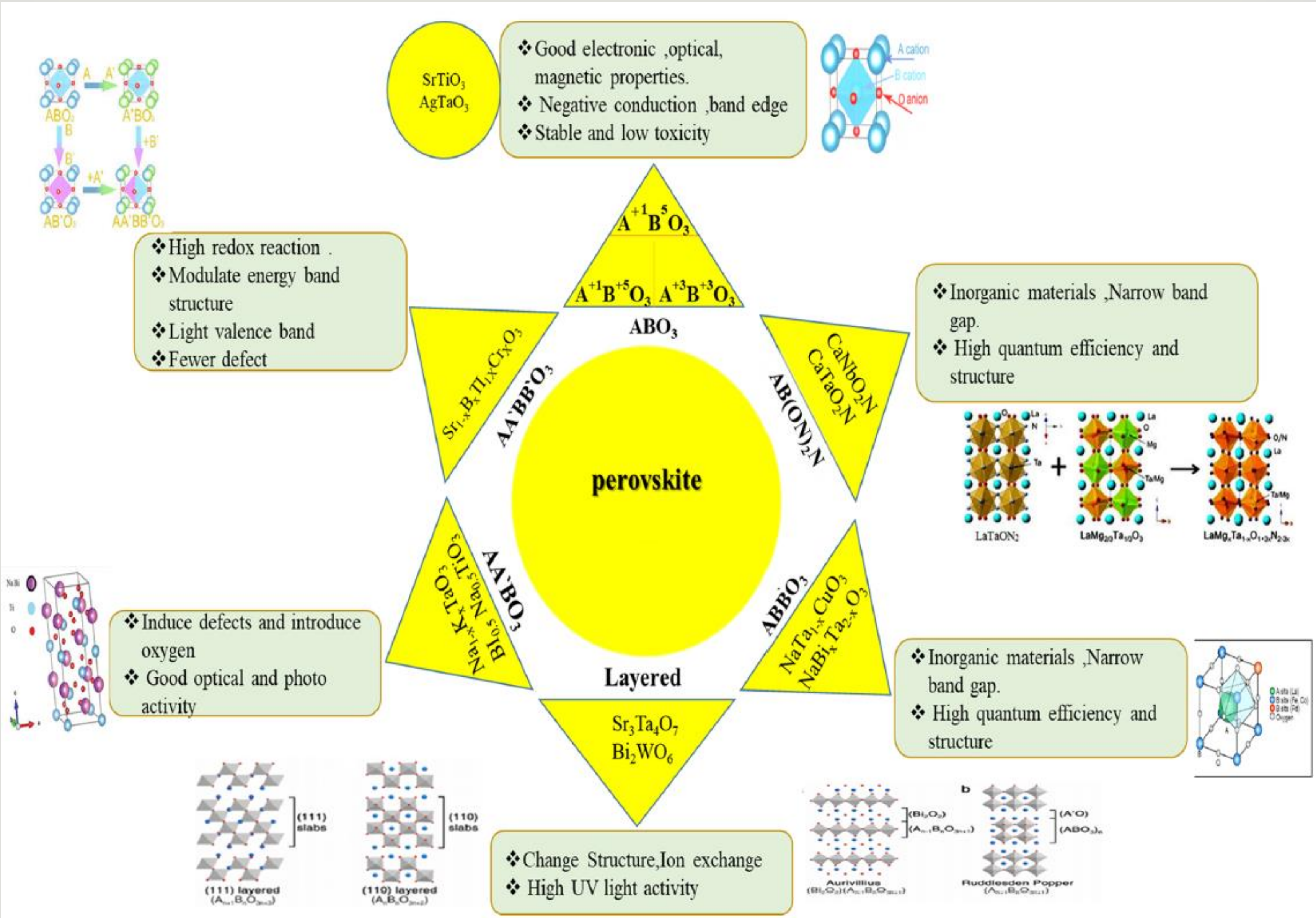
What is Perovskite? – Structure

ABO_3



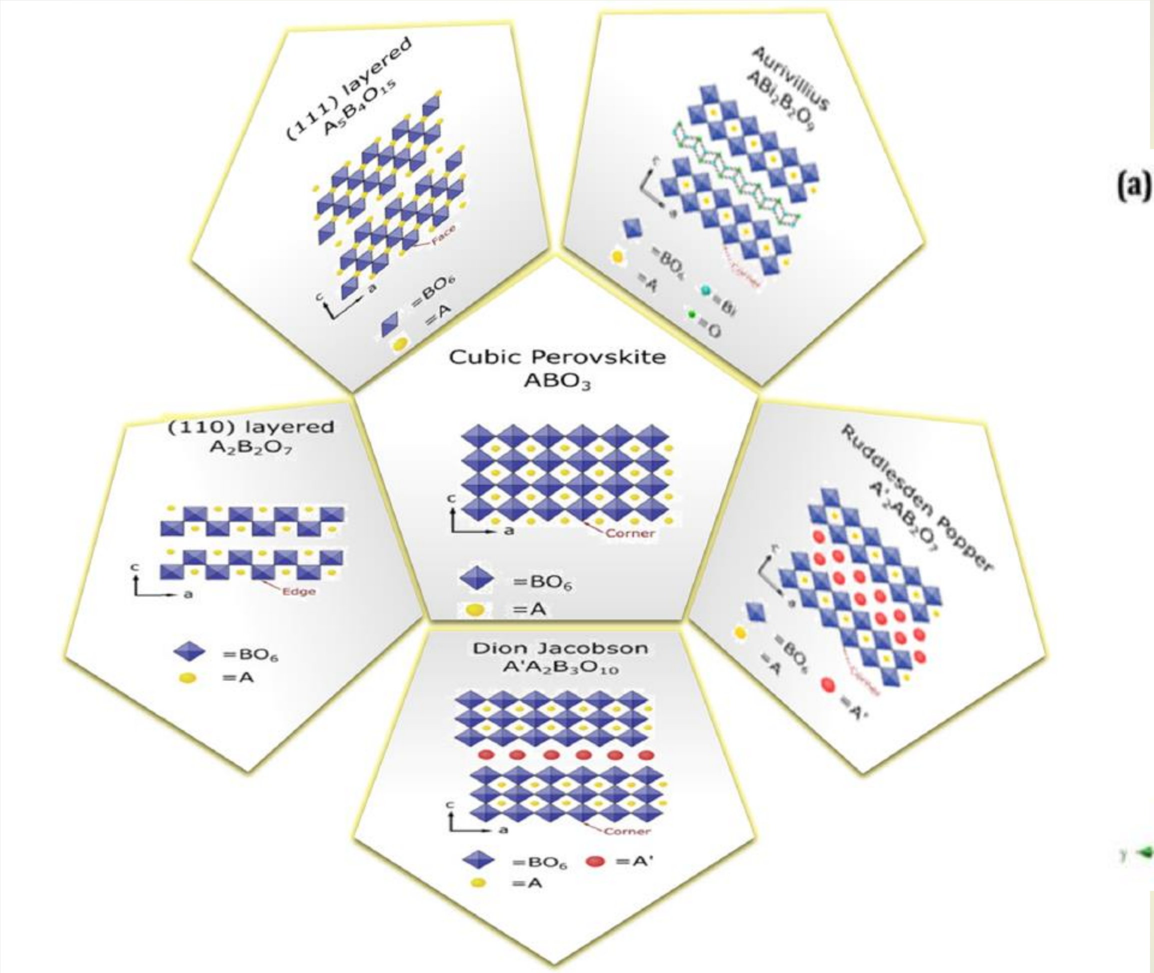
J. Environ. Chem. Eng. 2021, 9, 106264

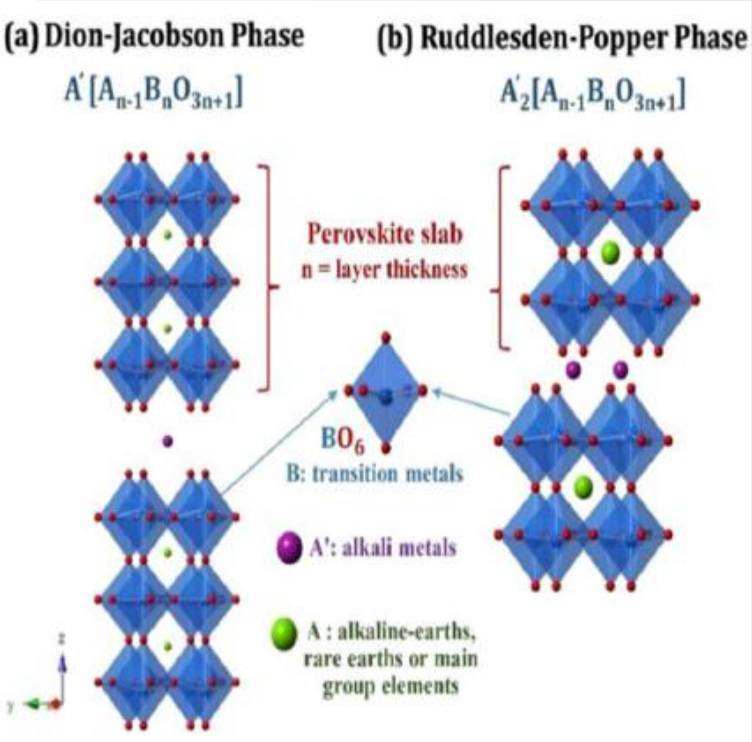
Oxide Perovskite Classification



J. Environ. Chem. Eng. 2021, 9, 106264

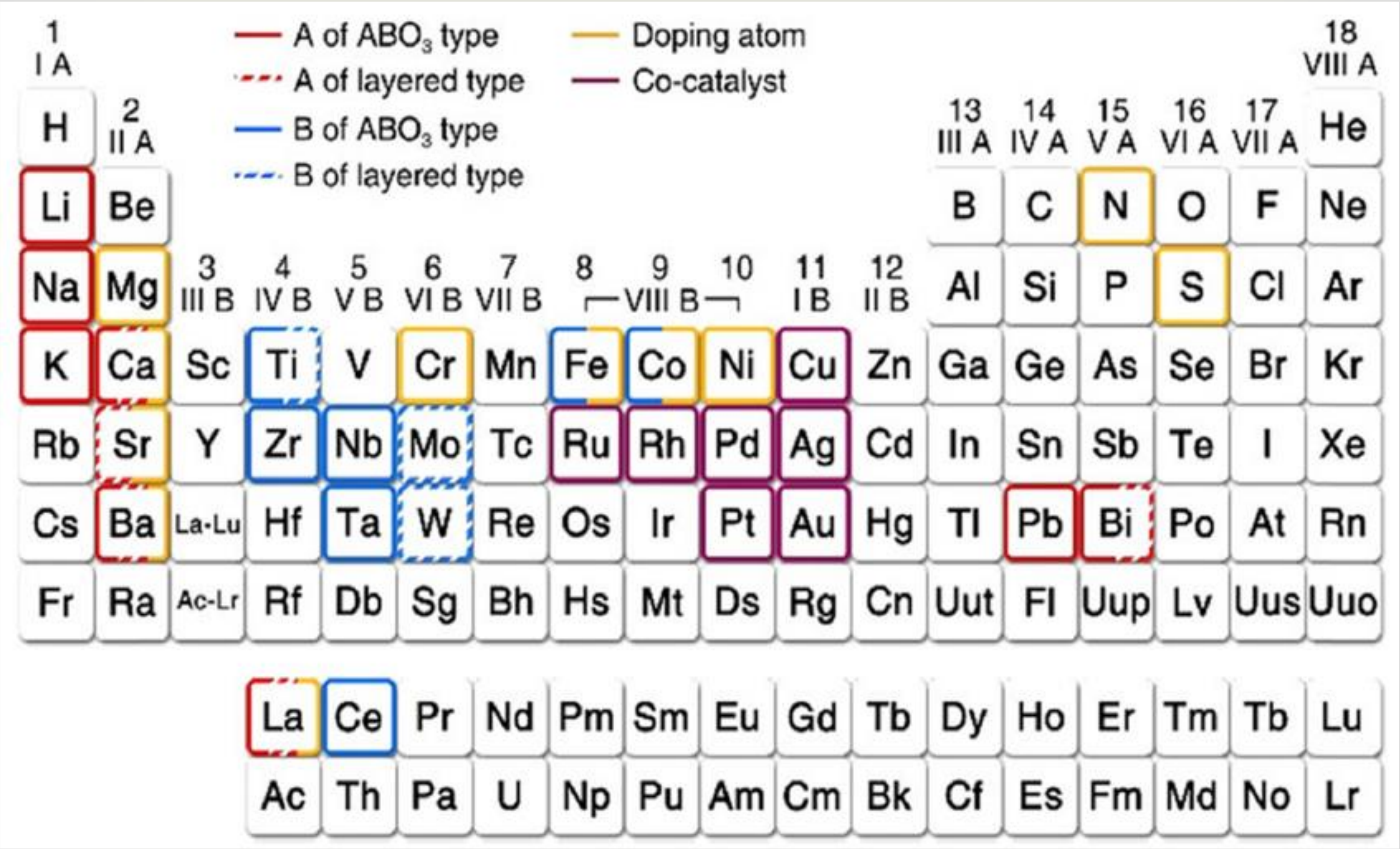
Cubic and Layered Perovskites





J. Environ. Chem. Eng. 2021, 9, 106264

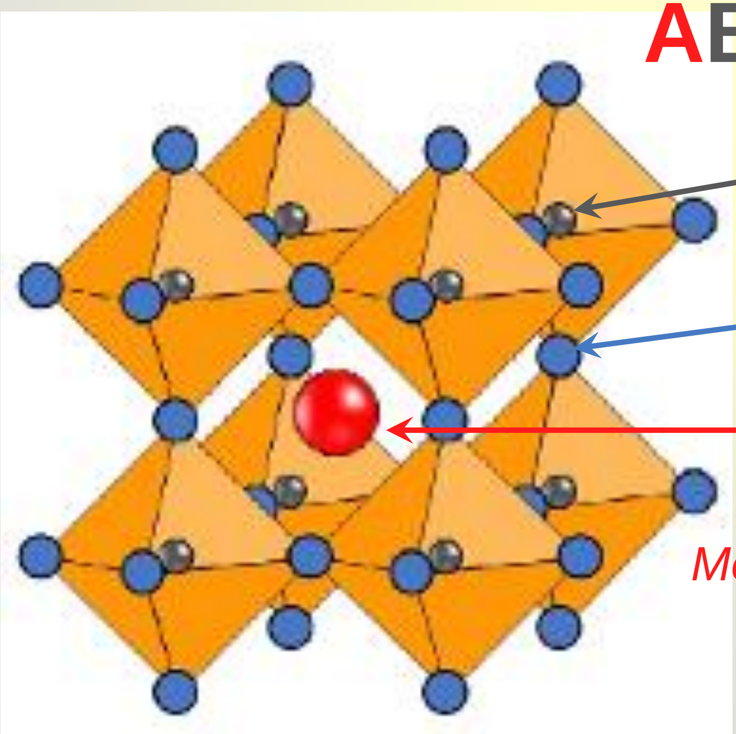
Element Composition of ABO_3



J. Environ. Chem. Eng. 2021, 9, 106264

Organic-Inorganic Hybrid Perovskite

1. Organic-Inorganic Hybrid Perovskite discovered by Diater Weber in 1978, by replacing cesium in $CsPbX_3$ (X=Cl, Br or I) with methyl ammonium cations (MA).
2. $MAPbI_3$ is commonly used for high efficiency perovskite solar cells.
3. $MAPbI_3$ has band gap of 1.55 eV with absorption coefficient as high as10^5 cm^{-1}.



ABX_3

(Sn^{2+}, Pb^{2+}…)

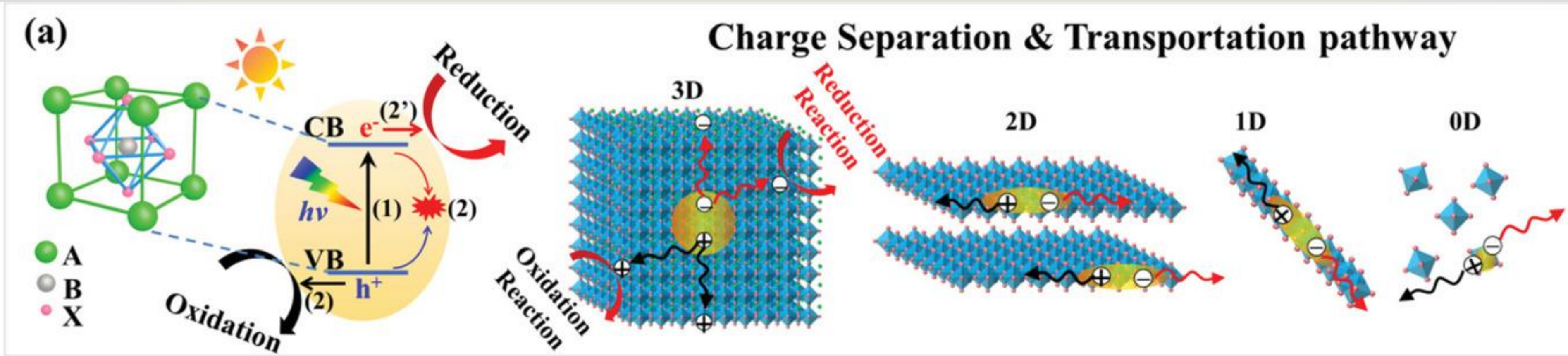
(Cl^-, Br^-, I^-)

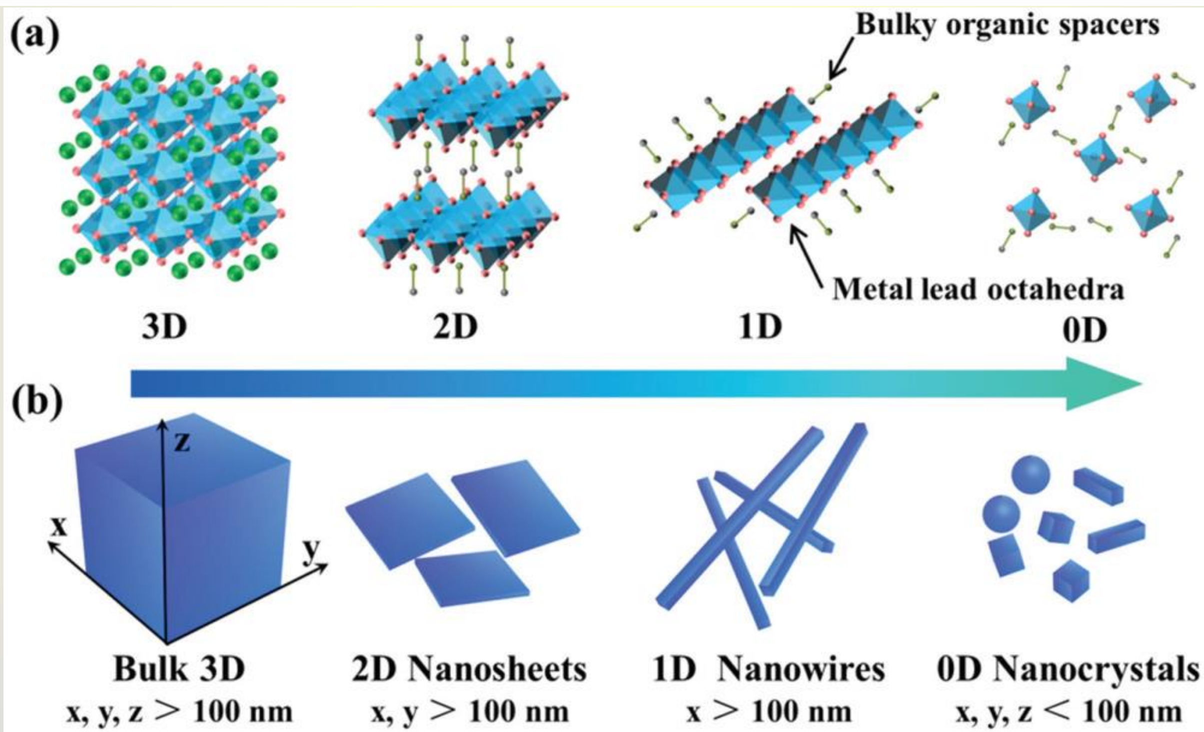
(MA, FA, Cs, Rb)

Methylammonium (MA), Formamidinium (FA)

Source: google image

Dimensionality of Halide Perovskites

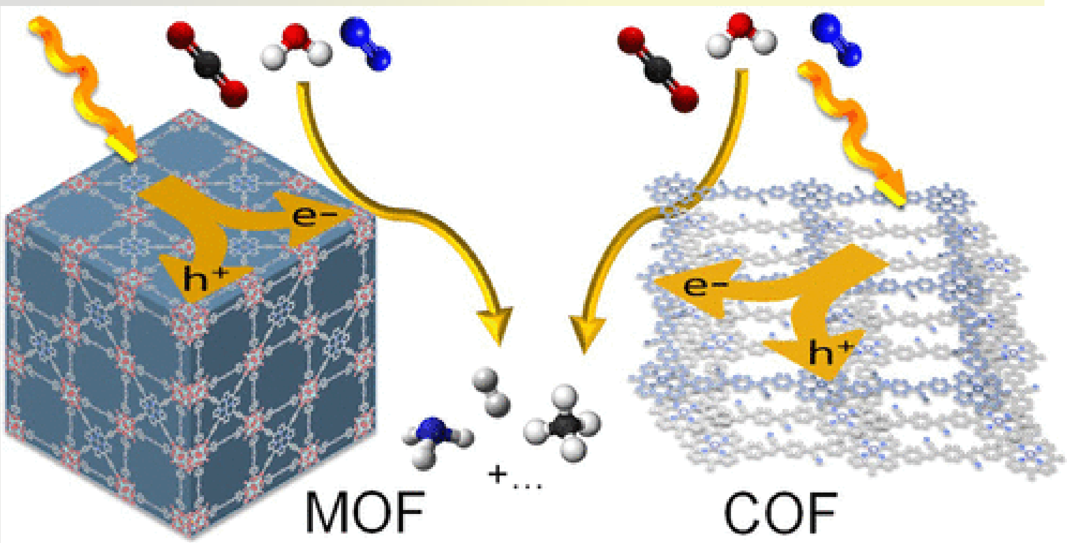


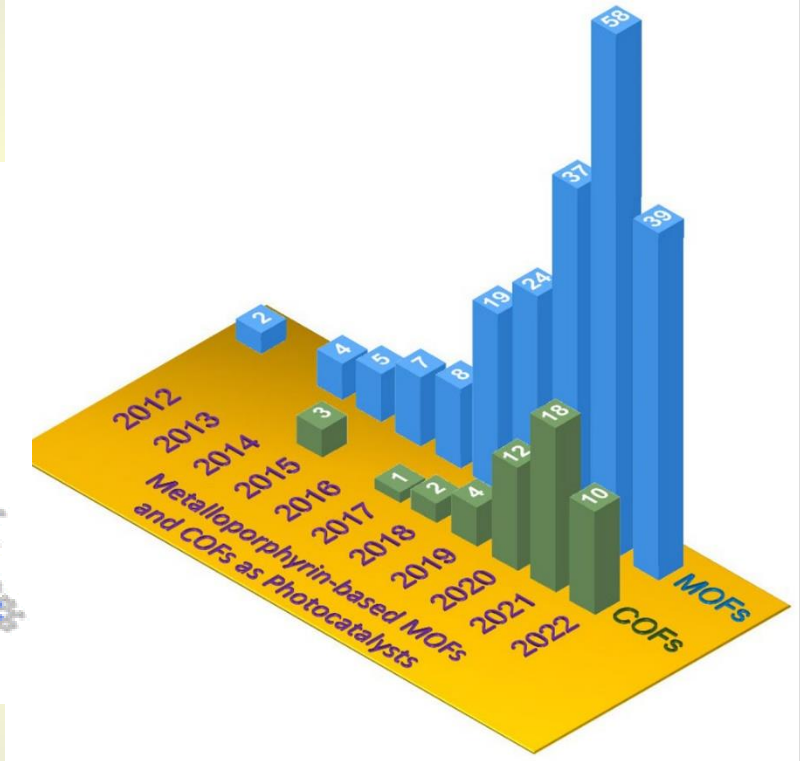


Adv. Energy Mater. 2022, 12, 2004002

Photocatalyst 4
MOF and COF

Metal-Organic Framework (MOF)
Covalent-Organic Framework (COF)



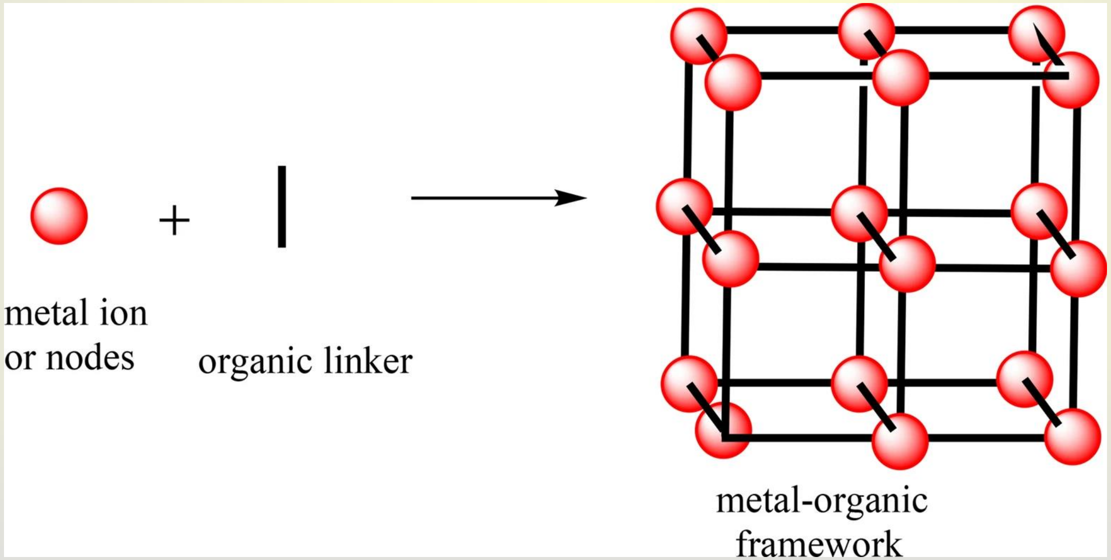


Scifinder, late March 2022

ACS Appl. Nano Mater. 2022, 5, 5, 6055-6082

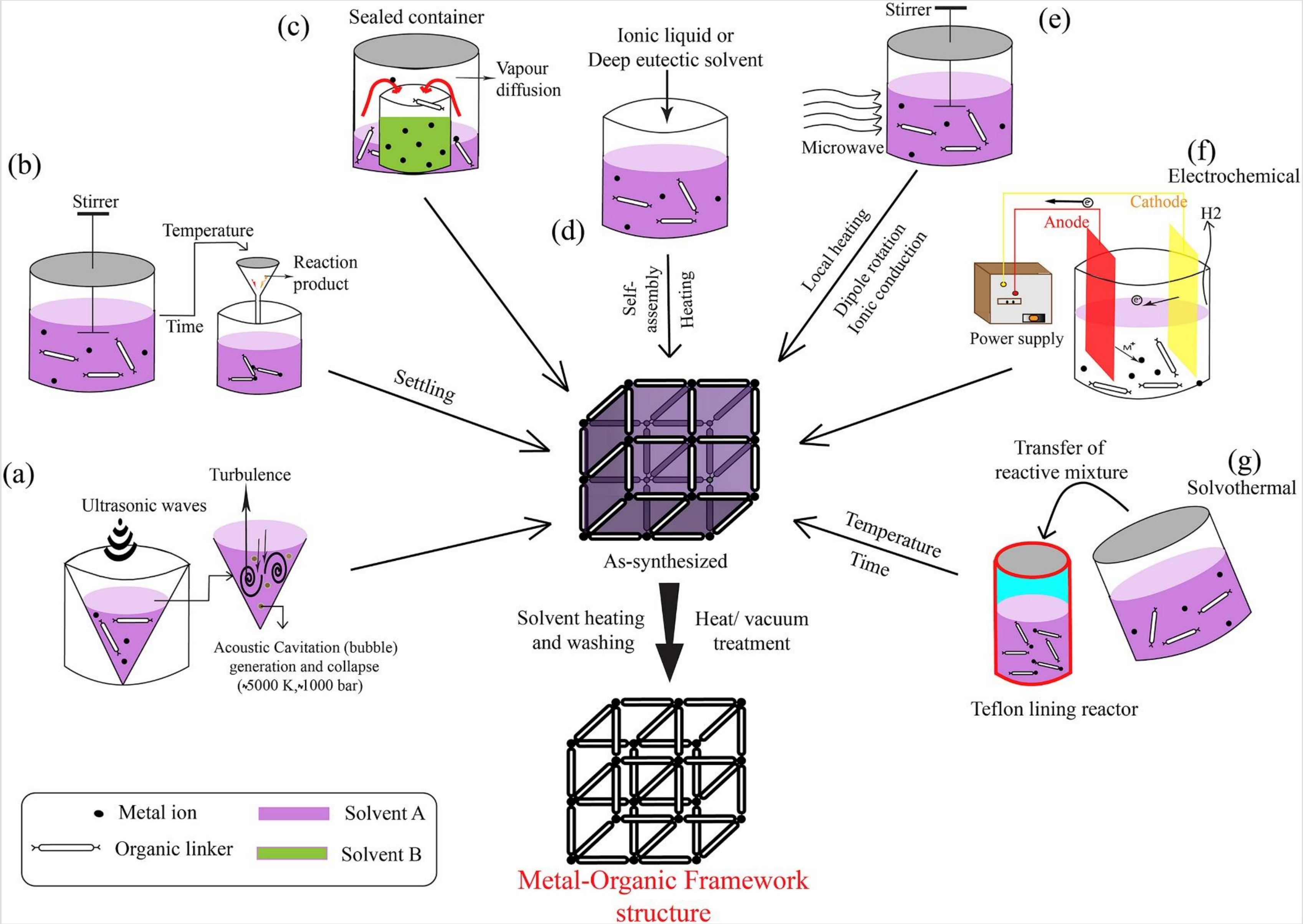
What is Metal-Organic Framework (MOF)?

- Porous coordination polymers.
- Constructed from organic linkers and metal nodes (metal ions or clusters).
- Porous crystalline inorganic–organic hybrid materials.
- High surface area, uniform and tunable porous structure, and high-density coordination-unsaturated metal sites.
- Easy facilitation of electrons between metal-ligands.



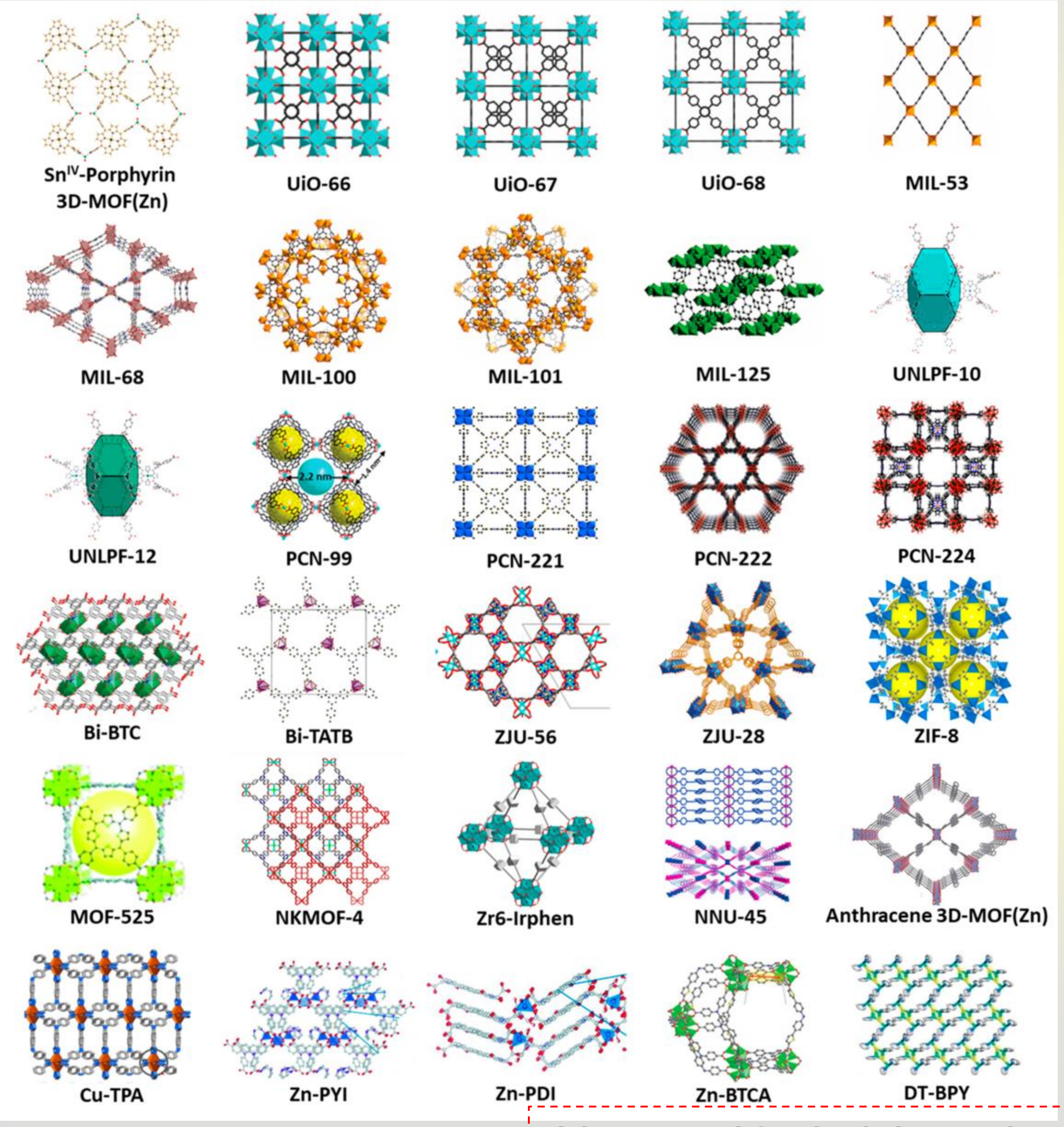
Building blocks and porous structure of a MOF.

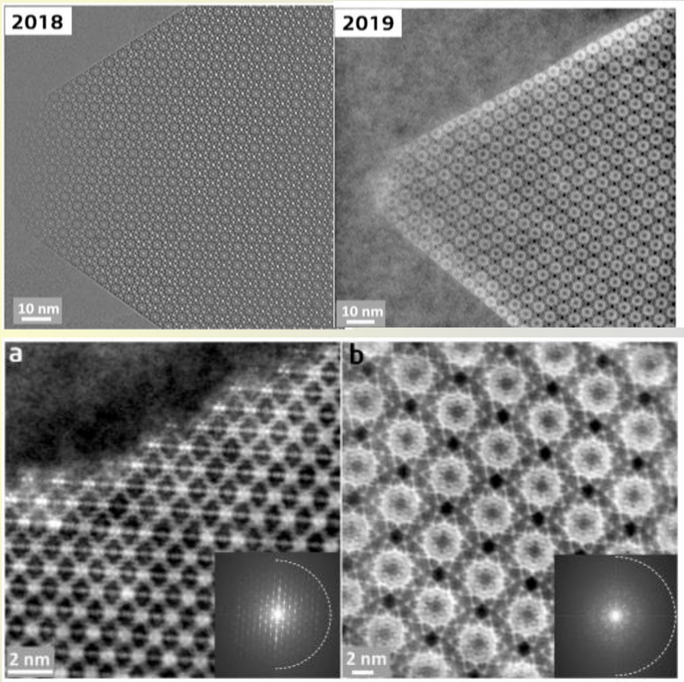
Synthesis of MOF Materials



Trends in Food Science & Technology 104 (2020) 102–116

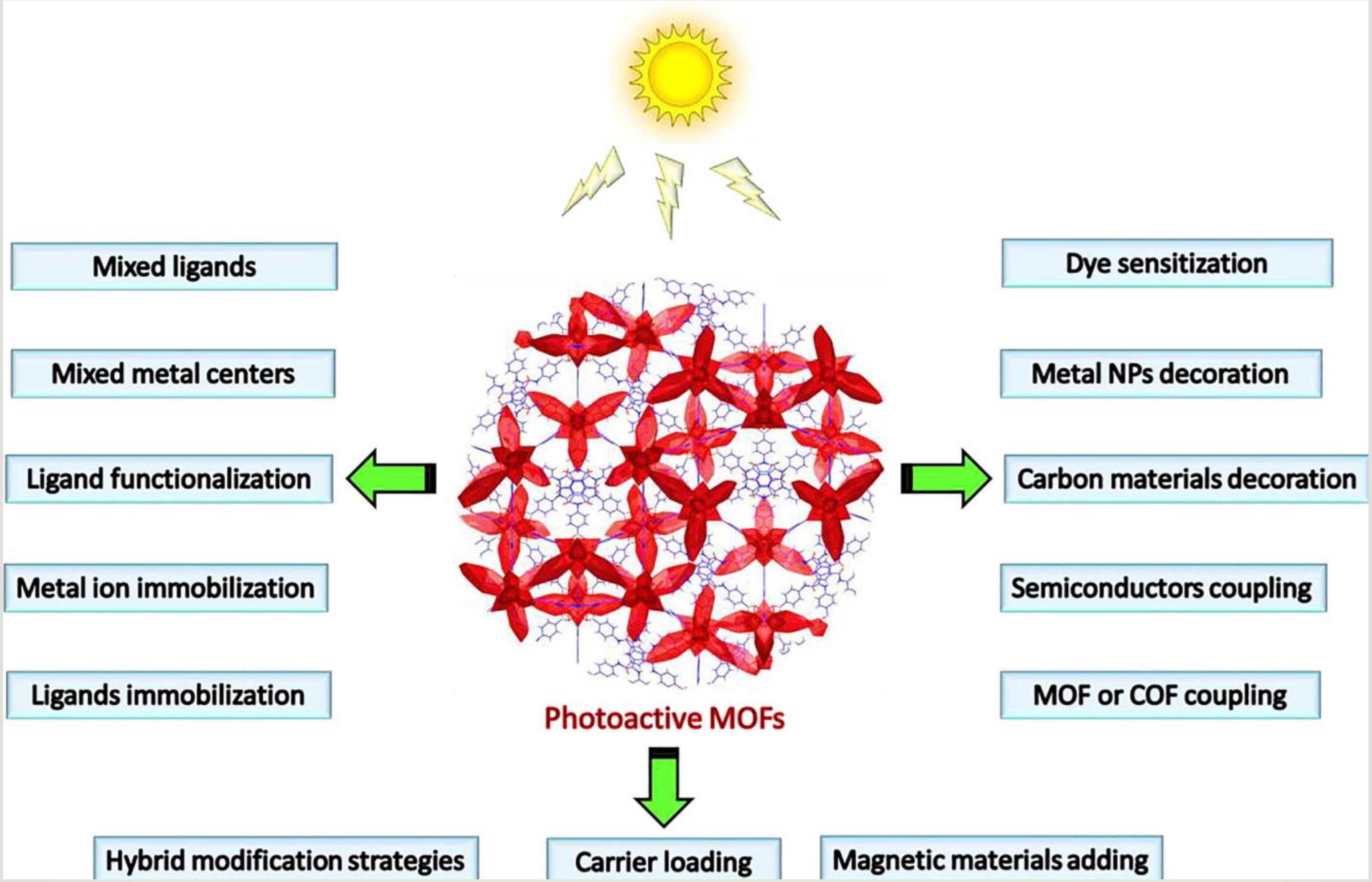
Examples of Varied Types of MOF





COMMUNICATIONS CHEMISTRY | https://doi.org/10.1038/s42004-020-00361-6

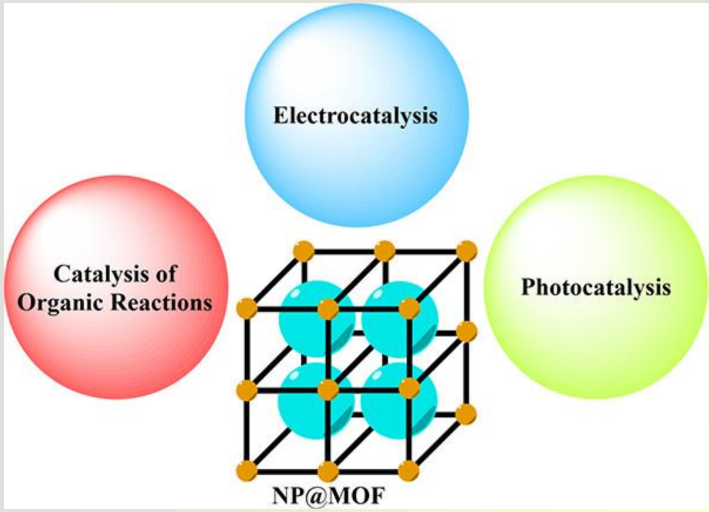
Engineering MOF Materials

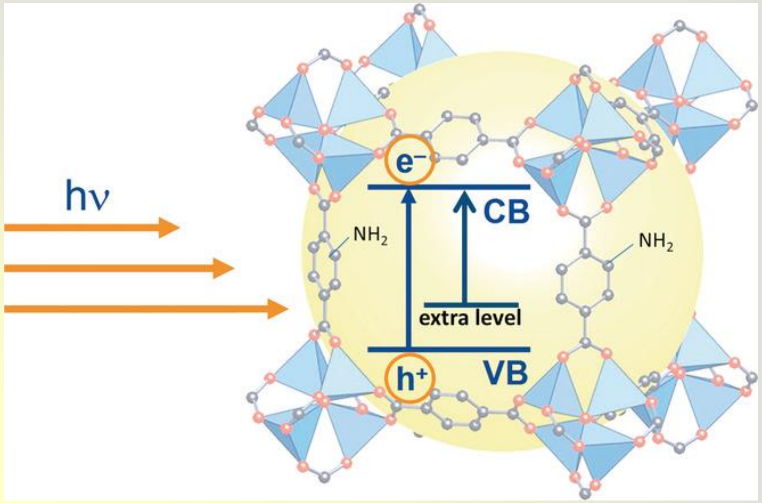


MOF engineering techniques as effective photocatalysts to split H_2O and reduce CO_2.

Coordination Chemistry Reviews 469 (2022) 214664

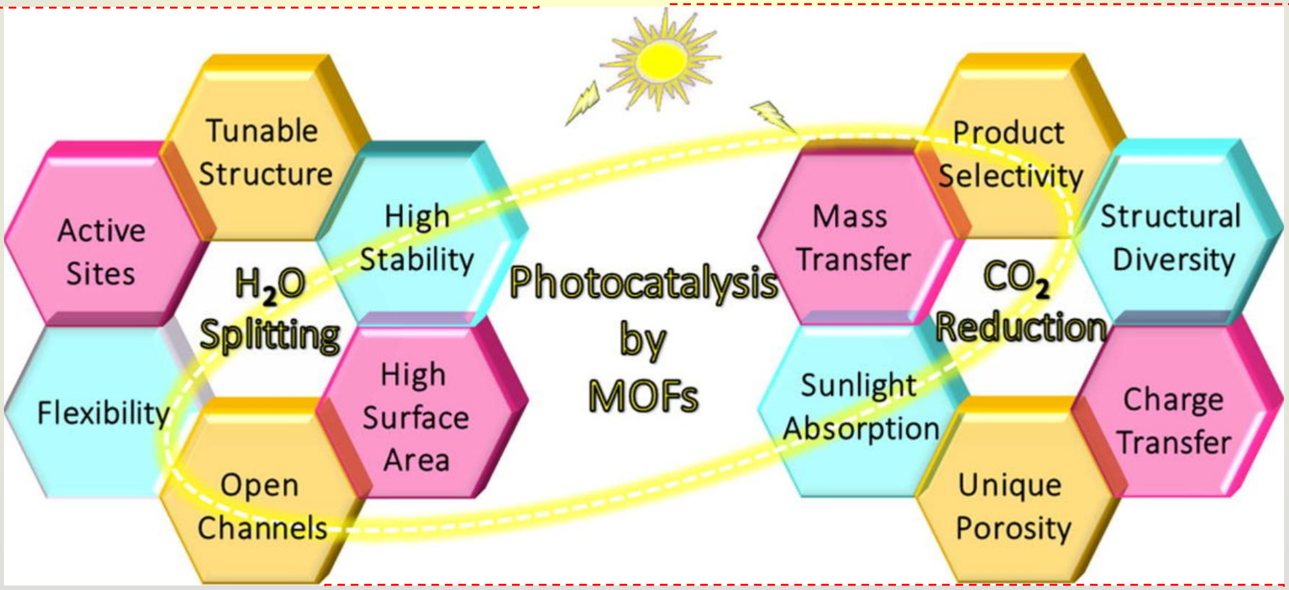
Applications of MOF Materials





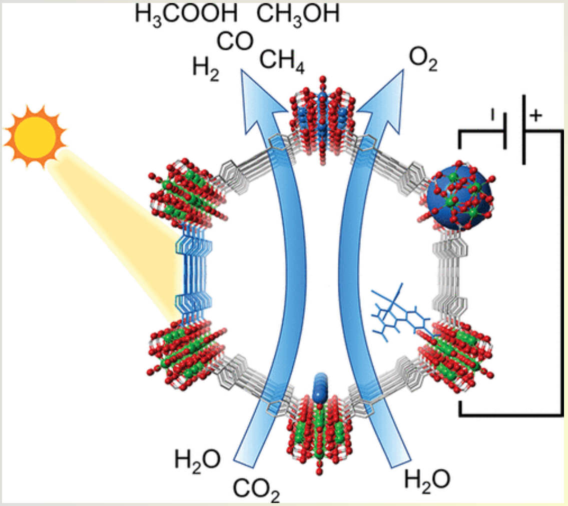
Chem. Rev. 2020, 120, 2, 1438-1511

Angew. Chem. Int. Ed. 2016, 55, 5414–5445

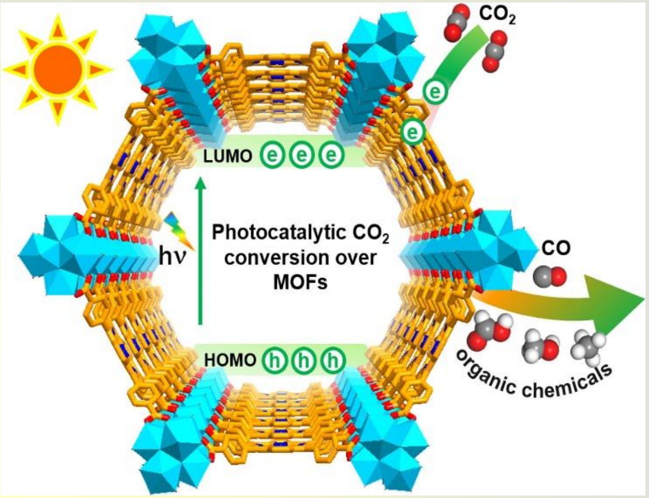


Coordination Chemistry Reviews 469 (2022) 214664

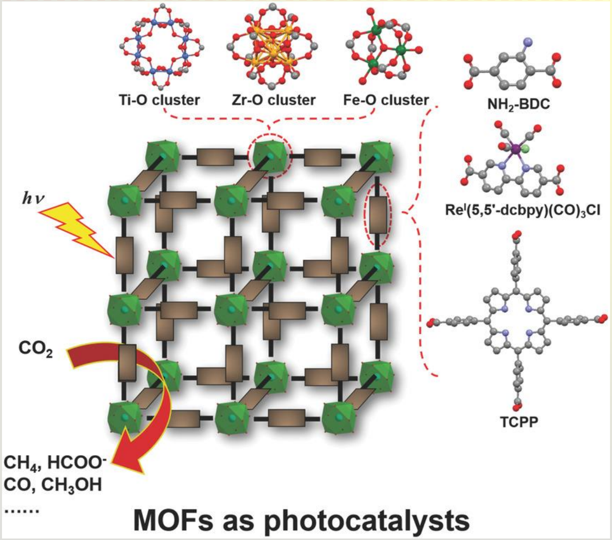
MOFs for CO_2 Reduction



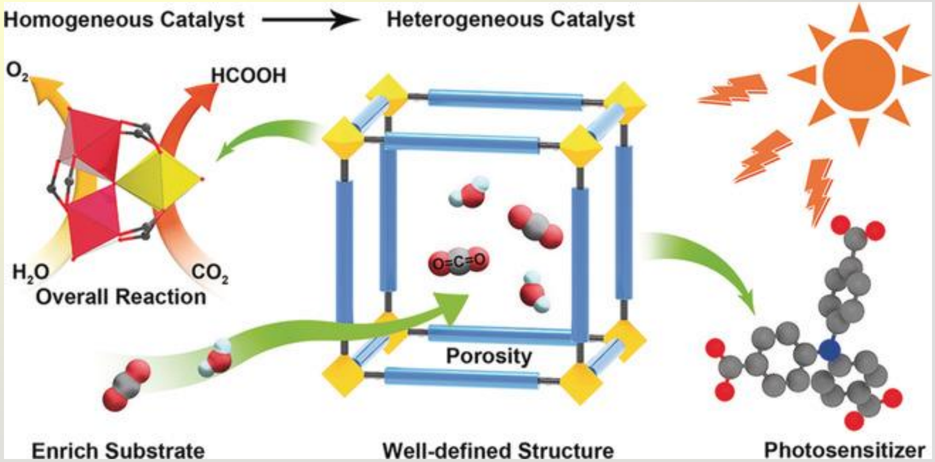
ACS Energy Lett. 2018, 3, 3, 598–611



Coordination Chemistry Reviews 412 (2020) 213262

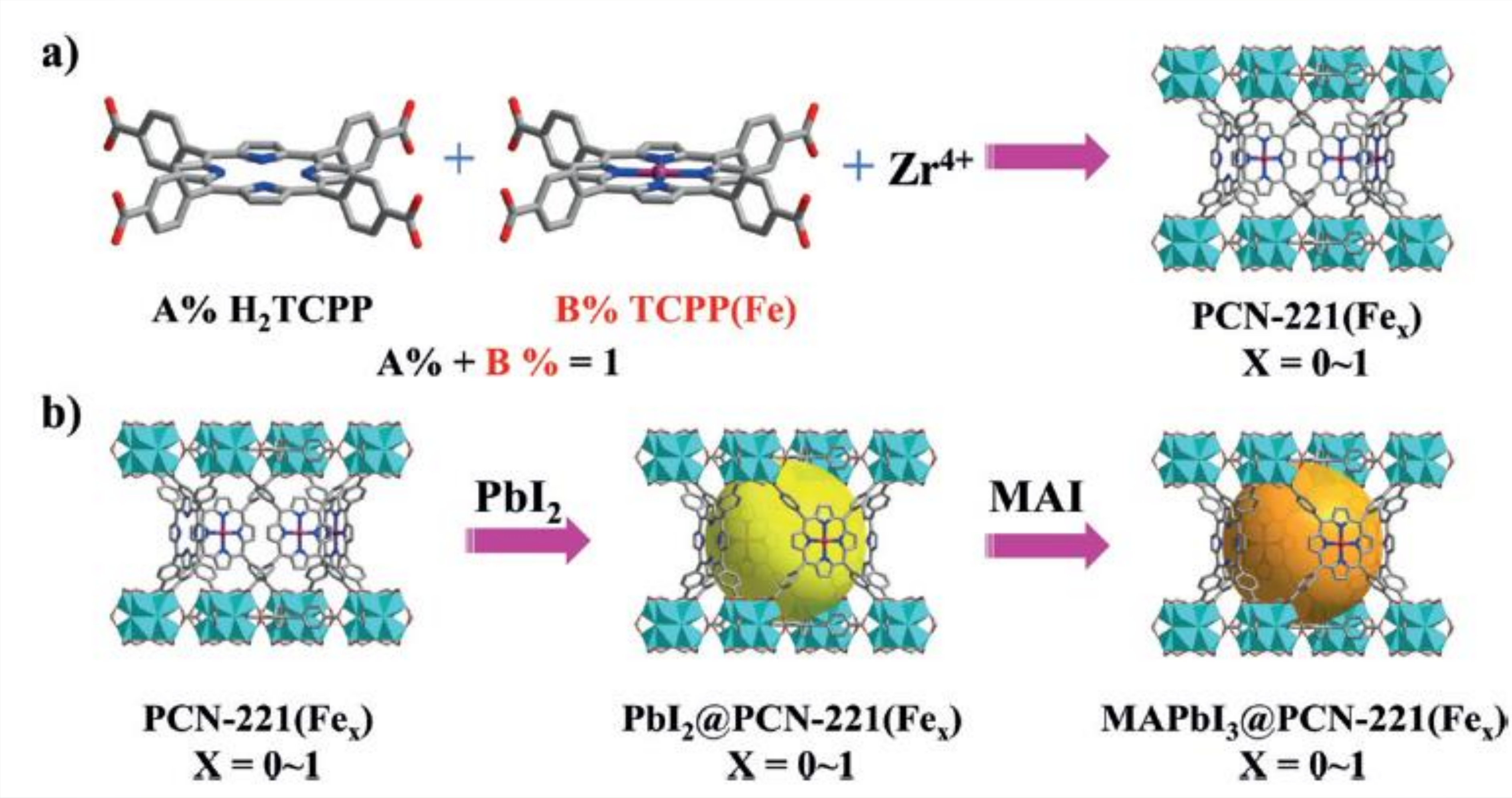


Adv. Mater. 2018, 30, 1705512



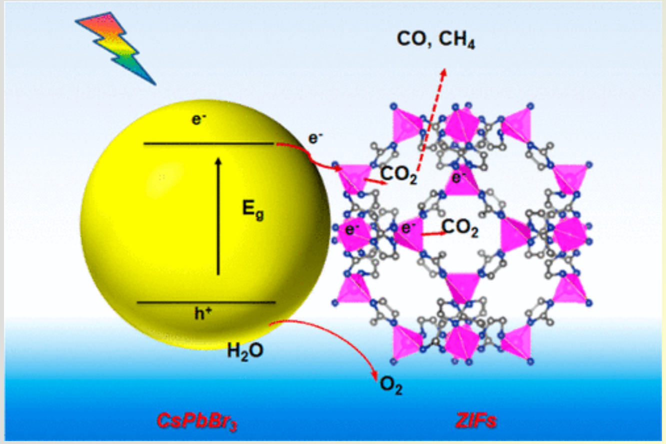
Angew. Chem. 2020, 132, 2681–2685

Synthesis of PeNC/MOF Heterojunctions

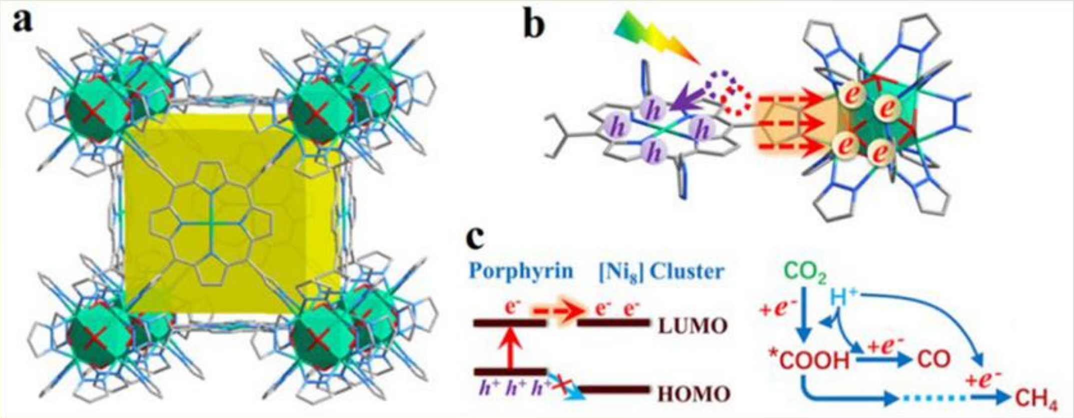


Angew. Chem. Int. Ed. **2019**, *58*, 9491–9495

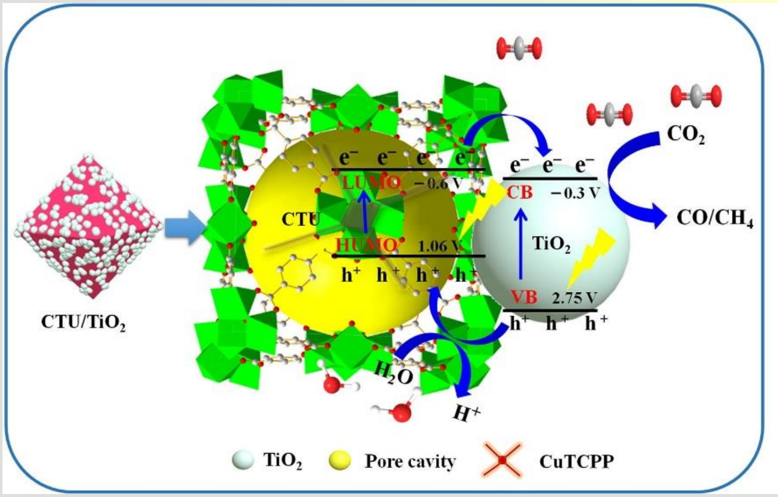
QD/MOF Heterojunctions



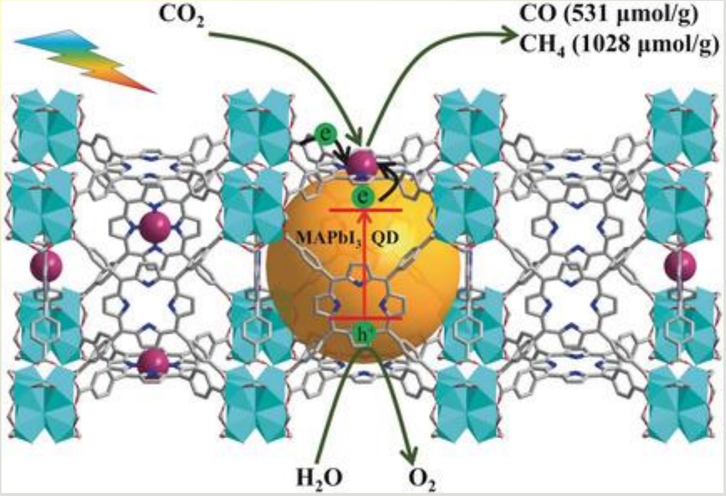
ACS Energy Lett. 2018, 3, 11, 2656-2662



J. Am. Chem. Soc. 2020, 142, 28, 12515-12523



Science Bulletin, 2019, 64, 13, 926-933



Angew. Chem. Int. Ed. 2019, 58, 9491–9495


(C)fuul
Thanks