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

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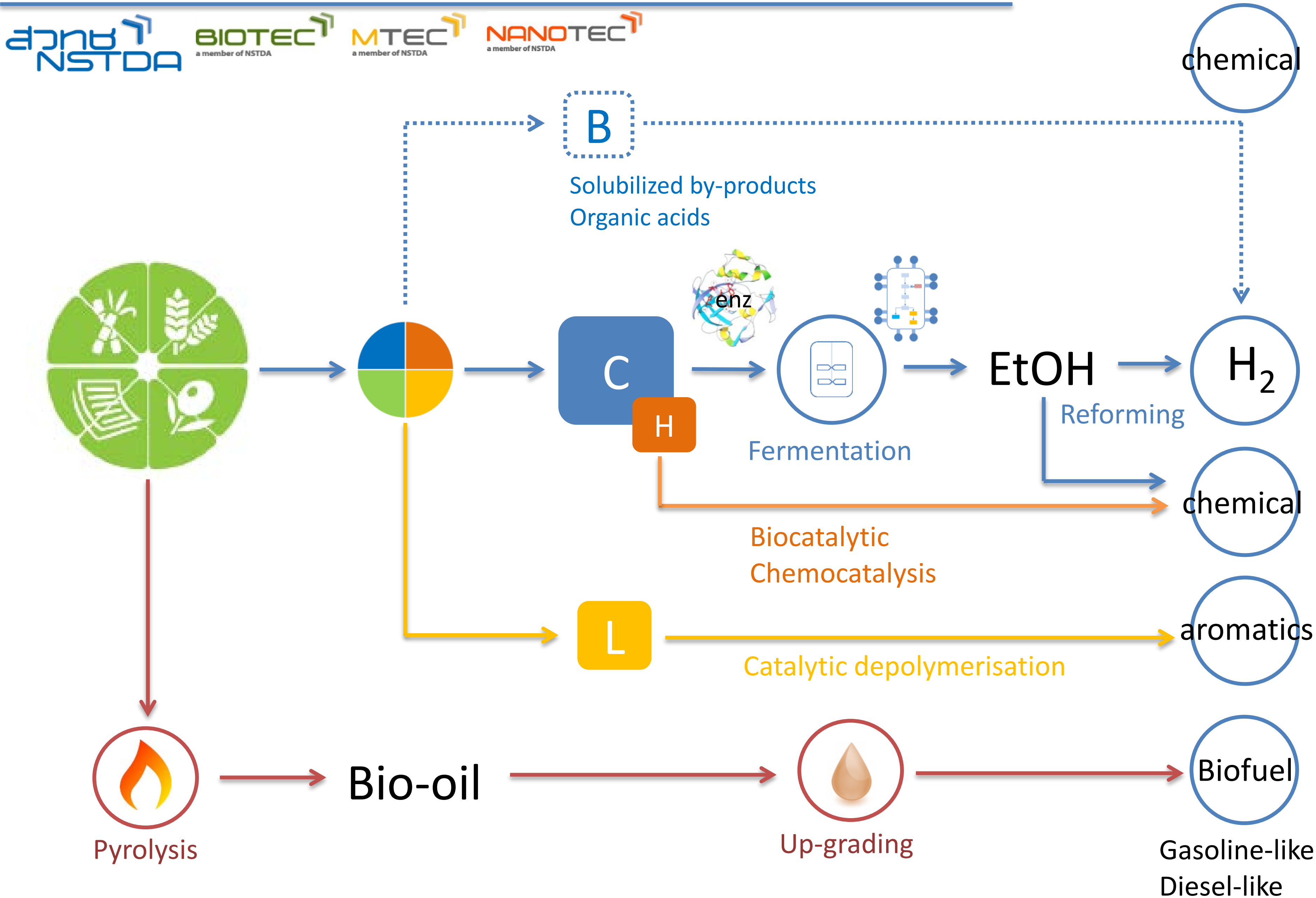
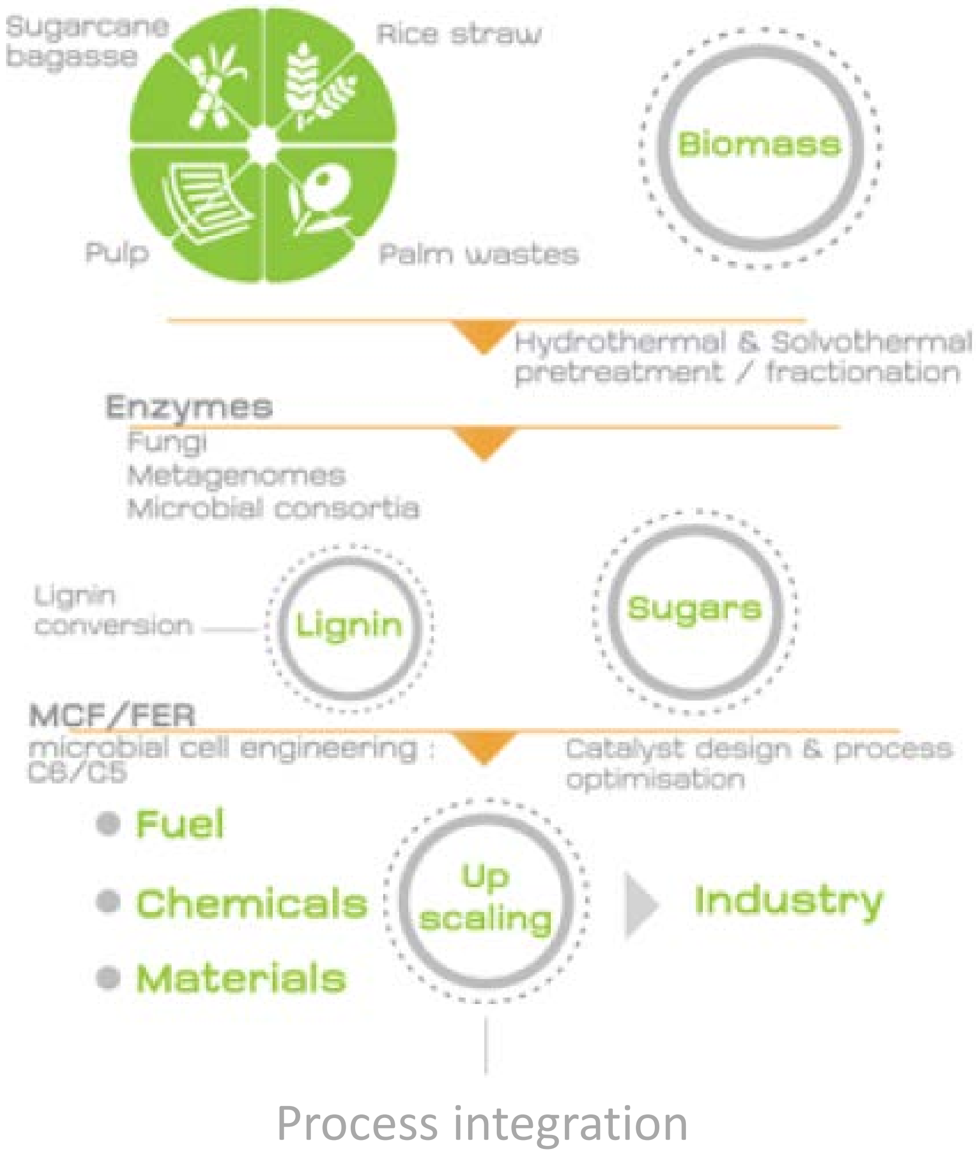
NSTDA Integrated biorefinery research network



IBL core research themes

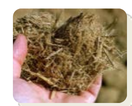


Pretreatment & Fractionation

- Green process: LHW/ORG
- Efficiency/Selectivity

Enzymatic hydrolysis

- Cellulolytic enzyme
- High solid hydrolysis process


Bagasse

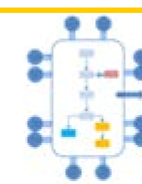

Cassava pulp

Catalysts & Biocatalysts for conversion

- Sugars: Cell factory
- Lignin: Catalytic conversion


Catalyst


Biocatalyst

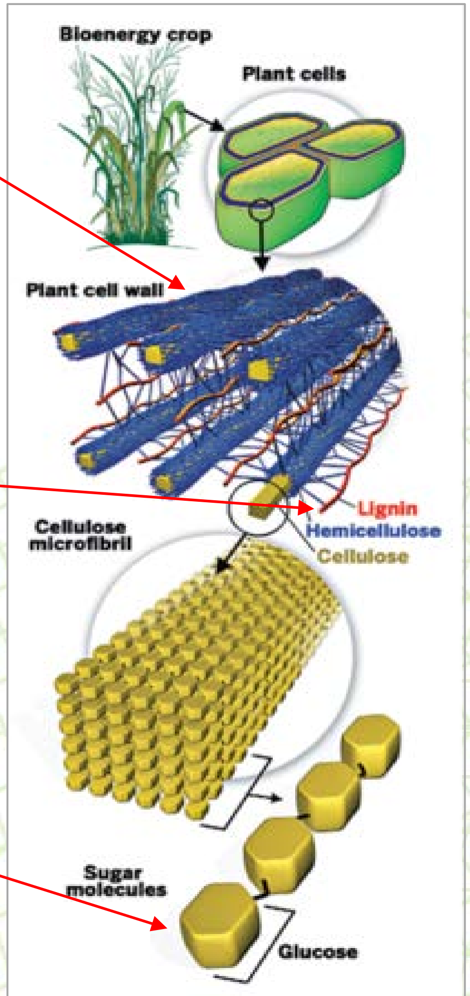

Cell factory [MCF]

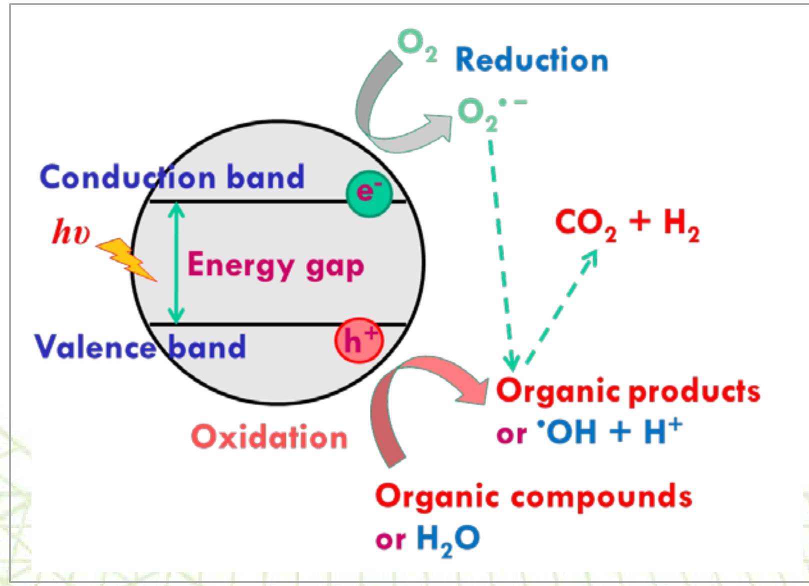
Research Themes

Theme 3
Biomass Pretreatment

Theme 2
Lignin Conversion

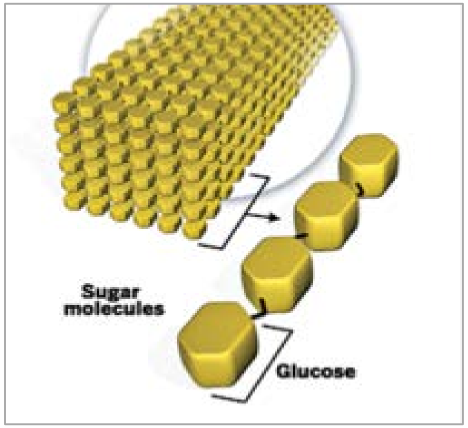
Theme 1
Sugar Conversion





Value-added Fuels & Chemicals

Theme 1: Sugar Conversion



Development of TiO_2 Fabrication with CTAB Surfactant

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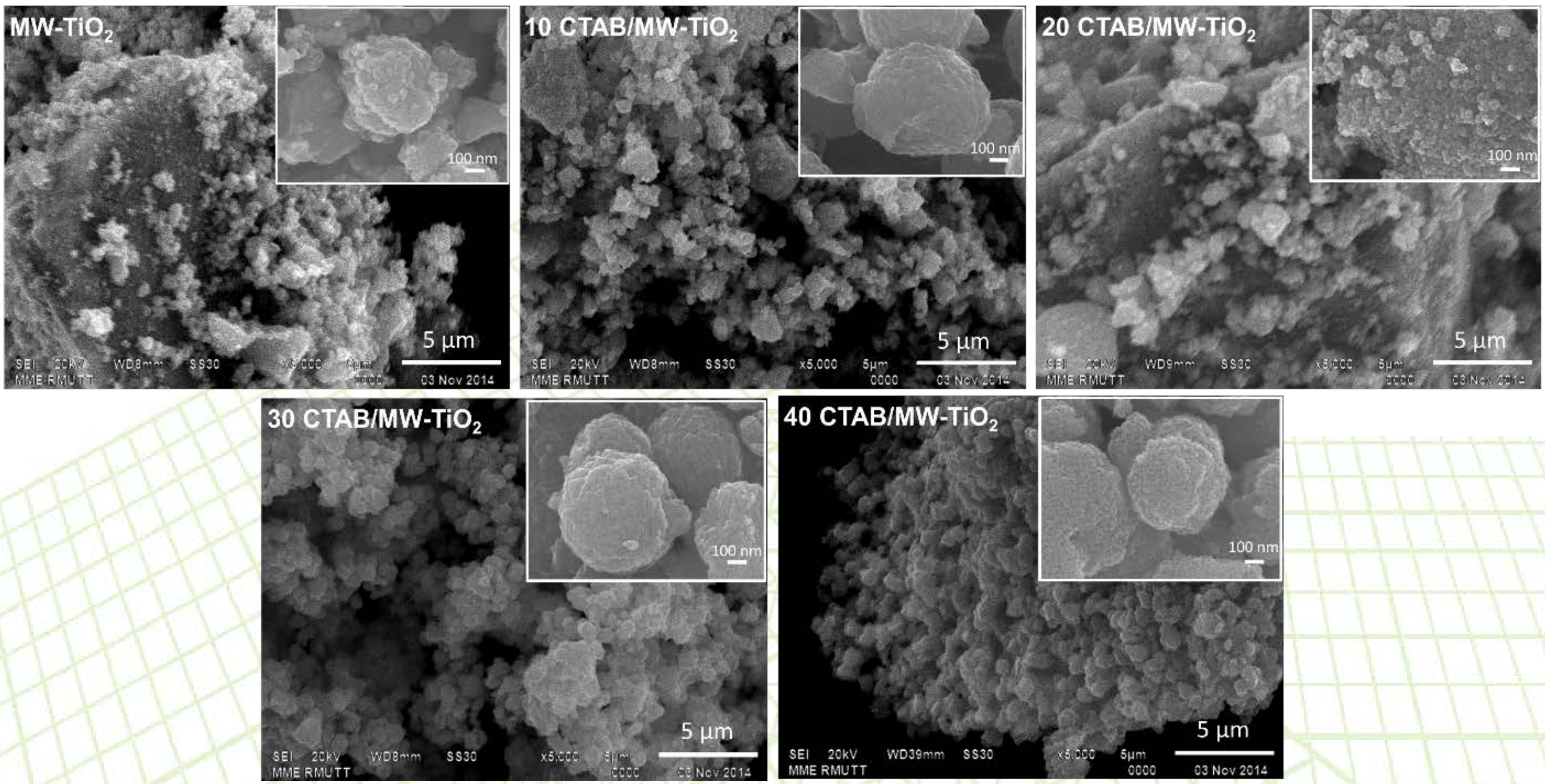

SEM and FESEM images of TiO_2 photocatalysts synthesized by different concentrations of CTAB

Photocatalytic Activity of TiO_2 Modified by CTAB

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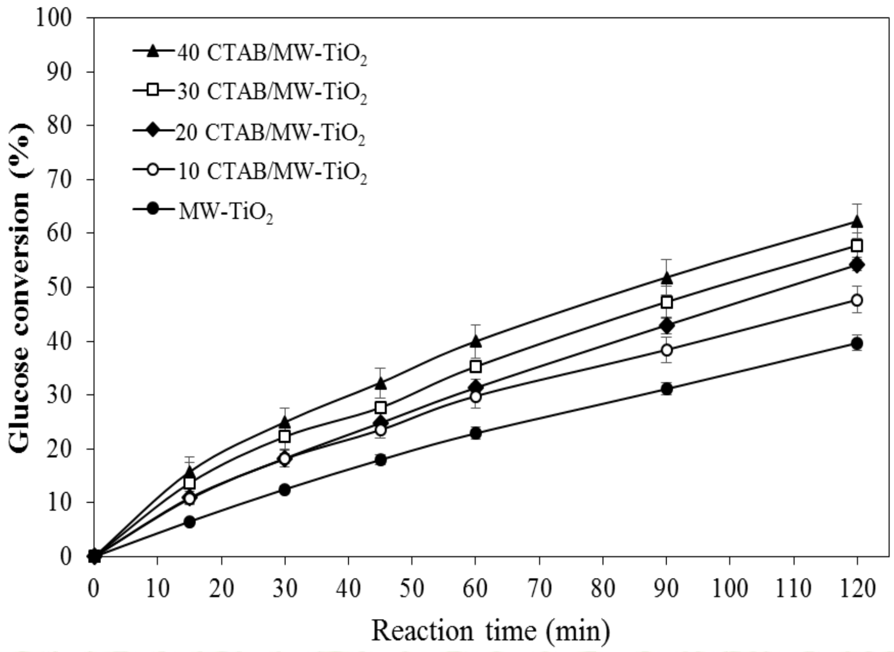
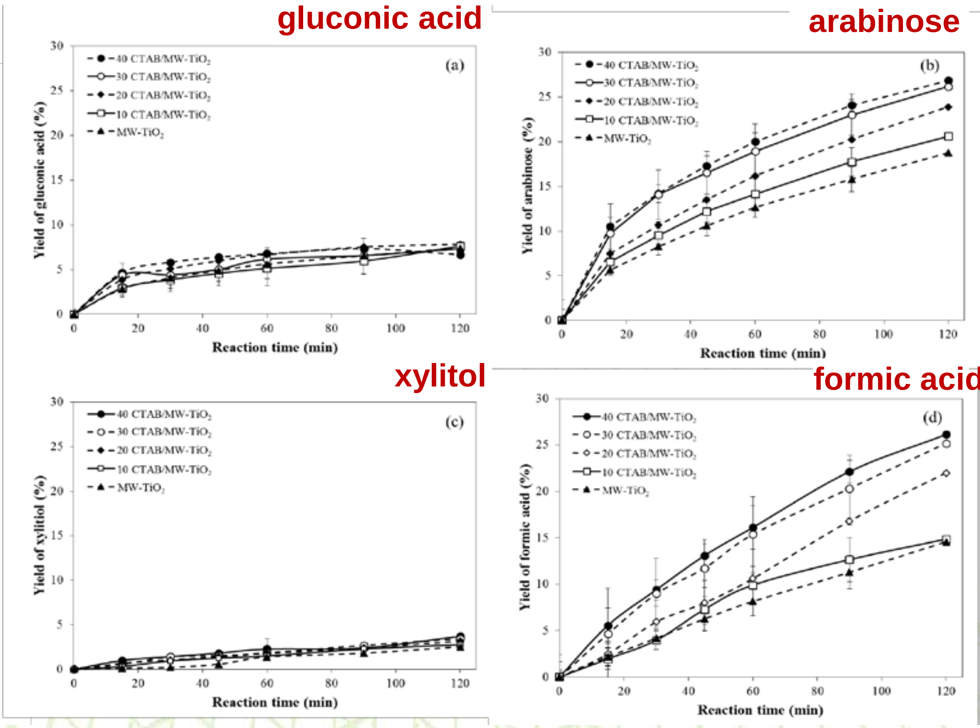
The results of development of TiO_2 fabrication with CTAB surfactant



Photocatalytic conversion of glucose with TiO_2 synthesized with different concentrations of CTAB in MW.



Product yields of photocatalytic conversion of glucose with TiO_2 photocatalysts synthesized by different concentrations of CTAB

Modification of TiO_2 with Zeolite Supporters

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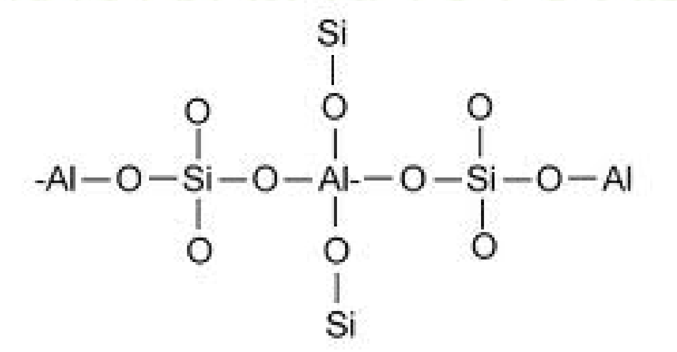
Zeolites

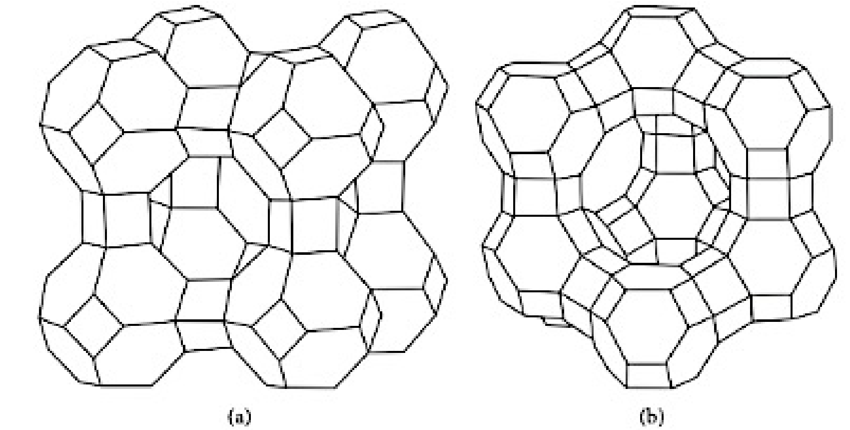
Zeolites are hydrated aluminosilicate minerals made from interlinked tetrahedral of alumina (AlO_4) and silica (SiO_4).

Advantages of Zeolites

- ✓ Improved selectivity
- ✓ High activity
- ✓ Excellent absorption ability



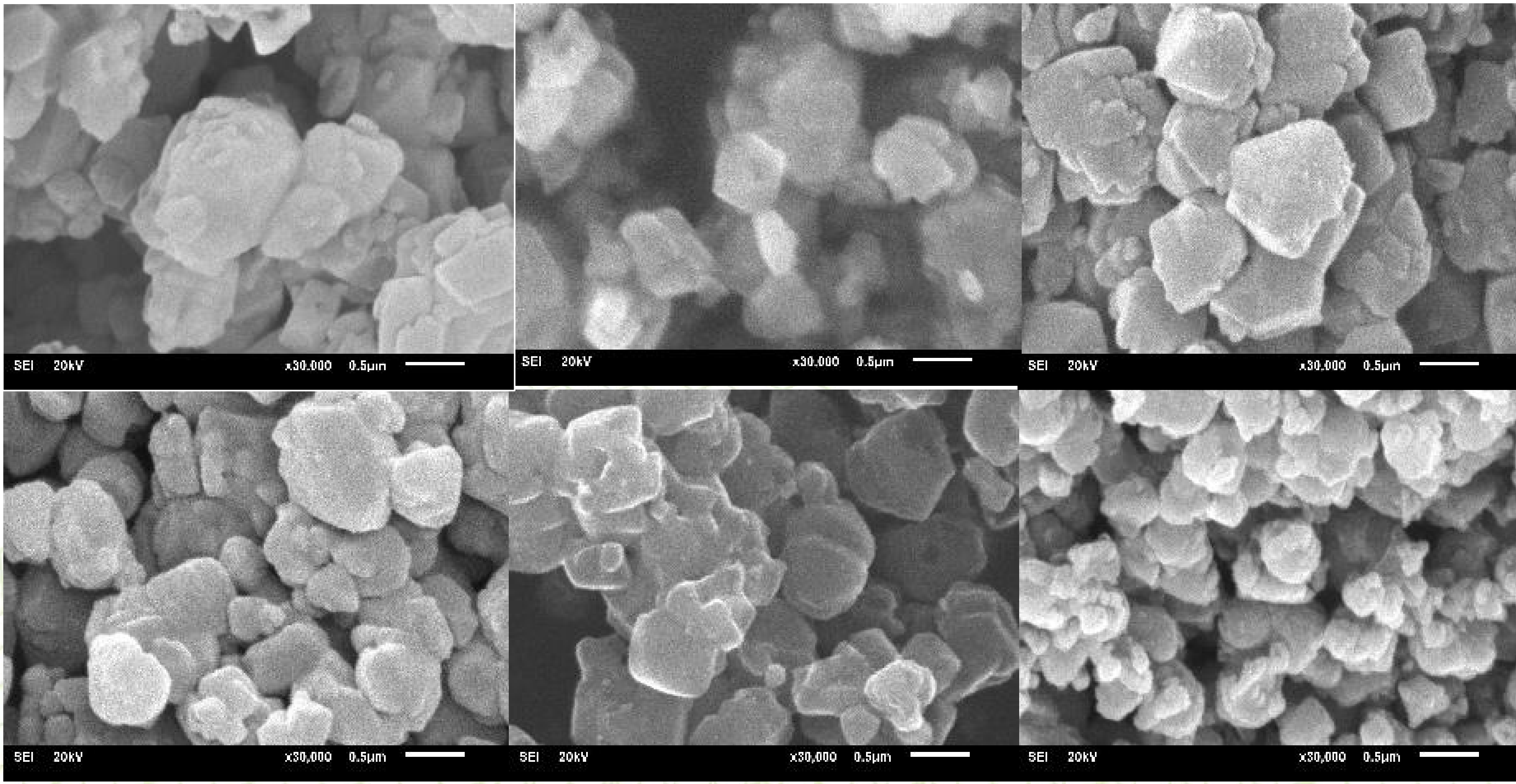
Basic Zeolite Structure



Structure of zeolite A (a) and faujasite-type zeolites X and Y (b) formed by sodalite cages

(Lutz, 2014).

Modification of TiO_2 with Zeolite Supporters



SEM images (30000x) of ZeY, TiO_2 (5%)/ZeY(95%), TiO_2 (15%)/ZeY(85%), TiO_2 (30%)/ZeY(70%), TiO_2 (45%)/ZeY(55%),and TiO_2.

Modification of TiO_2 with Zeolite Supporters

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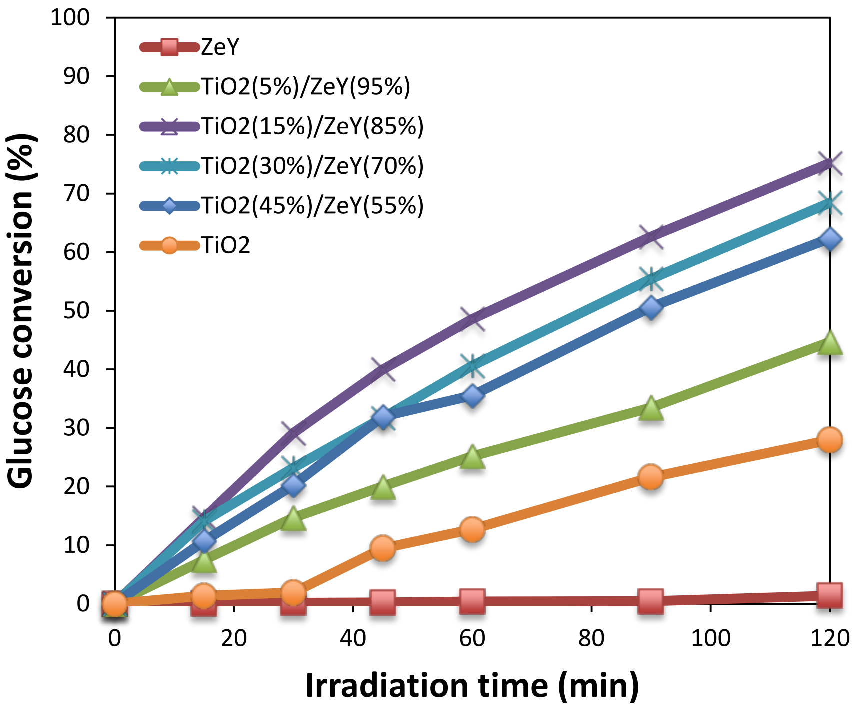
The results of modification of TiO_2 with zeolite supporter

Photocatalytic conversion of glucose



Photocatalyst	S_{BET} (m^2/g)
ZeY	590.76
TiO_2(5%) /ZeY(95%)	588.36
TiO_2(15%) /ZeY(85%)	524.41
TiO_2(30%) /ZeY(70%)	494.57
TiO_2(45%) /ZeY(55%)	419.44
TiO_2	34.38

Modification of TiO_2 with Zeolite Supporters

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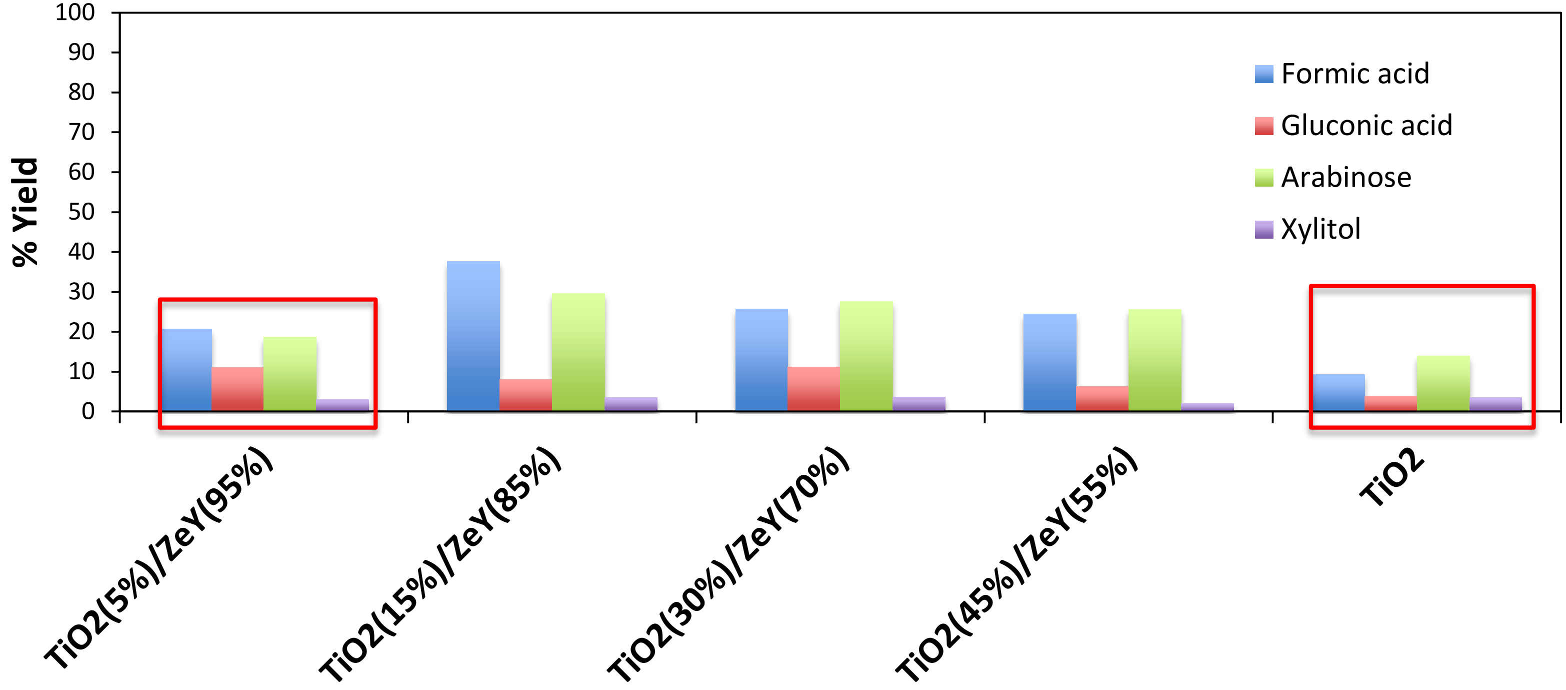
The results of modification of TiO_2 with zeolite supporter

Product Yields



Modification of TiO_2 with Zeolite Supporters

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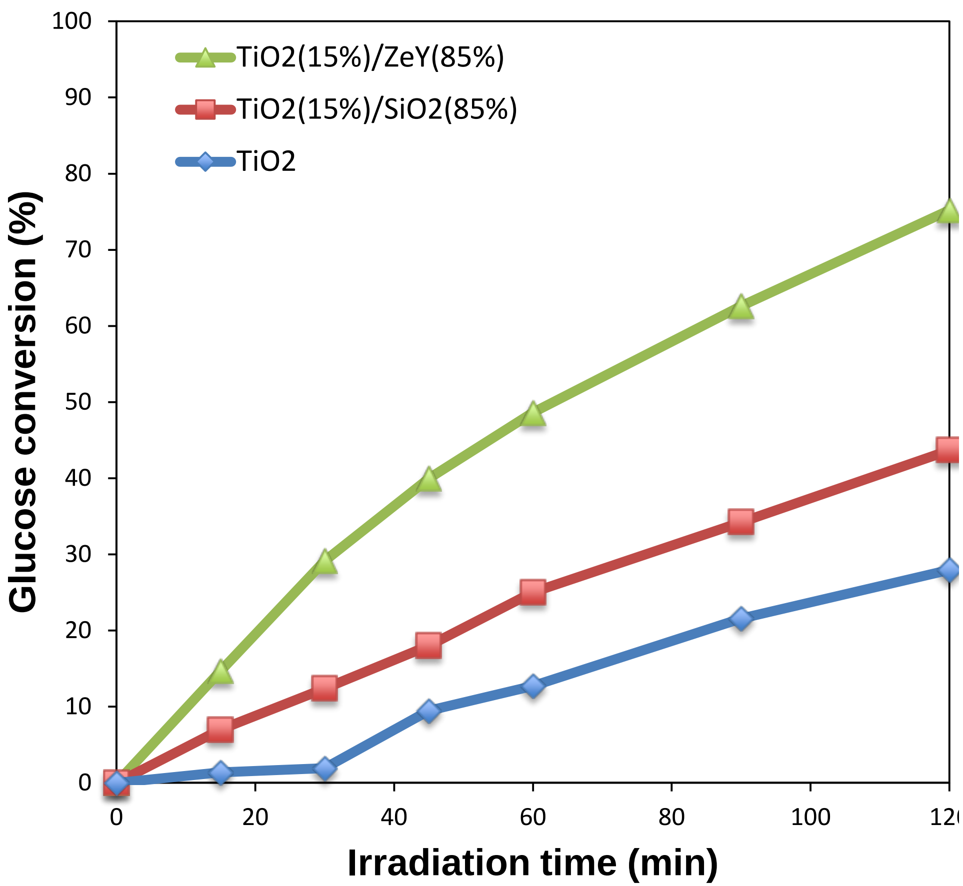
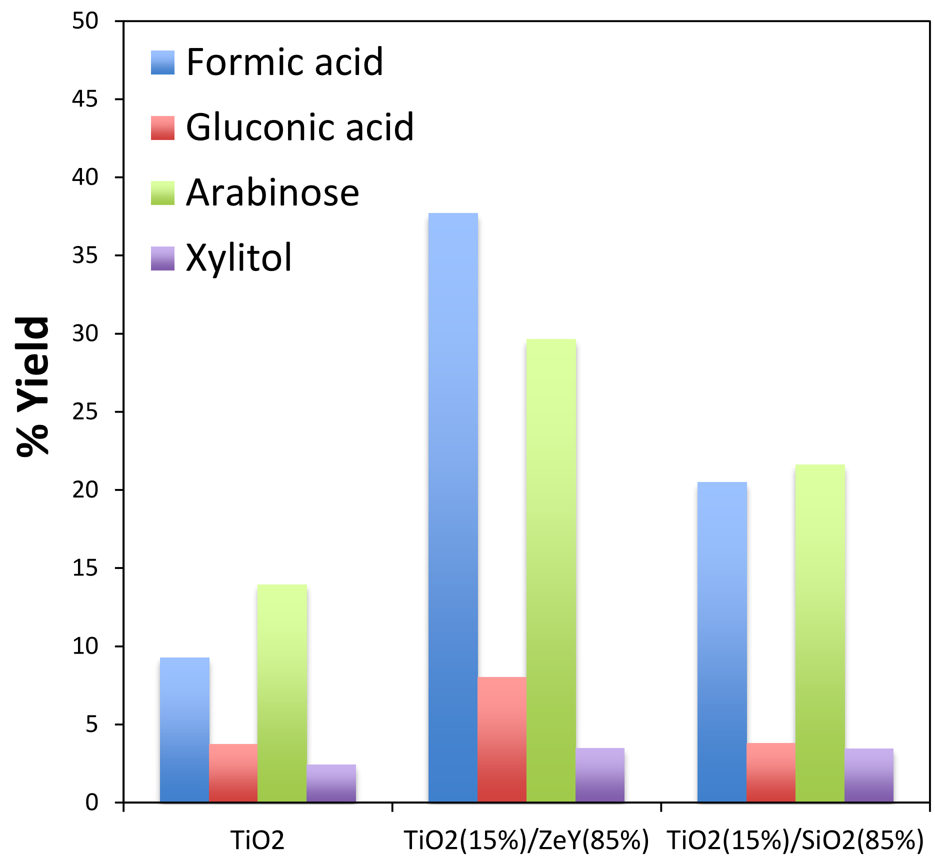
The results of modification of TiO_2 with zeolite supporter

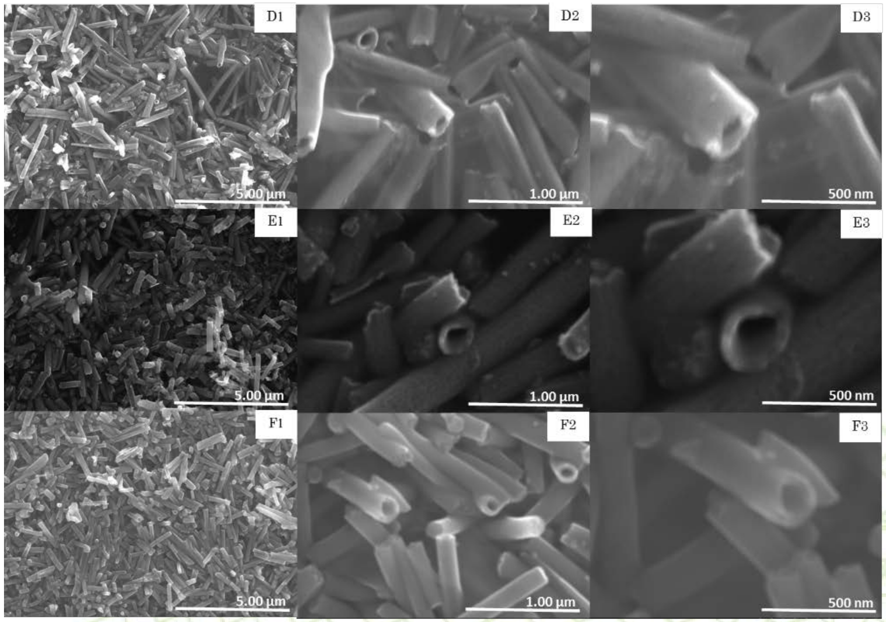
Photocatalytic conversion of glucose



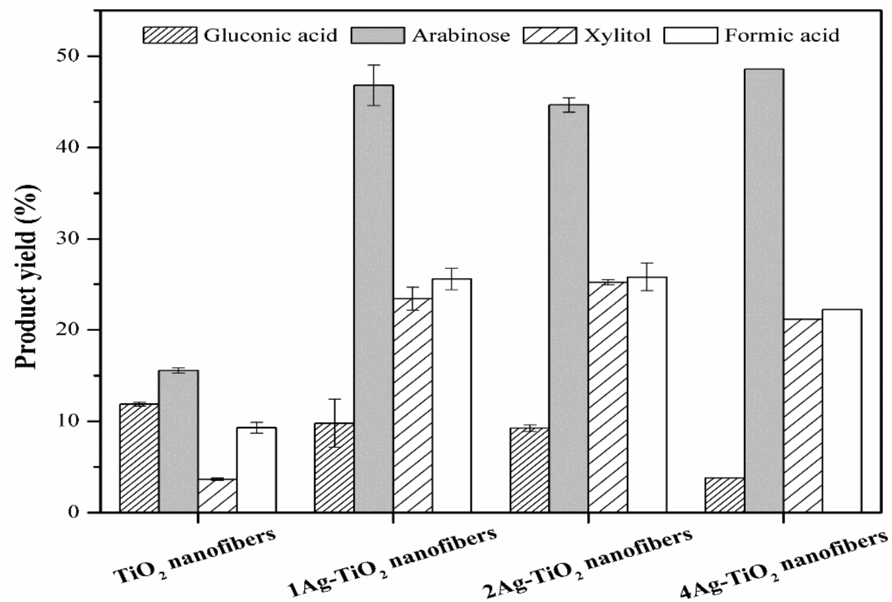
Product Yields



TiO_2 Nanofiber Photocatalysts

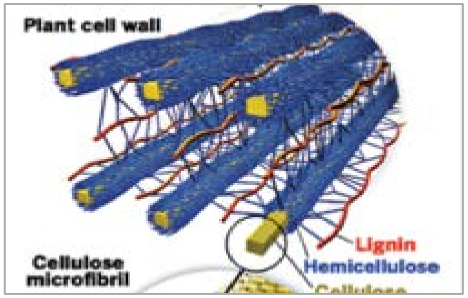


SEM images of TiO_2 nanofibers from co-axial horizontal electrospinning at inner flow rate 0.5 ml/h at magnifications of (D1) 10.0k, (D2) 50.0k and (D3) 100.0k, inner flow rate 1.0 ml/h at magnifications of (E1) 10.0k, (E2) 50.0k and (E3) 100.0k and inner flow rate 1.5 ml/h at magnifications of (F1) 10.0k, (F2) 50.0k and (F3) 100.0k.



Yields of formic acid, gluconic acid, arabinose, and xylitol from photodecomposition of glucose

Theme 2: Lignin Conversion



Photocatalytic Conversion of Lignin to High-value Products

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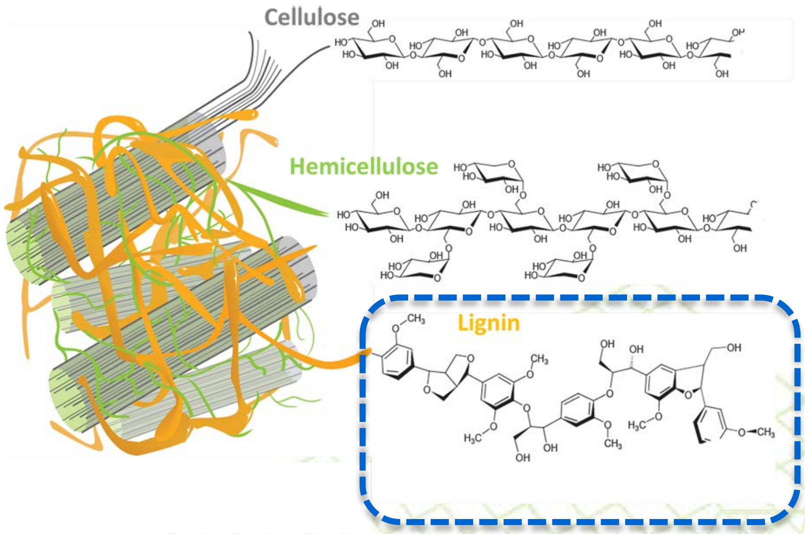
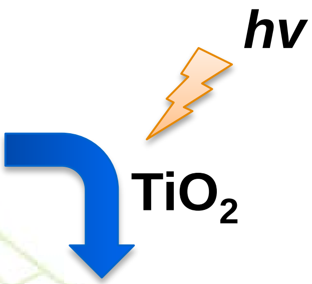


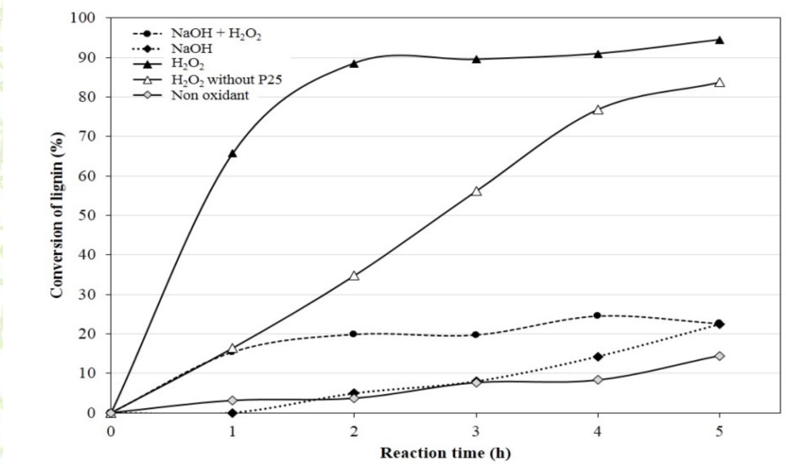


Photocatalytic activity

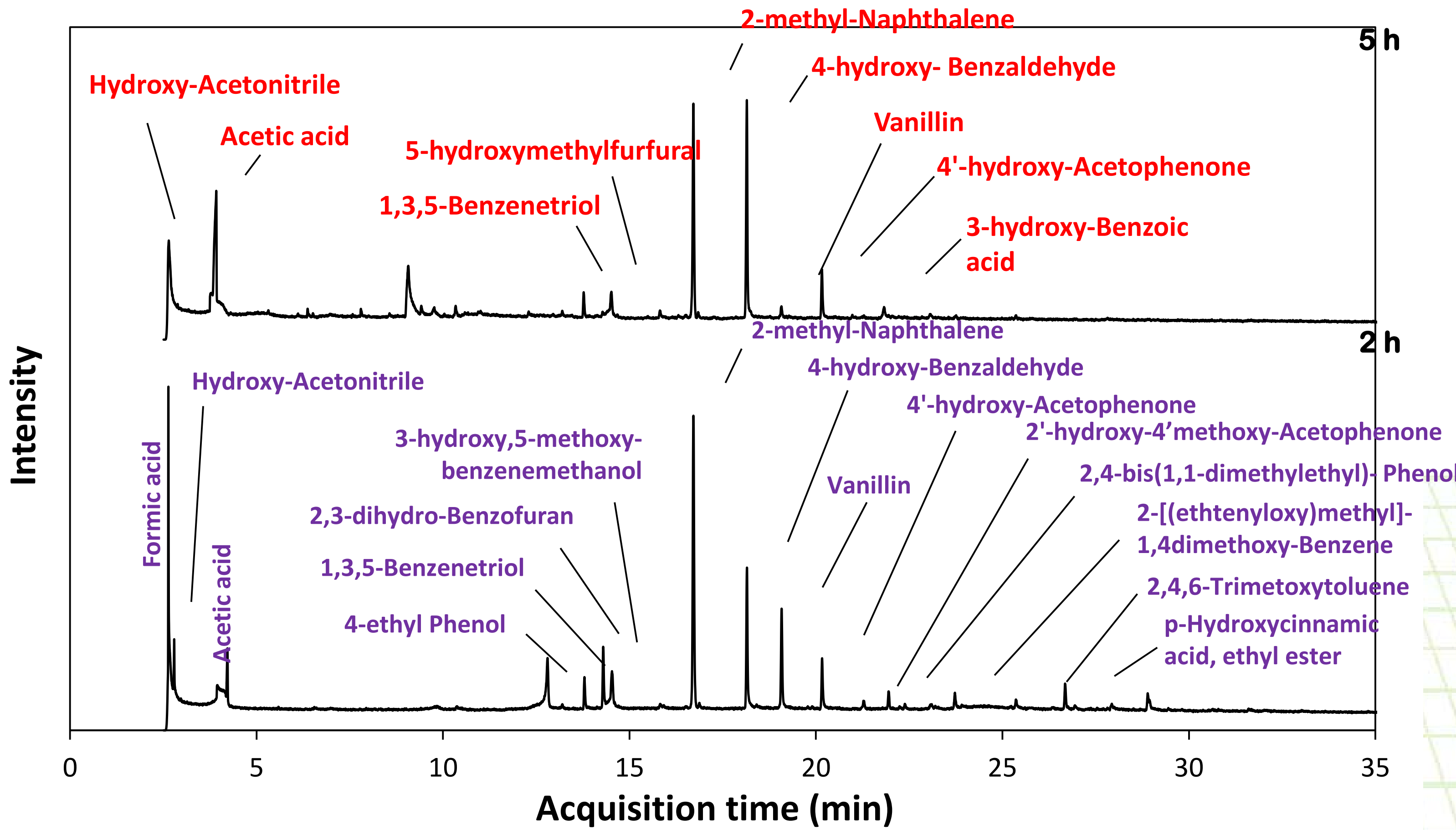
Composition of the biomass

http://www.psb.ugent.be/bio-energy/313-lignin

Effect of kraft lignin concentration on photocatalytic conversion of kraft lignin (reaction conditions: 1g/L of P25, 100/0 v/v of water to ACN and 400 W of UV-lamp).



Products from Conversion of Lignin



GC-MS spectra of hydrocarbon compounds derived from photocatalytic conversion of kraft lignin catalyzed by P25 under UV irradiation for 2 and 5 h.

Price of High-value Chemicals

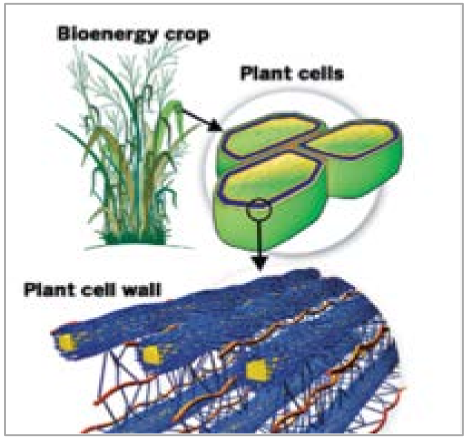
Chemicals from glucose conversion

Products	Price (THB)/kg	Applications
Gluconic acid	337	acidity regulator
Arabinose	1685-5055	sweetener
Xylitol	33.7-168.5	sweetener
Formic acid	16.513-18.53	preservative and antibacterial agent, use in cleaning products, dyeing and finishing textiles products, and use in direct formic acid fuel cell (DFAFC)

Chemicals from lignin conversion

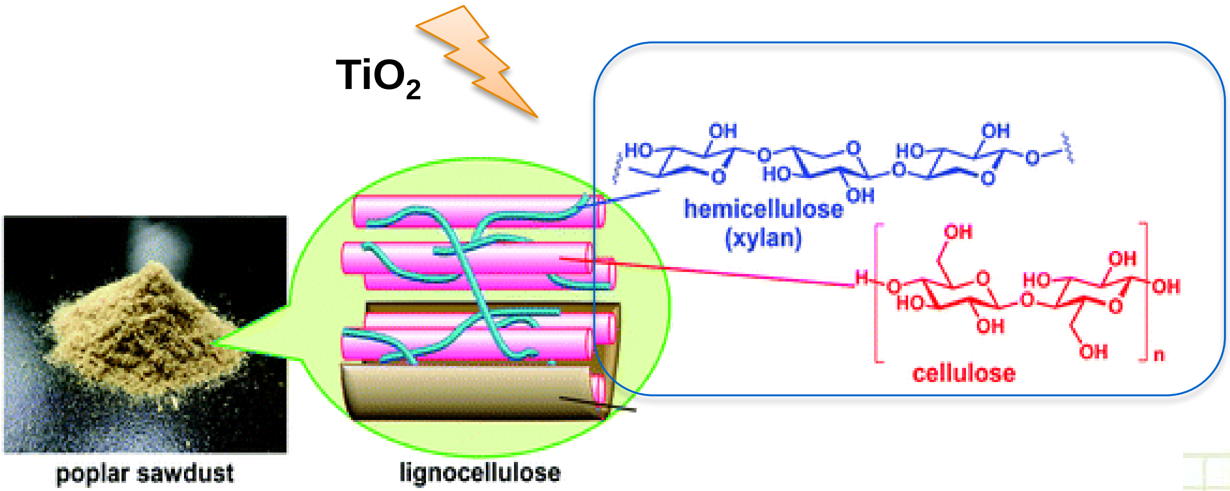
Products	Price (THB)/kg	Applications
2-methyl naphtalene	33.7-50.55	textile dyeing, printing and metal surface water treatment and chelating, used in organic synthesis,pesticide, pharmaceutical and dyne intermedite
4-hydroxy-benzaldehyde	33.7-3370	pharmaceutical intermediate, antiallergic agent blood system agent and anesthetic agents
Vanillin	33.7-505.5	synthetic flavor and fragrance
4'-hydroxy-acetophenone	3370	used in the manufacture of medicinal reagent

Theme 3: Biomass Pretreatment



Photocatalytic Pretreatment of Biomass

Concept of Photocatalytic Pretreatment of Biomass



Biomass structure

Enzymatic hydrolysis

Glucose, fructose, xylose

Photocatalytic process

High-value chemicals

Photocatalytic Pretreatment of Biomass

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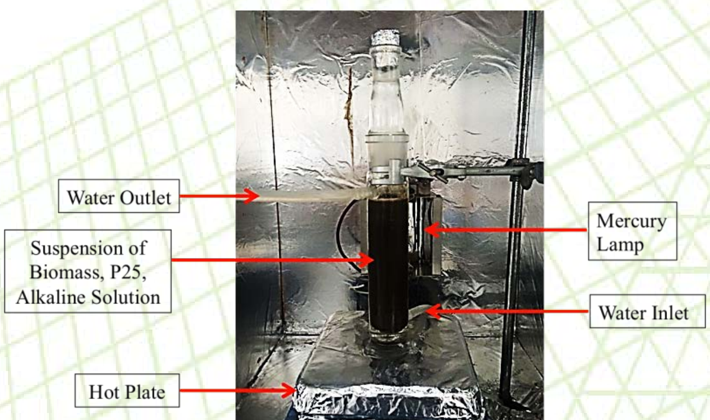
① **Blank Pretreatment**

② **Photocatalytic Pretreatment**



Pretreated suspension filtrated by vacuum filter

Filtration

Liquid Product

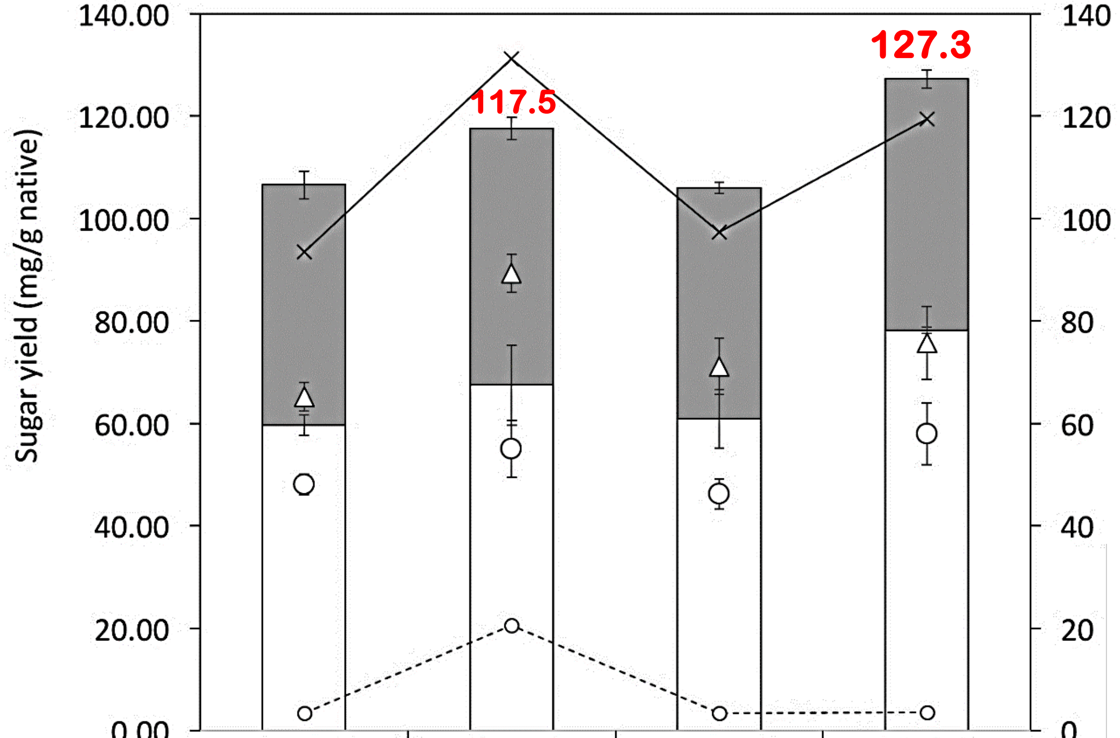
Further product analysis by HPLC

Dilute with DI water until neutral

Solid Product (neutral)

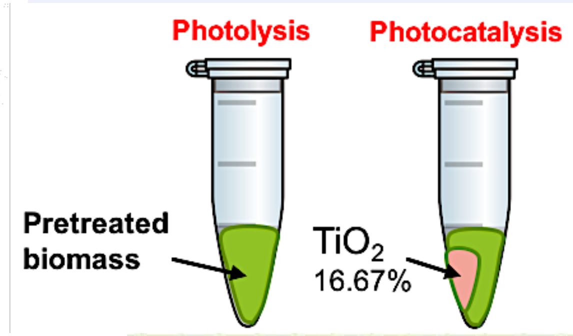
Further enzymatic hydrolysis

Photocatalytic Pretreatment of Biomass



	Bagasse + H2O	Bagasse + H2O + UV	Bagasse + H2O + TiO2	Bagasse + H2O + TiO2 + UV
Pentose(mg/g native)	47.00	50.09	45.12	49.07
Glucose(mg/g native)	59.60	67.46	60.88	78.18
O Pentose (mg/g pretreated)	48.11	55.00	46.23	57.91
Δ Glucose (mg/g pretreated)	65.18	89.36	71.09	75.71
Total sugar (mg/g pretreated)	93.53	131.22	97.27	119.49
Weight loss (%)	3.48	20.64	3.42	3.65
Catalyst in Solid Phase (%)	0.00	0.00	16.47	16.67

Condition:
Biomass = 7.5 g
Solvent (water) = 150 ml
TiO_2 = 1.5 g
Temperature = 25 °C
Time = 24 h



Sugar digestibility yields in photocatalytic pretreatment (solvent = water) compared with blanks (no catalyst and/or no UV irradiation).

Overall Research Outputs

Overall Research Outputs

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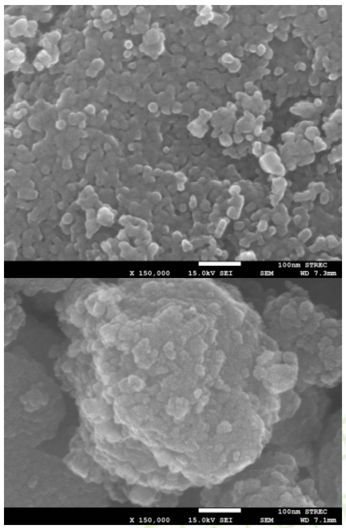
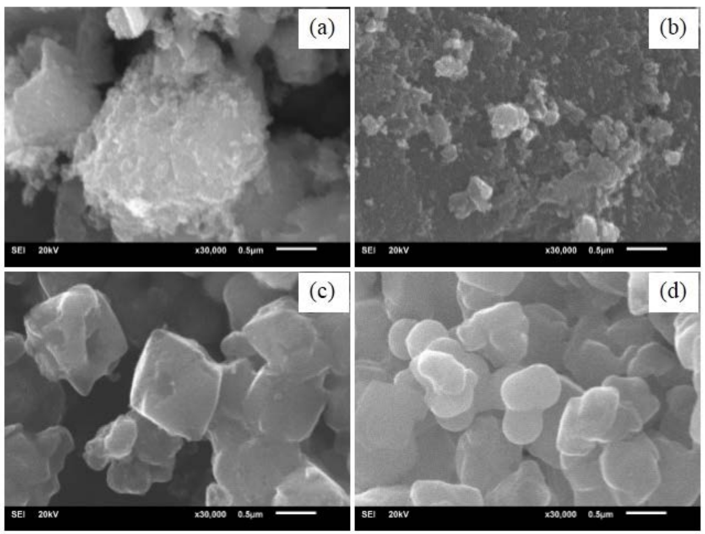
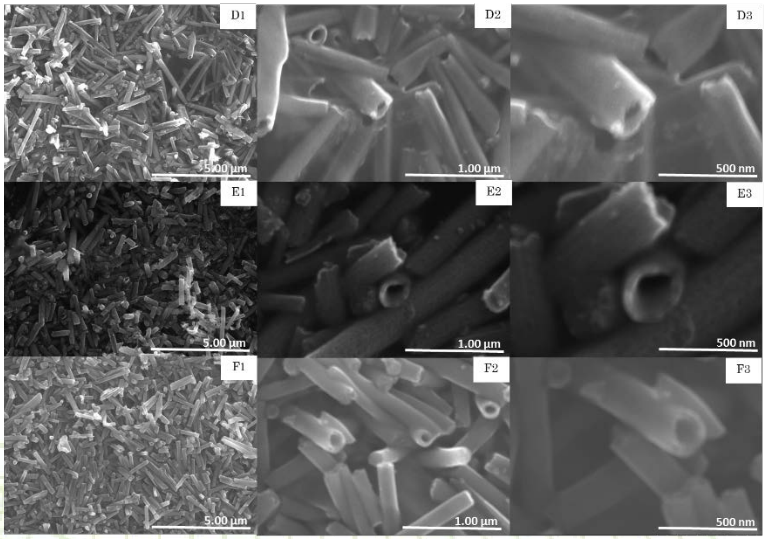
Synthesized Photocatalysts



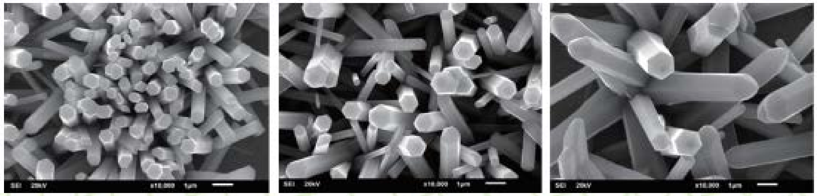
TiO_2 nanoparticles



Zeolite supported TiO_2



TiO_2 nanofibers and nanotubes



TiO_2 nanowires

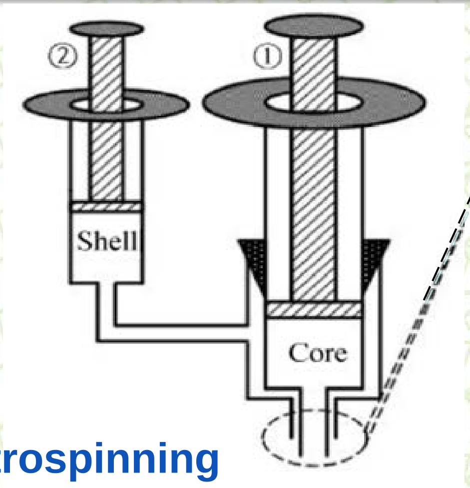
High-value chemicals

- Xylitol
- Gluconic acid
- Arabinose
- Formic acid
- Vanillin
- 2-methyl naphtalene
- 4-hydroxy-benzaldehyde
- *Etc.*

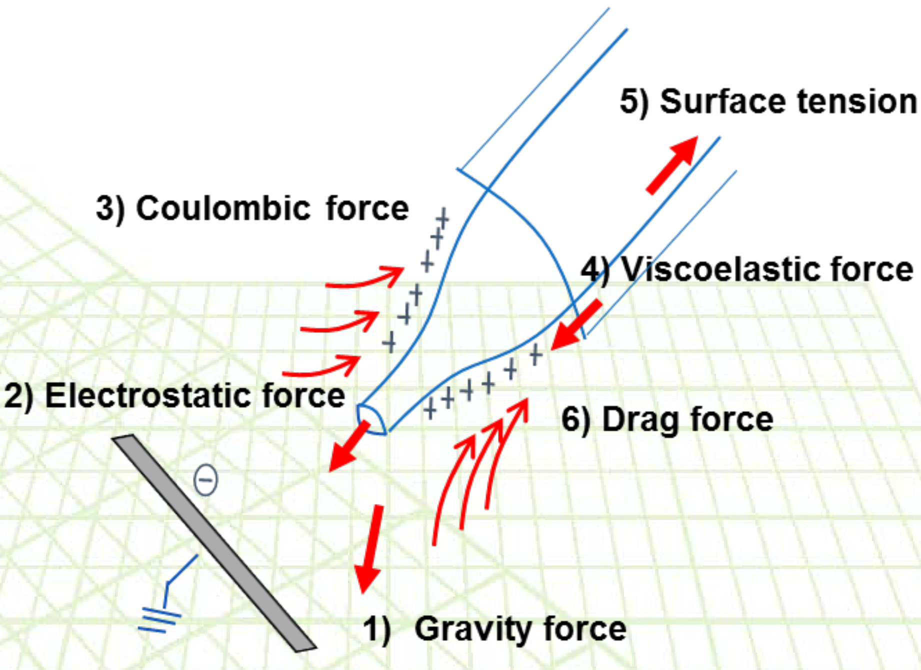
Electrospinning

Electrospinning is a technique to produce the polymer nanofibers from a wide variety of materials and versatile applications.
Different methods of electrospinning:

1. **Direct electrospinning**
2. **Emulsion electrospinning**
3. **Coaxial electrospinning**



Coaxial electrospinning with two-capillary spinneret.



Electrospinning force balance

Electrospinning

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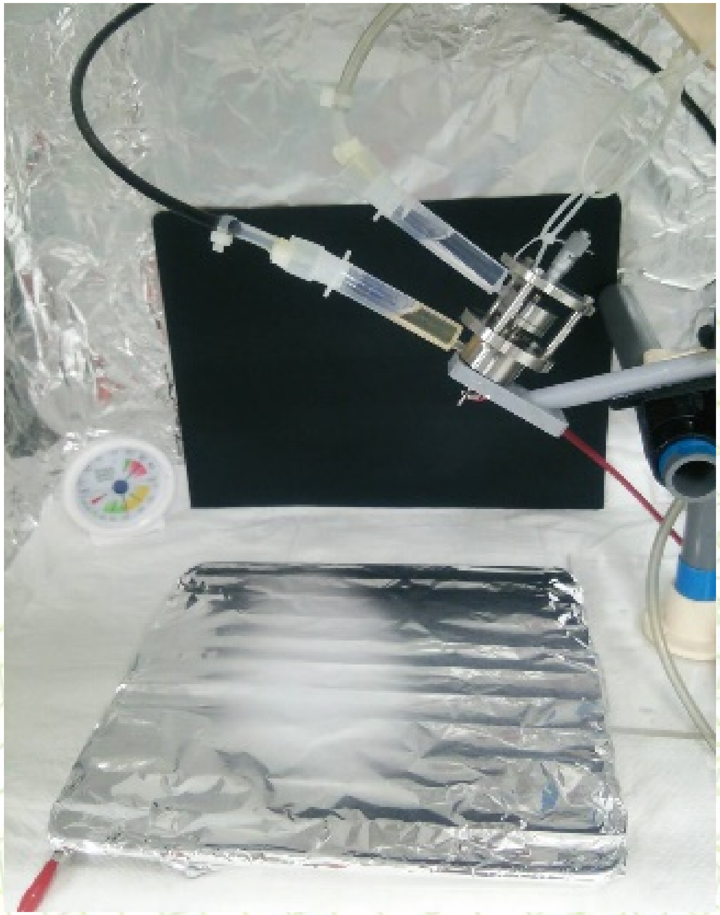

Experimental setup

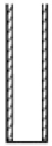
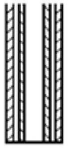
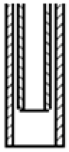
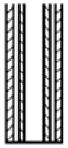
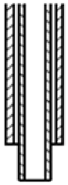
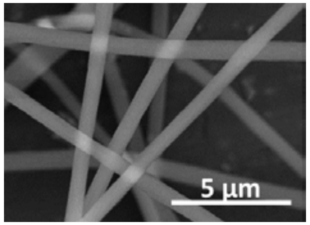
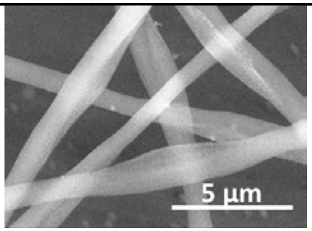
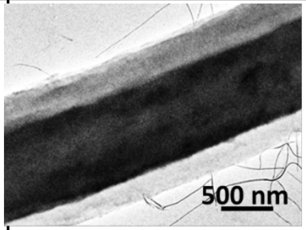
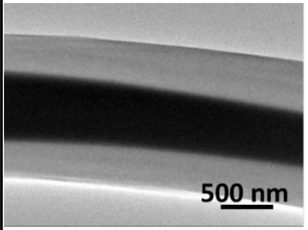
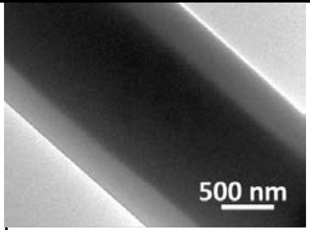
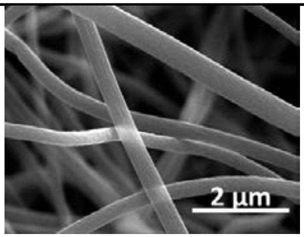
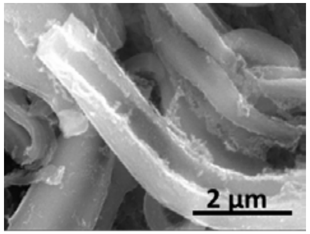
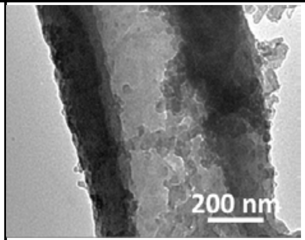
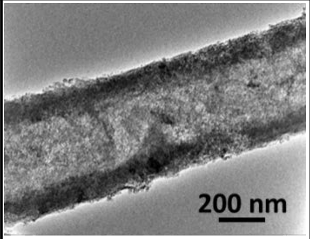
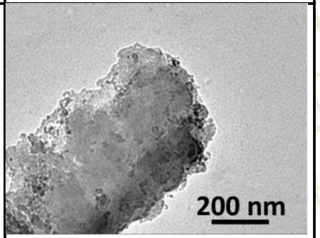
Internal factors:

- Type of polymer,
- Type of solvent,
- Solution concentration (viscosity),
- Solution conductivity, *etc.*

External factors:

- Collecting distance,
- Applied voltage,
- Solution flow rate,
- Ambient temperature, humidity, *etc*

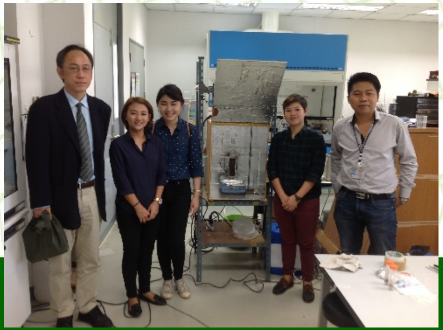
Balance levels of inner/outer nozzle end

	SEM Images		TEM Images		
Nanofibers	**PAN**	**PAN/PMMA**	**PAN/PMMA**		
Nozzle	**Single nozzle**	**Coaxial nozzle**	**Inward**	**Normal**	**Outward**
Illustration					
As spun nanofiber ***(Before calcination)***					
Carbon Nanofiber ***(After calcination)***					

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 – 31 May 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 Sanglee	6 Feb 2017 – 17 Mar 2017	Development of Visible-Light Irradiation Responded Metal Oxide for Photocatalytic and Photovoltaic Applications



Project Outputs

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Papers

- Navaporn Kaerkitcha, Surawut Chuangchote, and Takashi Sagawa (2016) "Control of physical properties of carbon nanofibers obtained from coaxial electrospinning of PMMA and PAN with adjustable inner/outer nozzle-ends," *Nanoscale Research Letters*, 11(1), 1-9.

- 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-TiO_2 Photocatalysts," *Applied Mechanics and Materials*, 839, 39-43.

- Mathana Wongaree, Siriluk Chiarakorn, Surawut Chuangchote, and Takashi Sagawa (2016) "Photocatalytic Performance of Electrospun CNT/TiO_2 Nanofibers in a Simulated Air Purifier under Visible Light Irradiation," *Environmental Science and Pollution Research*, 23, 21395-21406.

Patent

- Xylitol Production from Glucose and Xylose Using Titanium Dioxide Photocatalyst," Patent Submission No. 1401007893.