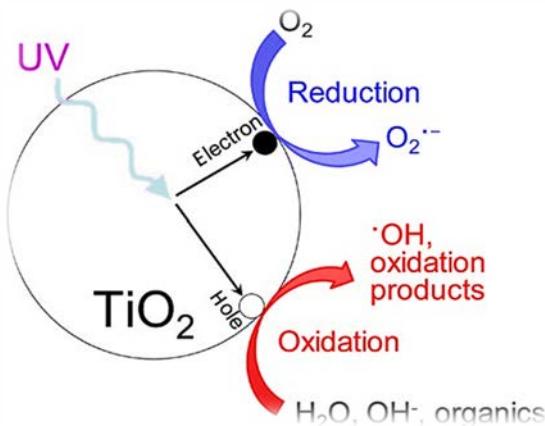
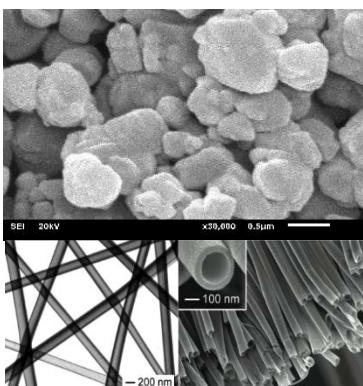


Modification of Visible-Light Photocatalytic Activity for Glucose and lignin Conversion to Value-Added Chemicals



Takashi Sagawa

Navadol Laosiripojana

Verawat Champreda

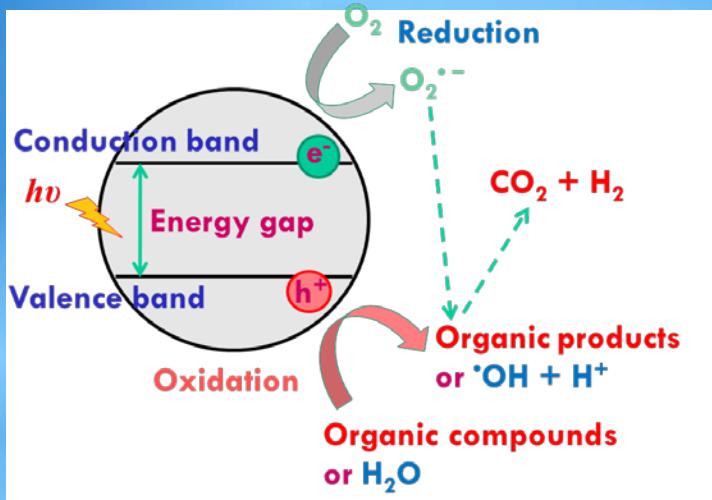
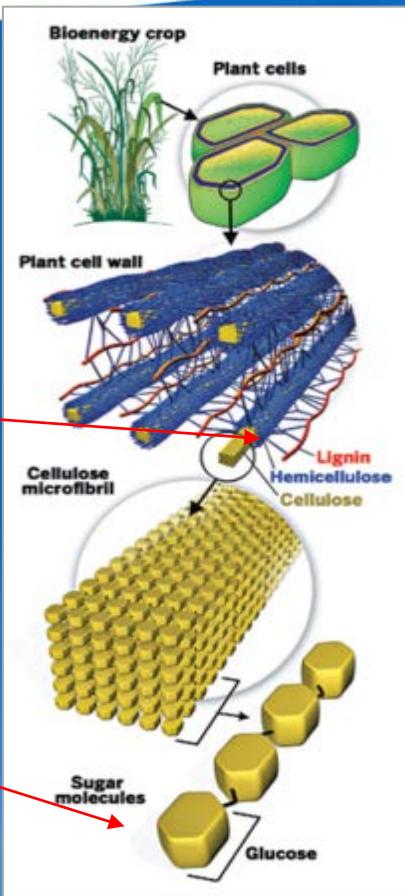
Surawut Chuangchote



Research Themes

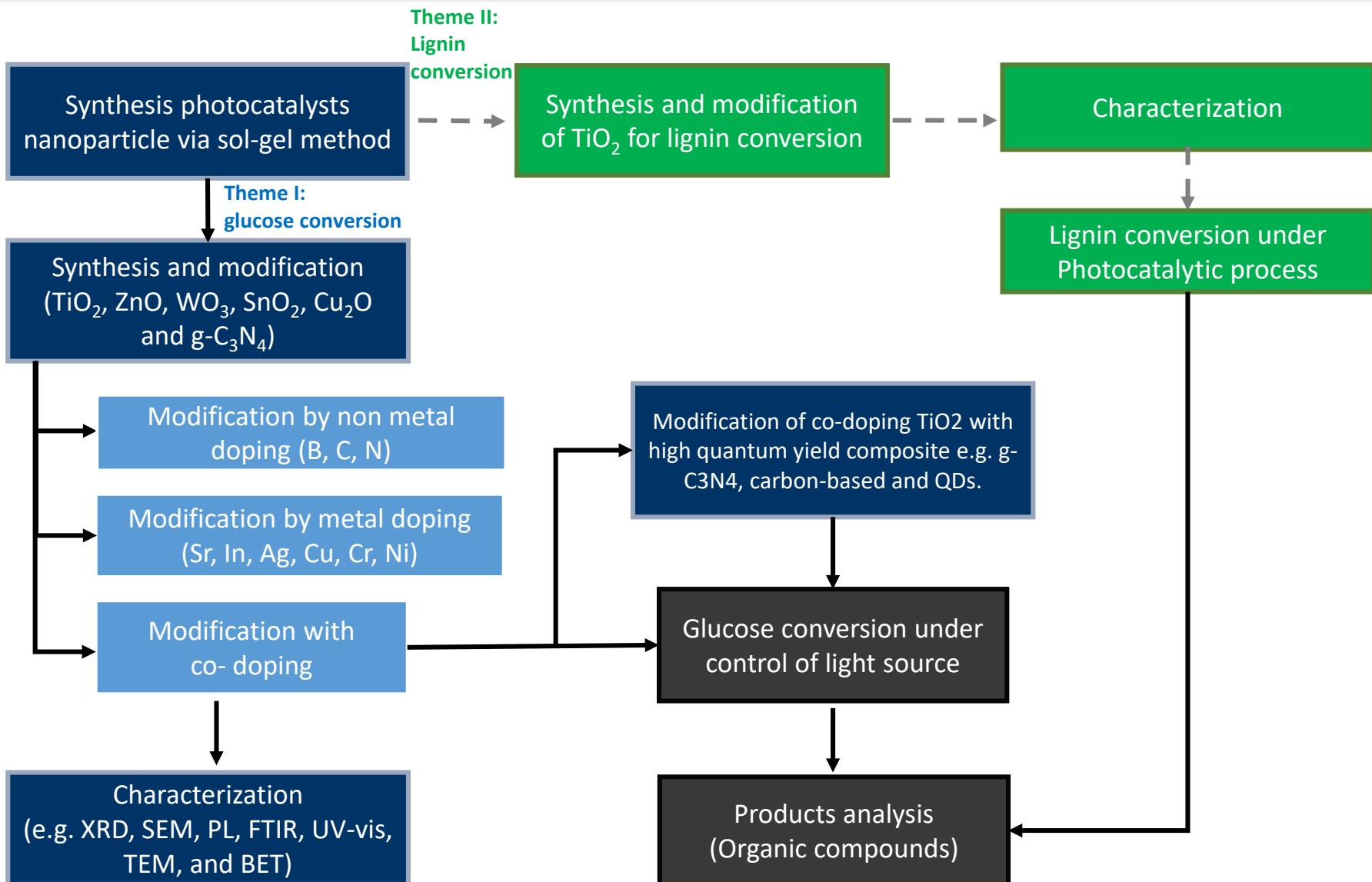
Theme 2
Lignin
Conversion

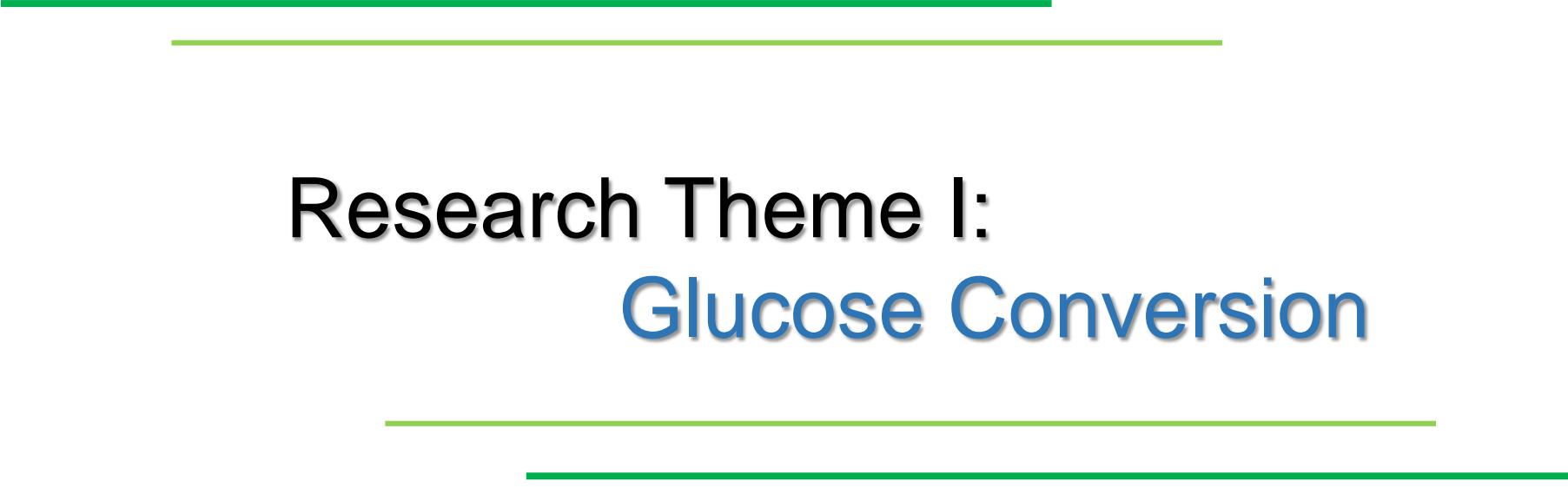
Theme 1
Sugar
Conversion



Value-added Fuels & Chemicals

Scope of Research Work



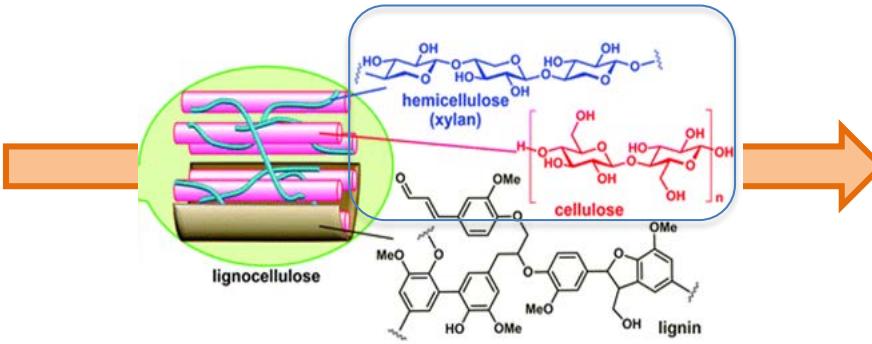


Research Theme I: Glucose Conversion

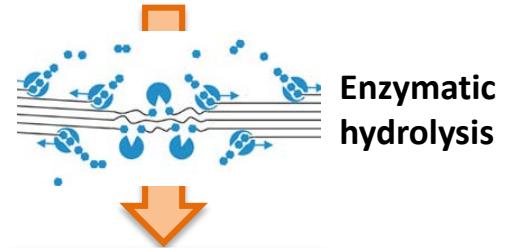
Photocatalytic Process for Biorefinery and value-added Chemicals



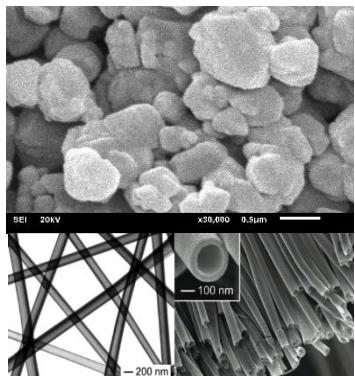
Biomass



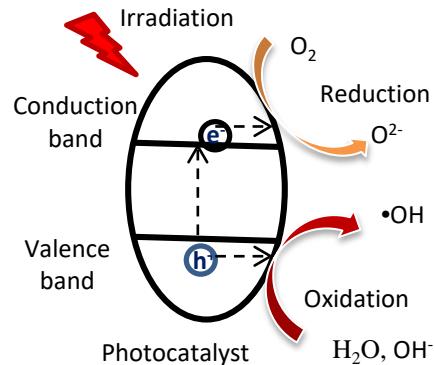
Carbohydrate structure



Enzymatic hydrolysis

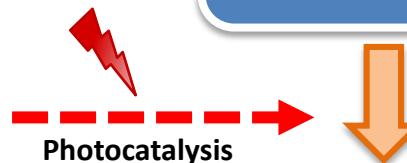


Photocatalyst



Photocatalytic process

*Sugars
Glucose (C₆)



Value-added Chemicals

- Xylitol, Gluconic acid, Formic acid, Arabitol

Proposed reaction pathways of photocatalytic glucose conversion with TiO_2 photocatalysts

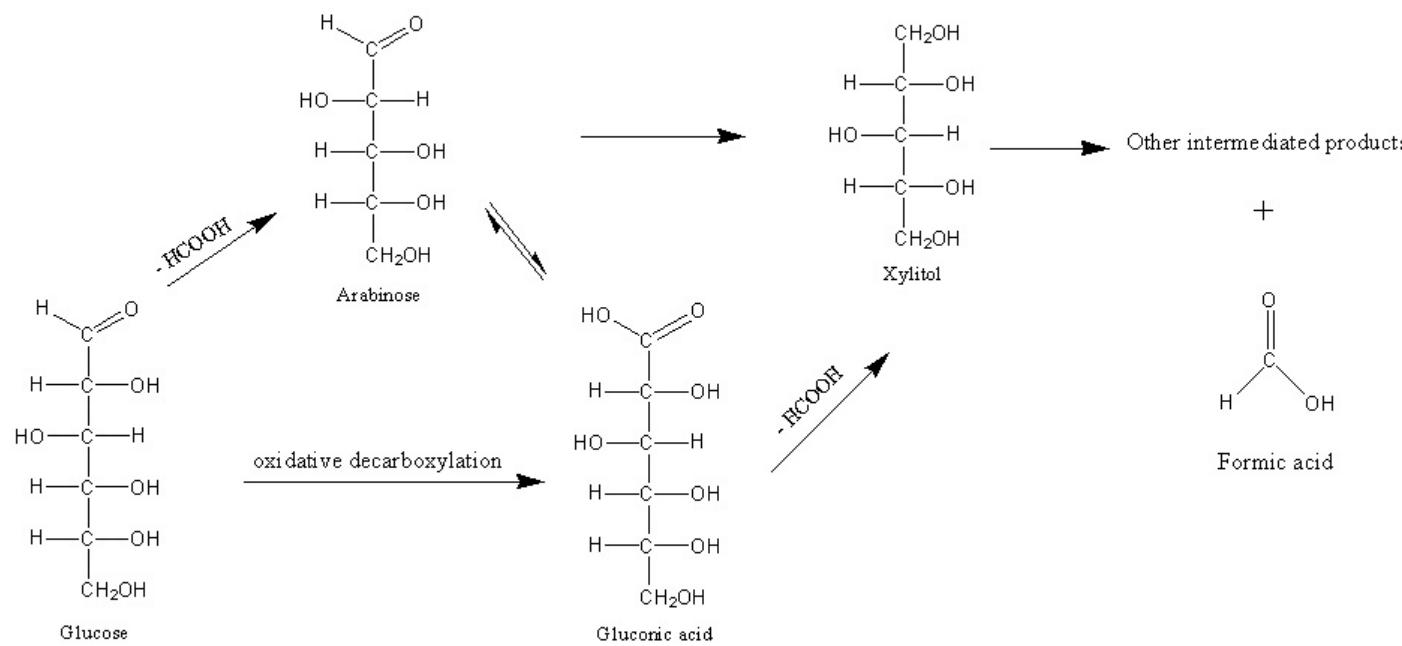
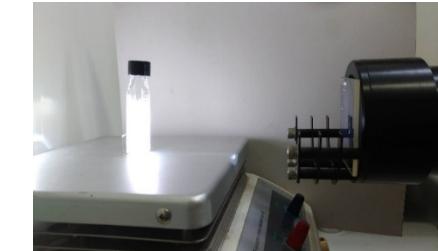
Photocatalytic reaction

Control under UV light
($\lambda=250\text{-}365 \text{ nm}$)

- Glucose concentration 1g/L
- Catalyst loading 1 g/L
- Mixture solvent (water:acetonitrile)
- Analysis products by HPLC

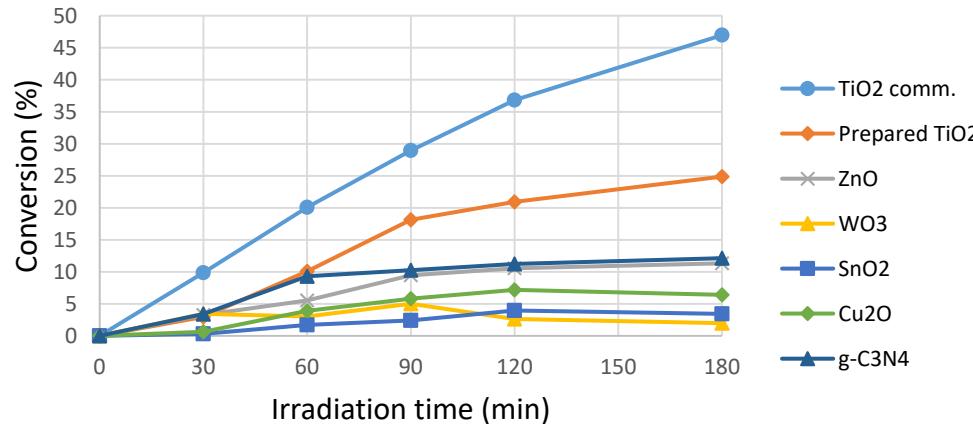


Control under visible light
(filter cut off $\lambda>380 \text{ nm}$)

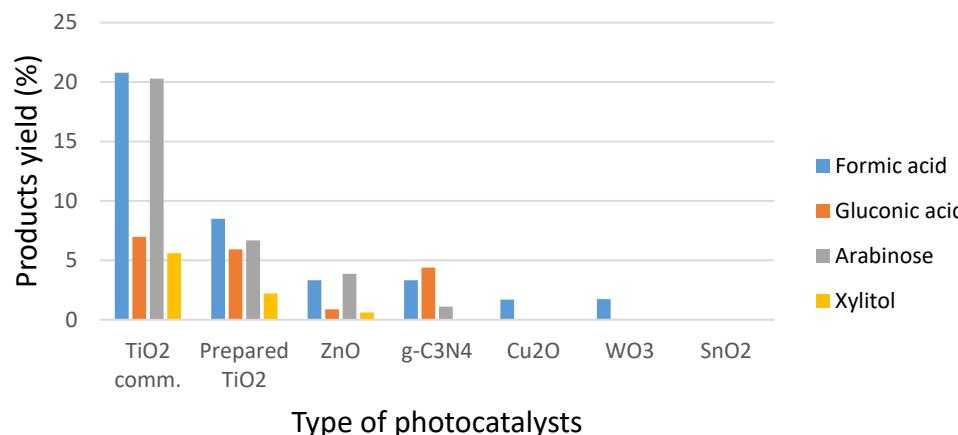


Photocatalytic conversion of glucose in the presence of various photocatalyst nanoparticles

Type of photocatalysts: TiO₂ commercial (anatase form), TiO₂, ZnO, WO₃, SnO₂, Cu₂O, g-C₃N₄ under **UV light (250-365 nm)** (difference in the relative band gap positions with various Redox potentials)



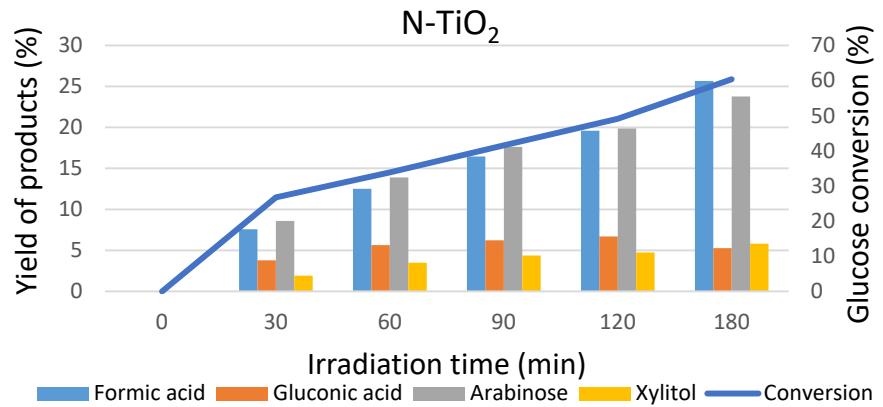
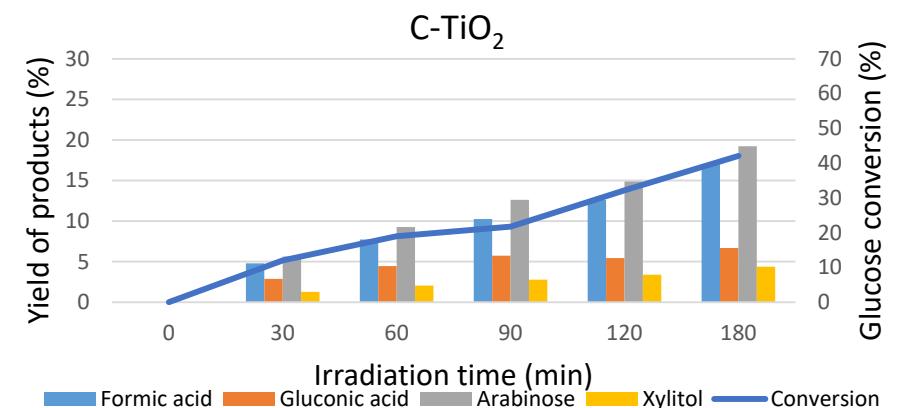
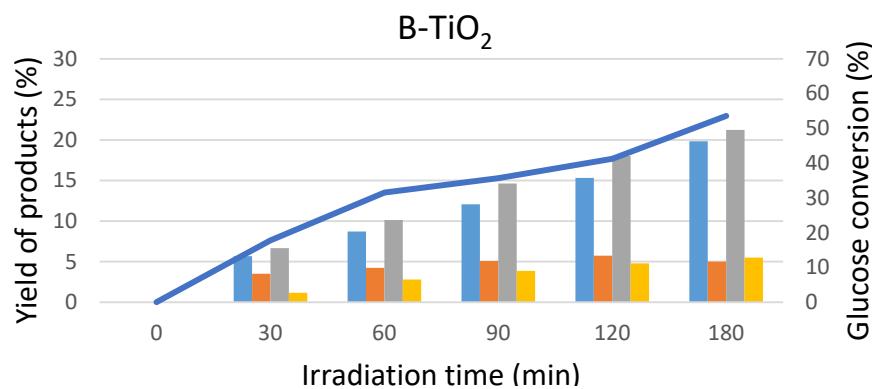
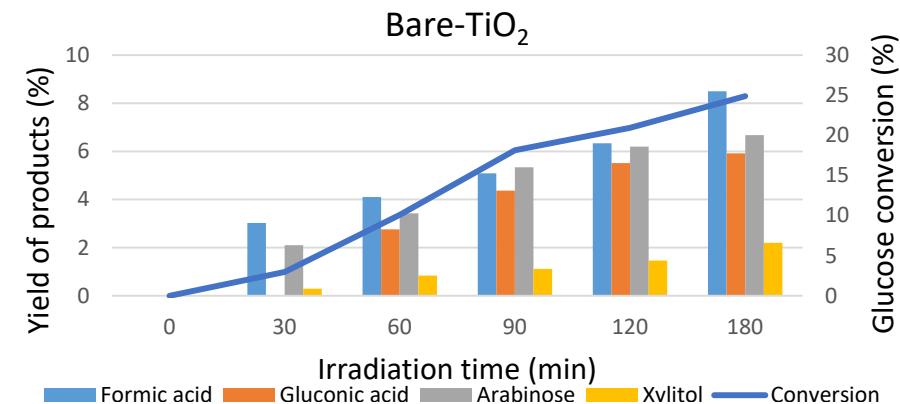
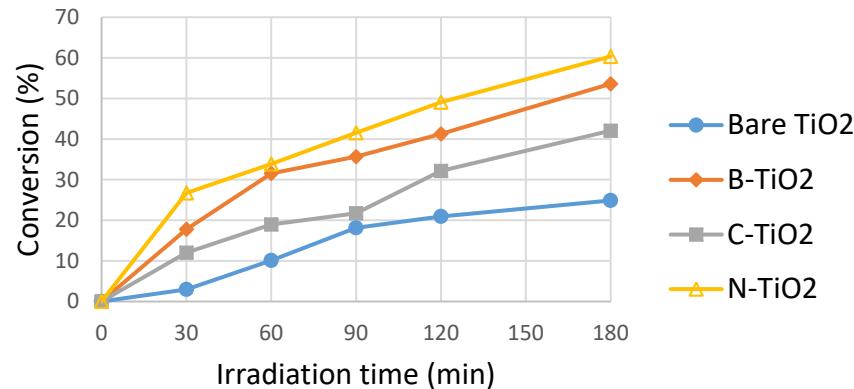
Glucose conversion using various type of photocatalysts under control light source ($\lambda=250-365$ nm).



Product yield of various type photocatalysts at specific time 180 min.

Doping of non-metal on TiO_2 nanoparticles

The effect of non-metal doped TiO_2 for glucose conversion control under UV light (250-365 nm)



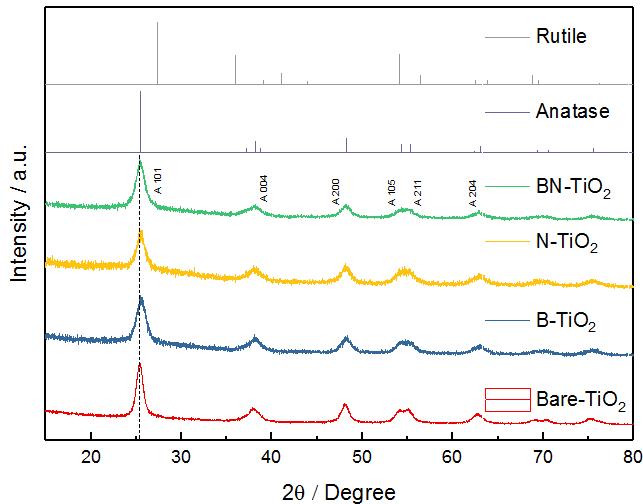
Doping of non-metal on TiO₂ nanoparticles

Characterization of non-metal doped TiO₂

BET analysis of non-metal doped TiO₂

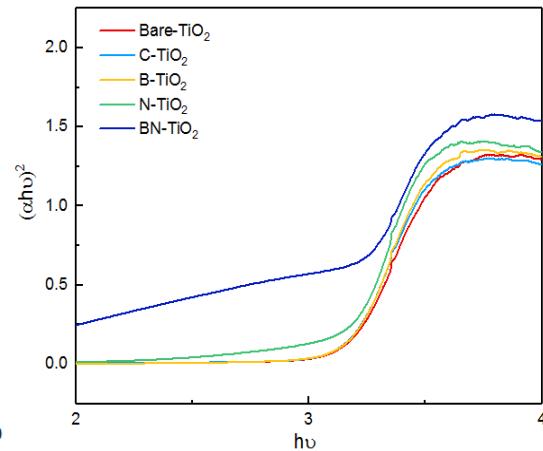
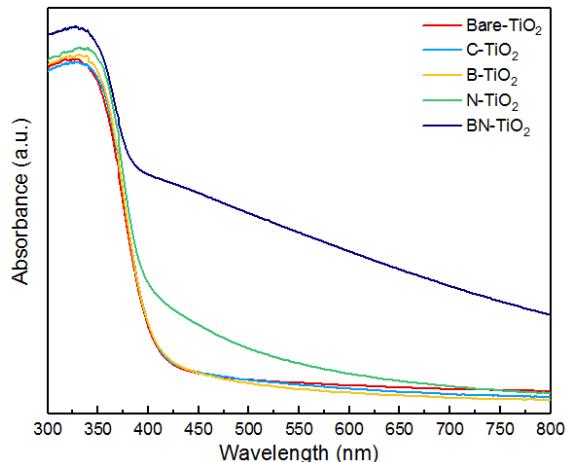
Samples	Pore size (nm)	Pore volume (cm ³ /g)	Surface area (m ² /g)
Bare TiO ₂	5.55	0.11	77.92
B-doped TiO ₂	3.99	0.15	147.37
C-doped TiO ₂	4.37	0.12	109.20
N-doped TiO ₂	5.47	0.21	153.04
BN-dopedTiO ₂	5.56	0.32	227.69

XRD analysis of non-metal doped TiO₂

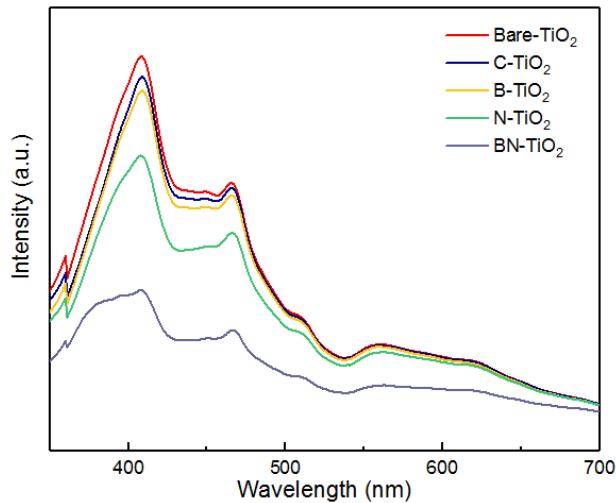


Photocatalysts	Crystal phase (%)		Crystallite size (nm)
	Anatase	Rutile	
Bare-TiO ₂	100	-	9.59
B-TiO ₂	100	-	7.31
N-TiO ₂	100	-	7.56
BN-TiO ₂	100	-	7.35

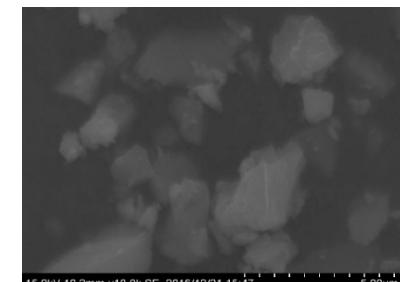
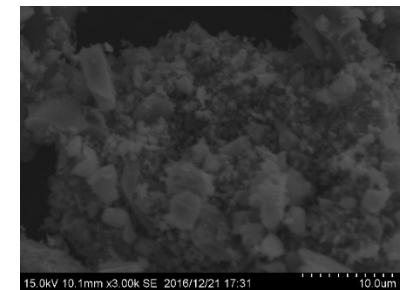
UV-vis diffuse reflectance spectra of non-metal doped TiO₂



Photoluminescence of non-metals doped TiO₂

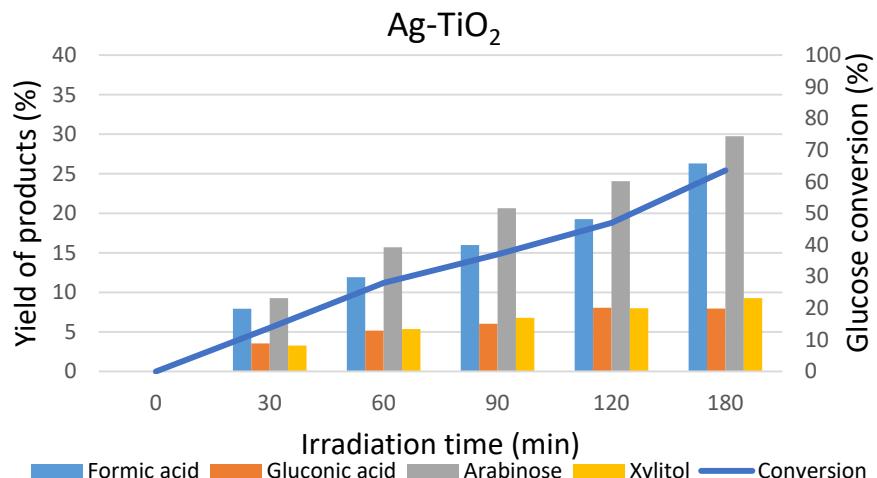
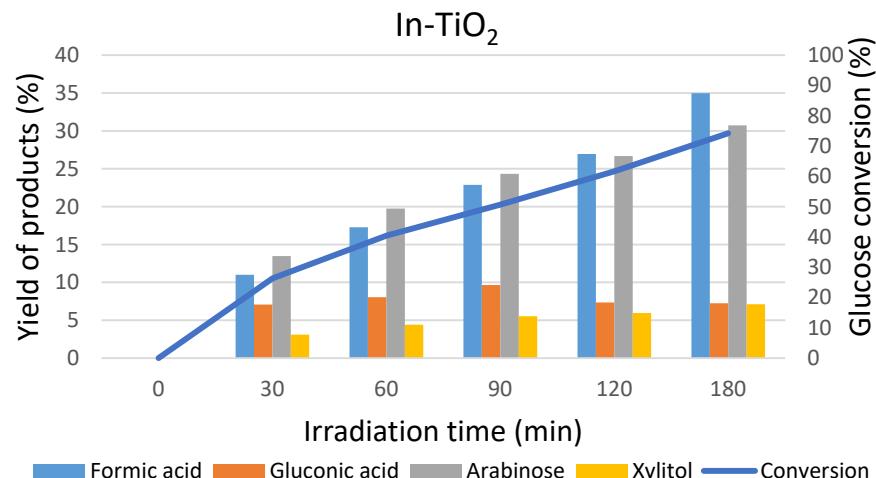
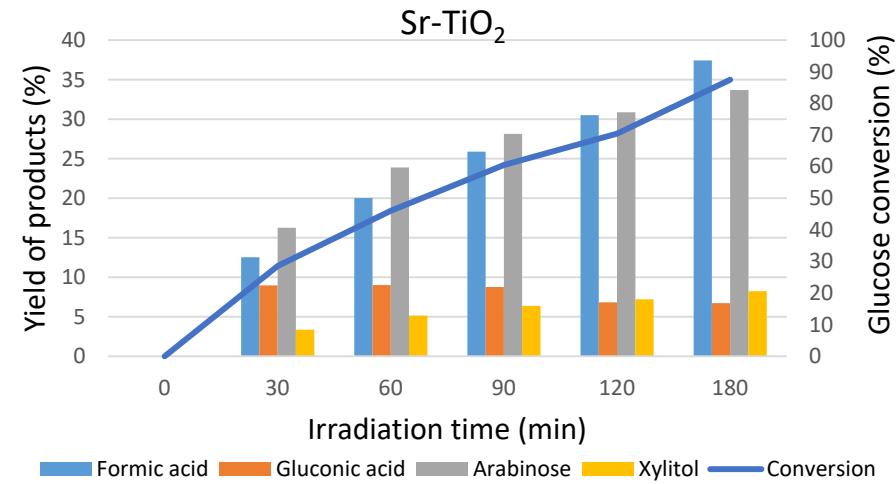
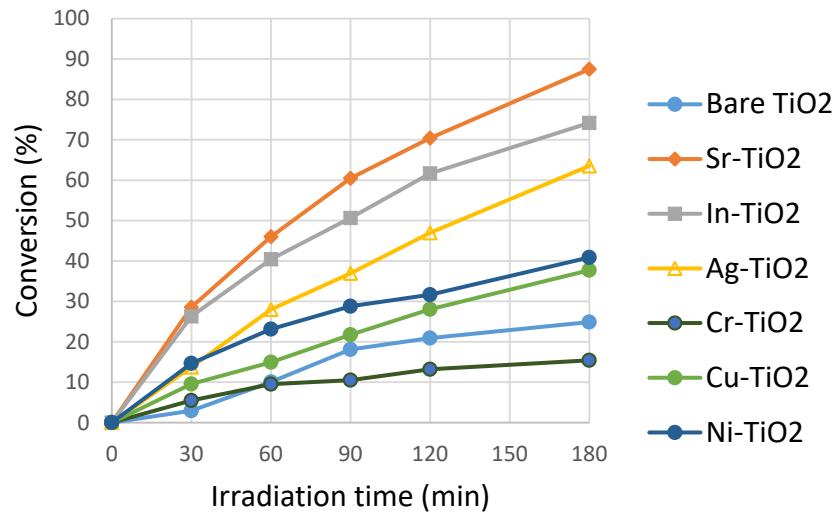


SEM image and EDX analysis



Doping of metals on TiO_2 nanoparticles

The effect of metal doped TiO_2 for glucose conversion control under UV light (250-365 nm)



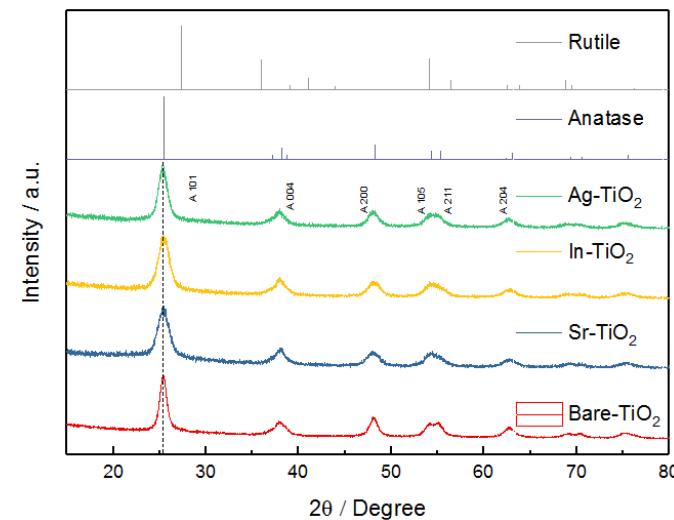
Doping of metals on TiO₂ nanoparticles

Characterization of metals doped TiO₂

BET analysis of non-metal doped TiO₂

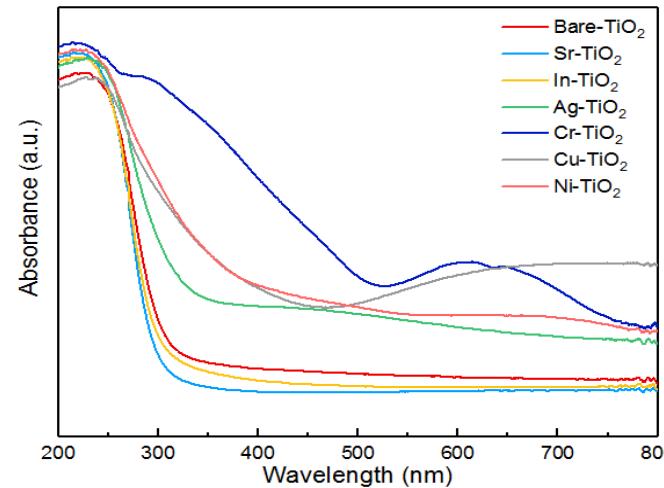
Samples	Pore size (nm)	Pore volume (cm ³ /g)	Surface area (m ² /g)
Bare TiO ₂	5.55	0.11	77.92
Sr-doped TiO ₂	4.55	0.24	210.60
In-doped TiO ₂	3.75	0.19	202.77
Ag-doped TiO ₂	3.76	0.11	114.95
Cr-doped TiO ₂	3.78	0.12	125.31
Cu-doped TiO ₂	3.96	0.12	124.07
Ni-doped TiO ₂	4.53	0.17	147.75

XRD analysis of metal doped TiO₂

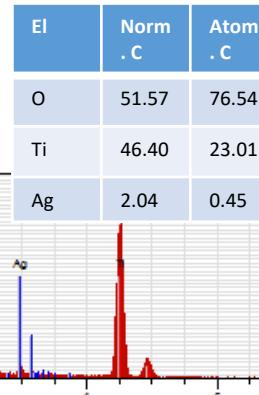
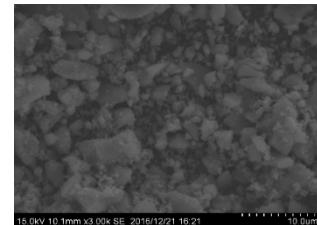


Photocatalysts	Crystal phase (%)		Crystallite size (nm)
	Anatase	Rutile	
Bare-TiO ₂	100	-	9.59
Sr-TiO ₂	100	-	5.81
In-TiO ₂	100	-	6.10
Ag-TiO ₂	100	-	7.41

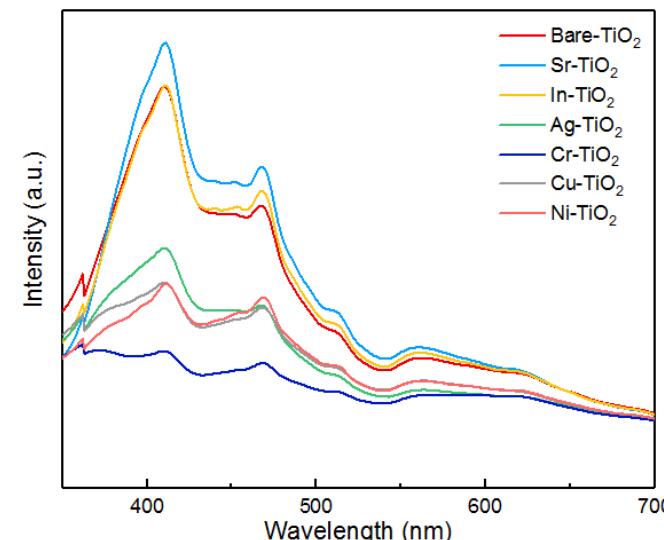
UV-vis diffuse reflectance spectra of metal doped TiO₂



SEM image and EDX analysis

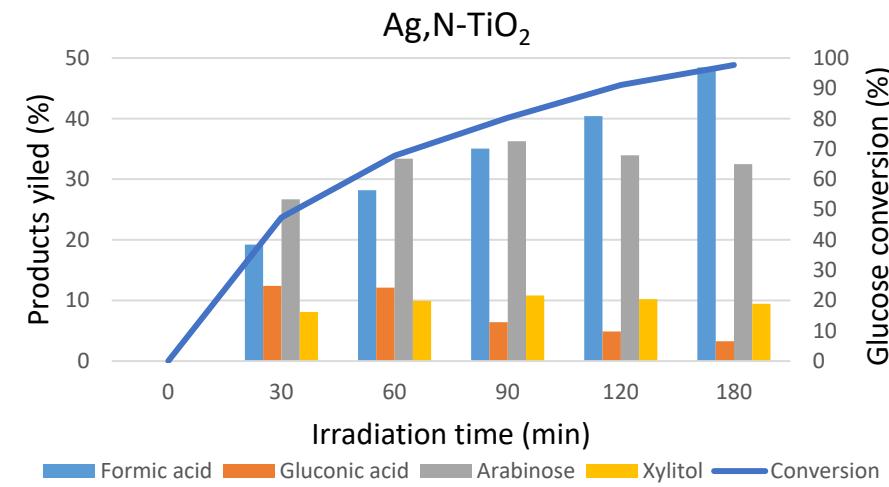
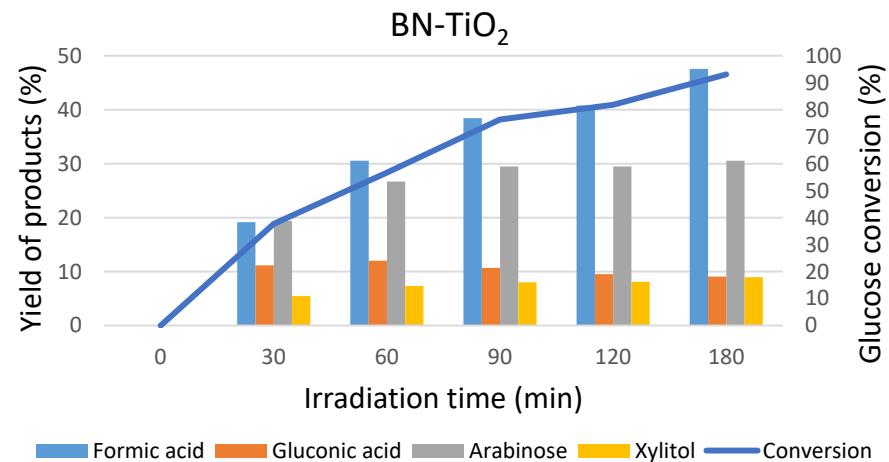
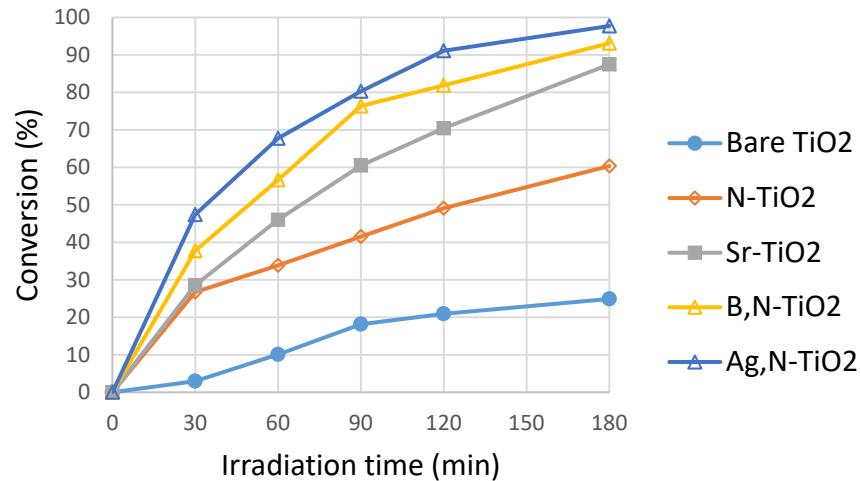


Photoluminescence of metals doped TiO₂



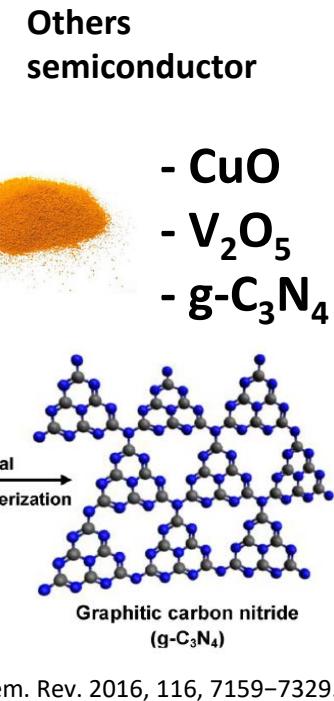
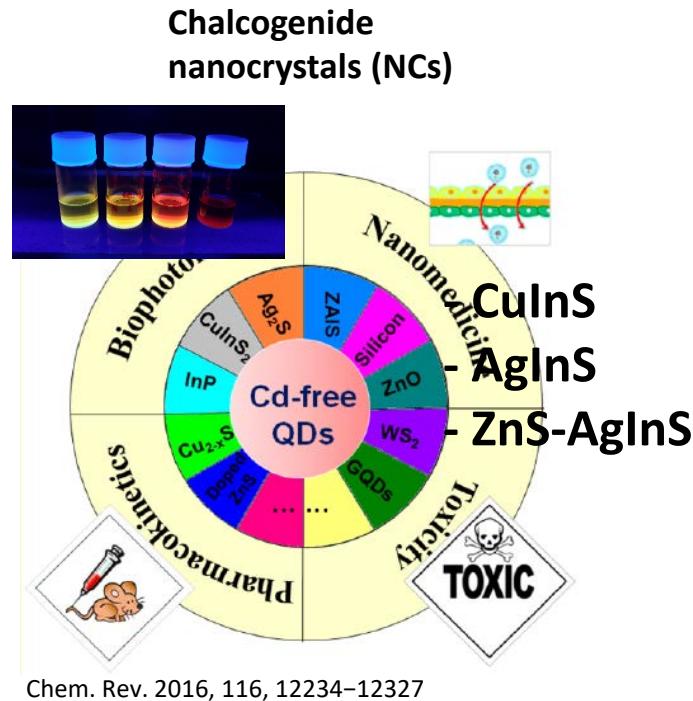
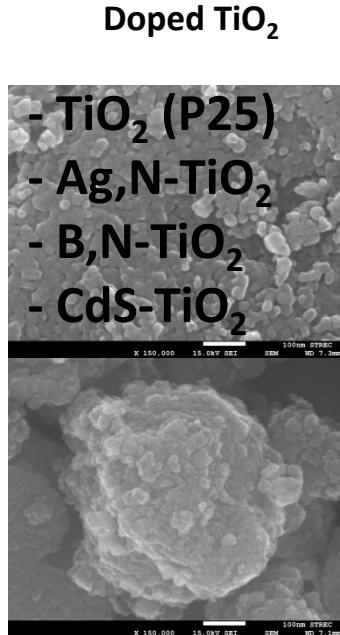
Co-doping on TiO_2 nanoparticles

The effect of co-doped TiO_2 for glucose conversion control under UV light (250-365 nm)



Glucose conversion under visible-light

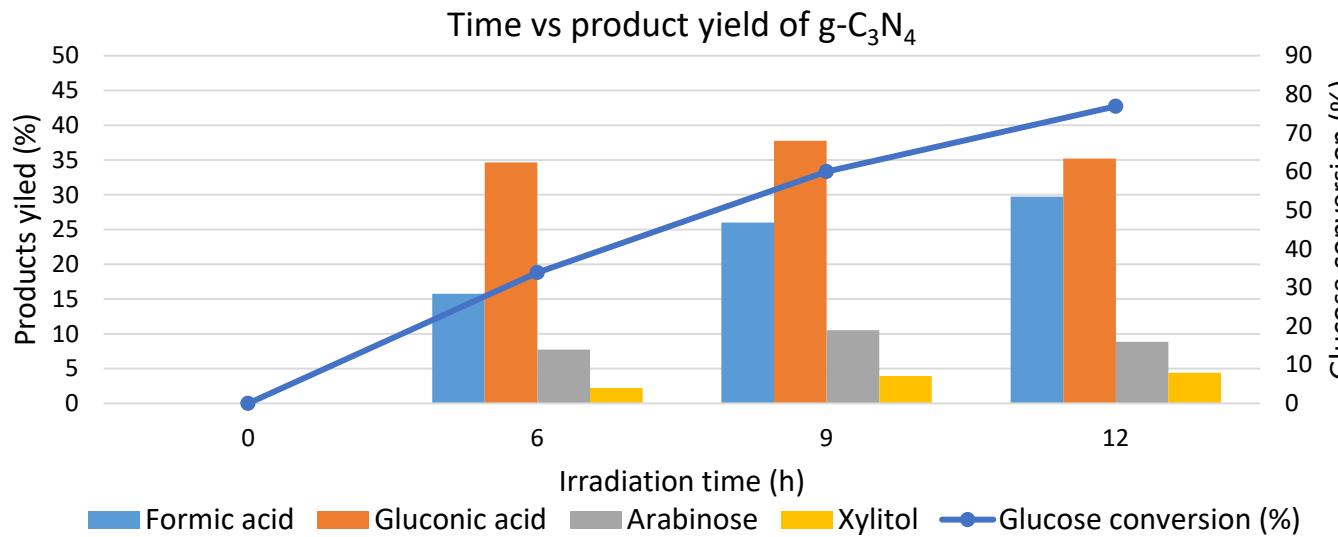
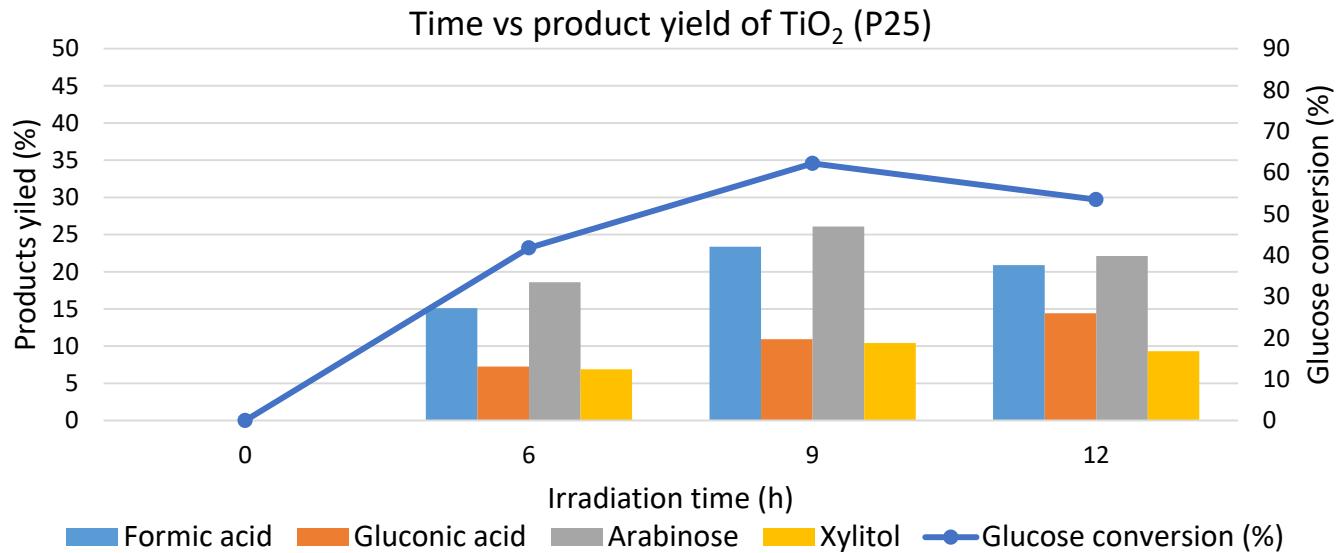
The effect of various photocatalysts on glucose conversion **under visible light ($\lambda>380$ nm)** for 6 h.



Photocatalysts	Glucose conversion (%)	Yield of products in aqueous phase (%)			
		Gluconic acid	Formic acid	Arabinose	Xylitol
TiO ₂ (P25)	40.8	7.4	15.4	18.9	7.0
CdS-TiO ₂	12.4	5.1	5.1	5.5	0.8
ZnS-AgInS ₂ (ZAlS x=0.4)	5.5	-	-	-	-
g-C ₃ N ₄ (From. Urea)	33.2 ± 0.32	34.6	14.7	7.2	2.7

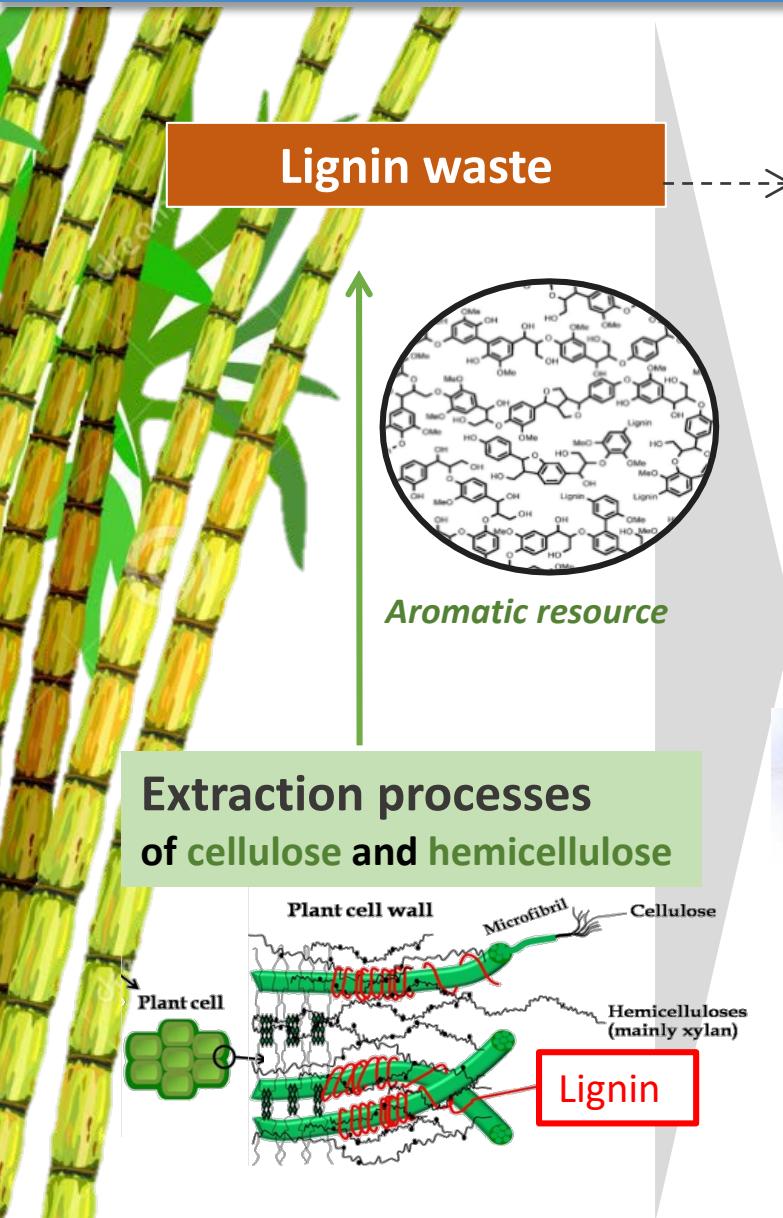
Glucose conversion under visible-light

To study the effect of irradiation time on product yield



Research Theme II: Lignin Conversion

Lignin Conversions

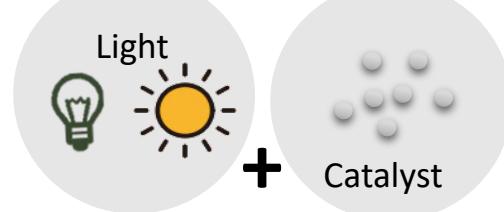


Photocatalysis

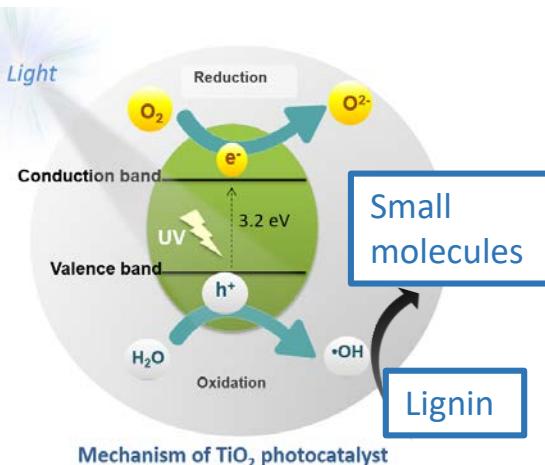
High value chemicals

-Small molecules

Basic concept:



UV and visible light

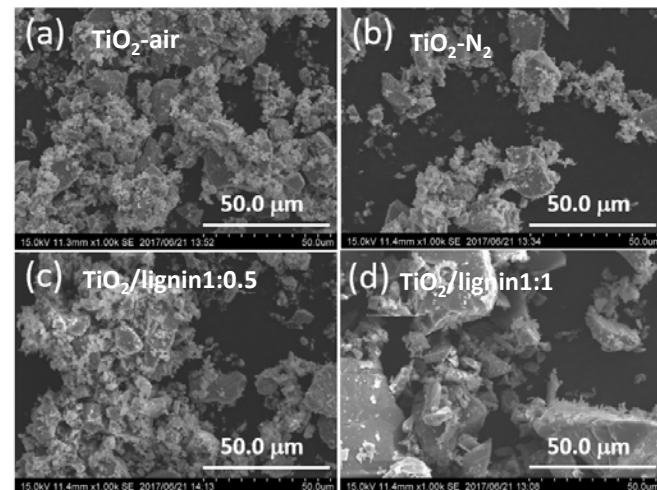


Analyses

-e.g. vanillin
(use in food industry)

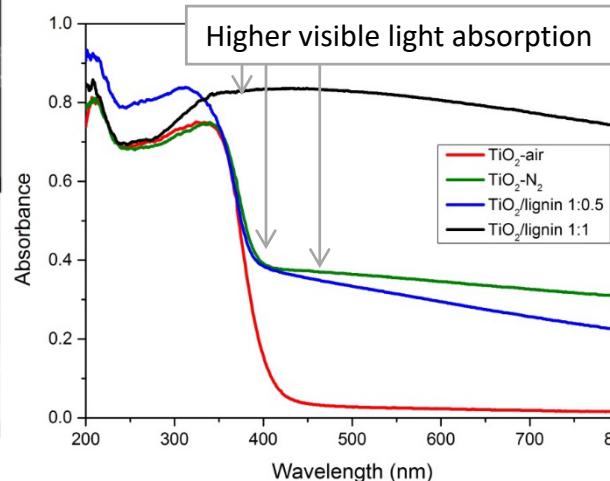
Lignin Conversions: Characteristics of photocatalysts

Scanning Electron Microscope (SEM)

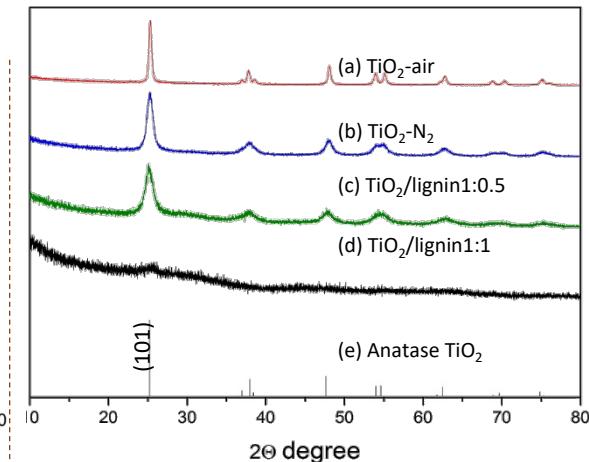


In Figure (d) $\text{TiO}_2/\text{lignin}1:1$

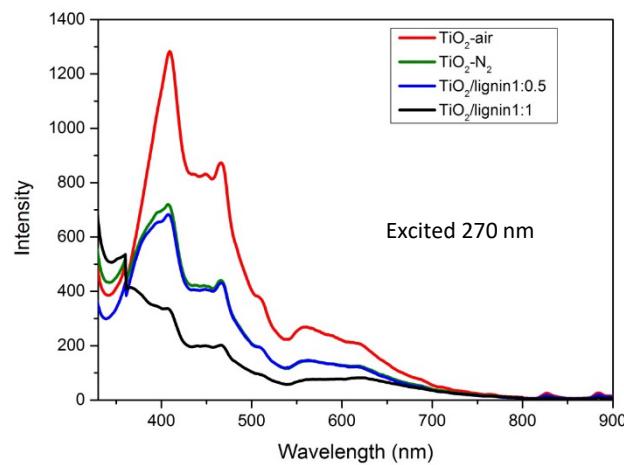
UV-Vis Diffuse Reflectance Spectroscopy (DRS)



XRD Analysis



Photoluminescence (PL)



Energy band-gap of photocatalysts

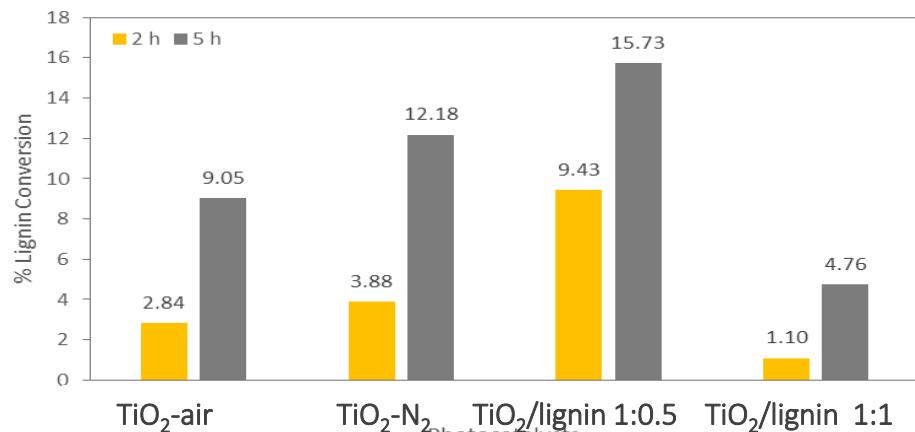
Photocatalysts	E_g (eV)
$\text{TiO}_2\text{-air}$	3.160
$\text{TiO}_2\text{-N}_2$	3.067
$\text{TiO}_2/\text{lignin}1:0.5$	3.076
$\text{TiO}_2/\text{lignin}1:1$	-

Photocatalysts	Crystallite size (nm)
$\text{TiO}_2\text{-air}$	23.6202
$\text{TiO}_2\text{-N}_2$	9.269
$\text{TiO}_2/\text{lignin}1:0.5$	7.0308
$\text{TiO}_2/\text{lignin}1:1$	ND

Show the decreasing of PL intensity corresponding with quenching.

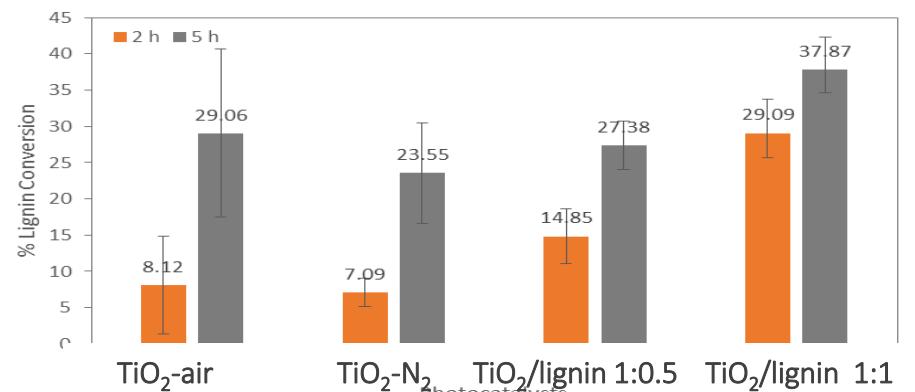
Lignin Conversions: Conversions & Product analysis

Visible irradiation



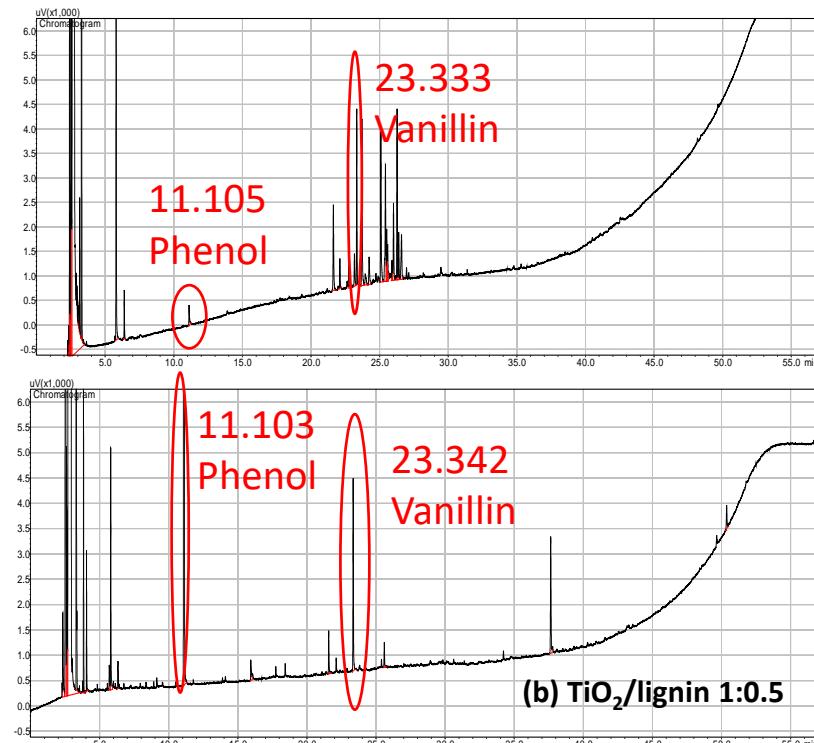
Photocatalytic lignin conversions under visible irradiation
(lignin concentration = 500 mg/L, catalyst content = 1,000 mg/L)

UV irradiation



Photocatalytic lignin conversions under UV irradiation
(lignin concentration = 500 mg/L, catalyst content = 1,000 mg/L)

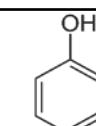
TiO₂/lignin 1:0.5 and TiO₂/lignin 1:1 showed the highest lignin conversions under visible and UV irradiations, respectively.



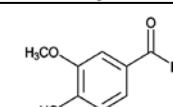
GC chromatogram of photocatalytic lignin conversion under UV irradiation at 5 h.

RT (min)	Compound	Structure
-------------	----------	-----------

11.073 Phenol



22.422 Vanillin



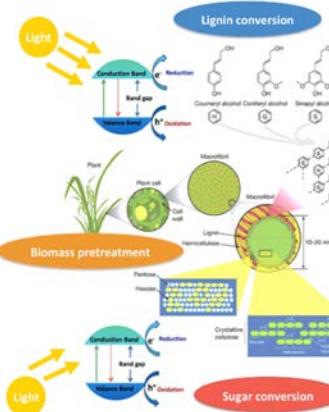
Confirm products by GC-MS in the next steps

1. Overview (STI for SDGs)

The project aims to develop improved technology for synthesis and fabrication of photocatalysts and development of photo bio-flow reactor for conversion of lignocellulose-derived components i.e. sugars and lignin to value-added chemicals e.g. functional sugar derivatives and phenolics. The work will integrate the technology on photocatalytic conversion to biorefinery which will lead to sustainable development of biomass-based industry targeting on multi-products i.e.fuels and chemicals from agricultural wastes



2. Japan - ASEAN STI Cooperation



- Catalyst synthesis and fabrication (TH)
 - Catalyst design and characterization for glucose and lignin conversion
- Photo-catalytic reactor design (JP)
 - Fibrous photocatalysts
 - Molecular imprinting & quantum dot
 - Composite photocatalysts

3. Best Practice of STI for SDGs

- international publications
= 2 accepted/1 in-prep(acknowledged to JASTIP)
- Graduate student training at KU
5 M.Sc/ 1 Ph.D
- 2 presentation in international conferences
- Photocatalytic technology on sugar conversion under proposed phase to TH industry

** Photocat team won 1st prize PTTGC Innovation award 2017 for smart eco-products



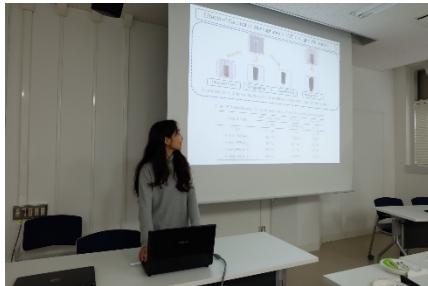
4. Challenging issues

- How to improve selectivity of the catalyst to specificity of products
- Downstream processing for separation of product mixtures
- Demonstration reactor design with catalyst recycling
- Technology demonstration plan to industry with feasibility evaluation

Project outputs

Exchange Researches

Name	Exchange Period	Research Topic
Ms. Kamonchanok Roongraung	18 Feb 2016 – 19 July 2016	Nano-scaled Photocatalysts for Energy Applications
Mr. Suriyachai Nopparat	28 Sep 2016 – 30 Sep 2017	Modification of Visible Light Photocatalytic Activity for Biomass Conversion to Value-added Chemicals
Ms. Nutsanun Klueb-arb	14 Nov 2016 – 23 Dec 2016	A Study of Reaction Pathways in Photocatalytic Conversion of Sugars to High-Value Fuels and Chemicals
Ms. Puangphen Hongdilokkul	14 Nov 2016 – 23 Dec 2016	Photocatalytic Upgrading of Lignin to High Value Products by Nanostructured Catalysts
Ms. Kanyanee Sangdee	6 Feb 2017 – 17 Mar 2017	Development of Visible-Light Irradiation Responded Metal Oxide for Photocatalytic and Photovoltaic Applications
Ms. Nattida Srisasiwimon	29 May 2017 – 30 June 2017	Enhancement of visible-light Photocatalytic Activity in TiO ₂ -based Catalysts for Lignin Conversion to Chemicals
Ms. Oranoot Sittipunsakda	29 May 2017 – 30 June 2017	Hydrogen Production from Wastewater via Photocatalytic Process



Research output

International publications

- ❑ Witchaya Arpavate, Surawut Chuangchote, Navadol Laosiripojana, Jatuphorn Wootthikanokkhan, and Takashi Sagawa (2016) "ZnO Nanorod Arrays Fabricated by Hydrothermal Method Using Different Thicknesses of Seed Layers for Applications in Hybrid Photovoltaic Cells," Sensors and Materials, 28(5), 403-408.
- ❑ Kamonchanok Roongraun, Navadol Laosiripojana, Surawut Chuangchote (2016) "Development of Photocatalytic Conversion of Glucose to Value-added Chemicals by Supported-TiO₂ Photocatalysts," Applied Mechanics and Materials, 839, 39-43.
- ❑ Mathana Wongaree, Siriluk Chiarakorn, Surawut Chuangchote, and Takashi Sagawa (2016) "Photocatalytic Performance of Electrospun CNT/TiO₂ Nanofibers in a Simulated Air Purifier under Visible Light Irradiation," Environmental Science and Pollution Research, 23, 21395-21406.
- ❑ Nutsanun Klueb-arb, Surawut Chuangchote, Kamonchanok Roongraung, Navadol Laosiripojana, Takashi Sagawa, Fabrication of Several Metal-Doped TiO₂ Nanoparticles and Their Physical Properties for Photocatalysis in Energy and Environmental Applications, Journal of Sustainable Energy & Environment, accepted.
- ❑ Puangphen Hongdilokkul, Surawut Chuangchote, Navadol Laosiripojana, Takashi Sagawa, Conversion of Lignin via Photocatalysis Using Synthesized Ag-TiO₂ Photocatalysts Sintered under Different Atmospheres, Journal of Sustainable Energy & Environment, accepted.

Research output

International conferences

- Puangphen Hongdilokkul, Surawut Chuangchote, Navadol Laosiripojana, Takashi Sagawa, Effects of Sintering Conditions in Ag-TiO₂ Nanoparticles on Photocatalytic Degradation of Lignin, International Conference on Materials Processing Technology 2017, November 30 - December 1, 2017, Bangkok, Thailand, 126-131.
- Nutsanun Klueb-arb, Surawut Chuangchote, Navadol Laosiripojana, Takashi Sagawa, Modifications of TiO₂ Nanoparticle Catalysts by Dopes with Transition Metals (Ag and Cu) or Alkali Metal (Rb), International Conference on Materials Processing Technology 2017, November 30 - December 1, 2017, Bangkok, Thailand, 132-140.