

FEBRUARY 17TH. 2021



*International Collaboration in the Era of COVID-19*

KYUSHU UNIVERSITY - UC SAN DIEGO JOINT WEBINAR SERIES

**SDGs THINK AND ACT TOGETHER**

**ENVIRONMENTAL MATERIALS FROM  
NATURAL RESOURCES FOR SDGs  
- SOLAR LIGHT DRIVEN CHEMICAL CONVERSION -**

DEPARTMENT OF EARTH RESOURCES

ENGINEERING

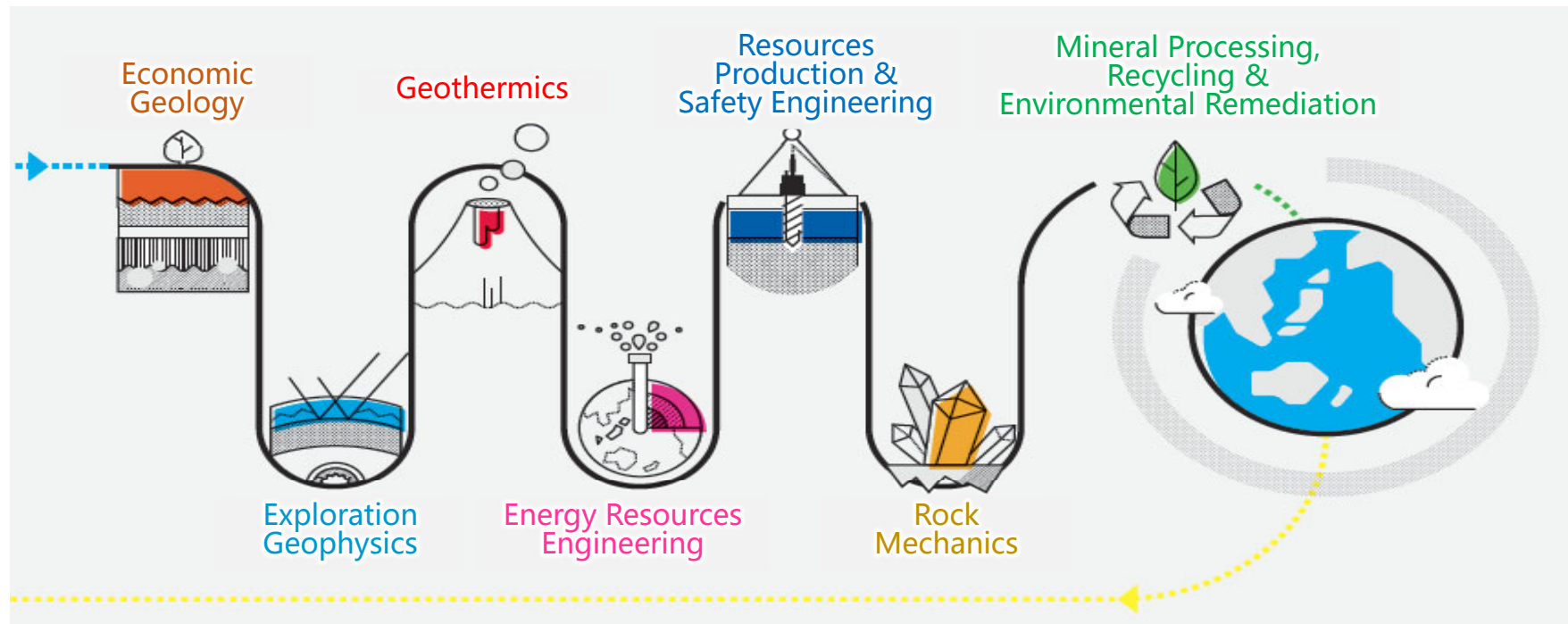
KYUSHU UNIVERSITY

**KEIKO SASAKI**

(PHD, PROF. DEPARTMENT CHAIR)

# ABOUT OUR DEPARTMENT

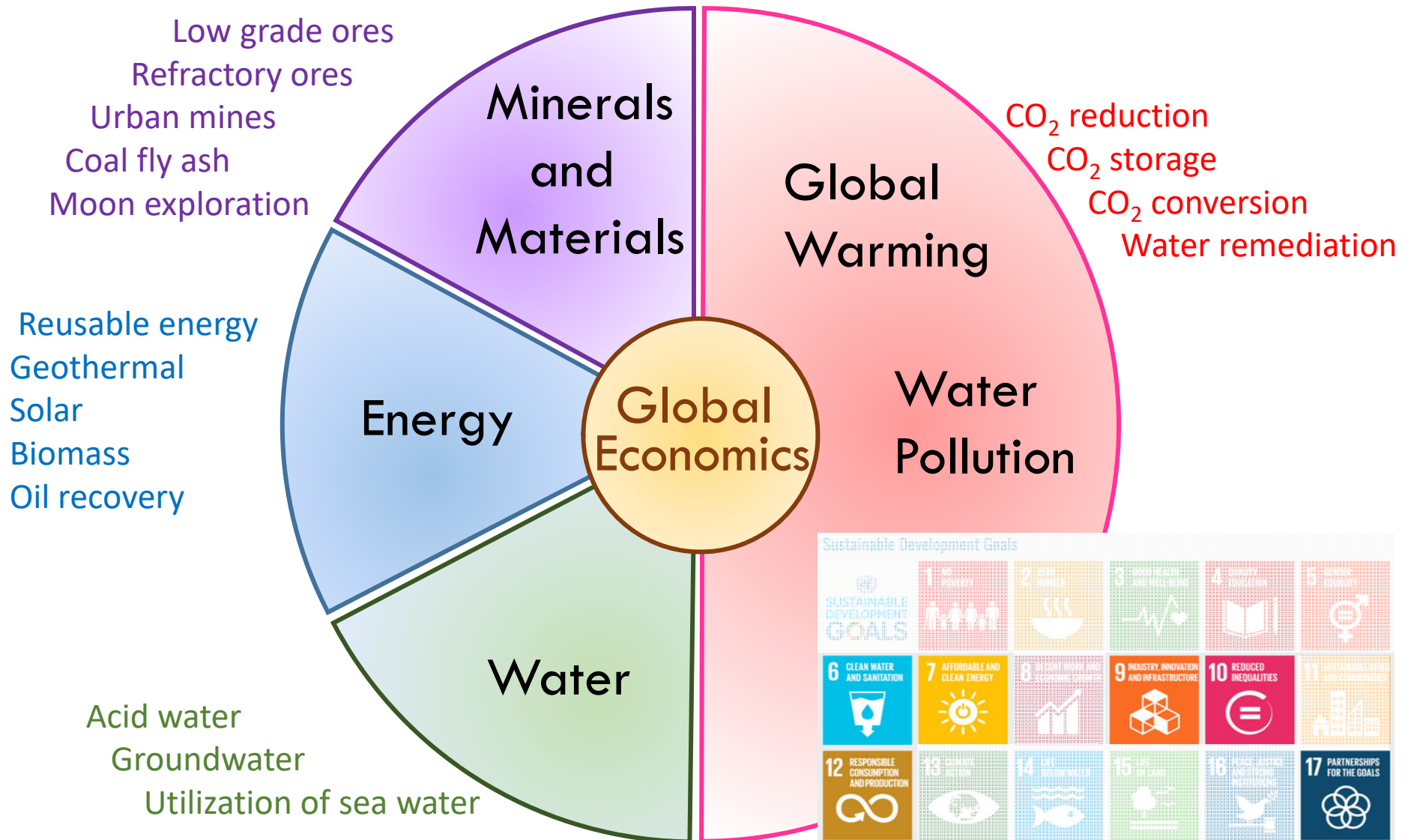
Department of **Earth Resources Engineering**, Kyushu University  
QS World Ranking 36<sup>th</sup> (**Mineral & Mining Engineering**)



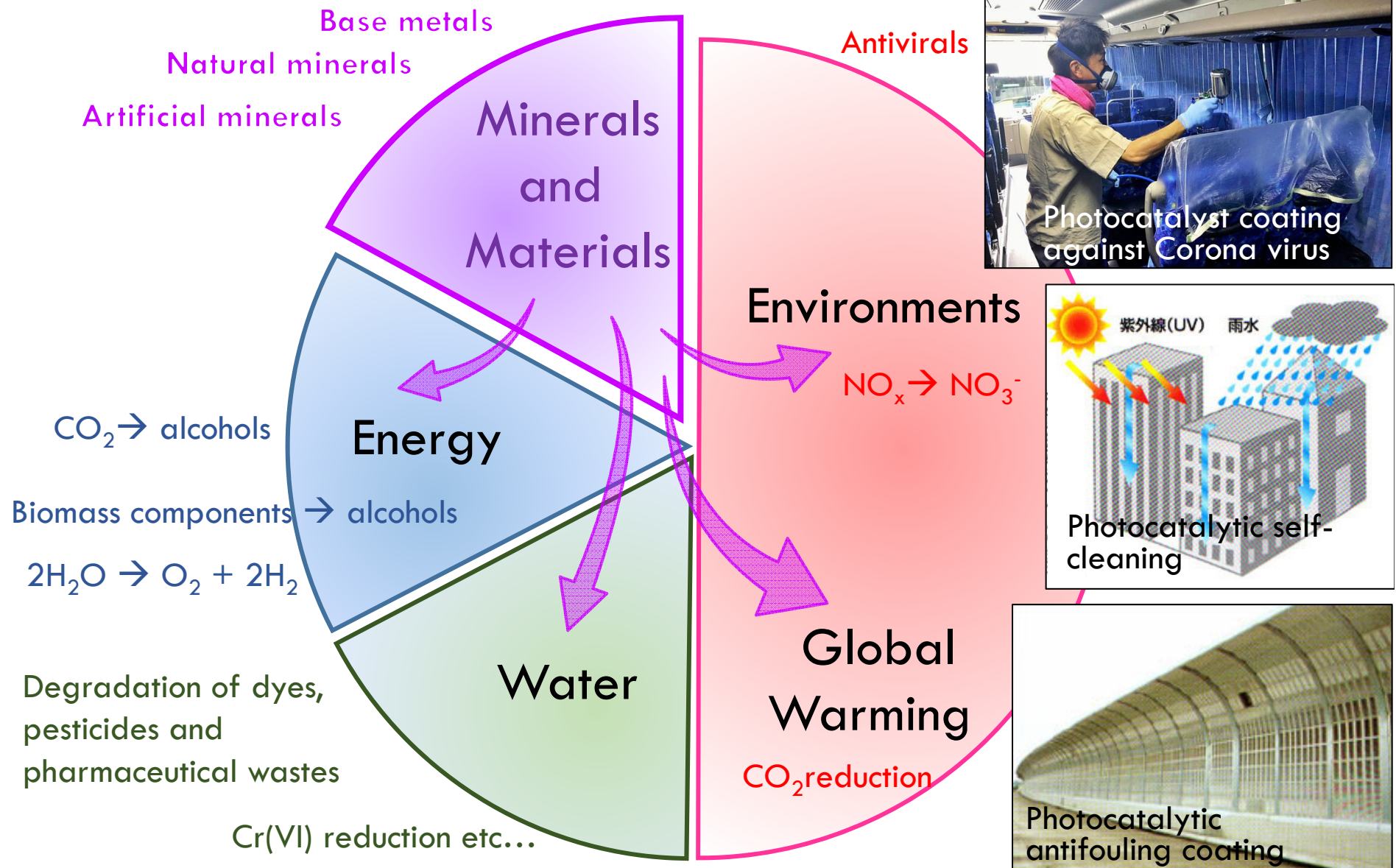
# WHAT ARE WE?: DEPARTMENT OF EARTH RESOURCES ENGINEERING

## Global Resources

## Global Environments

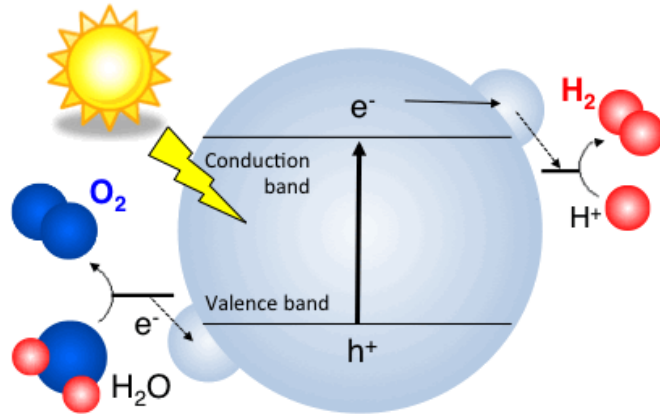


# Solar light driven chemical conversion



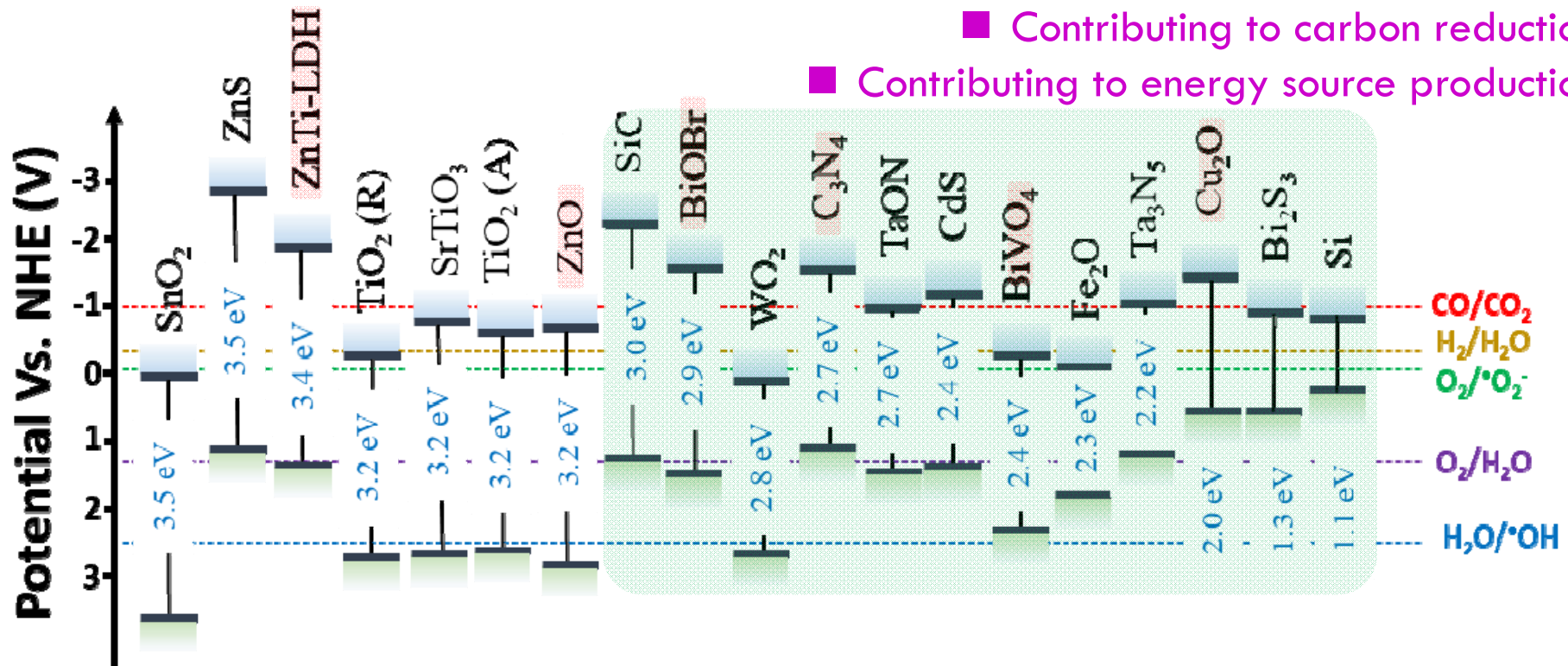
# Photocatalysis

*Fujishima and Honda, Nature, 1972, 238, 37-38.*

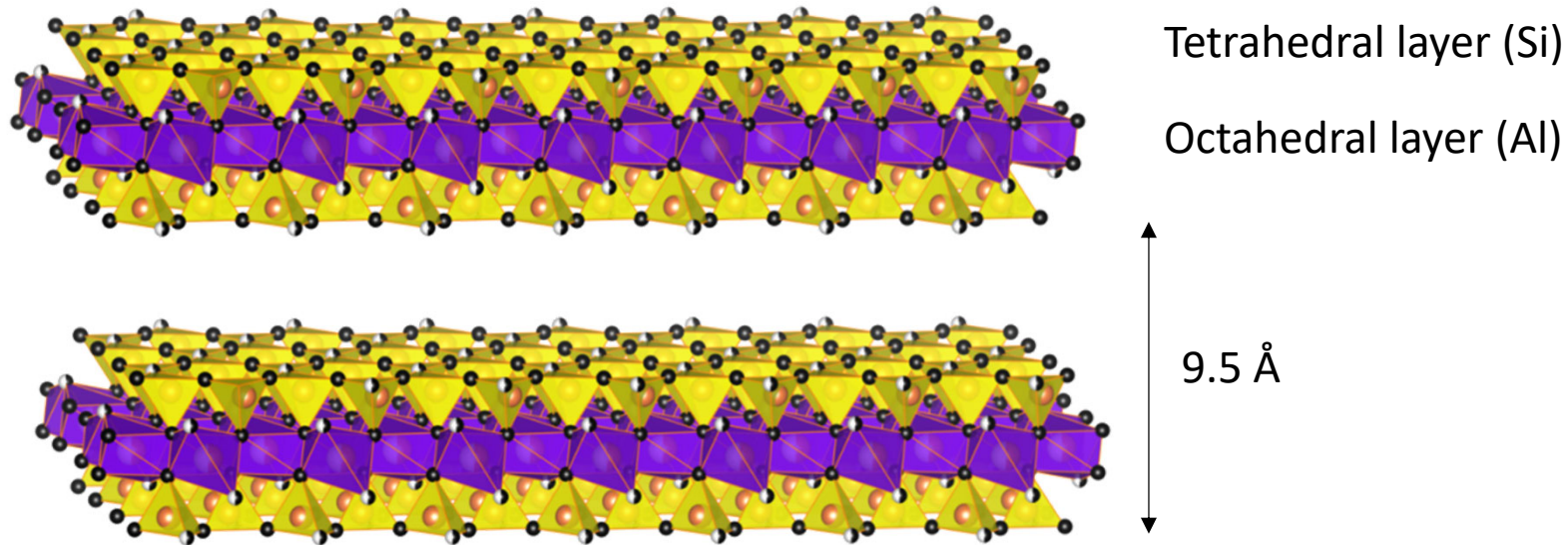


- i) light absorption (optical)
- ii) charge separation and transport (physicochemical)
- iii) surface chemical reaction (physical)

- Visible light driven
- Highly available
- Recyclability
- Contributing to carbon reduction
- Contributing to energy source production



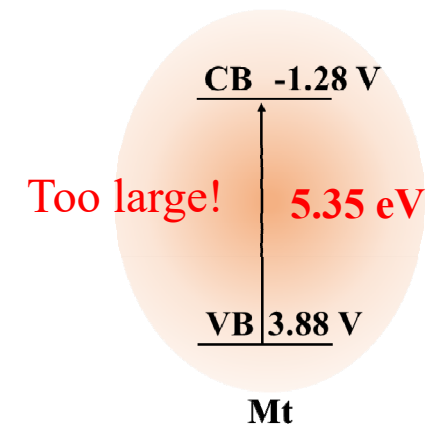
## Montmorillonite - 2:1 type clay-



😊 2D material  
High surface area  
Chemically and physically stable

😊 Fe contents  
Large charge density  
(1.15 meq/ g)

☹️ Large band gap



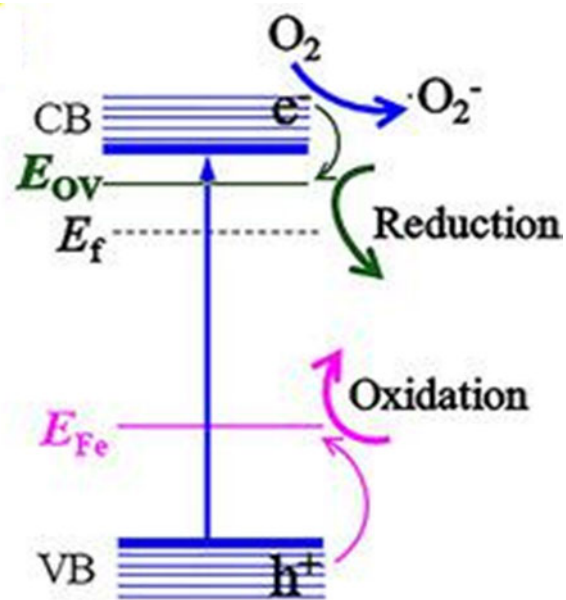
*Clay minerals have been believed as good supports for main photocatalysts in the composites. (i.e., TiO<sub>2</sub>-pillared clay)*

*Ding et al. 1999, JCIS, 209, 193. Ooka et al., 1999, JMC, 11, 2943.*

*Chuaicham et al. 2020*

## Modification: Heteroatom-doping

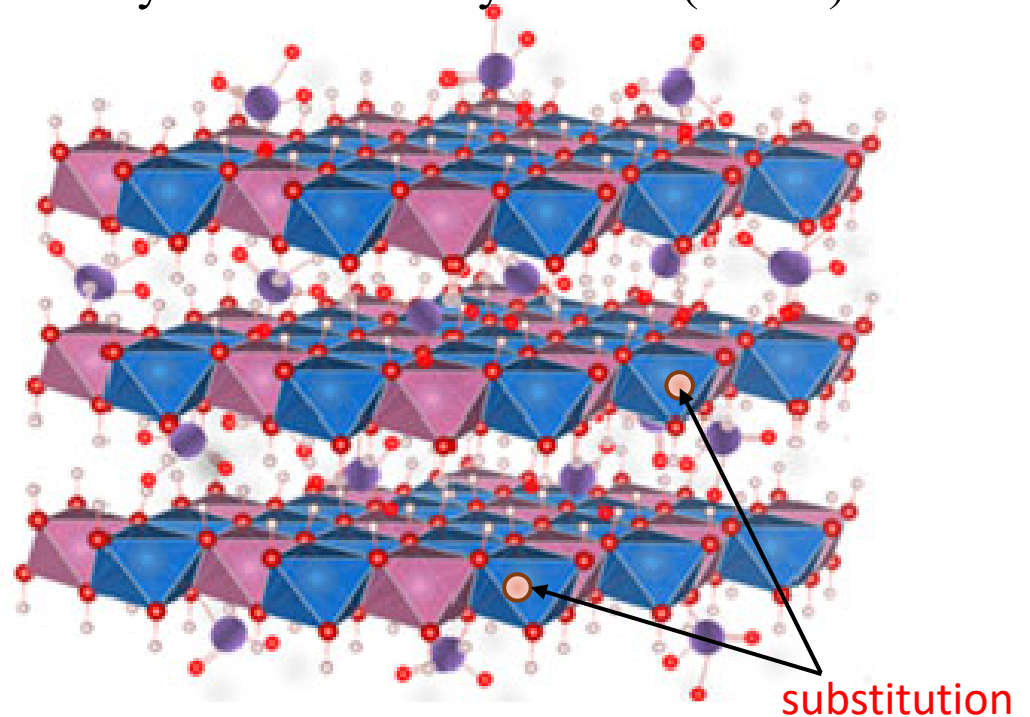
Fe-doped  $\text{Bi}_2\text{WO}_6$



Fe-doping on the  $\text{Bi}_2\text{WO}_6$  generates a new  $e^-$  donor level, Fermi level, and O vacancy.

*Hu et al. 2018, ChemCatChem, 10, 3040.*

Layered Double Hydroxide (LDHs)

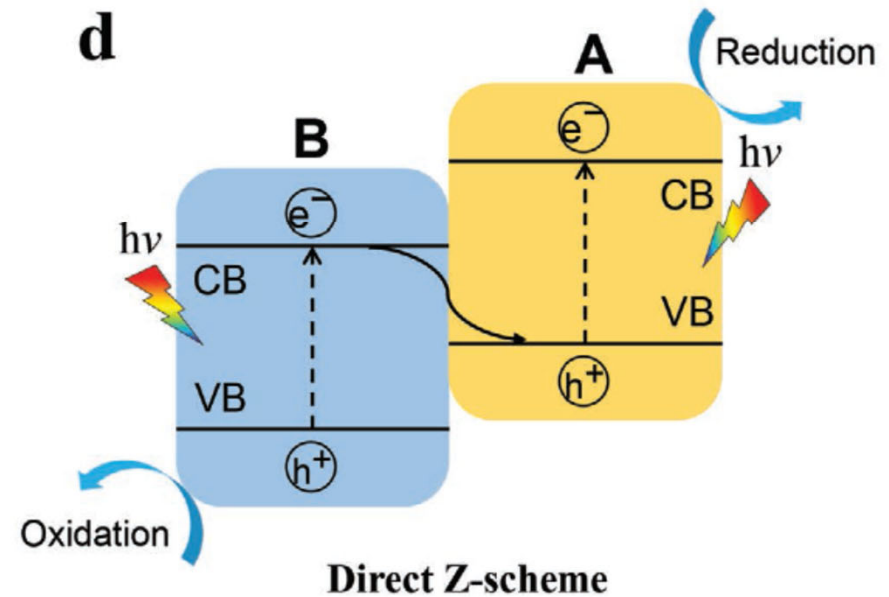
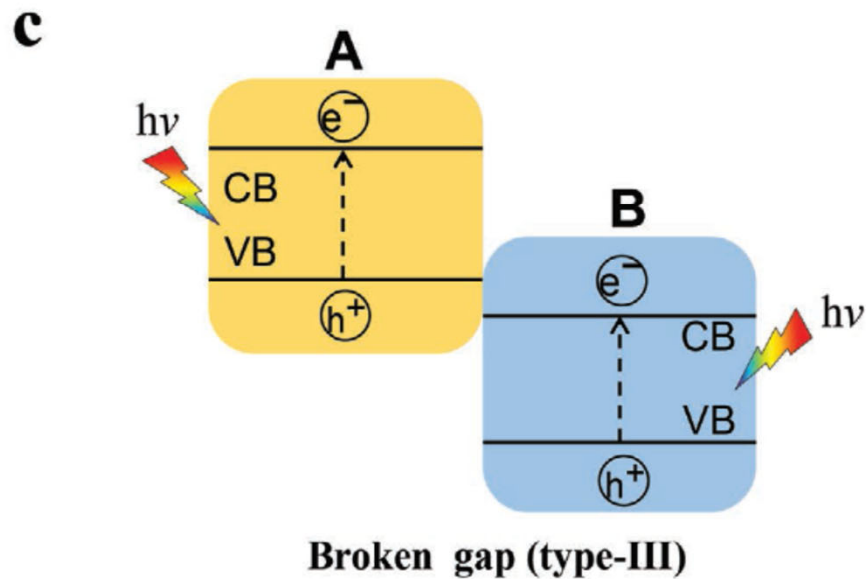
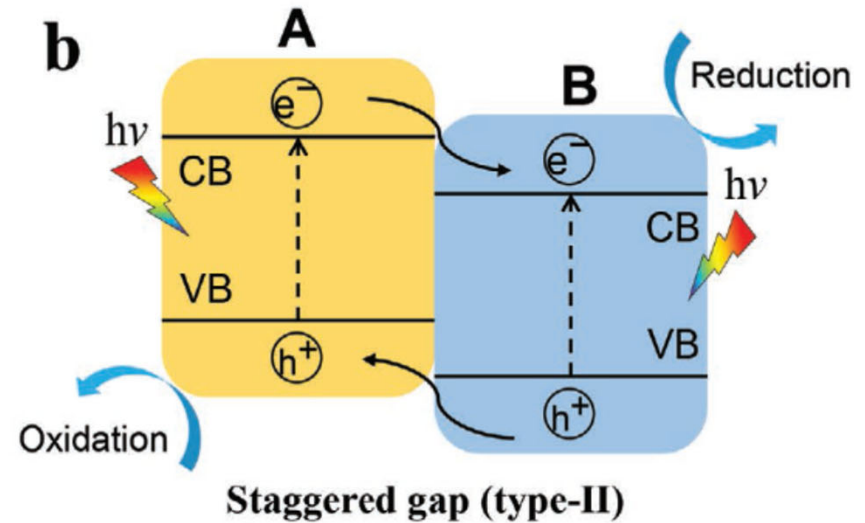
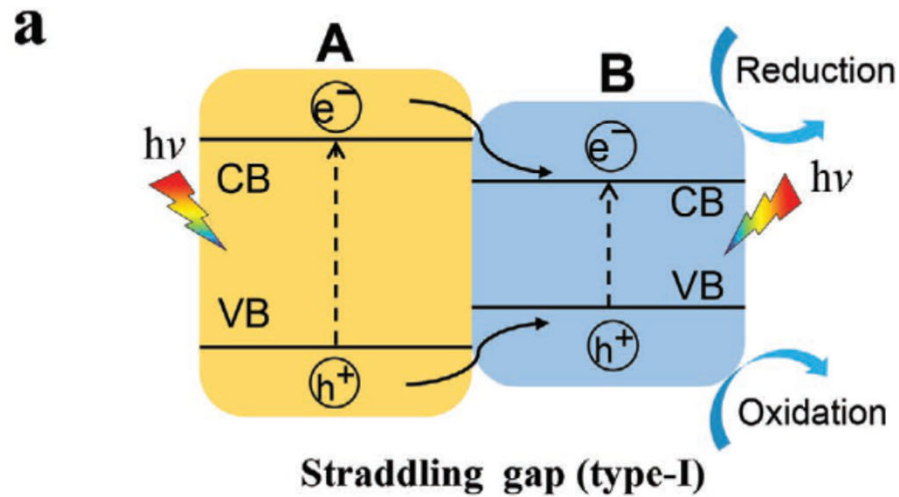


The  $\text{M}^{n+}\text{-O-Fe}^{3+}$  oxo-bridges can reduce or prevent the recombination of  $e^-$  and  $h^+$ .

*Meng, et al. 2019, Small, 15(41),1902551.*

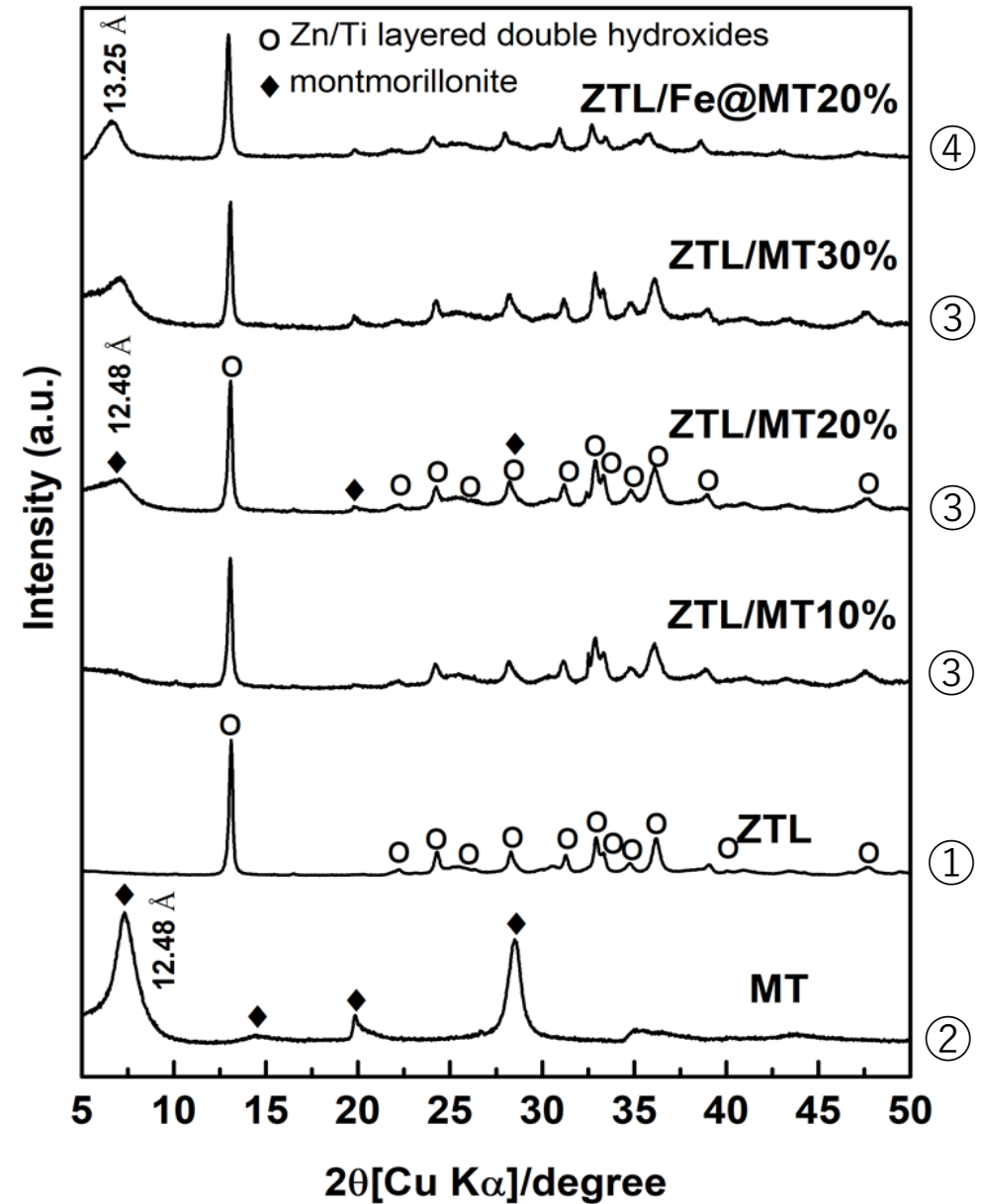
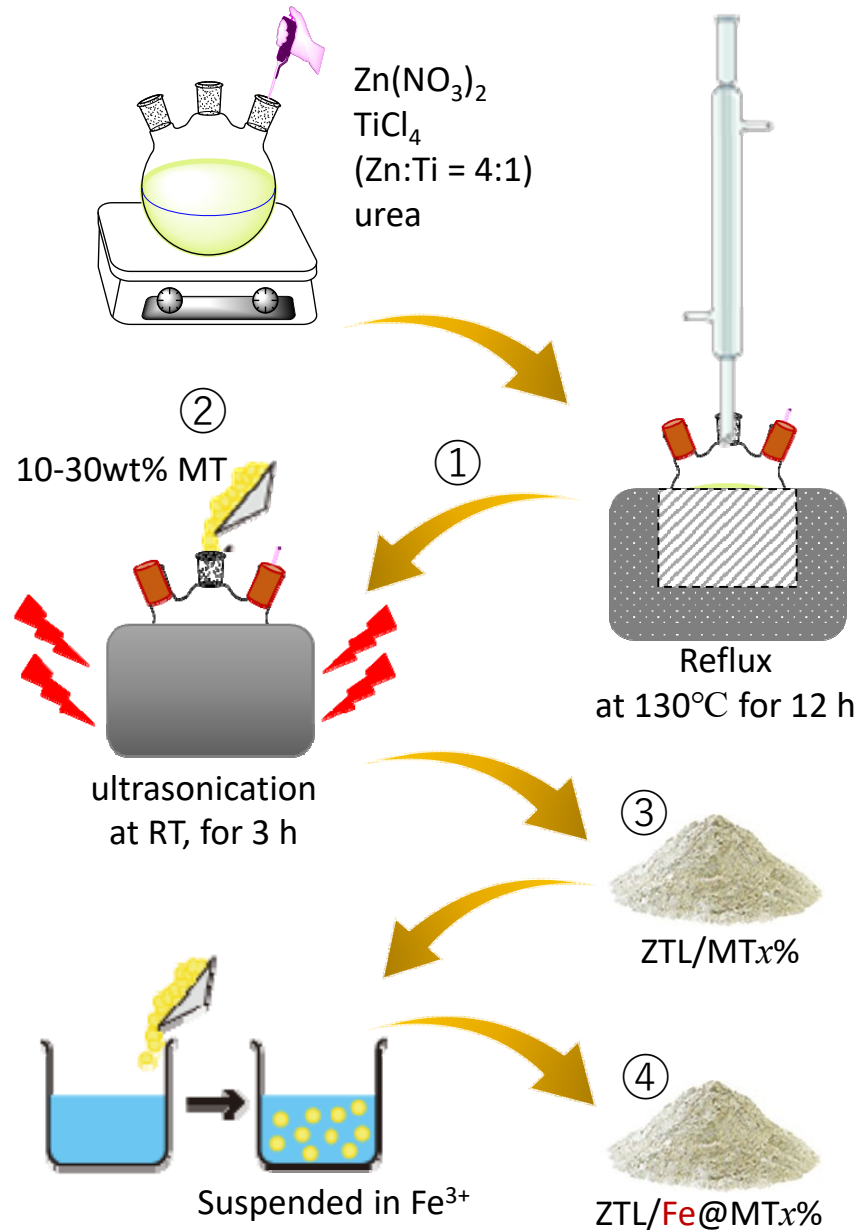
# Modification: Heterojunction

*Su et al., Adv. Sustainable Syst. 2020, 4, 2000130*

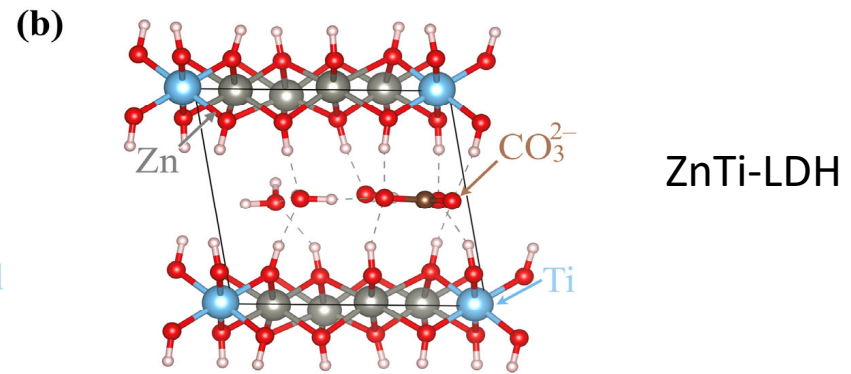
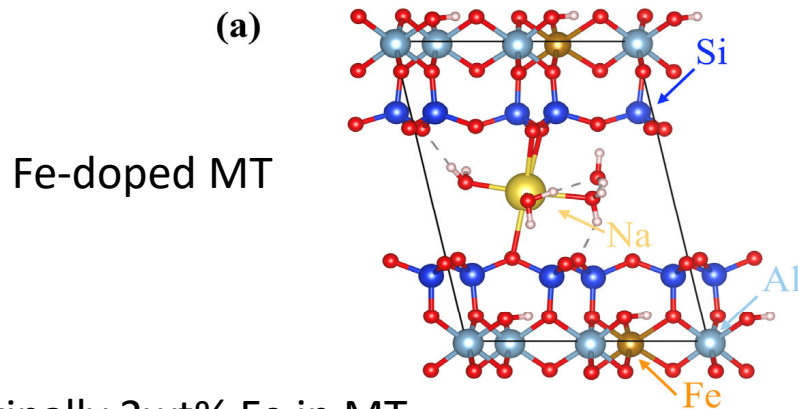




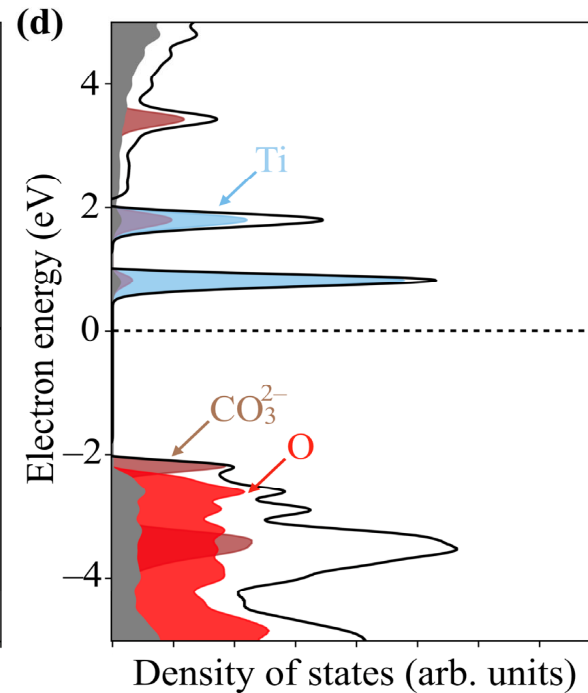
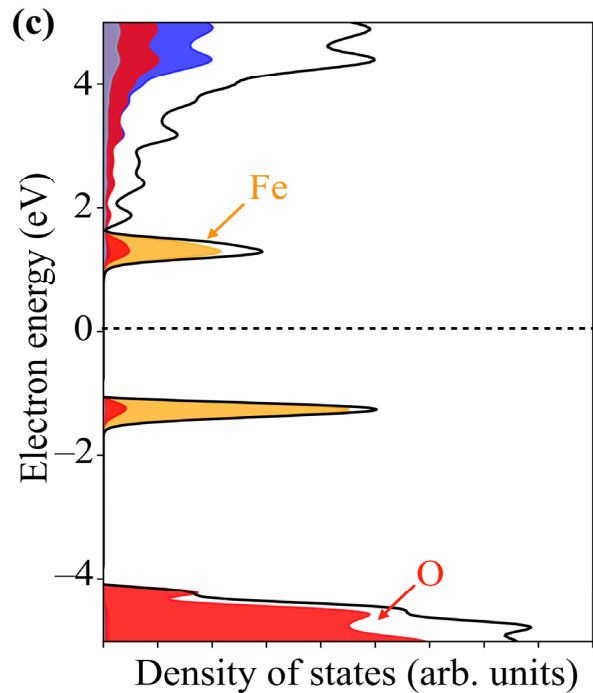
## Fabrication of ZnTi-layered double hydroxides (LDH) /Fe-doped montmorillonite (MT)



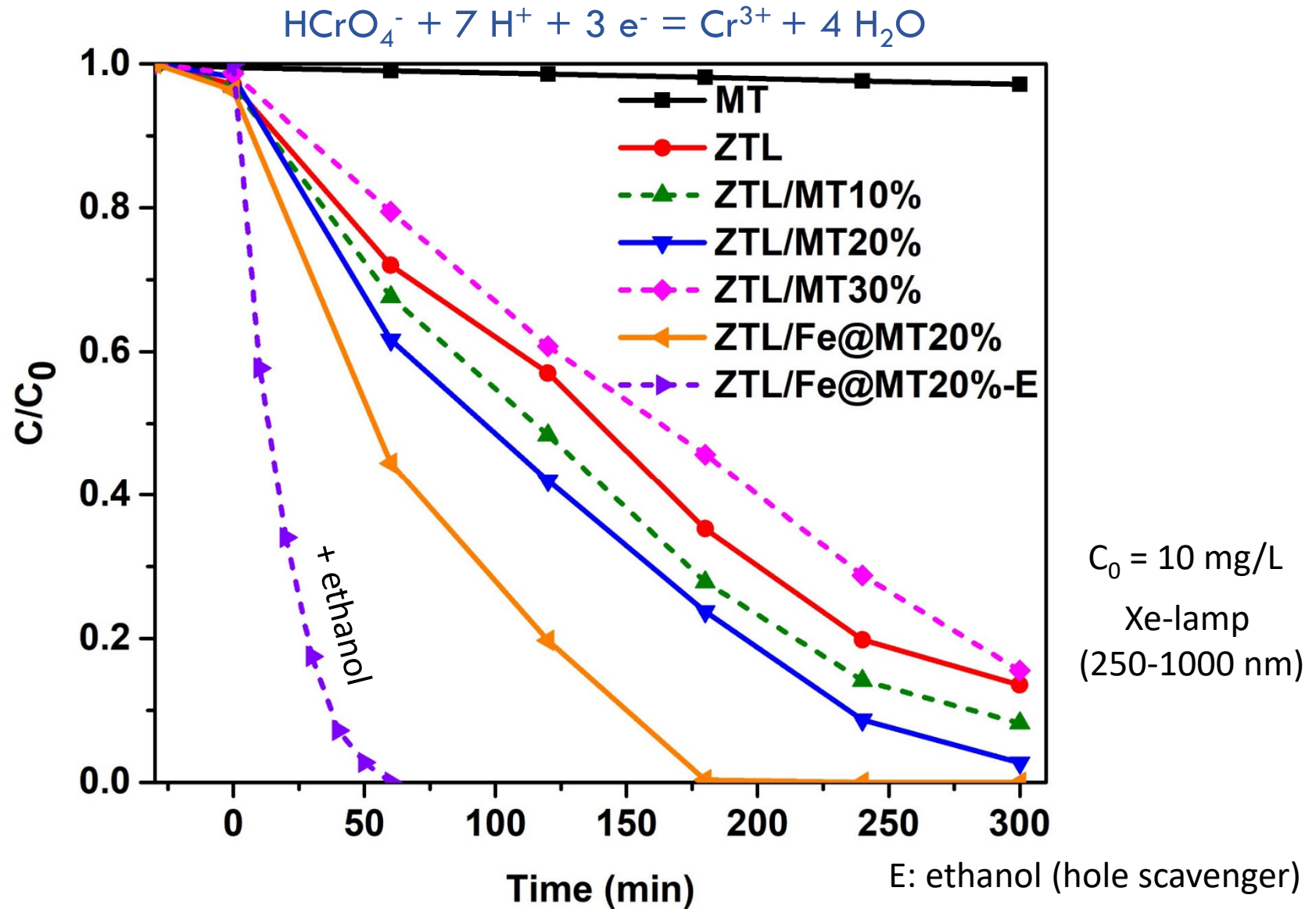
# DFT prediction of DOS for Fe-doped MT and ZnTi-LDH



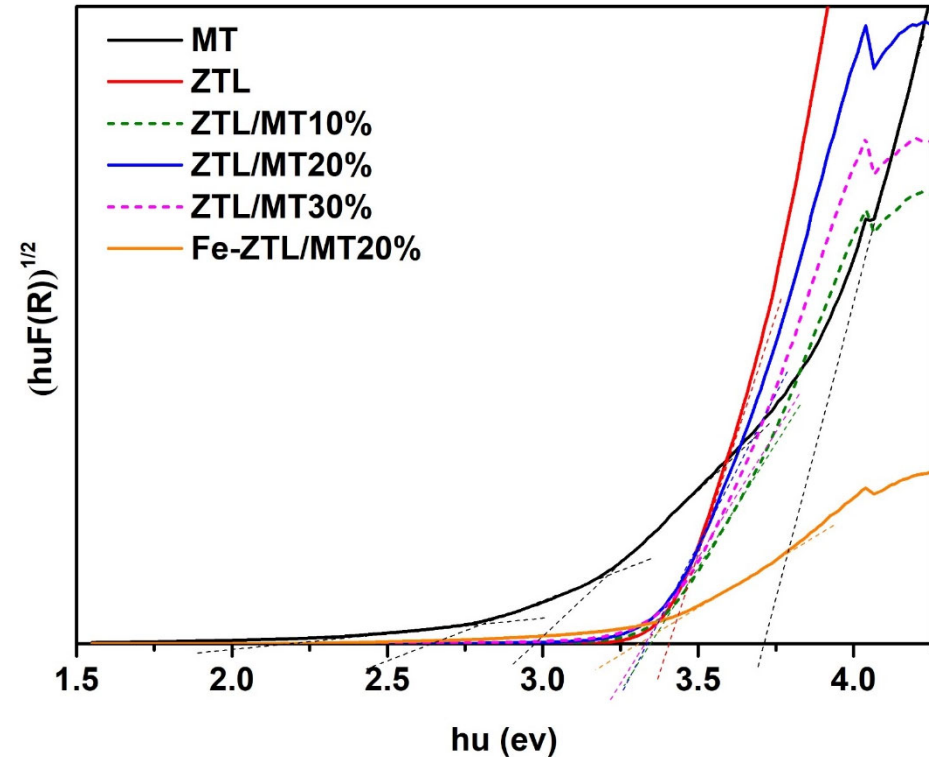
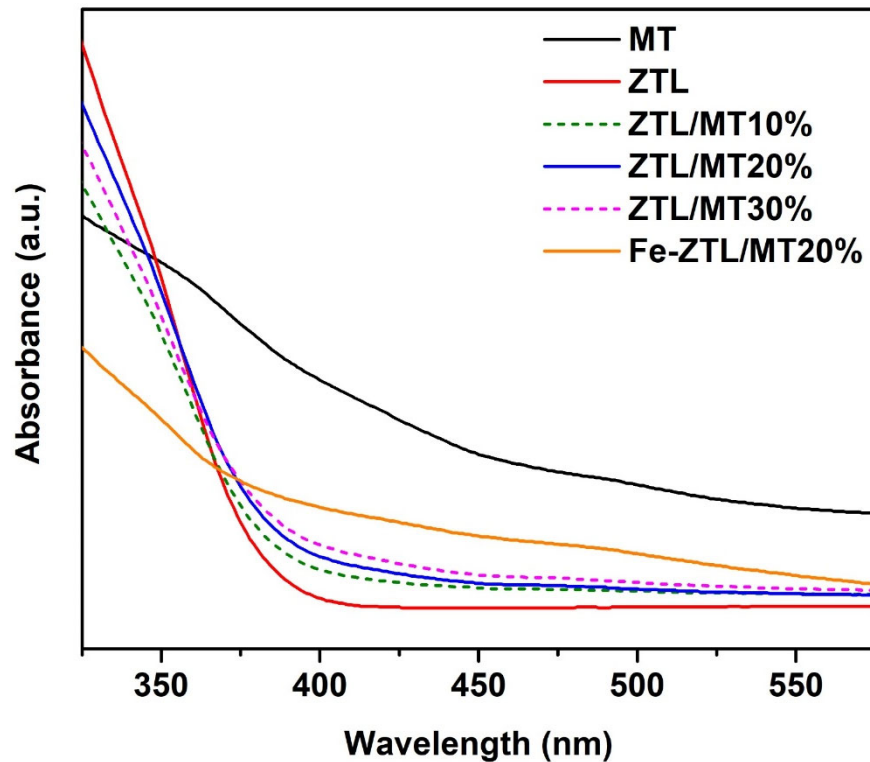
Originally 2wt% Fe in MT



## Photocatalytic reduction of Cr(VI) at pH 3



# Diffused Reflectance UV-VIS Spectroscopy (DRS)



Kubelka-Munk equation

$$\alpha hv = A(hv - E_g)^{n/2}$$

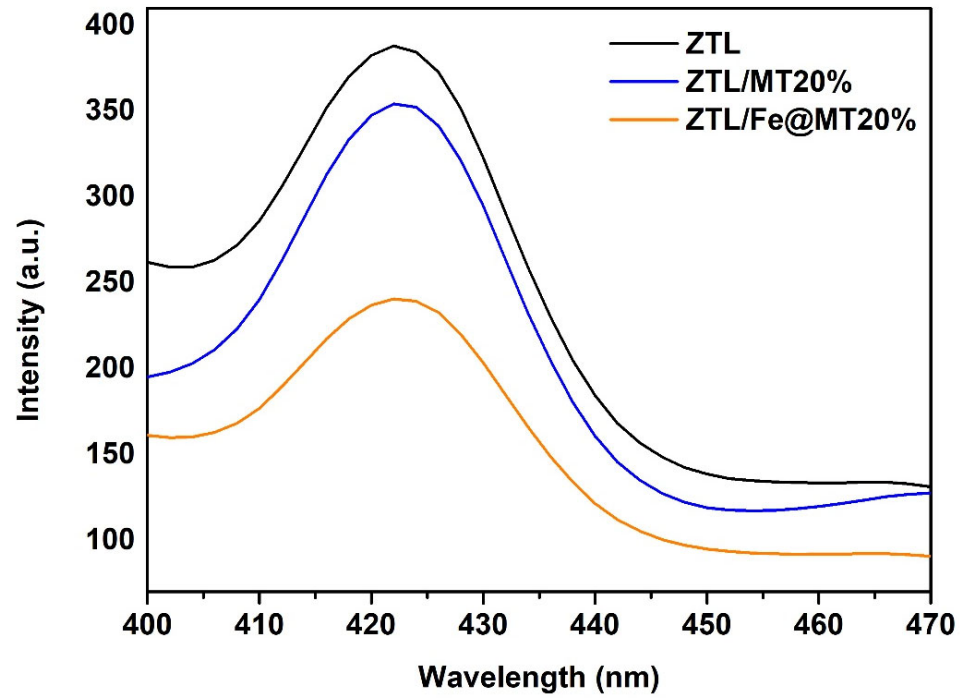
$\alpha$ , absorption coefficient

$\nu$ , light frequency

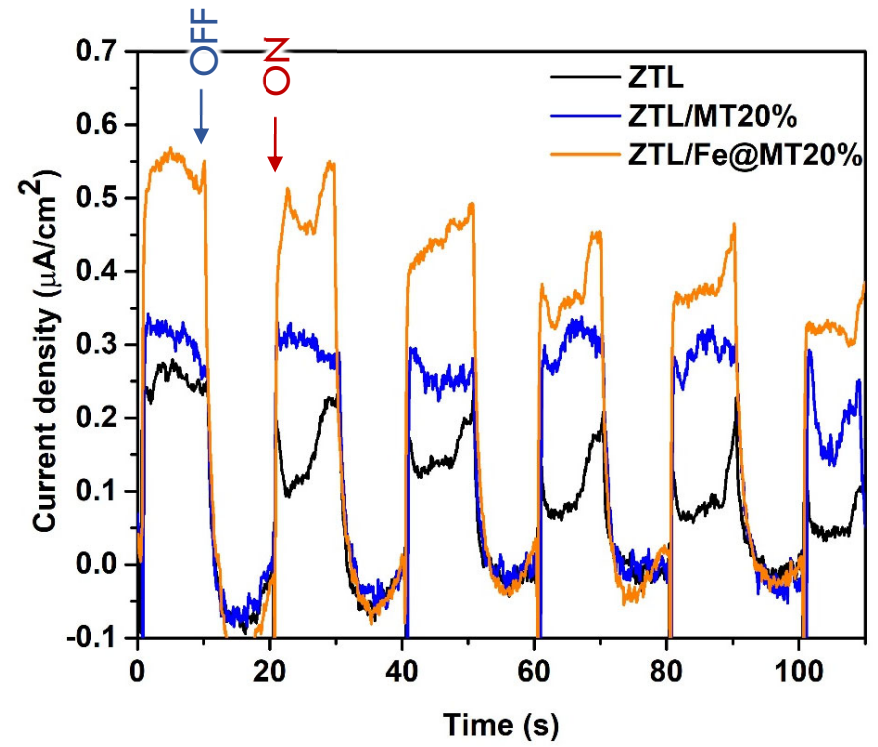
$A$ , proportionality constant

	$E_g$ (eV)
MT	2.56 and 3.72
ZTL	3.41
ZTL/MT20%	3.34
ZTL/Fe@MT20%	3.25

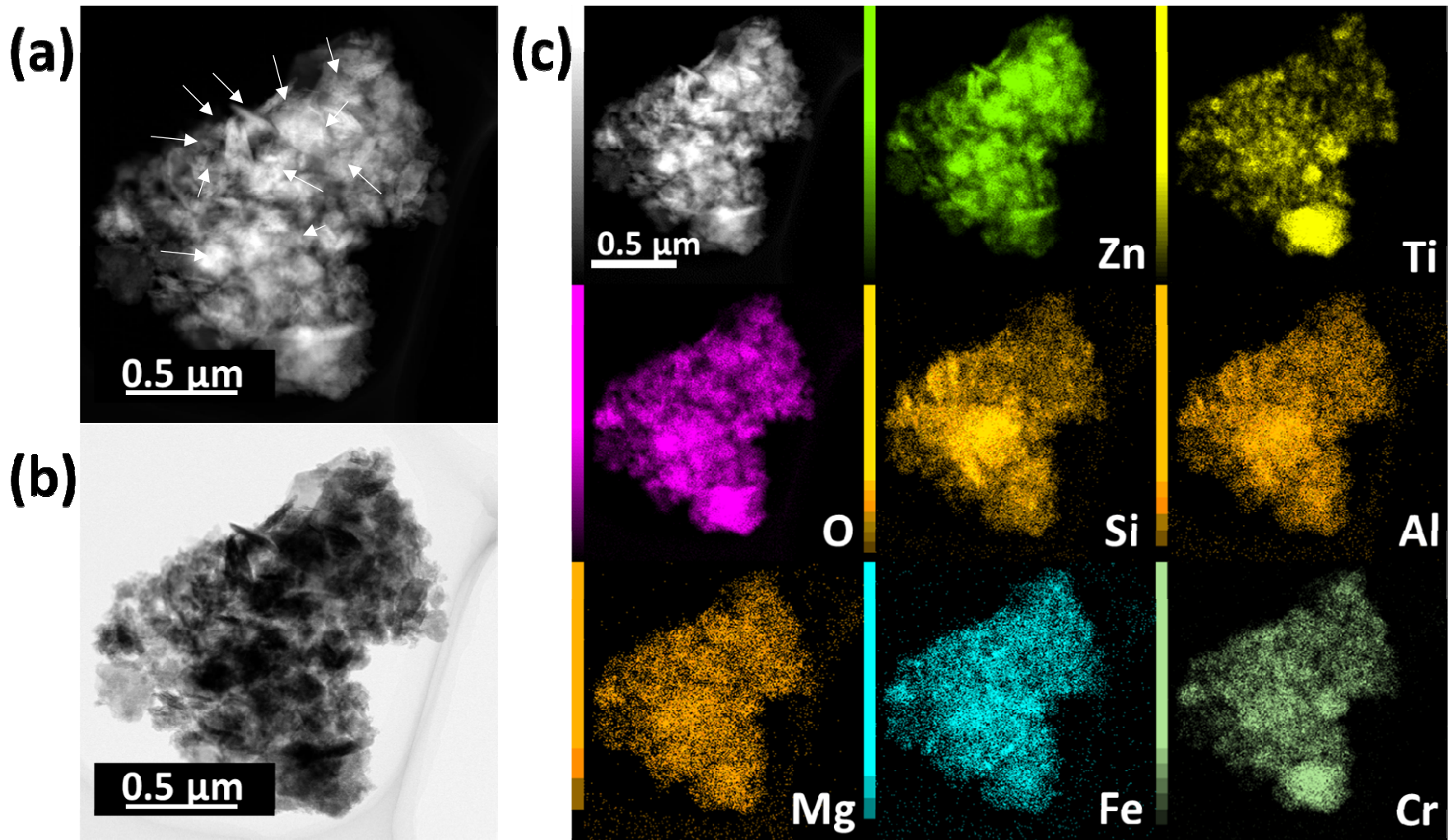
(a) Photoluminescence spectra



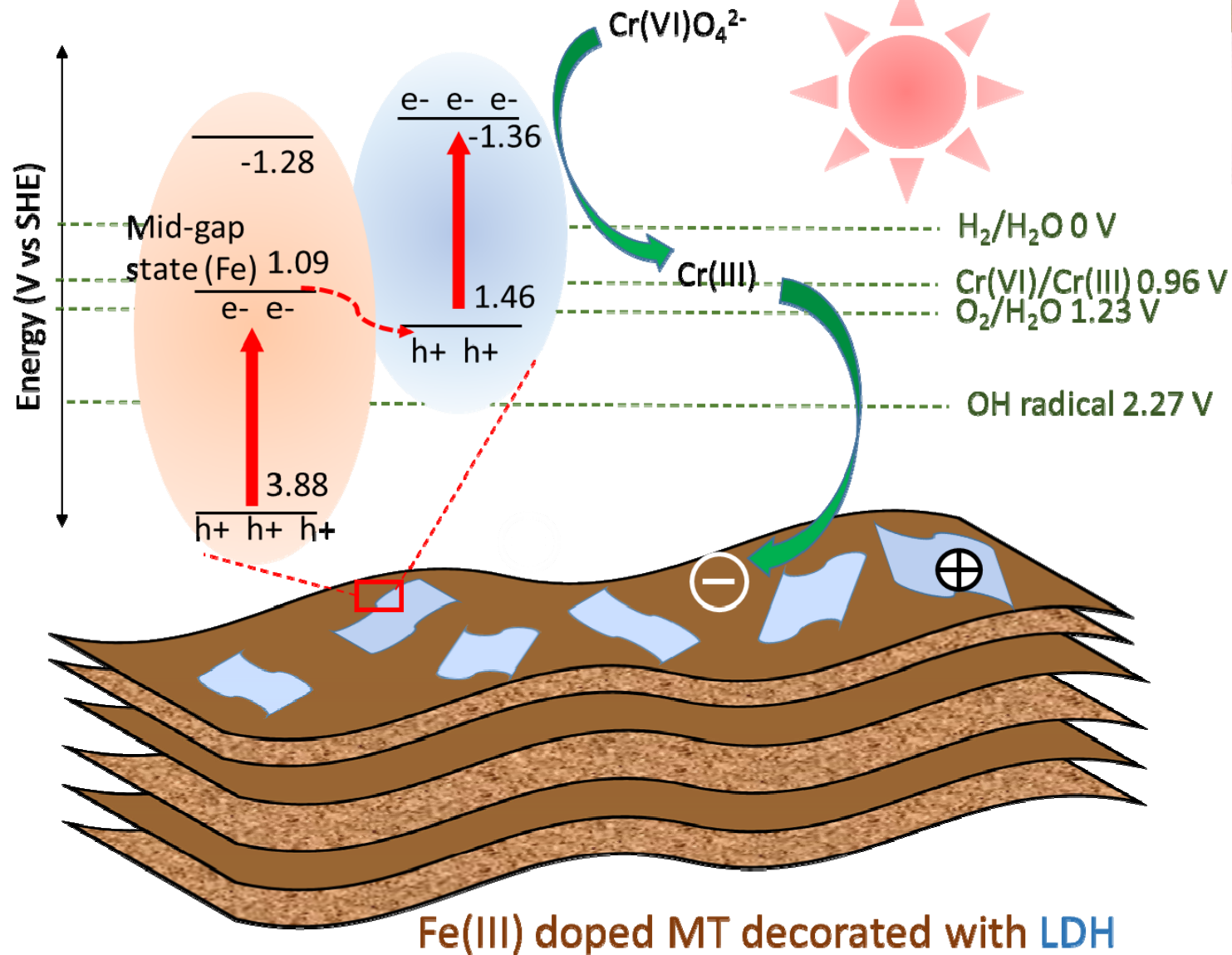
(b) Photocurrent



# TEM-EDX elemental mapping for spent ZTL/Fe@MT20%



# Z-scheme photocatalytic mechanism in Fe(III) doped MT decorated with LDH



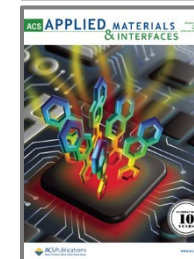
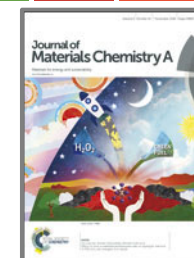
## Role of Fe(III) doped MT in the photocatalyst composites

Aspects	Advantages
(i) light absorption (optical)	<ul style="list-style-type: none"> <li>✓ Increased by composite with MT compared with ZnTi-LDH only</li> <li>✓ Increased by Fe-doping compared with no Fe-doping LDH/MT</li> </ul>
(ii) charge separation and transport (physicochemical)	<ul style="list-style-type: none"> <li>✓ <b>Generated the mid-trap state of electron by Fe</b> as an impurity in MT.</li> <li>✓ <b>Enhanced by Z-scheme heterojunction</b> for electron transfer and avoided the recombination of excited electron</li> </ul>
(iii) surface chemical reaction (physical)	<ul style="list-style-type: none"> <li>✓ Provided the large surface area</li> <li>✓ Enhanced the contact frequency with the main photocatalyst by 2D-2D materials</li> </ul>
(iv) others	<ul style="list-style-type: none"> <li>✓ Stabilized Cr(III) on the remaining surfaces of MT after photoreduction of <math>\text{Cr(VI)O}_4^{2-}</math></li> </ul>

Clay is not only a support for main photocatalyst in the composites, and involved in photochemical reactions.



- [Chitiphon Chuaicham](#), Radheshyam R Pawar, [Keiko Sasaki](#), Dye-sensitized photocatalyst of sepiolite for organic dye degradation, *Catalysts*, 9 (2019) 235-255.
- [Karthikeyan Sekar](#), [Chitiphon Chuaicham](#), Radheshyam R. Pawar, [Keiko Sasaki](#), Wei Li, Adam Lee, Karen Wilson, Template free mild hydrothermal synthesis of core-shell  $\text{Cu}_2\text{O}(\text{Cu})@\text{CuO}$  visible light photocatalysts for N-acetyl-para-aminophenol degradation, *J. Mater. Chem. A*, 7 (2019) 20767-20777.
- Sekar Karthikeyan, Kassam Ahmed, Amin Osatiashtiani, Adam F. Lee, Karen Wilson, [Keiko Sasaki](#), Ben Coulson, Will Swansborough-Aston, Richard E. Douthwaite, Wei Li, Pompon Dahlia-like  $\text{Cu}_2\text{O}/\text{rGO}$  nanostructures for visible light photocatalytic  $\text{H}_2$  production and 4-chlorophenol degradation, *Chem Cat Chem*, 12 (2020) 1699–1709.
- [Chitiphon Chuaicham](#), [Karthikeyan Sekar](#), Jun Tae Song, Tatsumi Ishihara, Bunsho Ohtani, [Keiko Sasaki](#), Importance of  $\text{ZnTiO}_3$  phase in ZnTi mixed metal oxide photocatalyst derived from layered double hydroxide, *ACS Appl. Mater. Interfaces*, 12 (2020) 9169–9180.
- [Chitiphon Chuaicham](#), Radheshyam R Pawar, [Karthikeyan Sekar](#), Yihuang Xiong, Ismaila Dabo, Bunsho Ohtani, [Keiko Sasaki](#), Energy-resolved distribution of electron traps for O/S-doped carbon nitrides by reversed double-beam photoacoustic spectroscopy and the photocatalytic reduction of Cr(VI), *Chem. Comm.*, 56 (2020) 3793–3796.
- [Chitiphon Chuaicham](#), Radheshyam R Pawar, [Sekar Karthikeyan](#), Bunsho Ohtani, [Keiko Sasaki](#), Fabrication and characterization of ternary sepiolite/g- $\text{C}_3\text{N}_4/\text{Pd}$  composites for improvement of photocatalytic degradation of ciprofloxacin under visible light irradiation, *J. Colloid. Interface Sci.*, 577 (2020) 397-405.
- [Sekar Karthikeyan](#); [Chitiphon Chuaicham](#); [Umamahesh Balijapalli](#); [Wei Li](#); [Adam Fraser Lee](#); [Keiko Sasaki](#), Surfactant- and template-free low-hydrothermal assembly of hierarchical to cubic nanostructured  $\text{CuO}/\text{Cu}_2\text{O}$  photocatalysts with uniformed sizes, *Appl. Cat. B: Environ.*, in press.
- [Chitiphon Chuaicham](#), Yihuang Xiong, [Sekar Karthikeyan](#), Weinan Chen, Li Zhang, Bunsho Ohtani, Ismaila Dabo, [Keiko Sasaki](#), A promising Zn-Ti layered double hydroxide/Fe-bearing montmorillonite composite as an efficient photocatalyst for Cr(VI) reduction: Insight into the role of Fe impurity in montmorillonite, *Appl. Surf. Sci.*, 546 (2021) 148835.
- [Sekar Karthikeyan](#); [Kassam Ahmed](#); [Yang Bai](#); [Keiko Sasaki](#), [Wei Li](#), Quantum dot bismuth vanadate/reduced graphene oxide photocatalyst for hydrogen evolution and bisphenol A degradation, *Appl. Mater. Today*, (2021) 100963.



# Solar light driven chemical conversion

