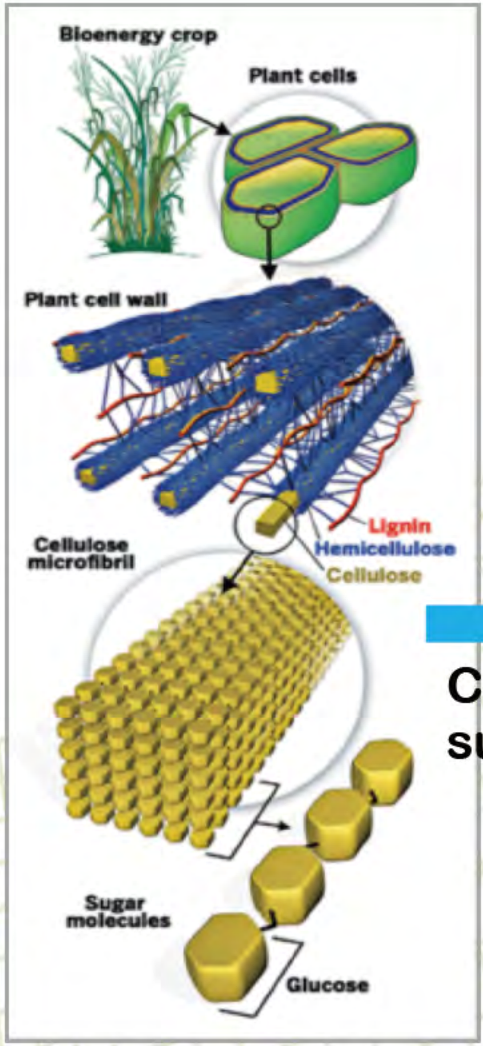
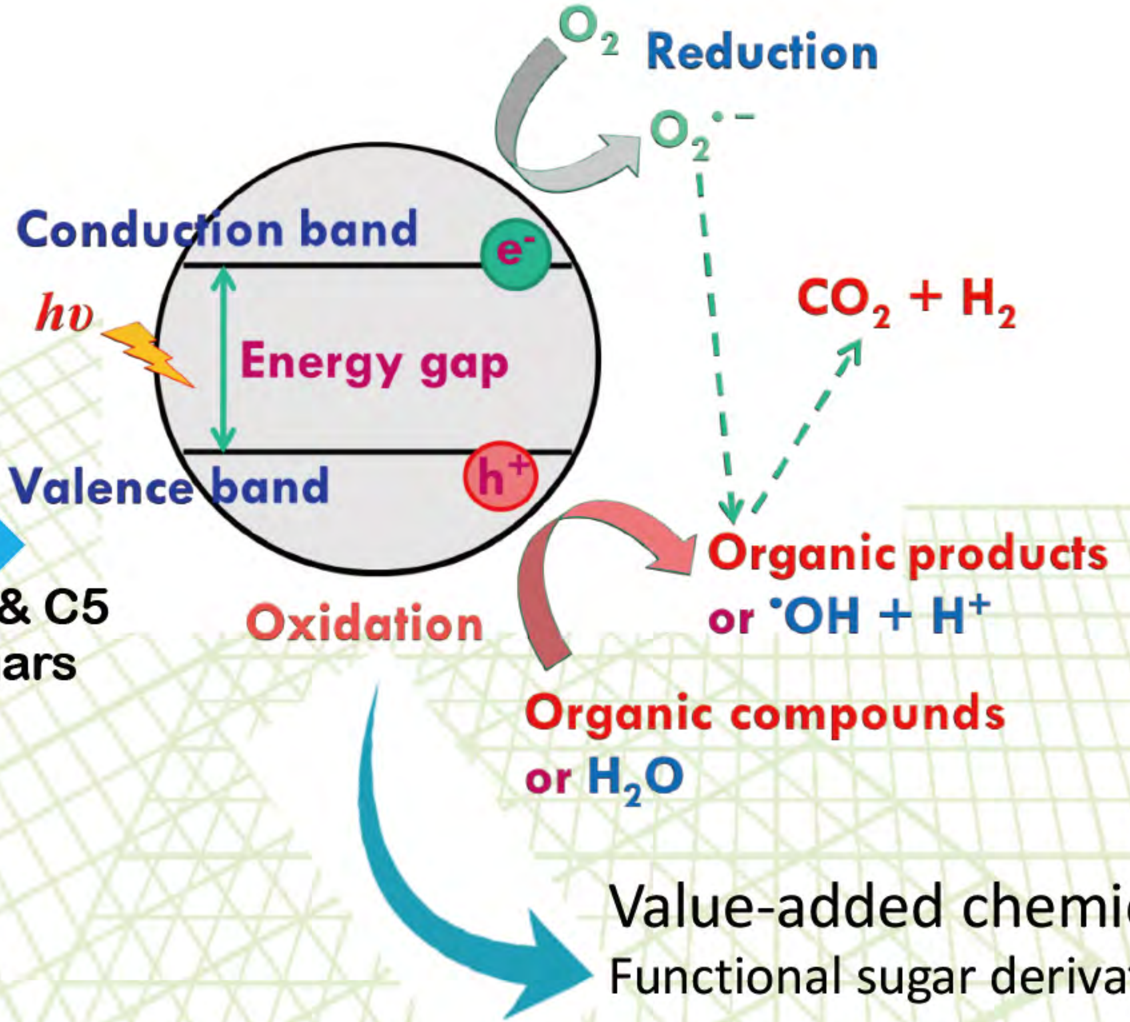
Innovations for conversion of sugar to high value chemicals by photocatalytic process

Prof.Takashi Sagawa
Assist.Prof.Surawut Chuangchote
Dr.Verawat Champreda
Prof.Navadol Laosiripojana

Photocatalytic conversion: sugars to chemicals



C6 & C5 sugars



Value-added chemicals

Functional sugar derivatives

Aims & Objectives

This project aims to develop high performance photocatalysts and photocatalytic reactor for production of target chemicals from glucose which can be obtained from 1st generation or 2nd generation raw materials in biorefinery. The project will focus on synthesis and fabrication of nano-scaled photocatalysts with improved performance and characterization of physicochemical properties of self-synthesized photocatalysts compared to commercial catalysts. The work will include the study of photocatalytic reactions on synthesis of high-value products (functional sugar derivatives) from glucose and application of the developed photocatalysts for production of target chemicals in photocatalytic reactor. The specific technical objectives are as follows:

(a) To study the effects of fabrication conditions, doping and surface modification on morphotological appearances, physico-chemical properties, photocatalytic activity and selectivity of the photocatalysts
(b) To study the effects of chemical structures of sugars on mechanisms of photocatalytic reactions
(c) To study the reaction pathways for photocatalytic conversion of sugars (e.g. glucose) to its derivatives or unconventional sugars
(d) To design and assemble a prototype laboratory-scale photocatalyic reactor (photo bio-flow reactor)
(e) To study the reaction kinetics on sugar conversion to target chemicals in photo-bio flow reactor

Project strategic plan

Glucose [Sucrose] → **Photocatalyst synthesis and fabrication** → **Photo-Bio flow Reactor** → **Crude product mixture** ⇒ **Product sepration**

Photocatalyst synthesis and fabrication

Fibrous catalyst design
Catalyst characterization

Synthesis

Sol-gel
Ultra-sonication
Hydrothermal
Sol-Microwave

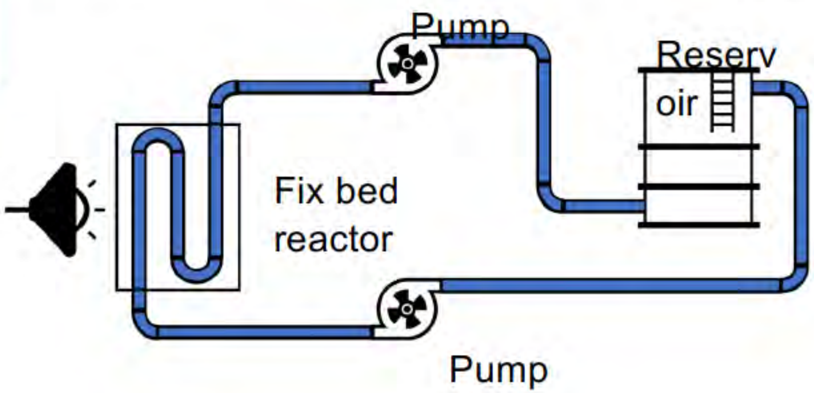
XRD/EDS/BET/TGA

Fabrication

Electrospinning
SEM/TEM/XRD/FT-IR/PL/
UV-Vis Diffuse Reflectance Spectra

Photo-Bio flow Reactor

Photo-Bio flow Reactor prototype (10 L) design
Operational parameters Optimization
- Light intensity
- Flowrate
- Reactant conc.



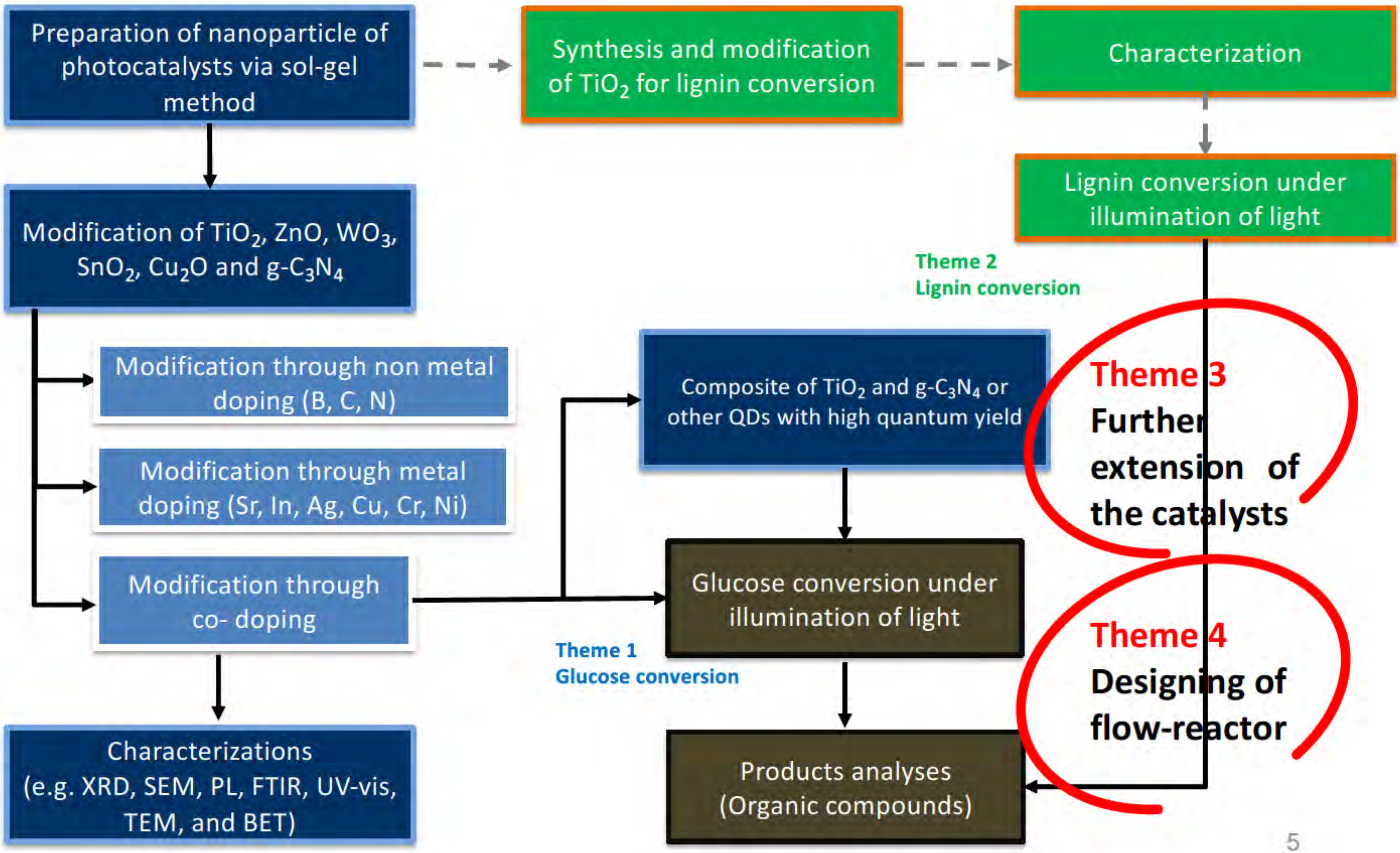
Crude product mixture

Functional sugar derivatives
Xylitol
Gluconic acid
Arabinose

→ Reaction kinetics
Process simulation
→ How to improve product selectivity

KU will involve in photocatalyst characterization and reactor design

Scopes of the research work



Glucose conversion to value-added chemicals

Sugar
- Glucose

UV light

Photocatalysis →

Value-added Chemicals
- Xylitol
- Gluconic acid
- Formic acid
- Arabinose

Research progress (Sep 2018 – Jan 2019)

Synthesis of TiO_2 nanofibers

Prepare solution

Add 0.8 g PVP

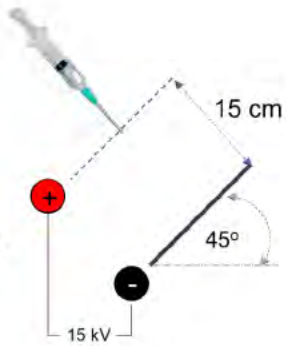
10 ml MeOH

→ Stir over night →

Add 4.000 g Titanium (IV) butoxide and 1.175 g Acetylacetone

→ Stir over night →

Electrospinning



↓

Electrospun fibers ← Calcination 500ºC, 2h ← Powder

*Polyvinylpyrrolidone (PVP)

Synthesis of B,N-TiO_2 nanofibers

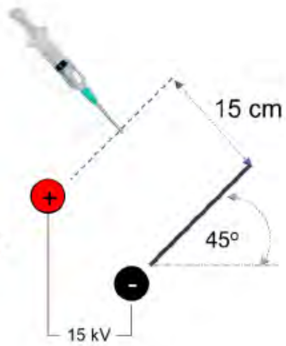
Prepare solution

Add 0.8 g PVP → 10 ml MeOH → Stir over night →

Add 4.000 g Titanium (IV) butoxide and 1.175 g Acetylacetone → Stir over night →

Add 0.02180 g Boric acid and 0.02396 g Ammonia → Stir over night →

Electrospinning



↓

Electrospun fibers → Calcination 500°C, 2h → Powder

*Polyvinylpyrrolidone (PVP)

Synthesis of TiO_2 hollow nanoribbons

Prepare solution

Add 0.8 g PVP

10 ml MeOH

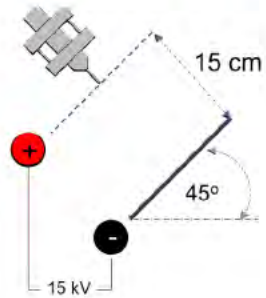
Stir
over night

Add 4.000 g
Titanium (IV) butoxide
and 1.175 g
Acetylacetone

Stir
over night

Electrospinning

Inner = mineral oil



Electrospun fibers

Calcination
500ºC, 2h

Powder

*Polyvinylpyrrolidone (PVP)

Synthesis of B,N-TiO_2 hollow nanoribbons

Prepare solution

Add 0.8 g PVP

10 ml MeOH

→ Stir over night →

Add 4.000 g Titanium (IV) butoxide and 1.175 g Acetylacetone

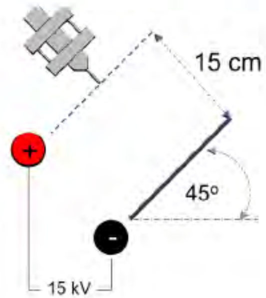
→ Stir over night →

Add 0.02180 g Boric acid and 0.02396 g Ammonia

→ Stir over night →

Electrospinning

Inner = mineral oil



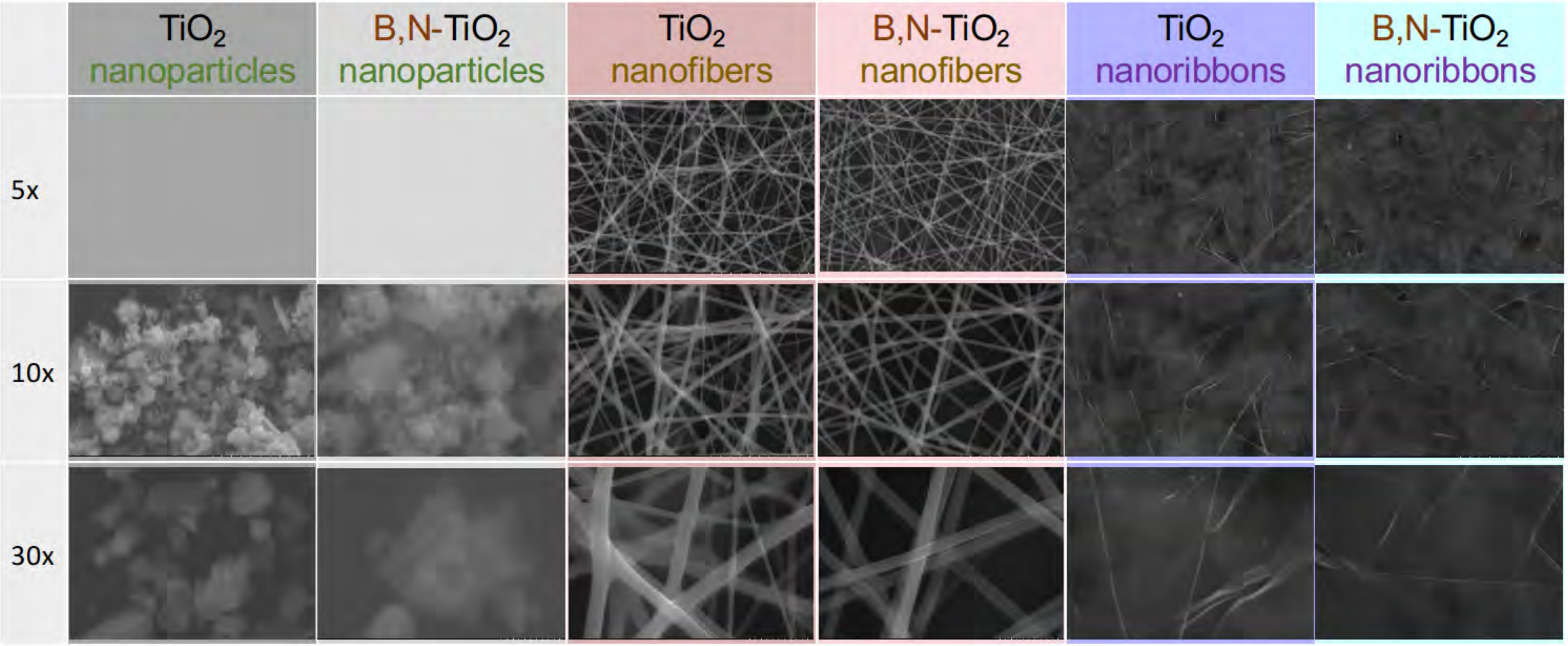
↓

Electrospun fibers → Calcination 500°C, 2h → Powder

*Polyvinylpyrrolidone (PVP)

Characterizations

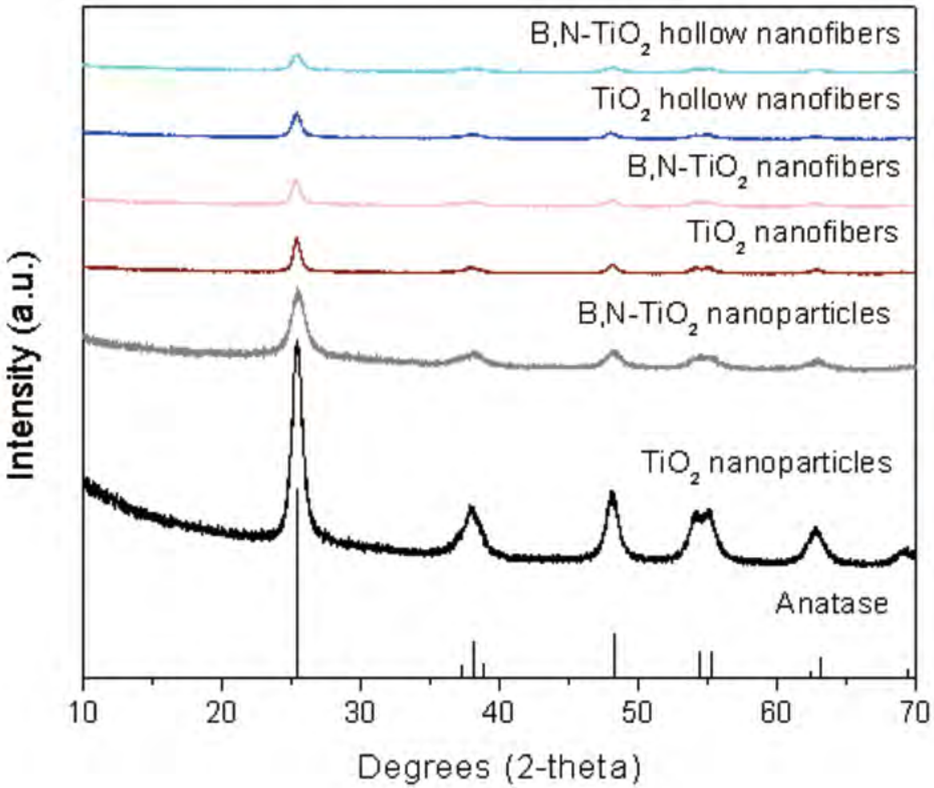
Scanning electron microscope (SEM) image



1.22um±0.30 1.50um±0.55 0.21um±0.10 0.14um±0.03 2.16um±0.21 1.70um±0.22

Characterizations

X-ray diffraction (XRD) pattern



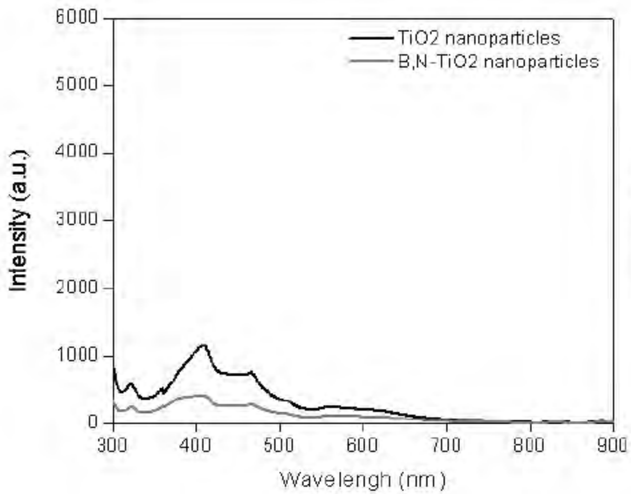
Crystallite size

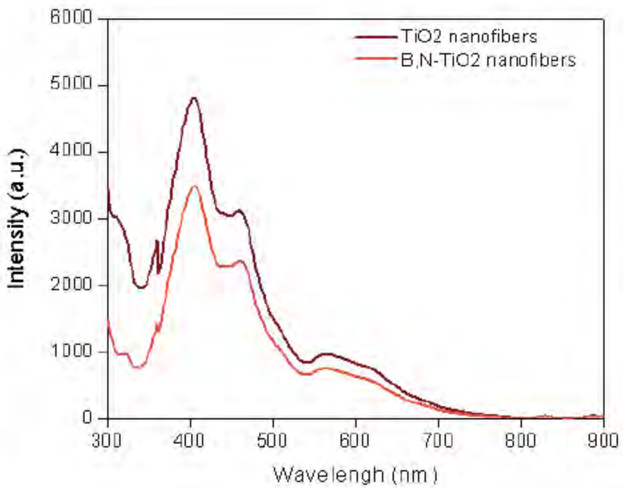
Materials	Crystallite size (nm)
TiO_2 nanoparticles	8.90
B,N-TiO_2 nanoparticles	6.74
TiO_2 nanofibers	12.79
B,N-TiO_2 nanofibers	10.66
TiO_2 nanoribbons	10.34
B,N-TiO_2 nanoribbons	9.77

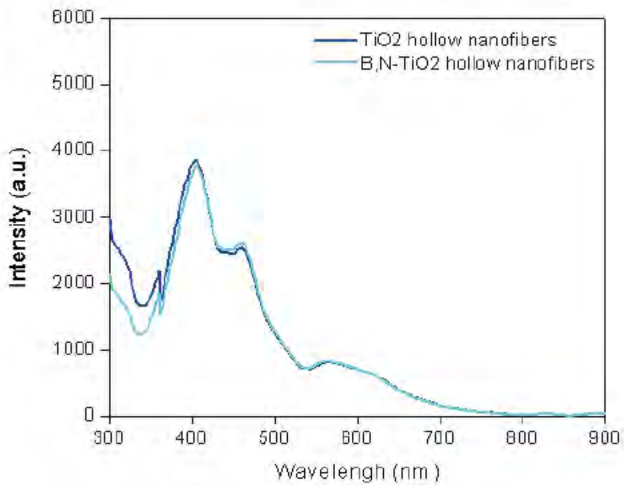
Characterizations

Photoluminescence spectra

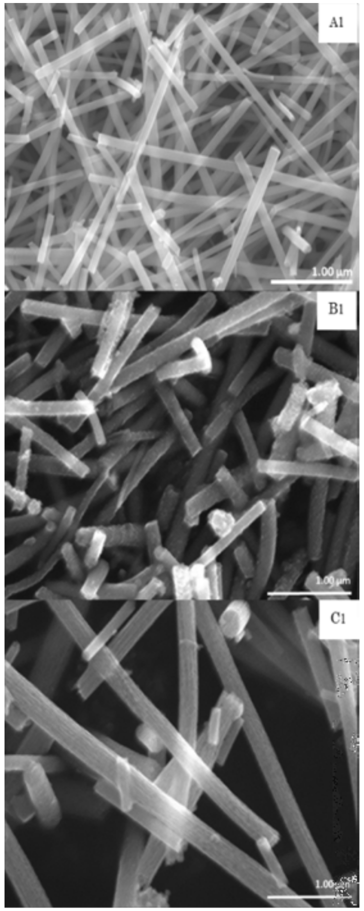
Nanoparticles	Nanofibers	Nanoribbons



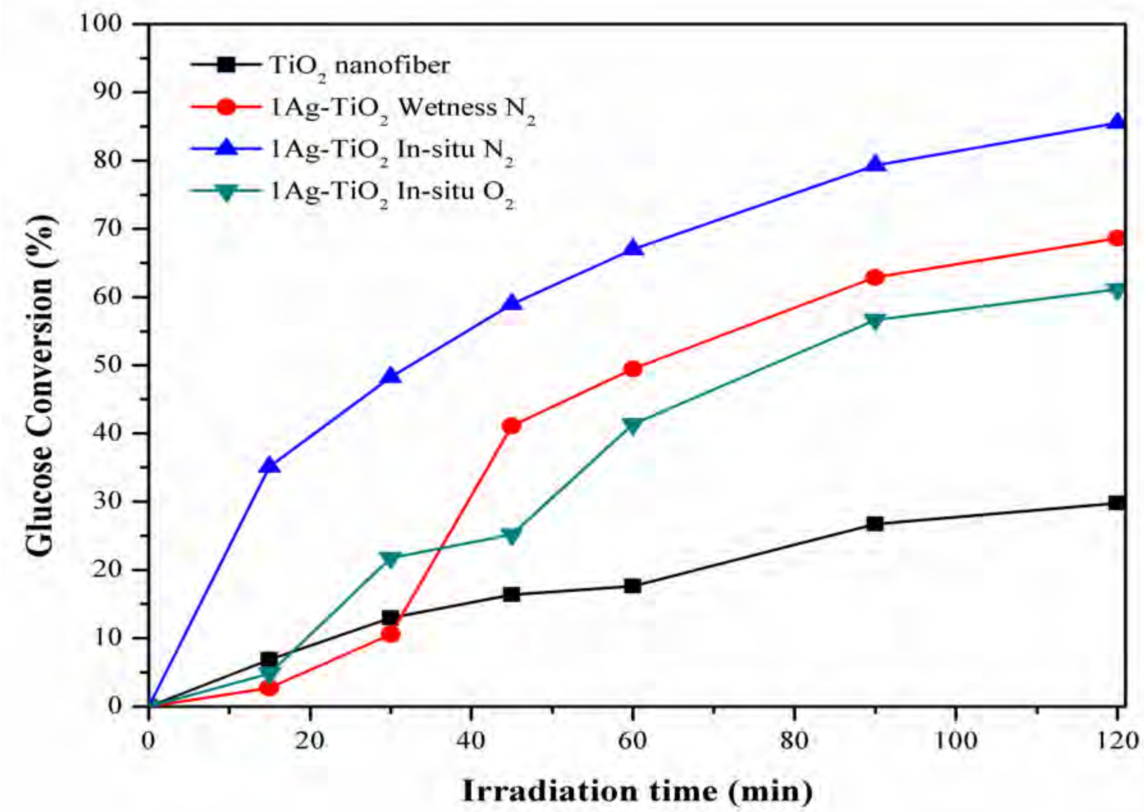




Photocatalytic Glucose Conversion on Pristine TiO_2 and Metal-doped Nanofibers



SEM images of Pristine TiO_2 and Metal-doped Nanofibers



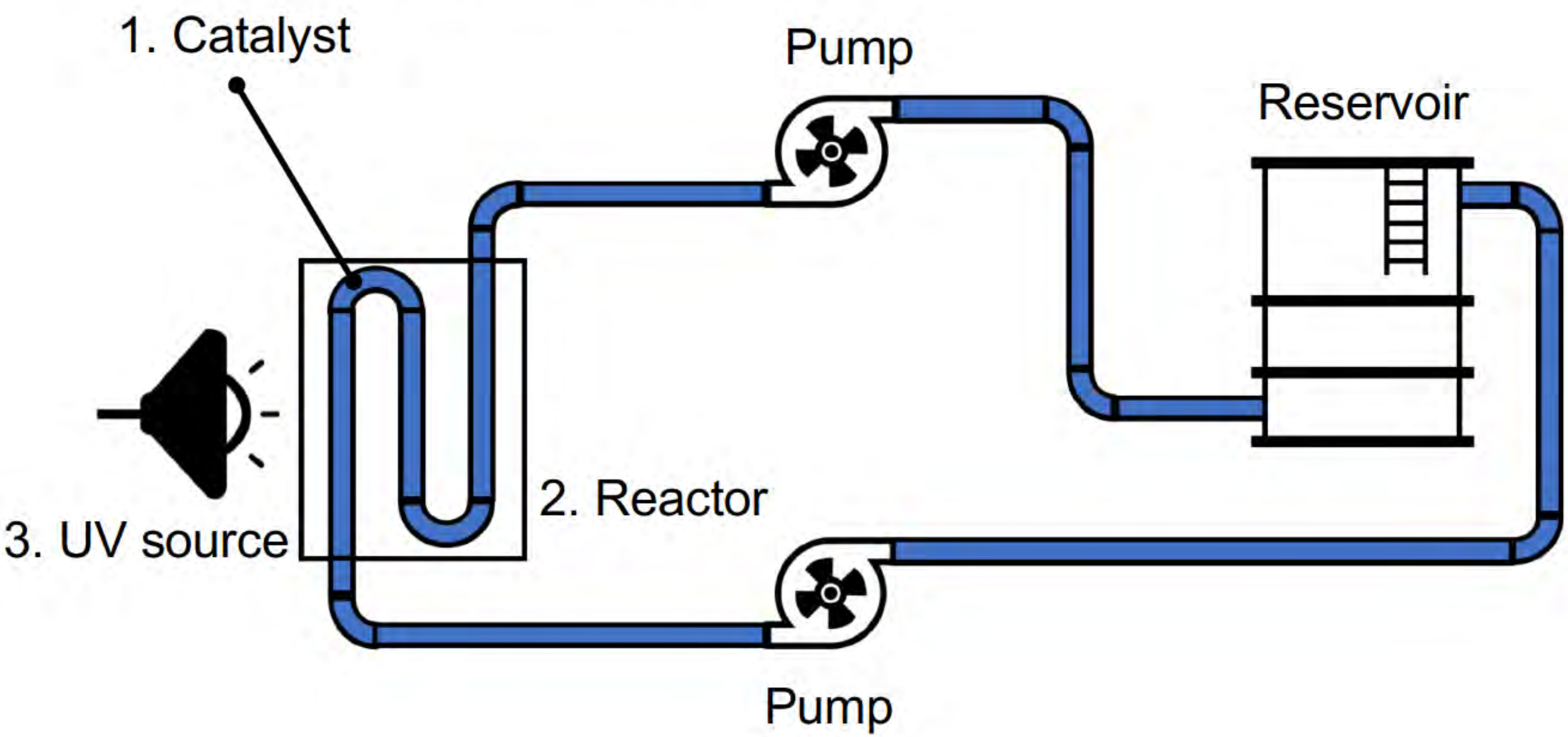
Photocatalytic conversion of glucose under UV irradiation for 120 min with Ag-loaded on TiO_2 nanofibers catalyst prepared by different techniques.

Future plan

- Optimization of percentage doping of nitrogen and boron in TiO_2 nanofibers and nanoribbons
- Characterizations of physio-chemical properties of photocatalytic materials.
- Synthesis of glucose-imprinted TiO_2 photocatalyst and characterization
- Study of the efficiency of photocatalyst on glucose conversion of other forms of fibers and further applications in photocatalytic bio-flow reactor

Design of photocatalytic bio-flow reactor

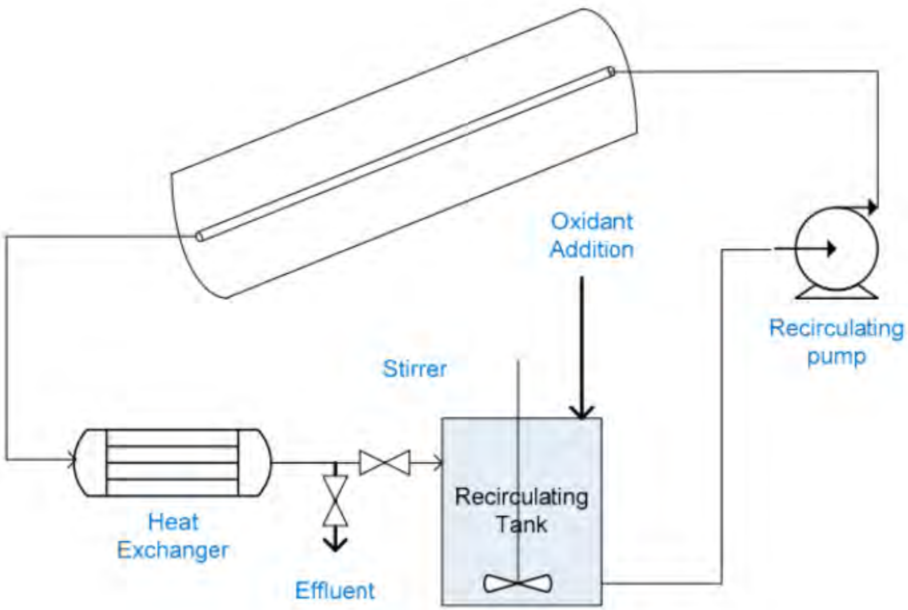
Overview of reactor design



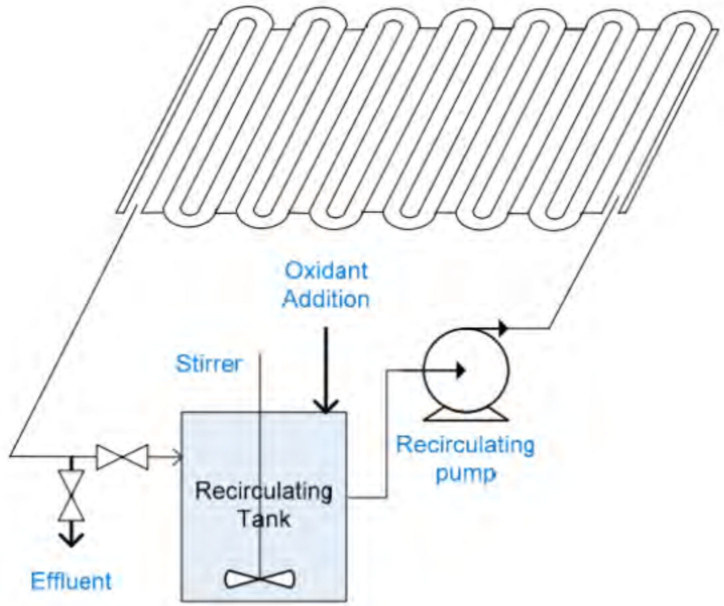
Design of photocatalytic bio-flow reactor

1. Photocatalytic slurry

Parabolic trough reactor



Compound parabolic concentrator

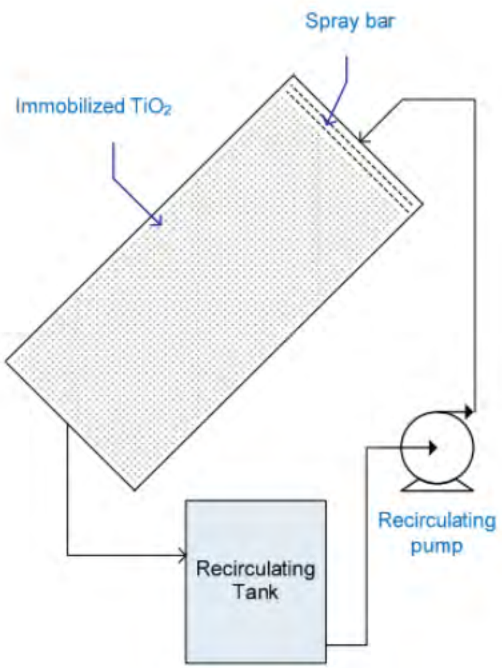


Alfano, et al., Catalysis Today 58 (2000) 199–230.

Design of photocatalytic bio-flow reactor

2. Photocatalyst immobilized on support

Thin-film fixed-bed reactor



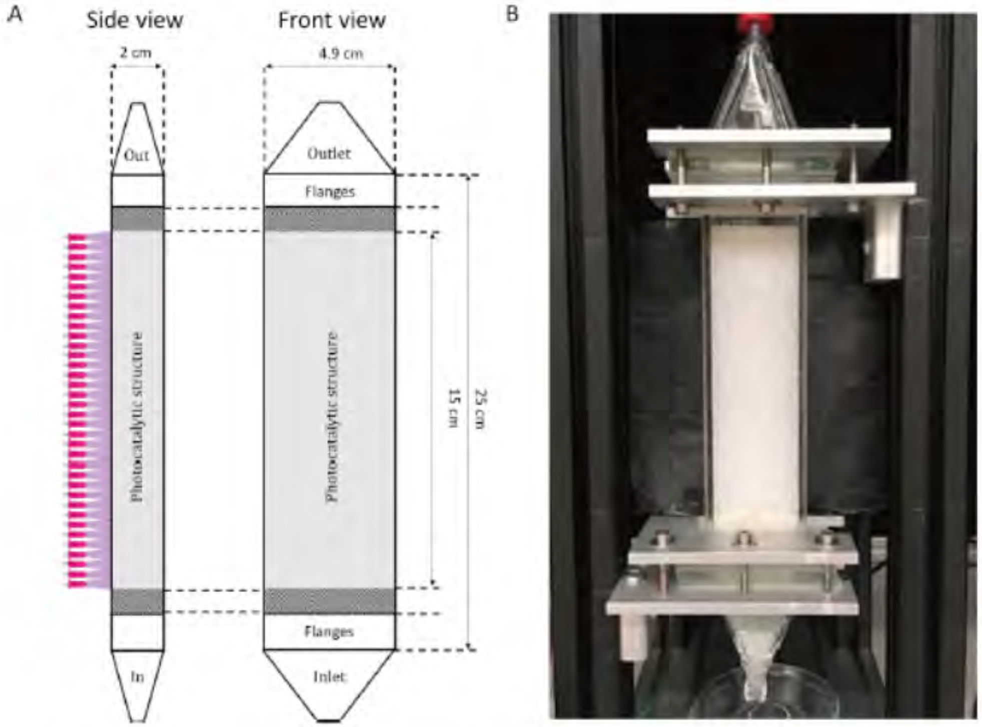


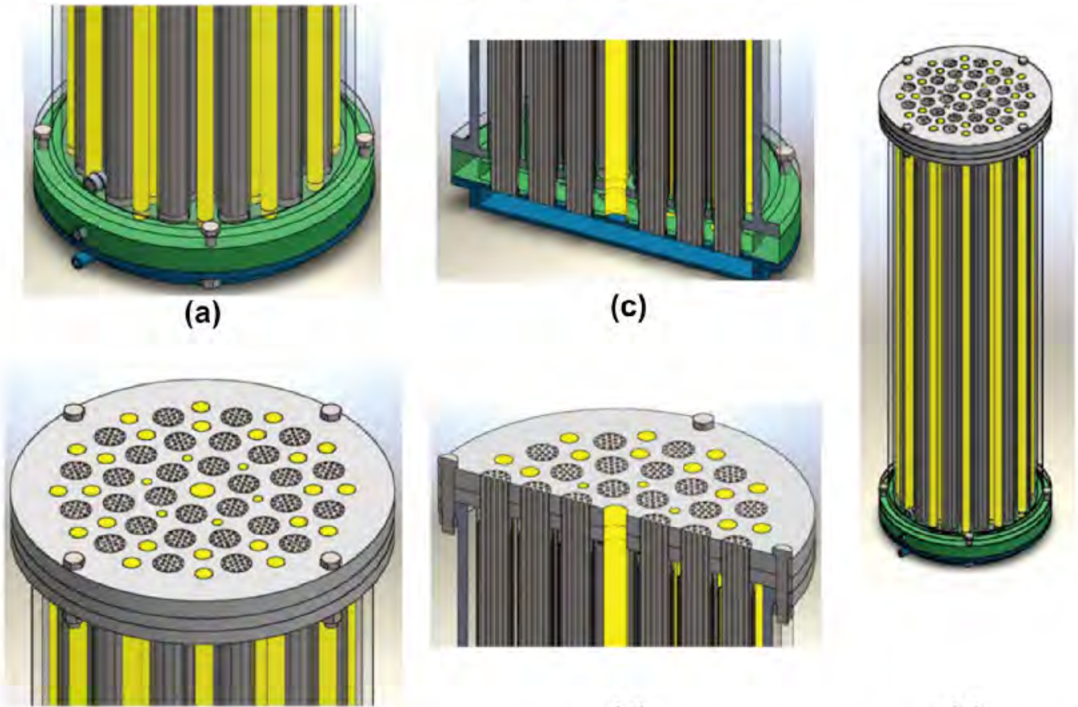
Fig. 3. (A) Schematic image of the used photocatalytic reactor. (B) picture of the photocatalytic reactor.

Alfano, et al., Catalysis Today 58 (2000) 199–230.
Claes, et al., Chemical Engineering Journal 361 (2019) 725-735.

Design of photocatalytic bio-flow reactor

2. Photocatalyst immobilized on support

Multi channel photocatalytic reactor



(a) (c)
(b) (d) (e)

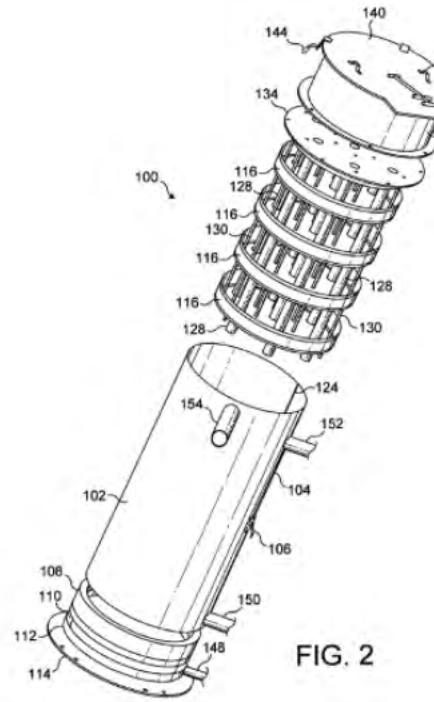


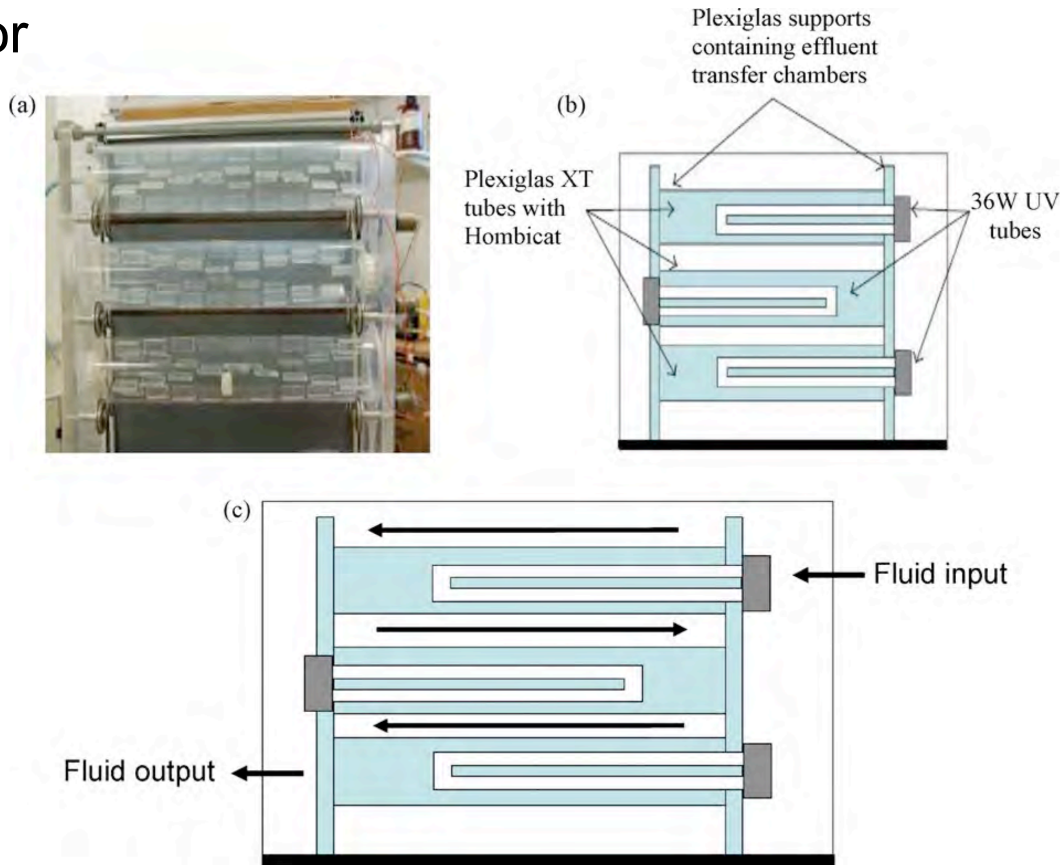
FIG. 2

A.A. Dimitrios et al., Chemical Engineering Journal 305 (2016) 92–103.
Foster et al., US Patent, US 2010/0003169 A1 (2010).

Design of photocatalytic bio-flow reactor

2. Photocatalyst immobilized on support

Flat plate reactor

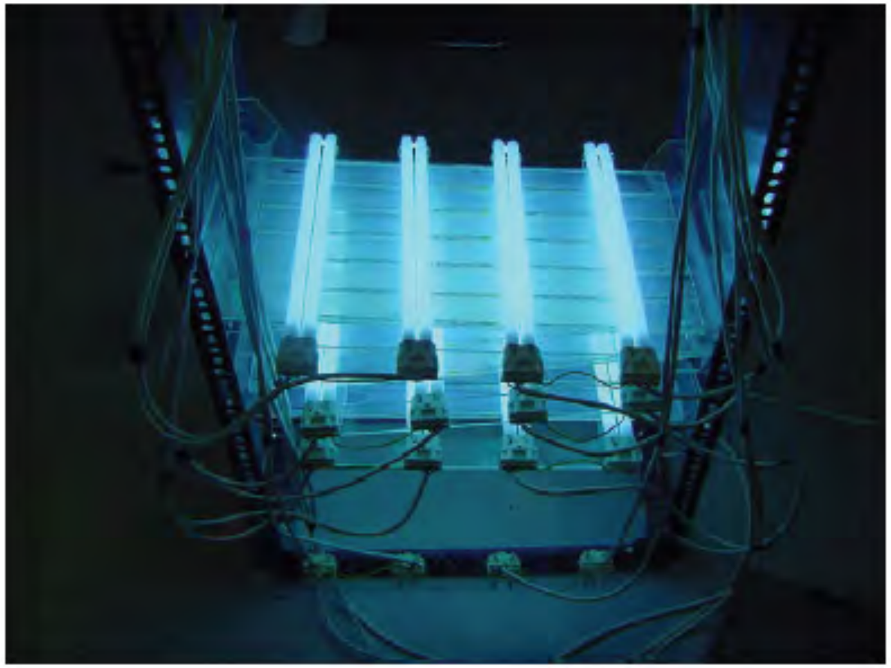


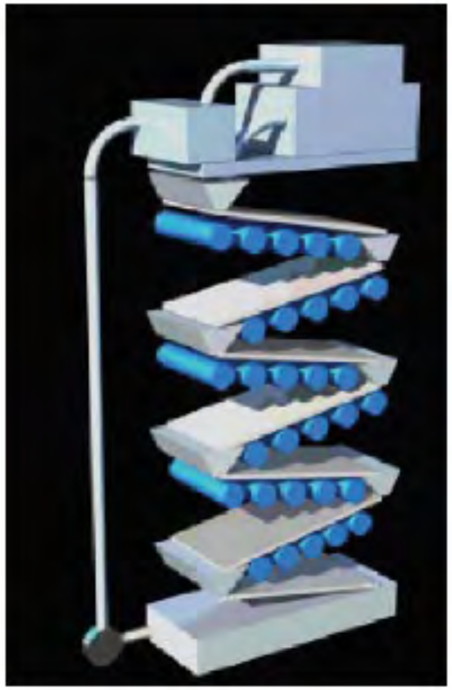
McCullagh, et al., Journal of Photochemistry and Photobiology A: Chemistry 211 (2010) 42–46.

Design of photocatalytic bio-flow reactor

2. Photocatalyst immobilized on support

Multiplate thin film reactor





Adams, et al., Hindawi Publishing Corporation
International Journal of Photoenergy 674537 (2008) 1-7.

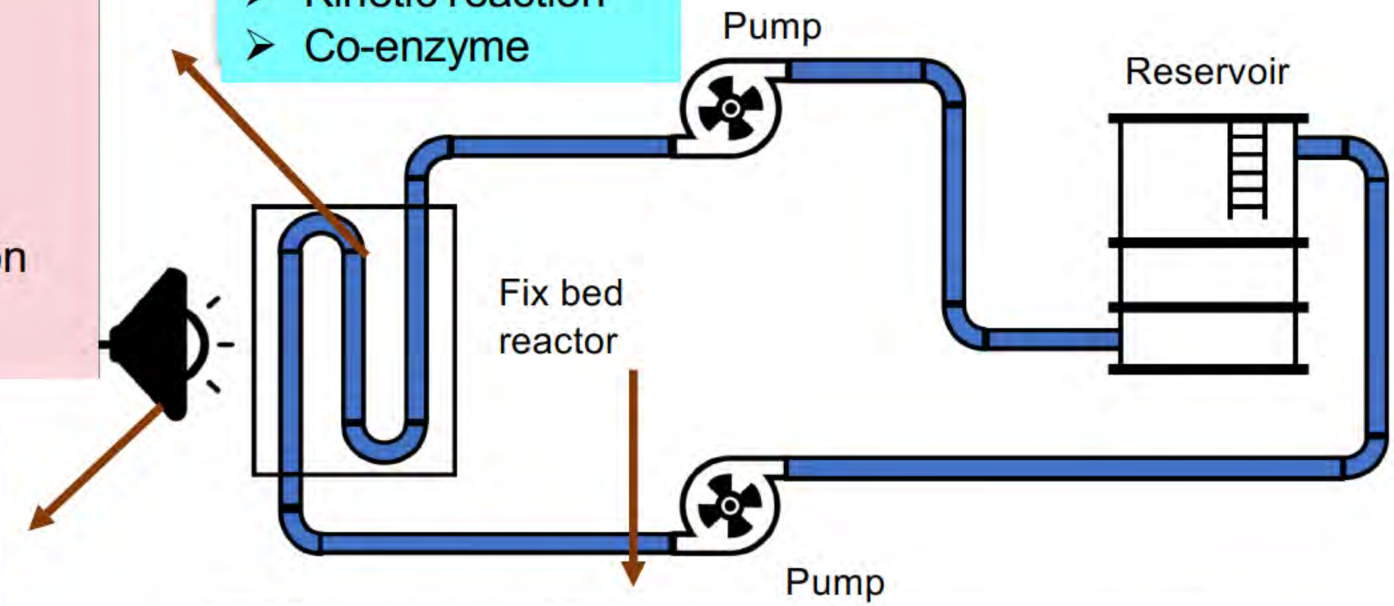
Summary

Photocatalyst modification
- ❖ Nanoparticles
- ❖ Nanofibers
  - ❖ Single fiber
  - ❖ Hollow fiber
- ❖ Surface modification
  - ❖ Mesoporous silica
- ❖ Applied techniques
  - ❖ Glucose imprinted on TiO_2

Light source
UV
&
Visible

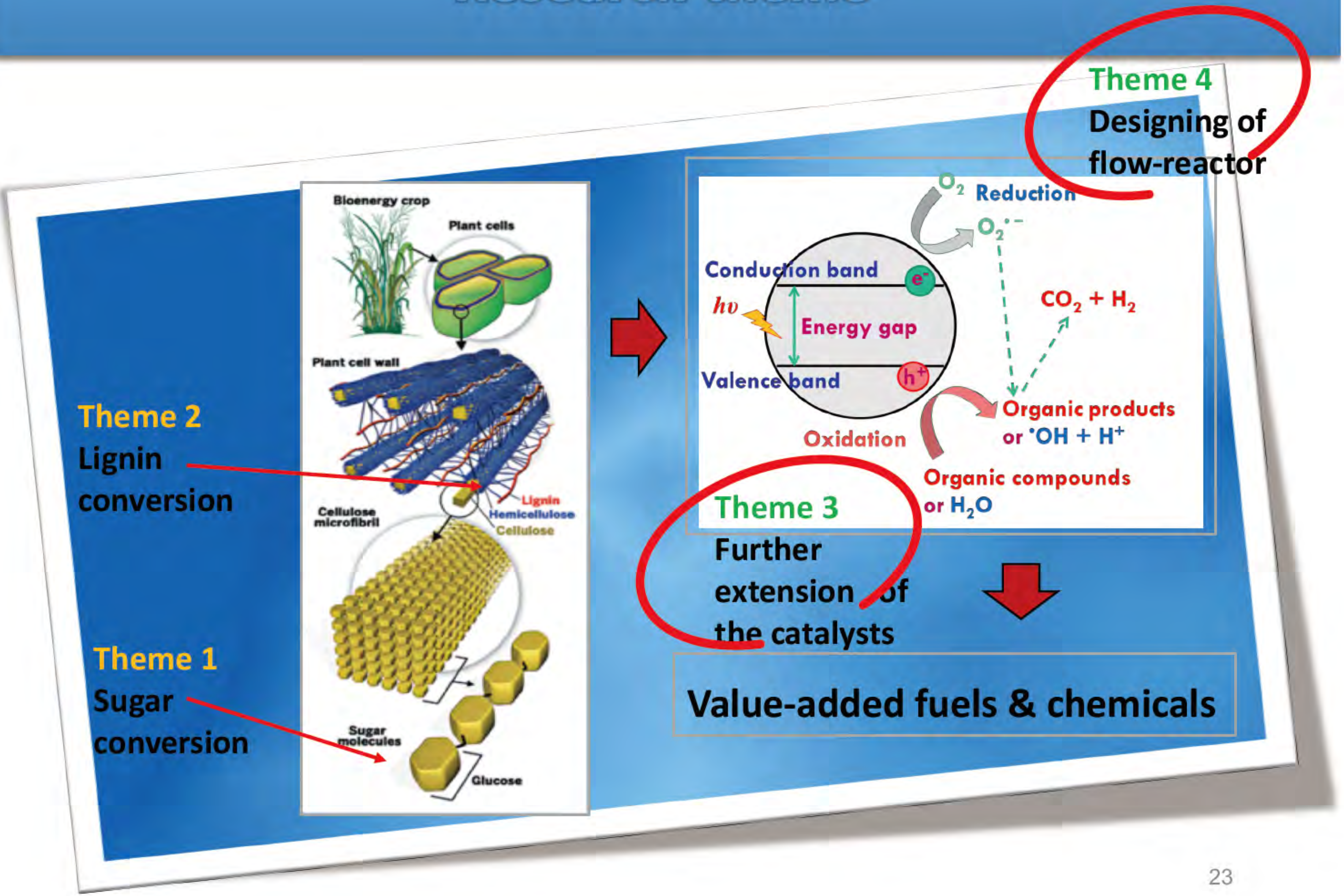
Flow-bed photo reactor

Proposed
- ➢ Kinetic reaction
- ➢ Co-enzyme



Materials and Methods
- ➢ Quartz plate
- ➢ Capillary column
- ➢ Coating and/or immobilized of photocatalyst

Research theme

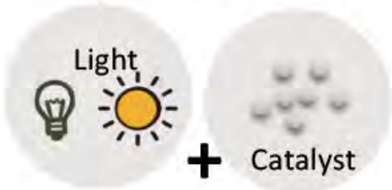


Innovations for Conversion of Sugars to High Value Chemicals by Photocatalytic Process

BIOTEC-JGSEE/KMUTT-Kyoto

Photocatalysis

Basic concept:



UV or visible light

Sugars (Glucose, etc.)

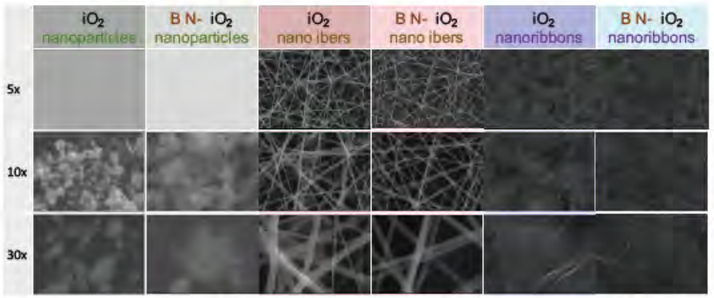
Light

Photocatalysts

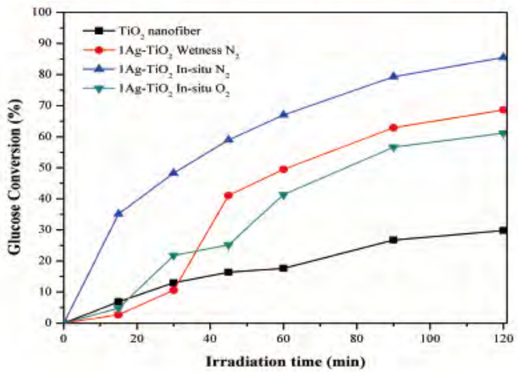
Value-added Chemicals

- Xylitol
- Gluconic acid
- Formic acid
- Arabinose

Photocatalysts



Sugar Conversions



Scientific Outputs

-Int. Journal : 2 papers + 2 submitted

-Int. Conf.: 2 invited + 3 orals

ACS Sustainable Chemistry & Engineering
Research Article

TiO_2/Lignin-Based Carbon Composited Photocatalysts for Enhanced Photocatalytic Conversion of Lignin to High Value Chemicals

Nattida Srisasiwimon,[†,‡] Surawut Chuangchote,[*,§] Navadol Laosiripojana,[†,‡] and Takashi Sagawa[∥]

[†]The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, 126 Prachauthit Rd., Bangmod, Thungkru, Bangkok 10140, Thailand

[‡]Center for Energy Technology and Environment, Ministry of Education, 126 Prachauthit Rd., Bangmod, Thungkru, Bangkok 10140, Thailand

[§]Department of Tool and Materials Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi, 126 Prachauthit Rd., Bangmod, Thungkru, Bangkok 10140, Thailand

[∥]Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

ABSTRACT: Upgrading of biomass wastes to be value-added materials has been attempted to apply in various applications. One of the interesting challenges is the effort to utilize biomass wastes to modify metal oxides to form composited photocatalysts to enhance the photoabsorption on the resultant catalysts. In this work, lignin-based carbon was used to modify TiO_2 and form the composite photocatalyst (TiO_2/lignin). A sol−gel microwave technique was used to prepare these catalysts. The effects of lignin-based carbon modification were investigated on their morphology, crystal structure, surface structure, optical properties, and photocatalytic activity. Characterizations of the obtained catalysts, including field emission scanning electron microscopy, high-resolution transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, UV−visible diffuse reflectance spectroscopy, photoluminescence, N_2 adsorption analyzed by the Brunauer−Emmett−Teller method, and UV−vis spectroscopy, were carried out. Here, lignin not only was used as a natural carbon source for modification of TiO_2 but also can be used as the biomass resource for green chemical production. Enhancement of photocatalytic performance of TiO_2 by carbon from sintered lignin was investigated from conversion of lignin to high value chemicals. It was found that carbon from lignin improved UVA irradiation photocatalytic performance of the TiO_2/lignin composite compared with the pristine TiO_2. The TiO_2/lignin composite with a TiO_2 to lignin ratio of 1:0.5 presented good characteristics and showed the highest photocatalytic activity under UVA irradiation for 5 h. After identification by gas chromatography mass spectroscopy, high value chemicals, such as vanillin, were found after photocatalysis.

KEYWORDS: *Lignin, TiO_2, Composite photocatalyst, Lignin conversion, High value chemical*

Thank you

Acknowledgement

- JASTIP program
- National Science and Technology Development Agency