Development of New Functional Materials for Energy and Environment

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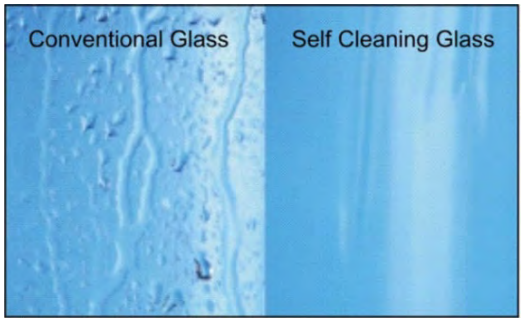
Outline

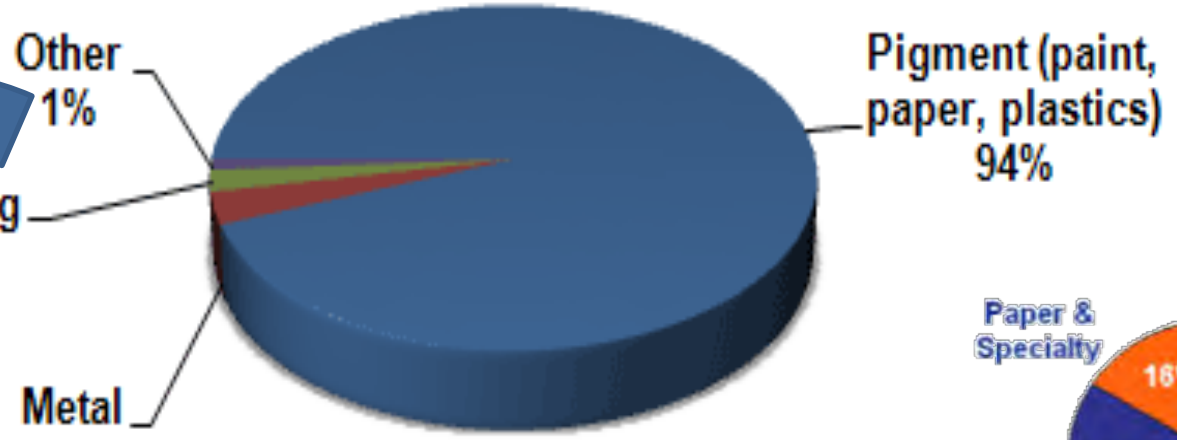
- ❑ Introduction
- ❑ Materials and methods
- ❑ Results and Discussion
- ❑ Conclusion

Introduction: TiO_2

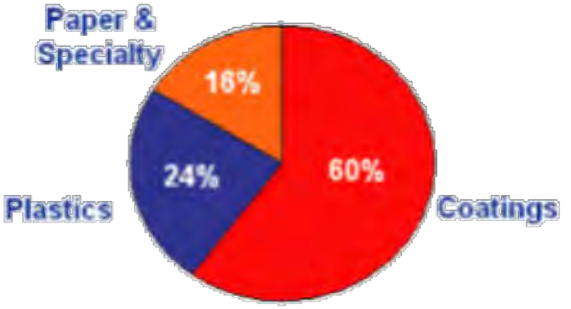
TiO_2



Global Consumption of Titanium



Titanium Market Supply/Demand
http://www.titaniumcorporation.com/s/Titanium.asp



food

cosmetics. sun screen lotions

Nano titanium dioxide

energy and environmental sciences

dye-sensitized solar cells

photovoltaic devices

photocatalysts

Energy storage

lithium/sodium storage

supercapacitors

Powder Technology 302 (2016) 254–260

Chem. Mater. 2015, 27, 6022−6029

J. Mater. Chem. A, 2015, **3**, 13807-13818

Introduction: TiO_2 in natural ores

Form of Titanium	TiO_2 %	Magnetic Susceptibility	Electrical Conductivity	Specific Gravity
Ilmenite - Sulphate - Chloride	 52 - 54 58 - 62	 High	 High	 4.5 - 5.0
Rutile	95 - 97	Low	High	4.2 - 4.3
Synthetic Rutile	88 - 95			
Leucoxene	70 - 91	Semi	High	3.5 - 4.1

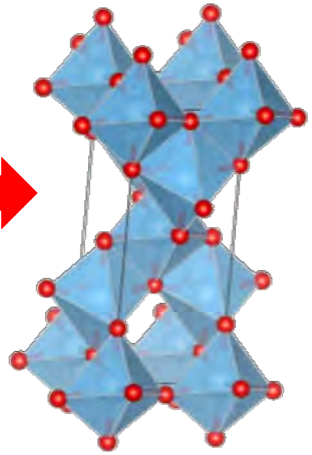
Sakorn Minerals Co., Ltd., Thailand

References;
http://metalpedia.asianmetal.com/metal/titanium/resources&production.shtml
http://www.mindat.org/photo-95122.html
http://www.mine-engineer.com/mining/mineral/rutile.htm

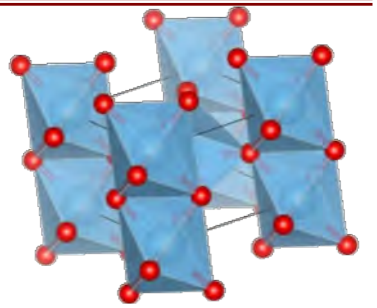
Introduction: TiO_2-based natural minerals

Ilmenite

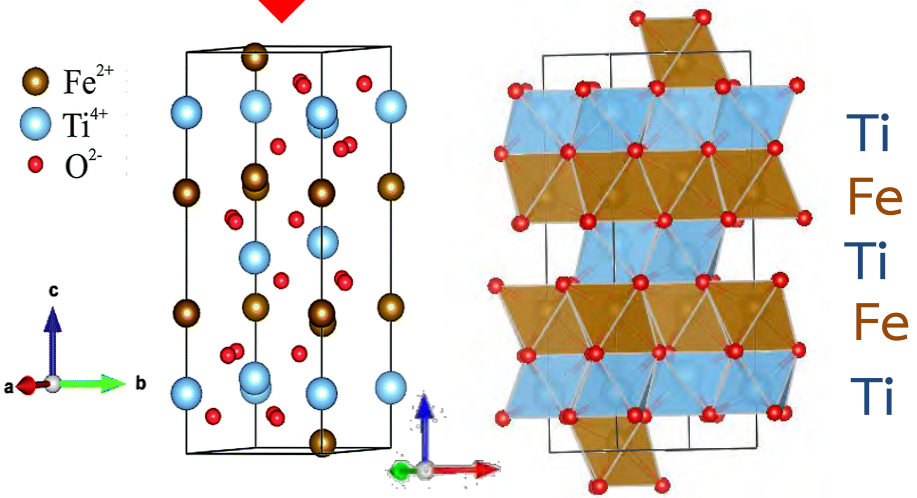
Leucoxene



Anatase TiO_2



Rutile TiO_2

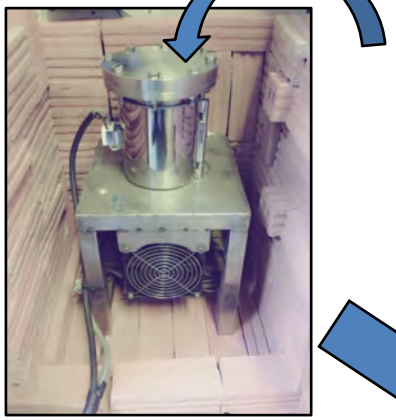


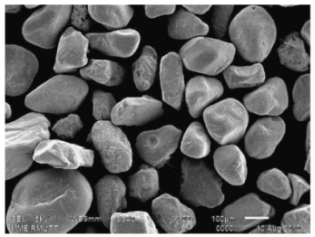
Ti
Fe
Ti
Fe
Ti

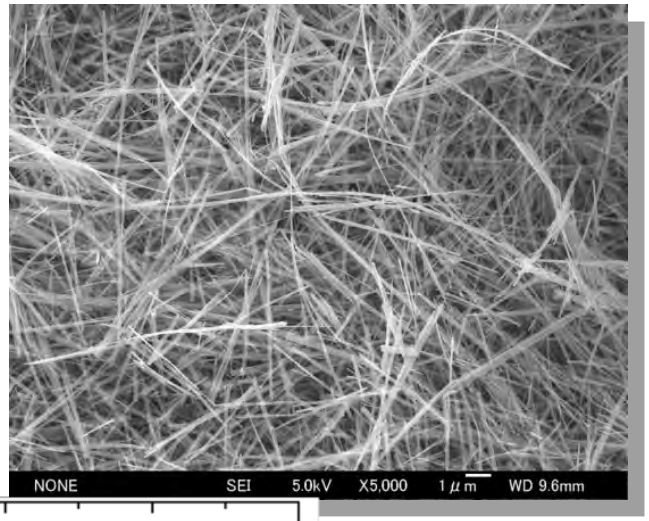
Mg, Al, Mn, Si impurities

Introduction: TiO_2 -based natural minerals

- TiO_2 nanofibers derived from ilmenite mineral by hydrothermal





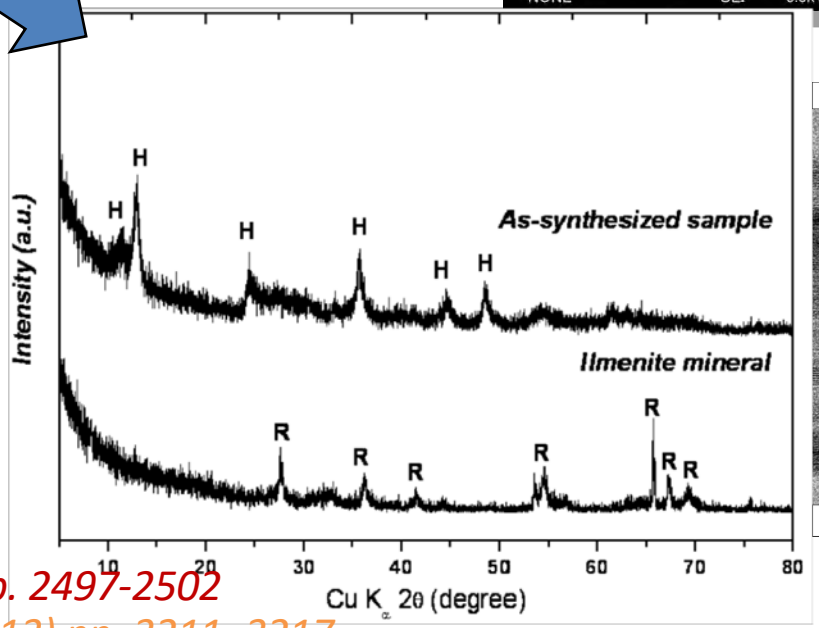


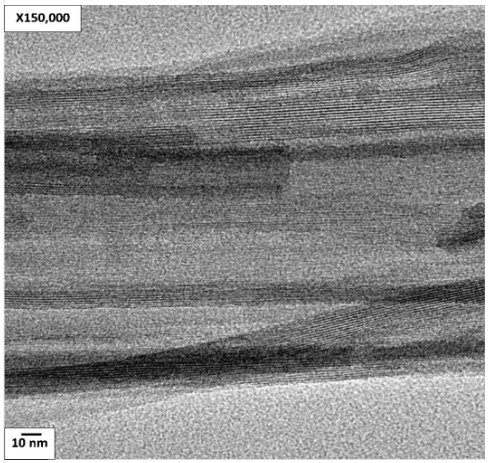
Ilmenite powder

+

NaOH (10M)

Hydrothermal
110-150 °C

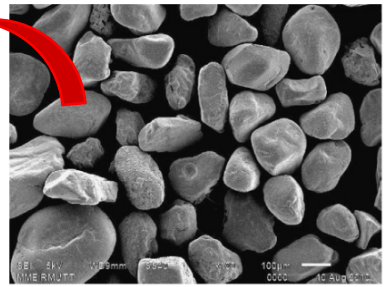


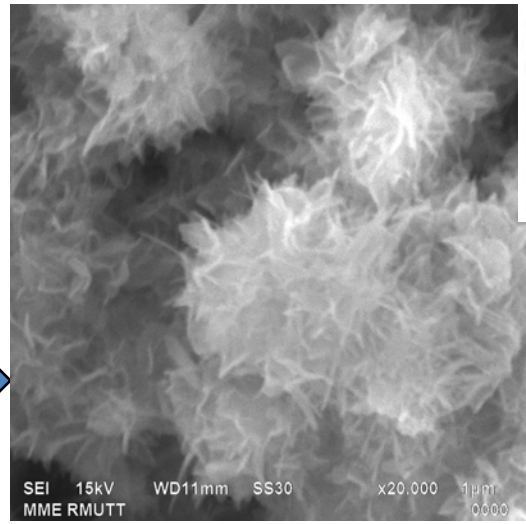


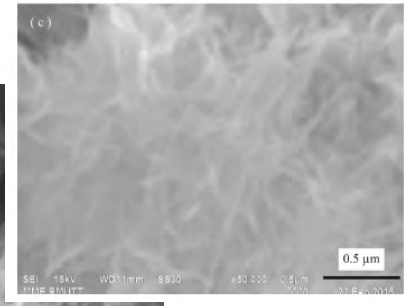
Ceramic International, 39 (2013) pp. 2497-2502
Materials Research Bulletin, 48 (2013) pp. 3211–3217

Introduction: TiO_2 -based natural minerals

- TiO_2 nanosheets from hydrothermal process





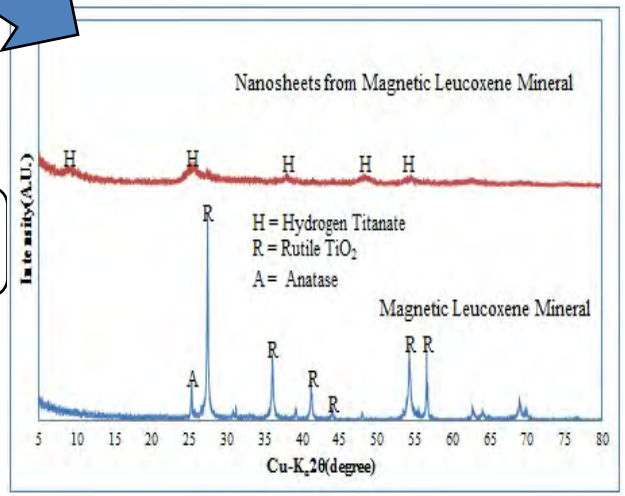


Leucoxene powder

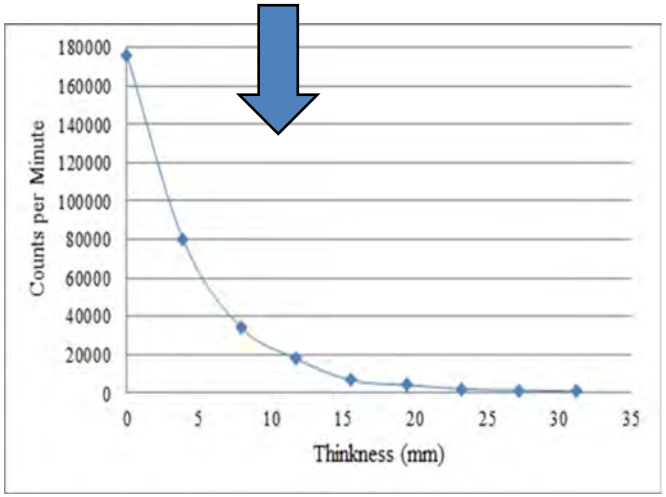
+

NaOH (5 M)

Hydrothermal
100°C 5 h



γ-ray shielding property



Synthesized process

- TiO_2 particles by chemical process

Sulphate/Chloride processes

Titanium Ore

H_2SO_4

Solution

Crystallization

Precipitation

Filtration and Washing

Calcination

Ferrous Sulfate Crystals

Intermediate TiO_2

Ferrous sulphate crystallisation

$FeSO_4 + 7H_2O \rightarrow FeSO_4 \cdot 7H_2O$

Calcination

$TiO(OH)_2 \rightarrow TiO_2 + H_2O$

Leaching

$TiFeO_3 + 2H_2SO_4 \rightarrow FeSO_4 + TiOSO_4 + 2H_2O$

Titanyl sulphate precipitation

$TiOSO_4 + H_2O \rightarrow TiOSO_4 \cdot 2H_2O$

Hydrolysis

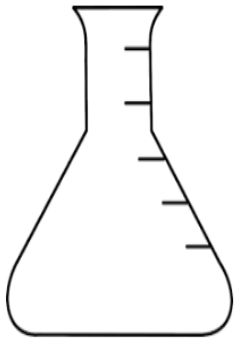
$TiOSO_4 + 2H_2O \rightarrow TiO(OH)_2 + H_2SO_4$

Calcination

$TiO(OH)_2 \rightarrow TiO_2 + H_2O$

Synthesized process

- Synthetic rutile powder by milling process with ultrasonic assisted route



Ultrasonic assisted

Leaching

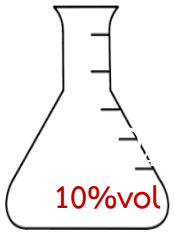
Milling

$$FeTiO_{3(s)} + 2H_2SO_4 \longrightarrow FeSO_{4\,(aq)} + TiOSO_{4\,(aq)} + 2H_2O_{\,(l)}$$

$$Fe_2O_{3(s)} + 3\,H_2SO_4 \longrightarrow Fe_2(SO_4)_{3\,(aq)} + 3\,H_2O_{\,(l)}$$

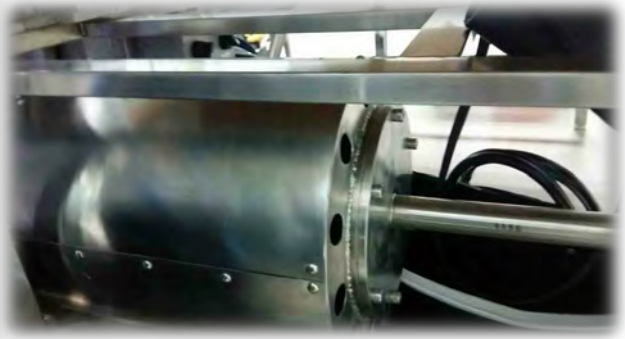
Synthesized process

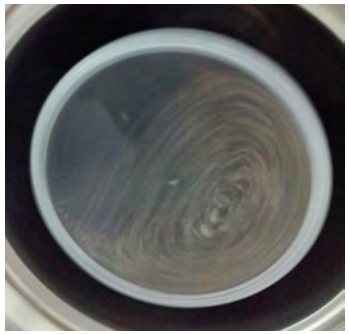
Ultrasonic-assisted process



Ultrasonic Probe

Leaching





20 h with ultrasonic for 1 h and 3 h

Polypropylene B

Results and discussion

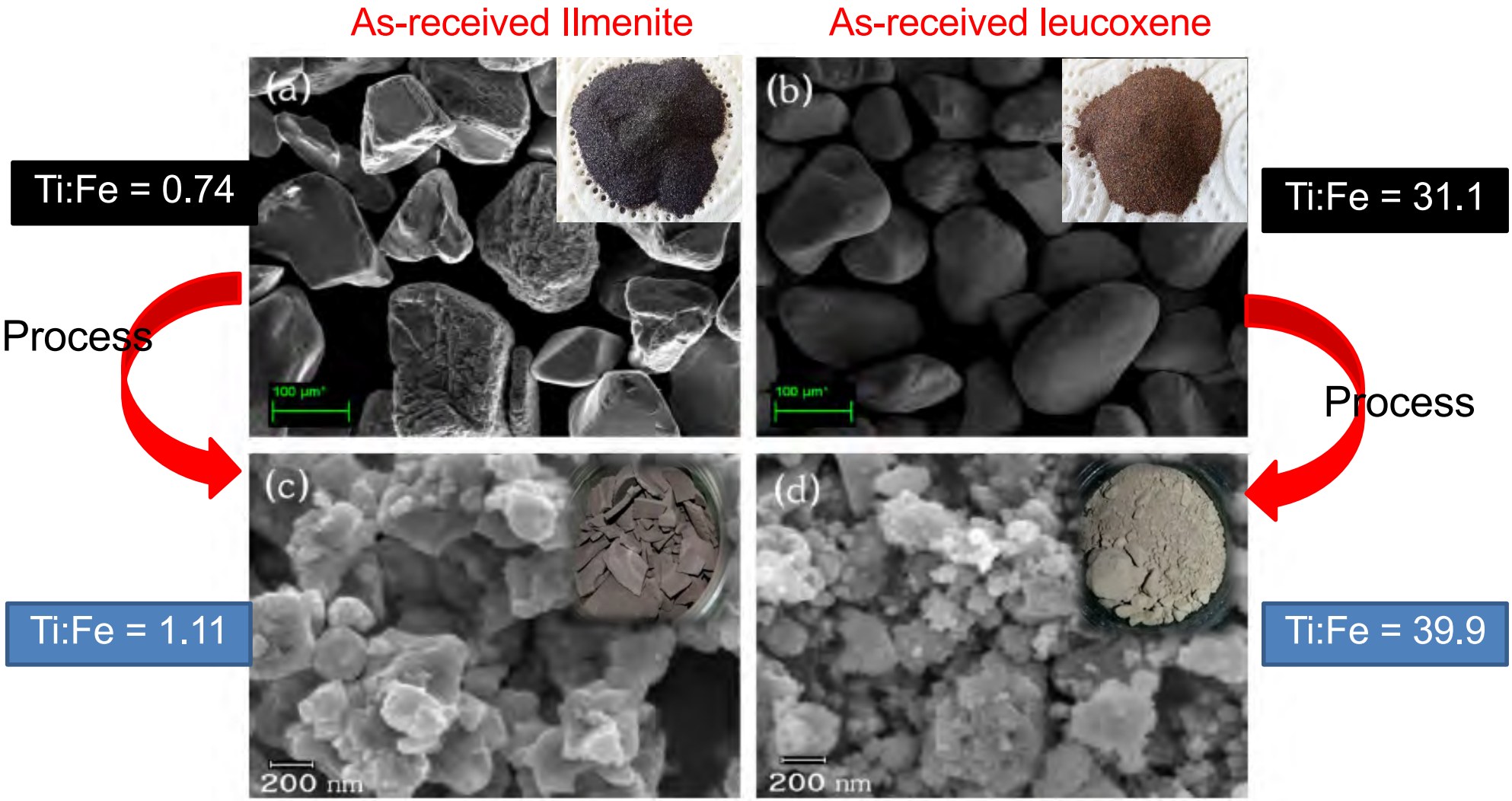
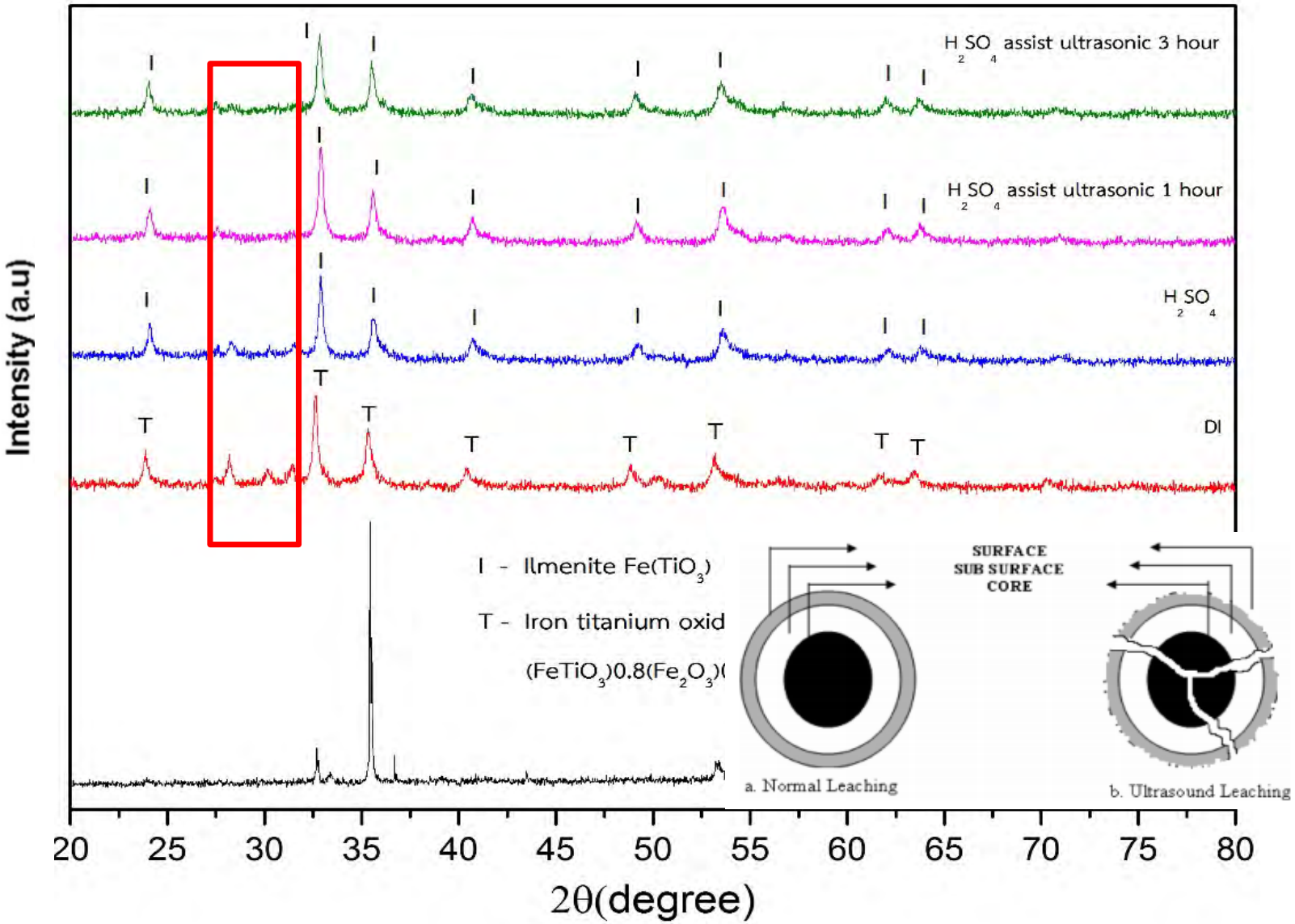


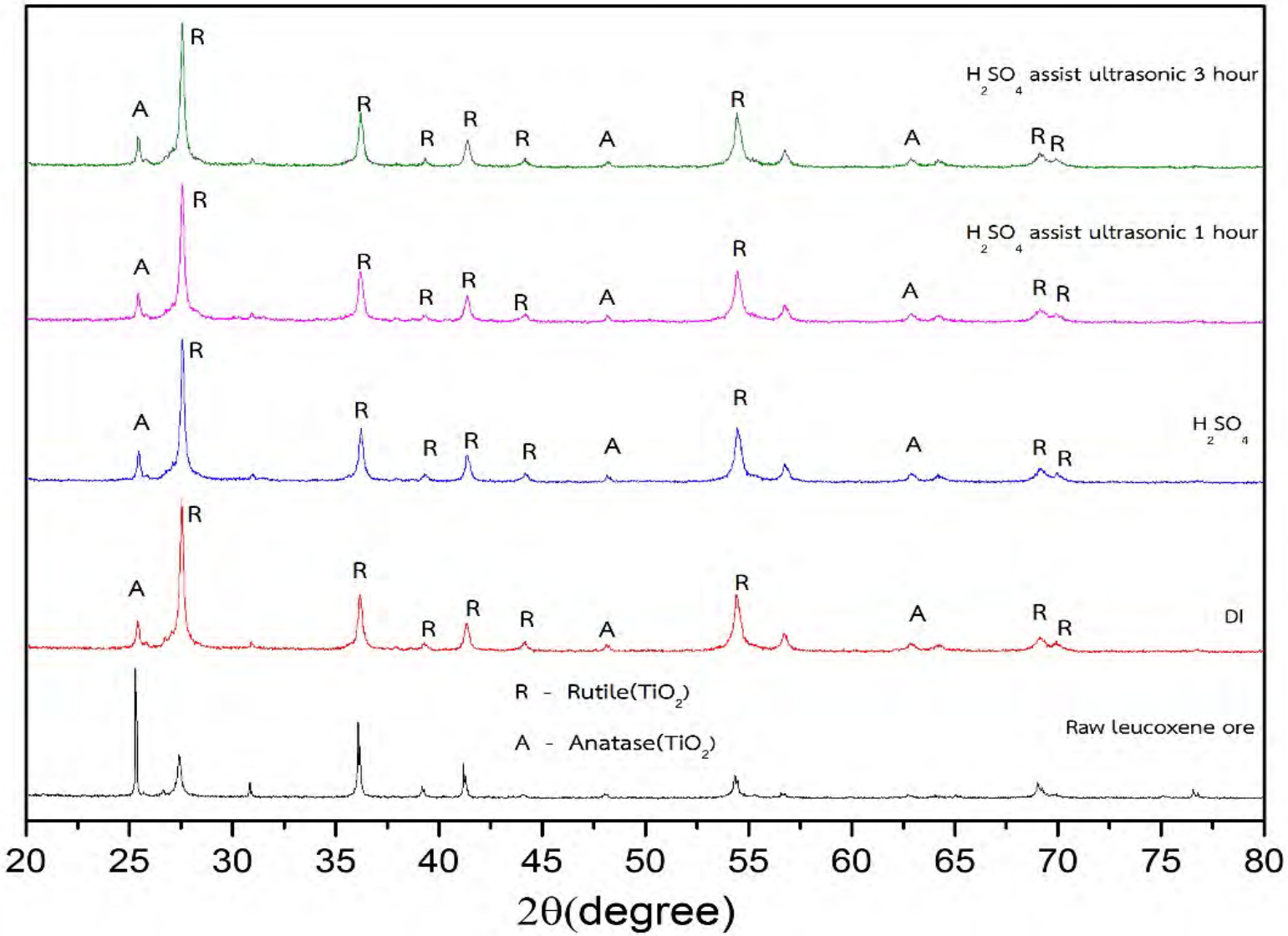
Fig. 1. SEM images of starting raw ilmenite ore (a), leucoxene ore (b), milled-ilmenite (a) and milled-leucoxene (b).

Results and discussion



XRD patterns of the products from **ilmenite ore** at different conditions.

Results and discussion



XRD patterns of the products of **leucoxene ore** at different conditions.

Results and discussion

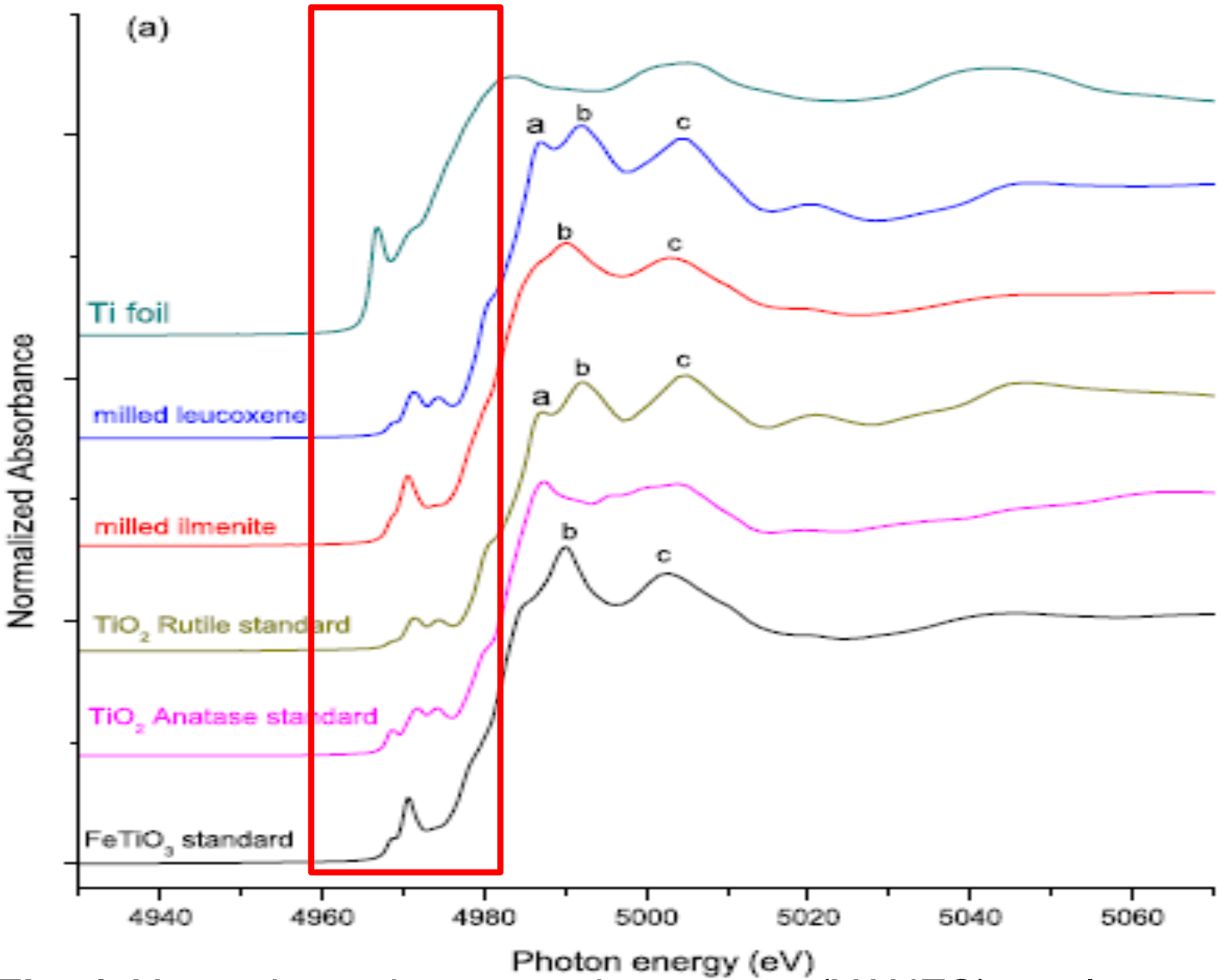
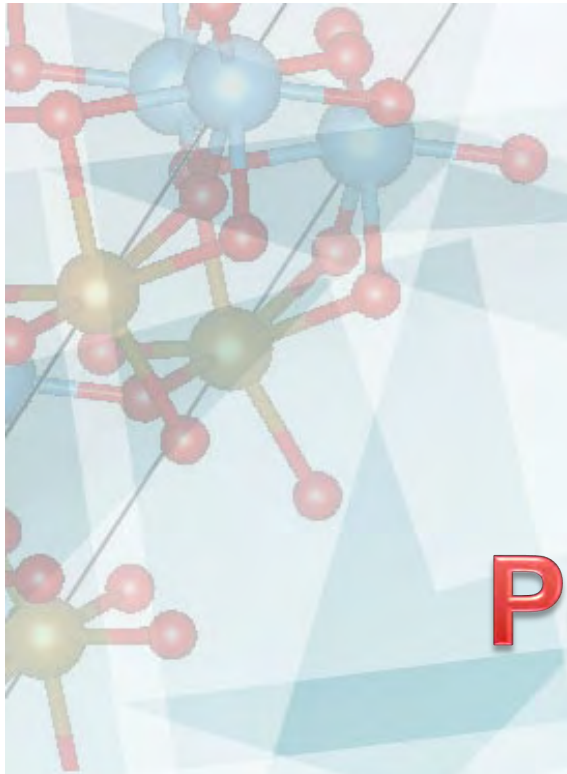


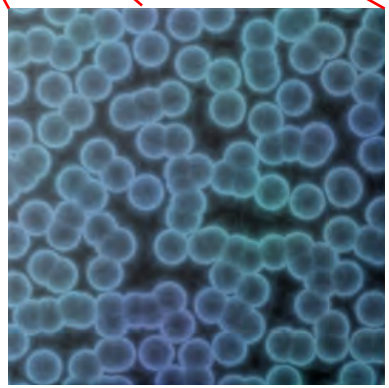
Fig. 4. X-ray absorption near edge spectra (XANES) results.



Possible applications and Proposal project

Feasible applications

- **Topic 1:** Coating of activated mineral-derived TiO_2 particles on earthenware-roof tiles



http://www.wisegeek.com/what-are-ceramic-tiles.htm
http://www.gettyimages.co.jp/detail
https://www.zazzle.co.uk/blue_bacteria_background_small_square_tile-227996258974984605

Discussion: Possible applications

- **Topic 1:** Coating of activated mineral-derived TiO_2 particles on earthenware-roof tiles

- Polyethylene glycol (PEG)
- Polyvinylpyrrolidone (PVP)

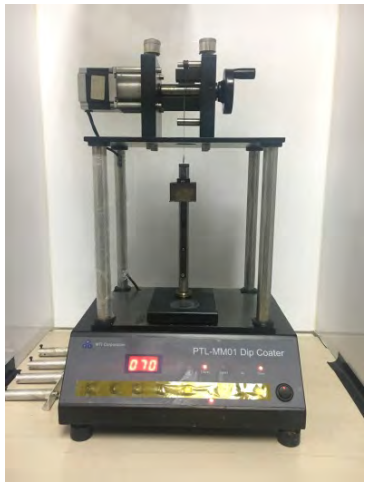
Activated Minerals + Binder solution

↓ Dip coating

Coating process

↓

Characterizations



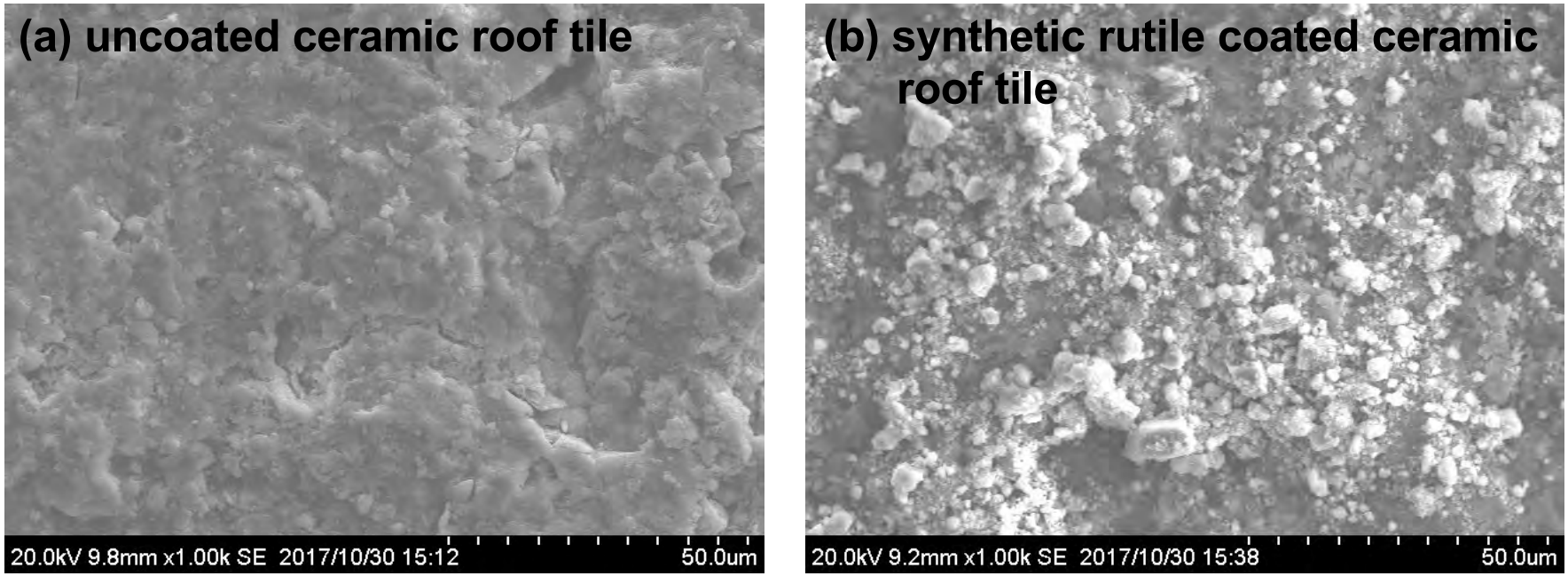
Uncoated ceramic

LEU/PEG coated ceramic

LEU/PVP coated ceramic

Discussion: Possible applications

- **Topic 1:** Coating of activated mineral-derived TiO_2 particles on earthenware-roof tiles

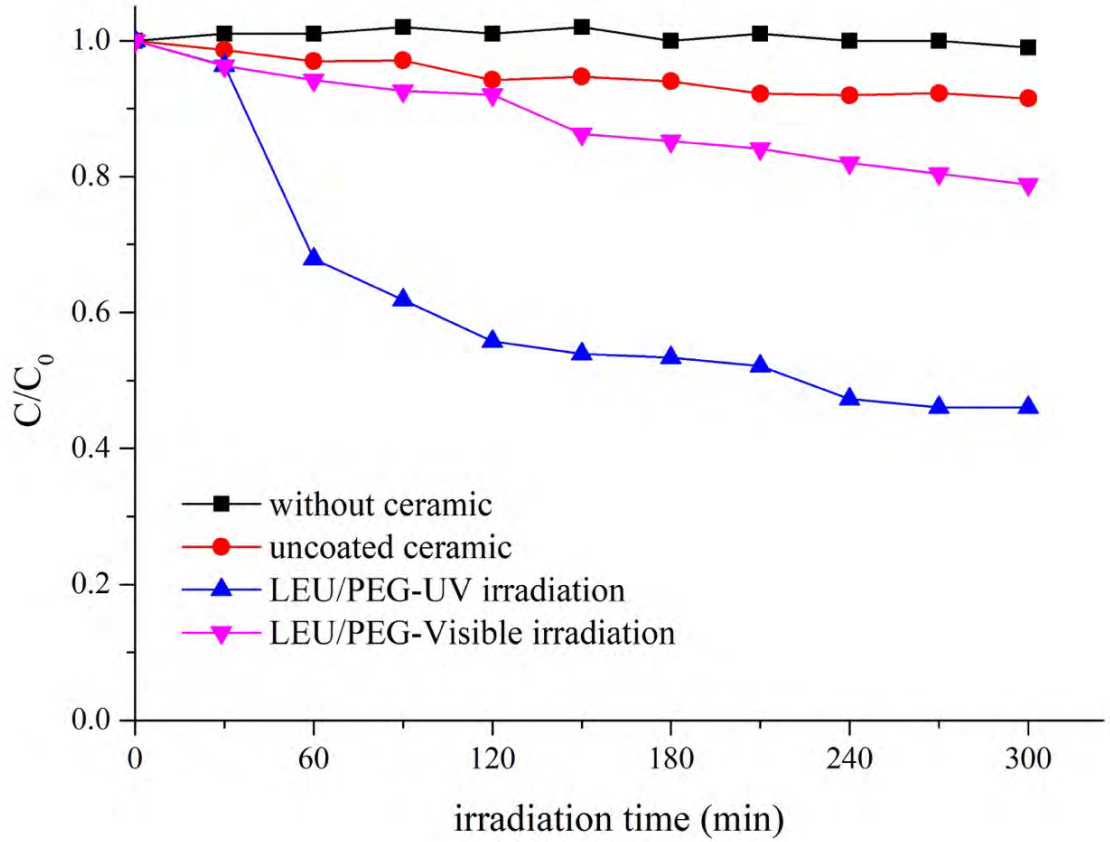


Surface morphologies by SEM images of (a) uncoated ceramic roof tile and (b) synthetic rutile coated ceramic roof tile.

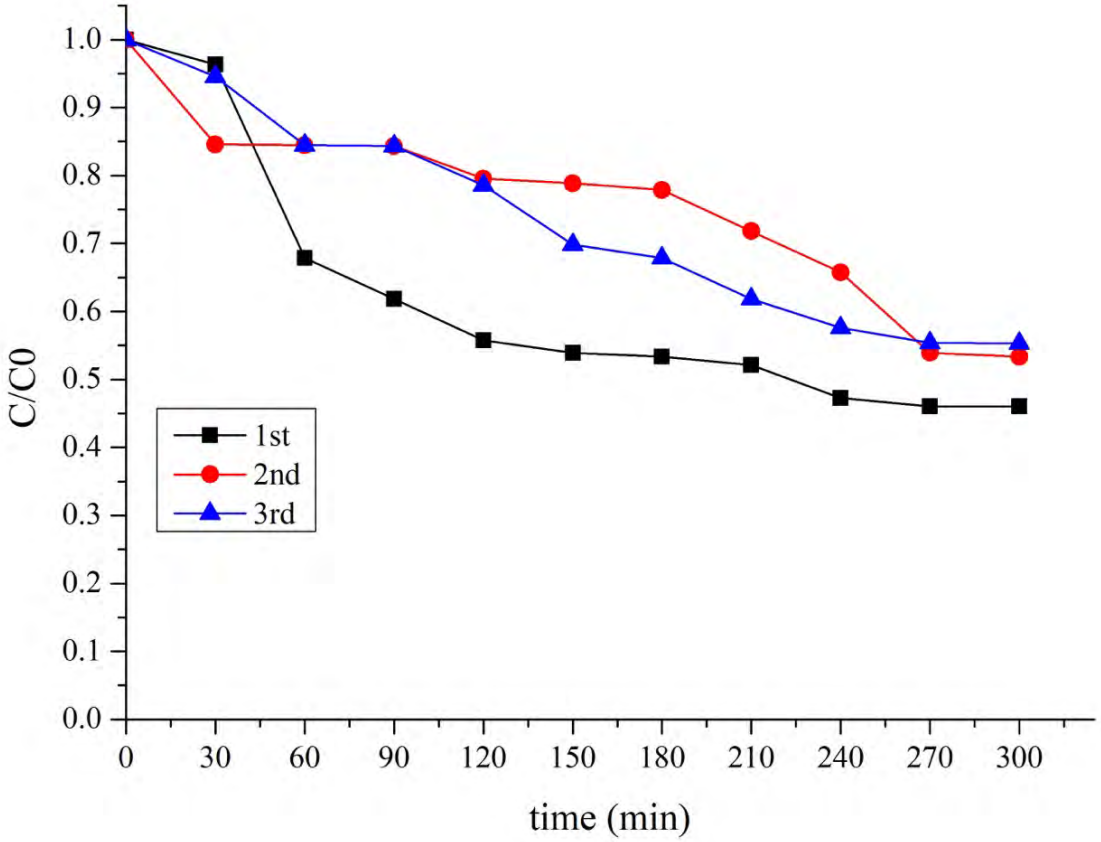
Chemicals composition

Element (% wt)	PEG binder		PVP binder	
	Uncoated	Coated	Uncoated	Coated
Silicon (Si)	24.96	16.84	24.96	18.52
Aluminum (Al)	12.99	11.79	12.99	10.81
Oxygen (O)	44.93	39.09	44.93	42.20
Iron (Fe)	5.63	5.13	5.63	5.32
Titanium (Ti)	0.48	17.85	0.48	13.34
Gold (Au)	5.50	5.72	5.50	6.84
Magnesium (Mg)	1.33	0.63	1.33	0.82
Calcium (Ca)	1.91	0.49	1.91	1.68
Potassium (K)	2.22	2.42	2.22	0.41

Photocatalytic activity of coated ceramic tile

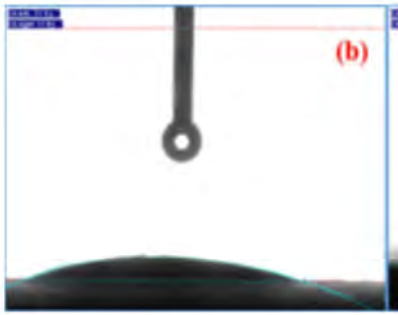


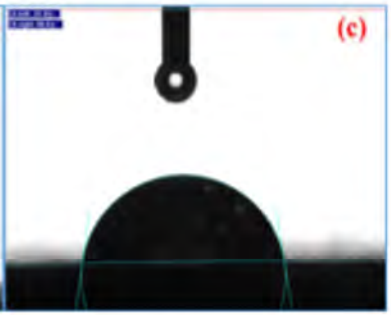
Results : Repeatability of coated ceramic tile

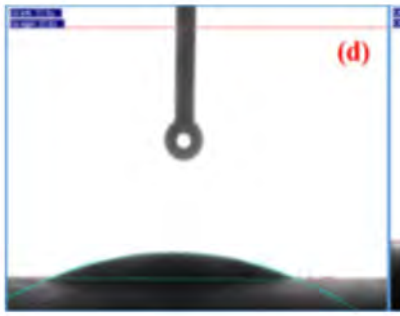


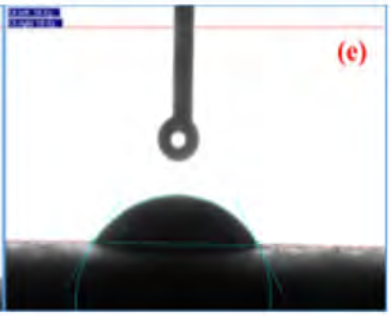
Hydrophobic property of coated ceramic tile

Specimen	Contact angle measurement (degree)
(a) Uncoated ceramic	26.4
(b) PEG coated ceramic	21.6
(c) PEG/LEU coated ceramic	80.7
(d) PVP coated ceramic	21.9
(e) PVP/LEU coated ceramic	58.1

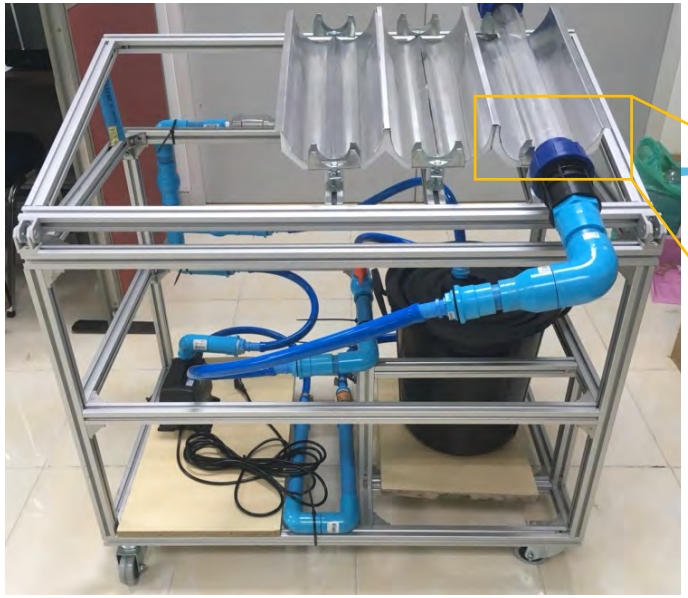








Feasible applications: 2.CPC photoreactor

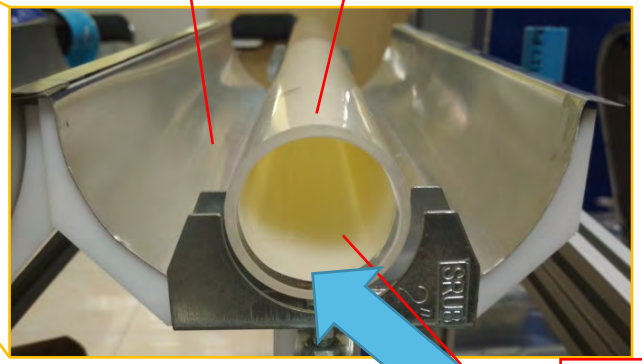


reflecting surface

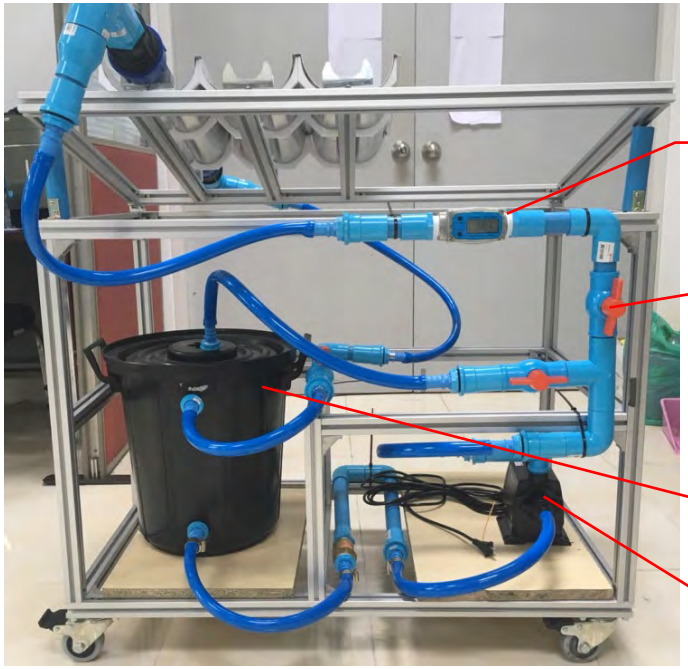
(aluminium plate)

reaction tube

(acrylic)



tube holder

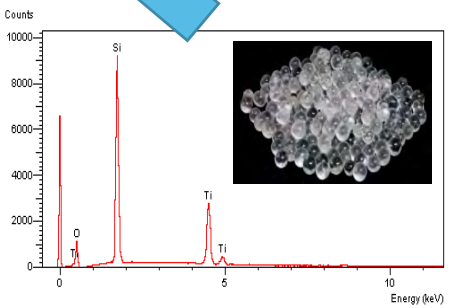


Flow meter

valve

solution tank

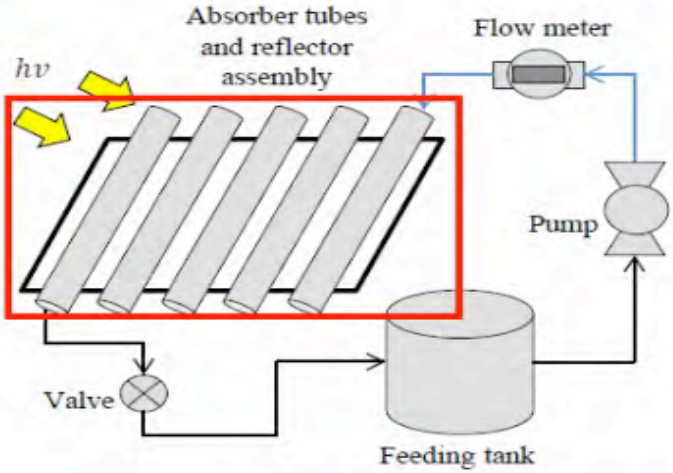
pump



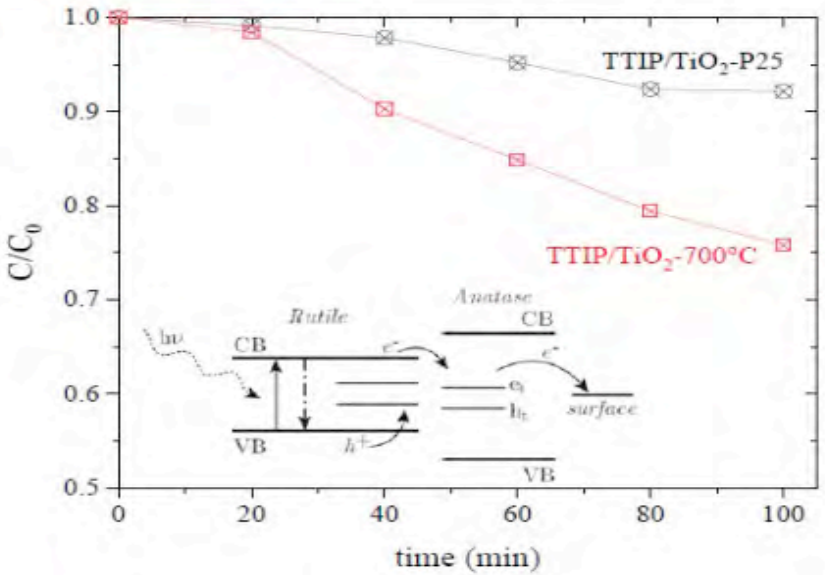
Feasible applications:

- **Topic 2: CPC Photoreactor**

Photocatalytic activity on CPC photoreactor



$$Degradation = \frac{C_t - C_0}{C_t}$$



Photodegradation of mixed phase TiO_2 calcined in CPC solar photoreactor.

Feasible applications:

- **Topic 3: UV-shielding Materials**

Extraction of cellulose (chemical treated)

I. Sample preparation

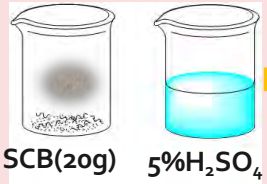
Sugarcane bagasse

Washing

Blending

Dry at 60°C
2days

II. Dewaxing



SCB(20g)

5%H_2SO_4 solution

stirring at
60°C for 2h

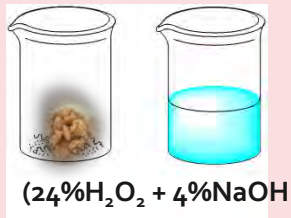
Washing until the neutral pH

The residue (previous step)

cellulose

Washed until the neutral pH

stirring at
60°C for 2h



(24%H_2O_2 + 4%NaOH)

III. Removal lignin & hemicellulose

Dewaxing with mild acid hydrolysis

Removal lignin and hemicellulose

Ultrasonic milling treatment

Chemical treated sample

Ultrasonic-assisted milling

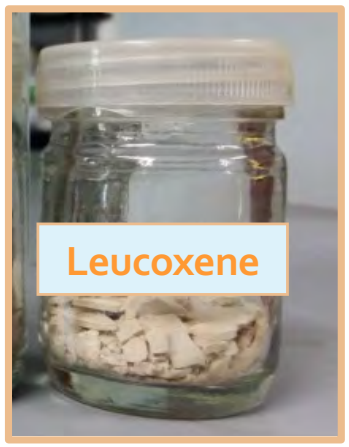
Ball milling : 5 h
600 RPM with
10% H_2SO_4

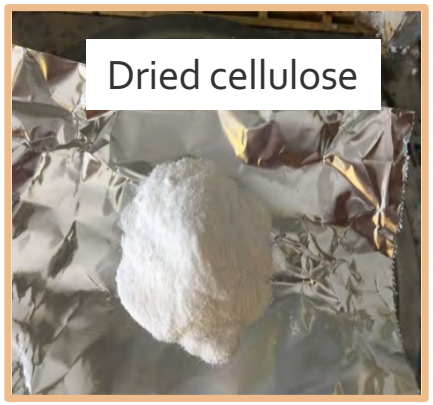
Washed until the neutral pH

After ultrasonic milling treatment

Preparation of composite films

Twin screw extruder with cast film machine



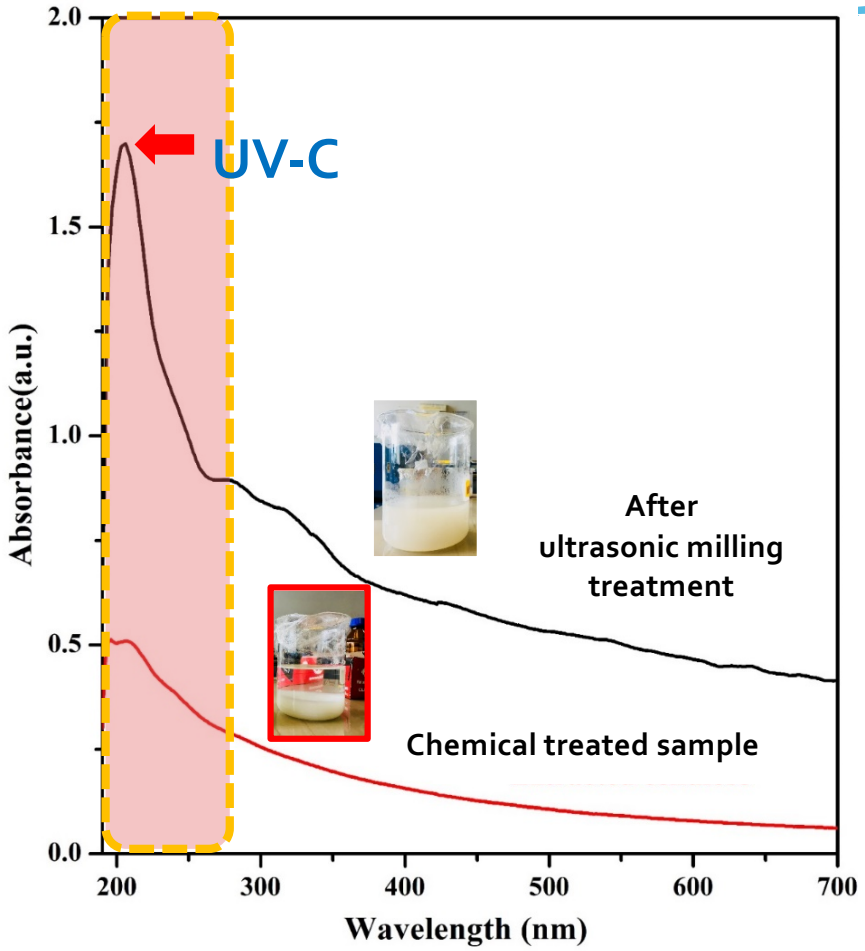


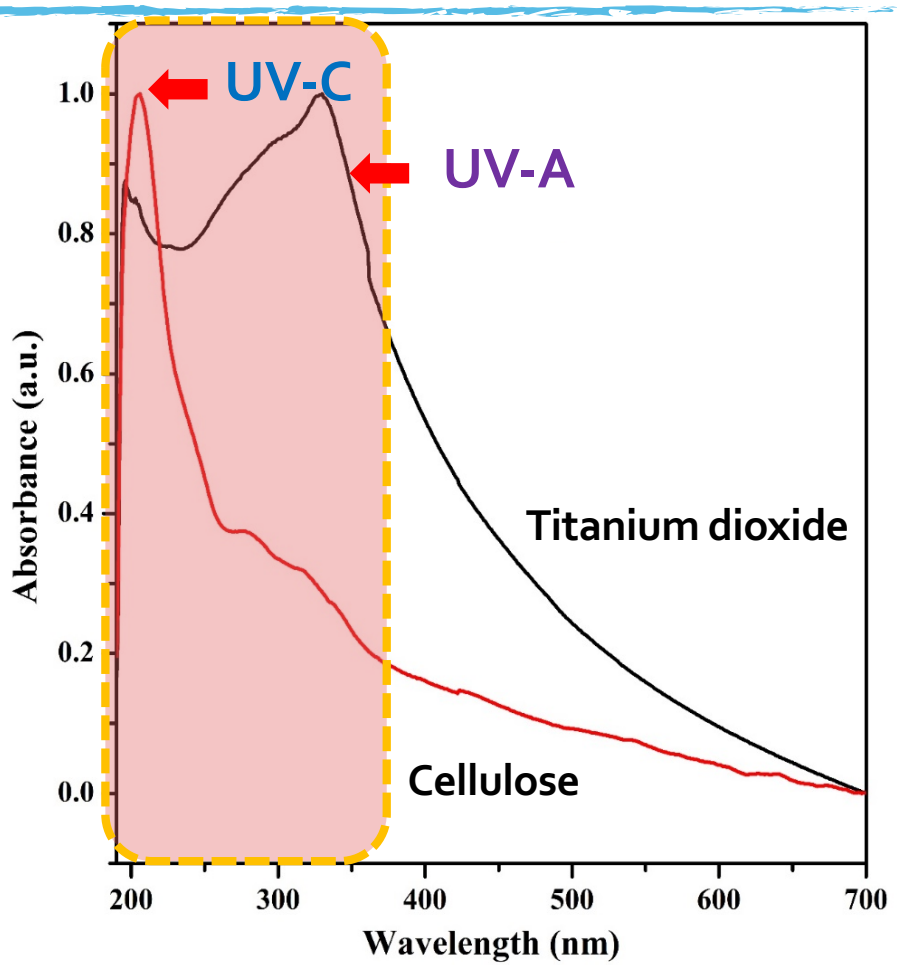
PLA (matrix)

LDPE (matrix)

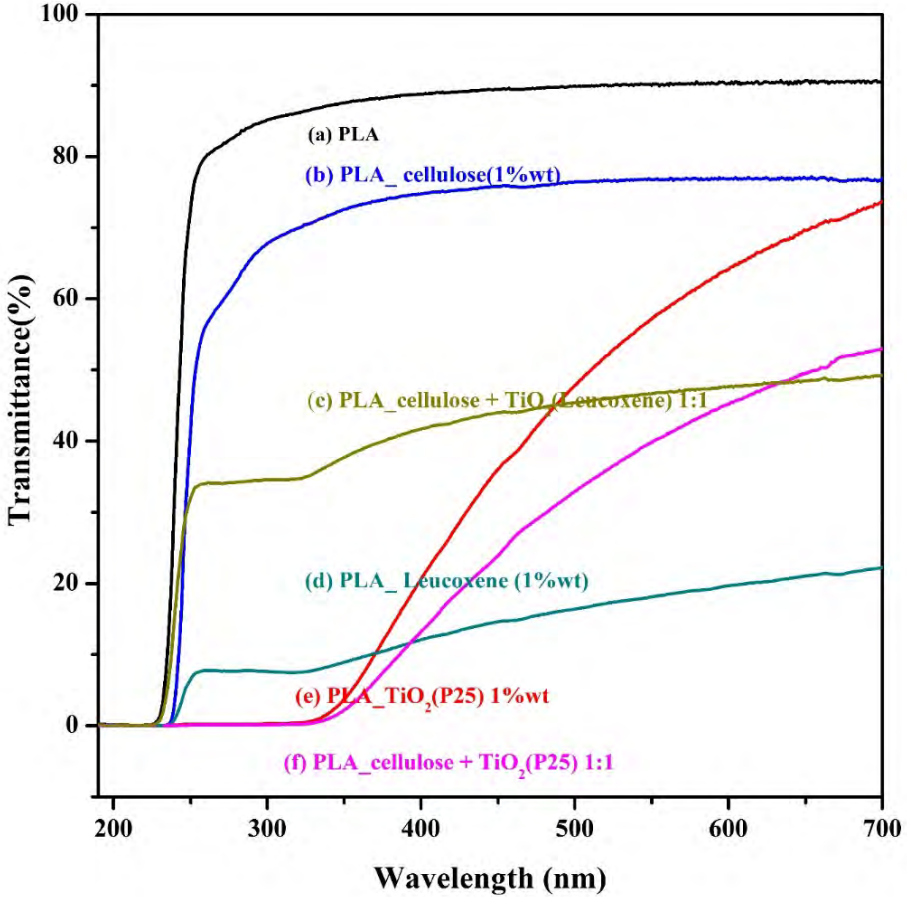
Composite film

Optical property of cellulose and Titanium dioxide





Optical property of composite films (PLA matrix)



(b) PLA_cellulose (1%wt)

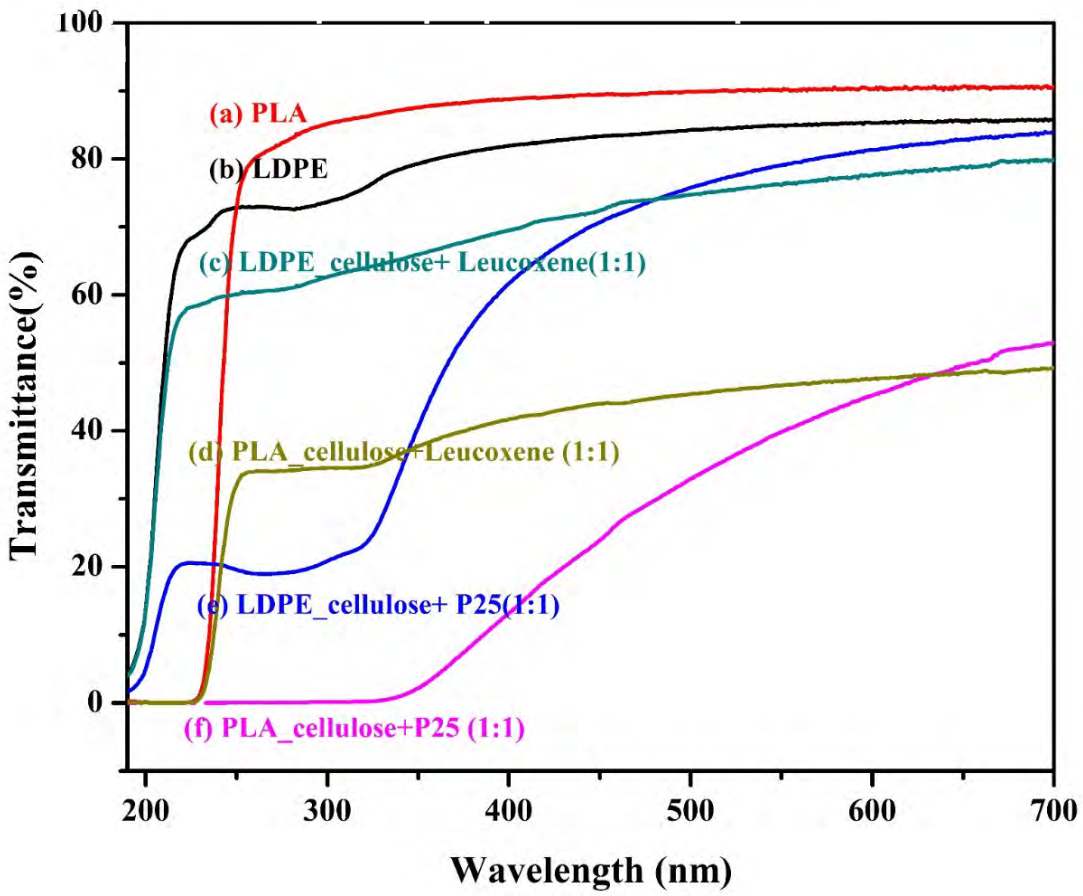
(c) PLA_ cellulose +Leucoxene(1:1)

(d) PLA_ Leucoxene(1%wt)

(e) PLA_ P25(1%wt)

(f) PLA_ cellulose +P25(1:1)

Optical property of composite films (LDPE matrix)



(a) PLA

(c) LDPE_ cellulose+Leucoxene (1:1)

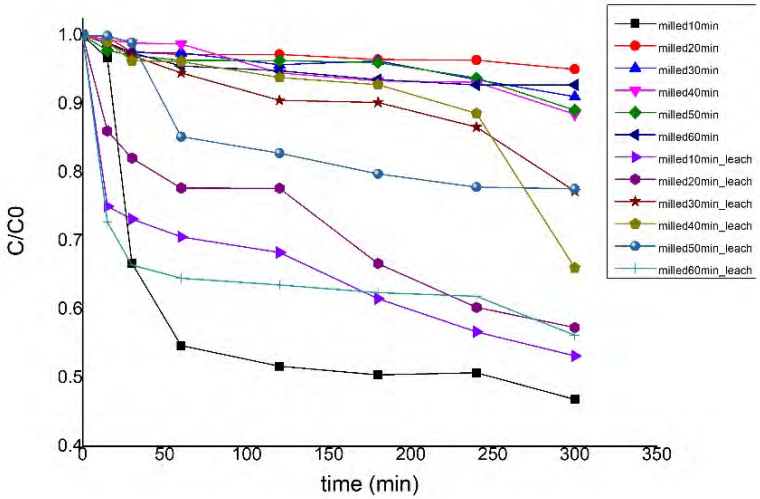
(d) PLA_ cellulose+Leucoxene (1:1)

(e) LDPE_ cellulose+P25 (1:1)

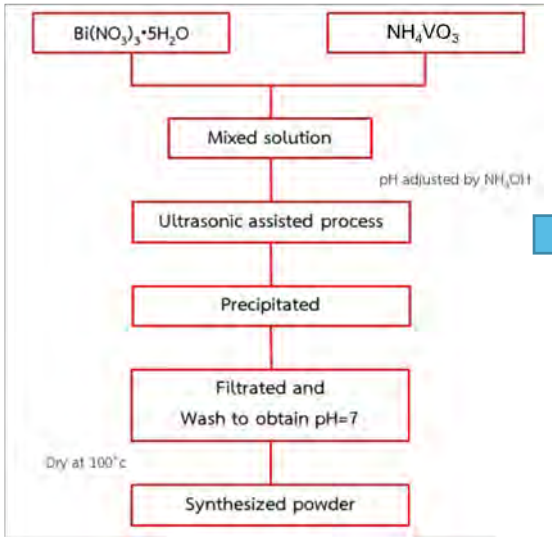
(d) PLA_ cellulose+P25(1:1)

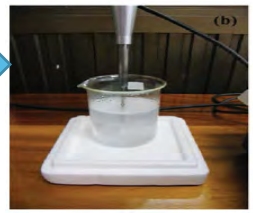
Other materials

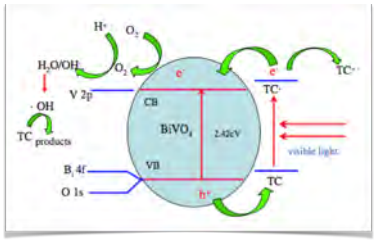
- Activated Magnetic Leucoxene

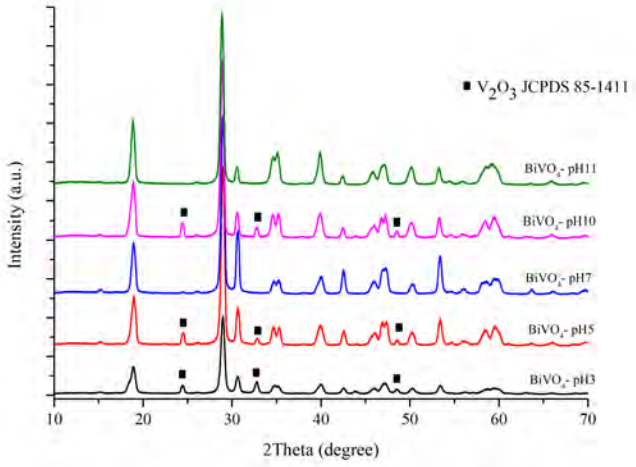


- BiVO4, BiWO4 catalyst









Scientific Output

- Int. Journal : 2 papers + 1 In press
- Int. Conf.: 2 orals
- Exchanged Researcher: 1
- Int. Conference : 1

ACTIVE ILMENITE SURFACE STRUCTURE INFLUENCE OF ACID ASSISTED BALL MILLING

WEERACHON PHOOHINKONG[1]*, SORAPONG PAVASUPREE[2], KANOKTHIP BOONYARATTANAKALIN[1], WANICHAYA MEKPRASART[1], WISANU PECHARAPA[1]
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Received (Day Month Year)

Active-ilmenite powder derived from natural ilmenite sand was prepared by ball milling process with acid- solution and DI water. Morphology and particles size of active-ilmenite product in acid/DI assisted ball milling process were monitored by field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). Surface atomic component and chemical bonding was investigated by X-ray photoelectron spectroscopy (XPS). Meanwhile, bulk chemical oxidation and fine structure of active-ilmenite were studied by X-ray absorption near edge structure (XANES) and extended X-ray absorption ne-structure spectroscopy (EXAFS) to confirm oxidation state and local active species structure at surface. Active-ilmenite by acid-assisted ball milling process is distinctive method for the preparation of active ilmenite product with high active surface. Moreover, the distortion of TiO_6 and FeO_6 octahedral cluster on sample surface was detected in all milled samples with acid-assisted ball milling process. While, the presences of Fe^{2+}, Fe^{3+} ions and miniature sulfate were also detected on sample surface by milled product with acid-assisted method.

Keywords: Ilmenite; $FeTiO_3$; Ball milling; XANES; EXAFS.

Current Applied Physics 18 (2018) 544–554

Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/cap

Synthesis of low-cost titanium dioxide-based heterojunction nanocomposite from natural ilmenite and leucoxene for electrochemical energy storage application

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[b] Department of Materials and Metallurgical Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Klong 6, Pathumthani 12110, Thailand

Applied Surface Science xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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Full Length Article

X-ray absorption spectroscopy analysis and photocatalytic behavior of $ZnTiO_3$ nanoparticles doped with Co and Mn synthesized by sonochemical method

Chakkaphan Wattanawikkam *, Thanaphon Kansa-ard, Wisanu Pecharapa

College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520 Thailand

Conclusion

- This work was carried out to synthesize activated ilmenite and leucoxene from natural ores by acid leaching-assisted ultrasonic ball-milling process.

- Impurity phases in as-received ores were significantly leached after increasing ultrasonic time and milling in acid solution.

- The feasible applications of the material are proposed.

Acknowledgment

- College of Nanotechnology, KMITL
- National Science and Technology Development Agency, NSTDA
- Rajamangala University of Technology Thanyaburi
- Graduate School of Energy Science, Kyoto University
- JASTIP fund and Kyoto University
- Research Staff at NMRL, KMITL

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YOUR KIND ATTENTION