Technological concepts and future applications of Ag and TiO_2 anatase nanoparticles produced by Green methods

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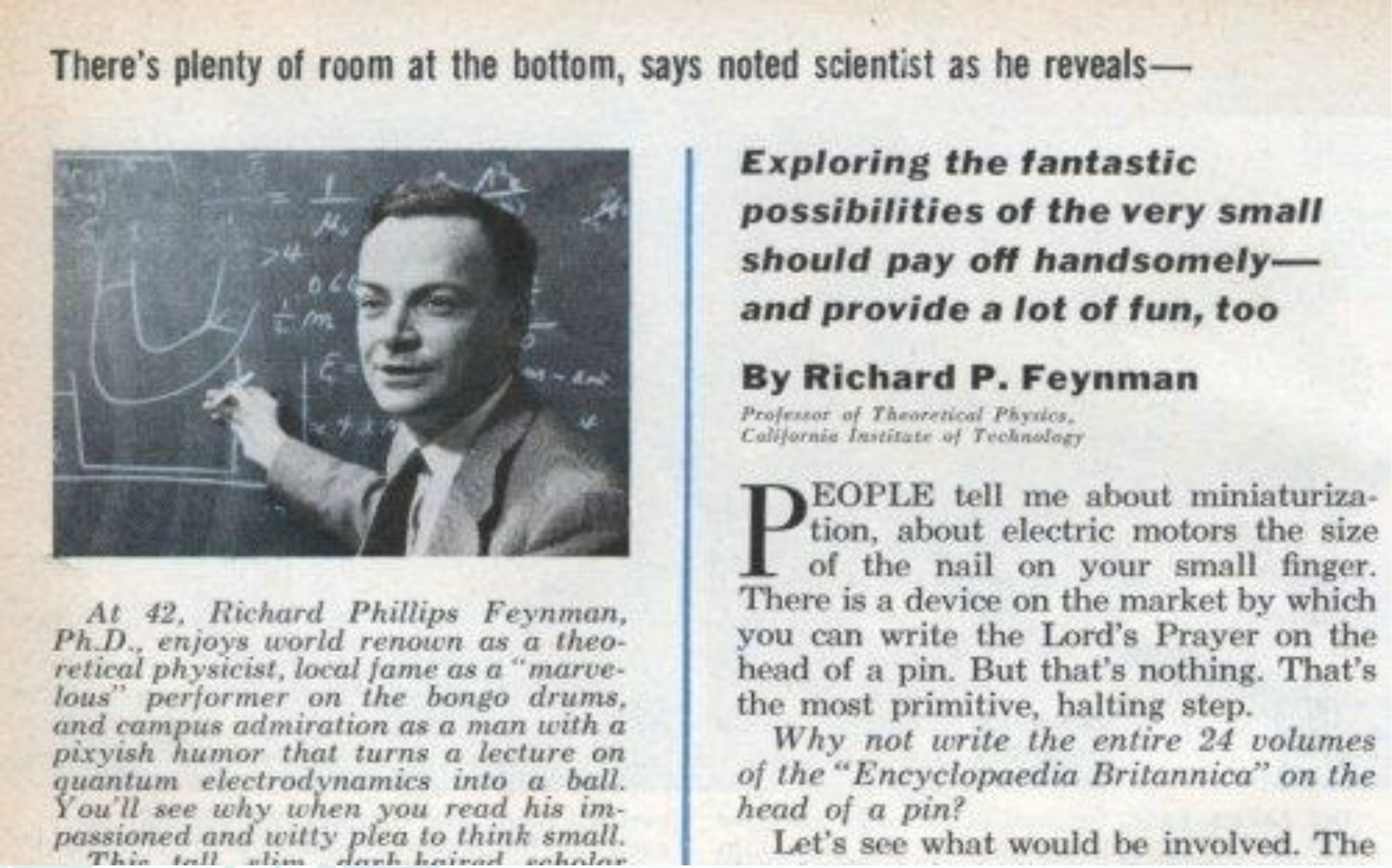
November, 2017



There's plenty of room at the bottom, says noted scientist as he reveals—

Exploring the fantastic possibilities of the very small should pay off handsomely—and provide a lot of fun, too

By Richard P. Feynman

Professor of Theoretical Physics, California Institute of Technology

At 42, Richard Phillips Feynman, Ph.D., enjoys world renown as a theoretical physicist, local fame as a "marvelous" performer on the bongo drums, and campus admiration as a man with a pixyish humor that turns a lecture on quantum electrodynamics into a ball. You'll see why when you read his impassioned and witty plea to think small.

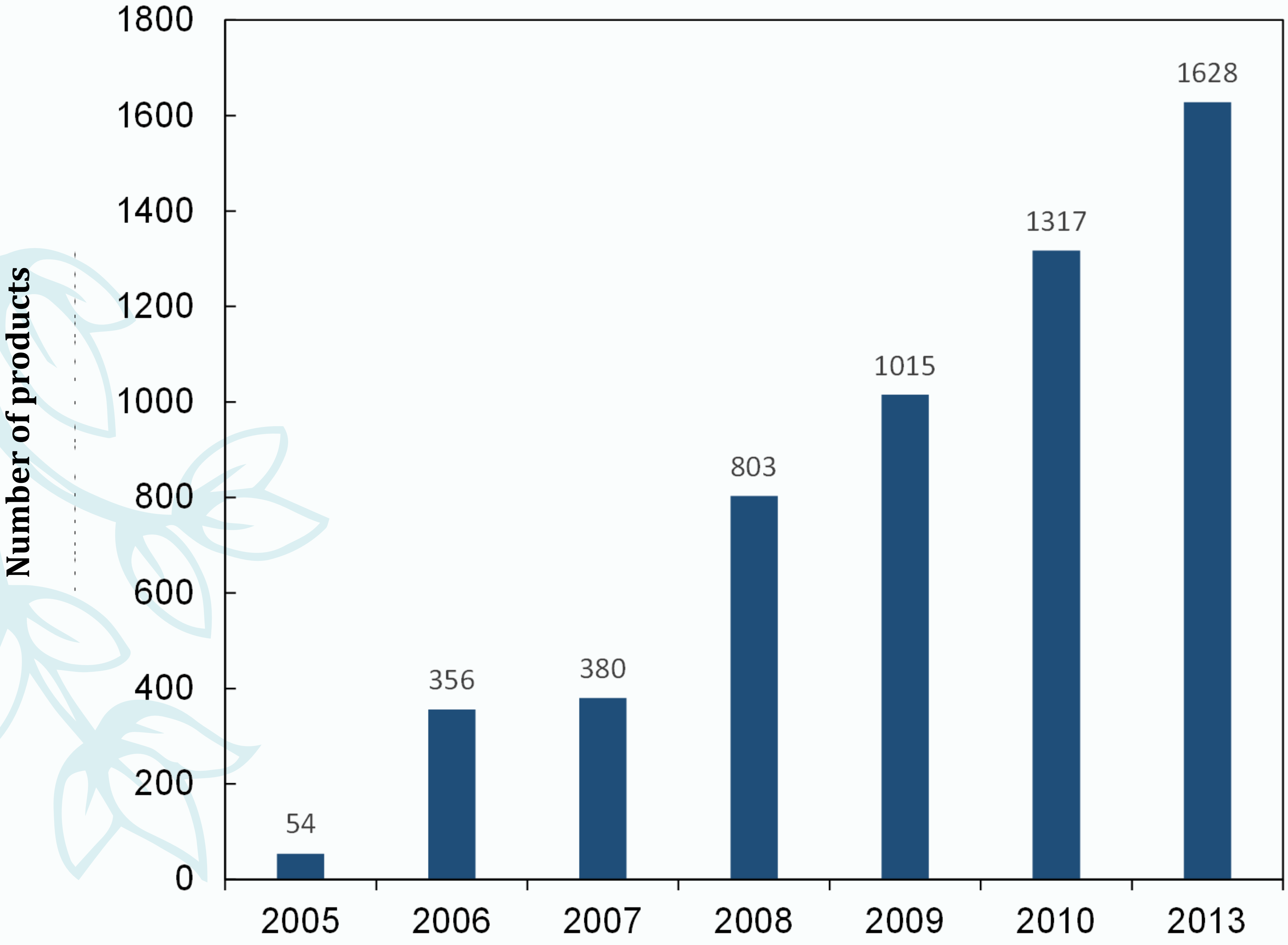
PEOPLE tell me about miniaturization, about electric motors the size of the nail on your small finger. There is a device on the market by which you can write the Lord's Prayer on the head of a pin. But that's nothing. That's the most primitive, halting step.

Why not write the entire 24 volumes of the "Encyclopaedia Britannica" on the head of a pin?

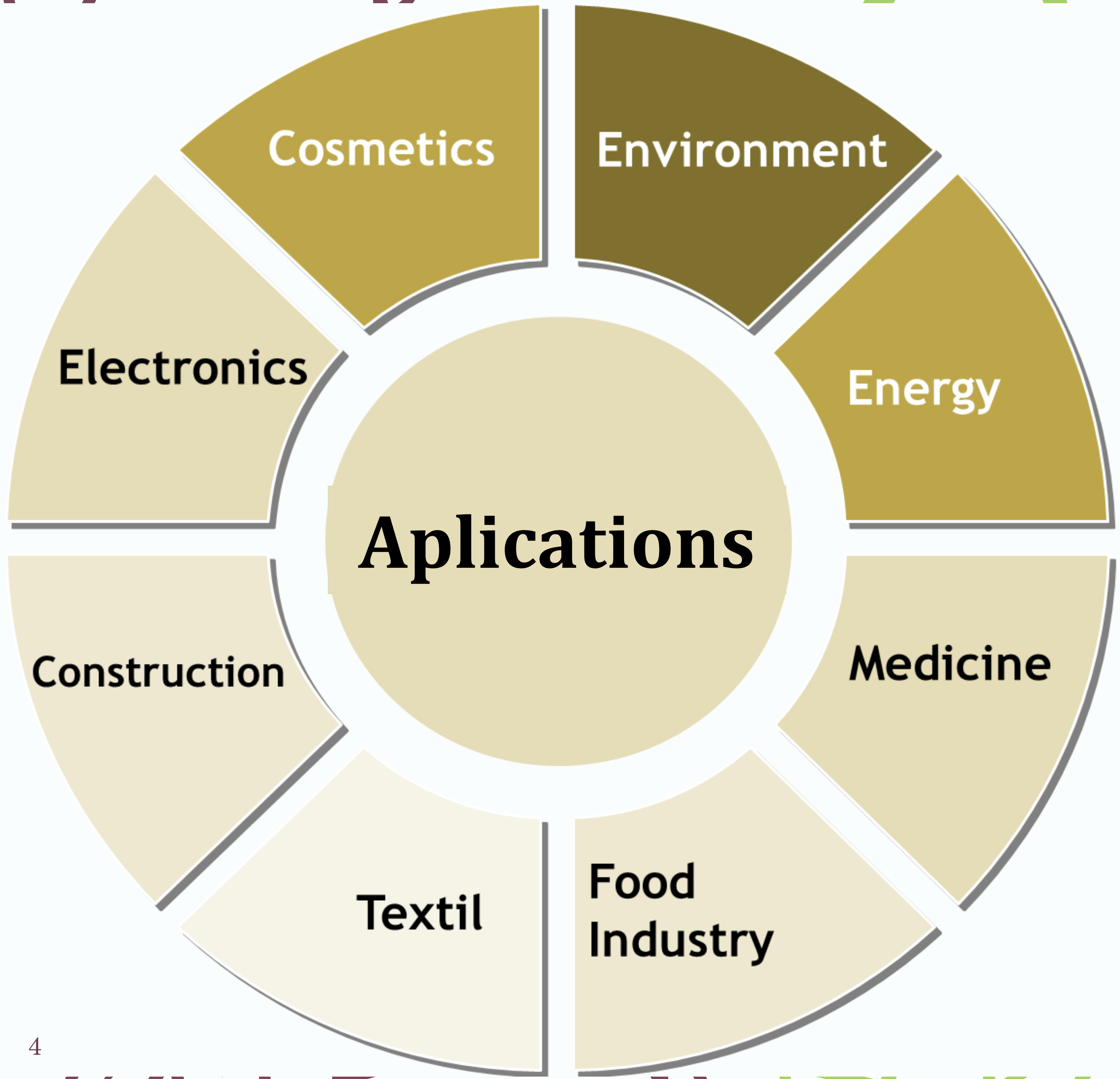
Let's see what would be involved. The

http://www.cnano.fr/spip.php?article8&lang=en

"I don't know how to do this on a small scale in a practical way, but I do know that computing machines are very large; they fill rooms. Why can't we make them very small, make them of little wires, little elements, and by little, I mean little?" R.F.



Project on Emerging Nanotechnologies http://www.nanotechproject.org/cpi (Tomado el 19 de mayo del 2014)

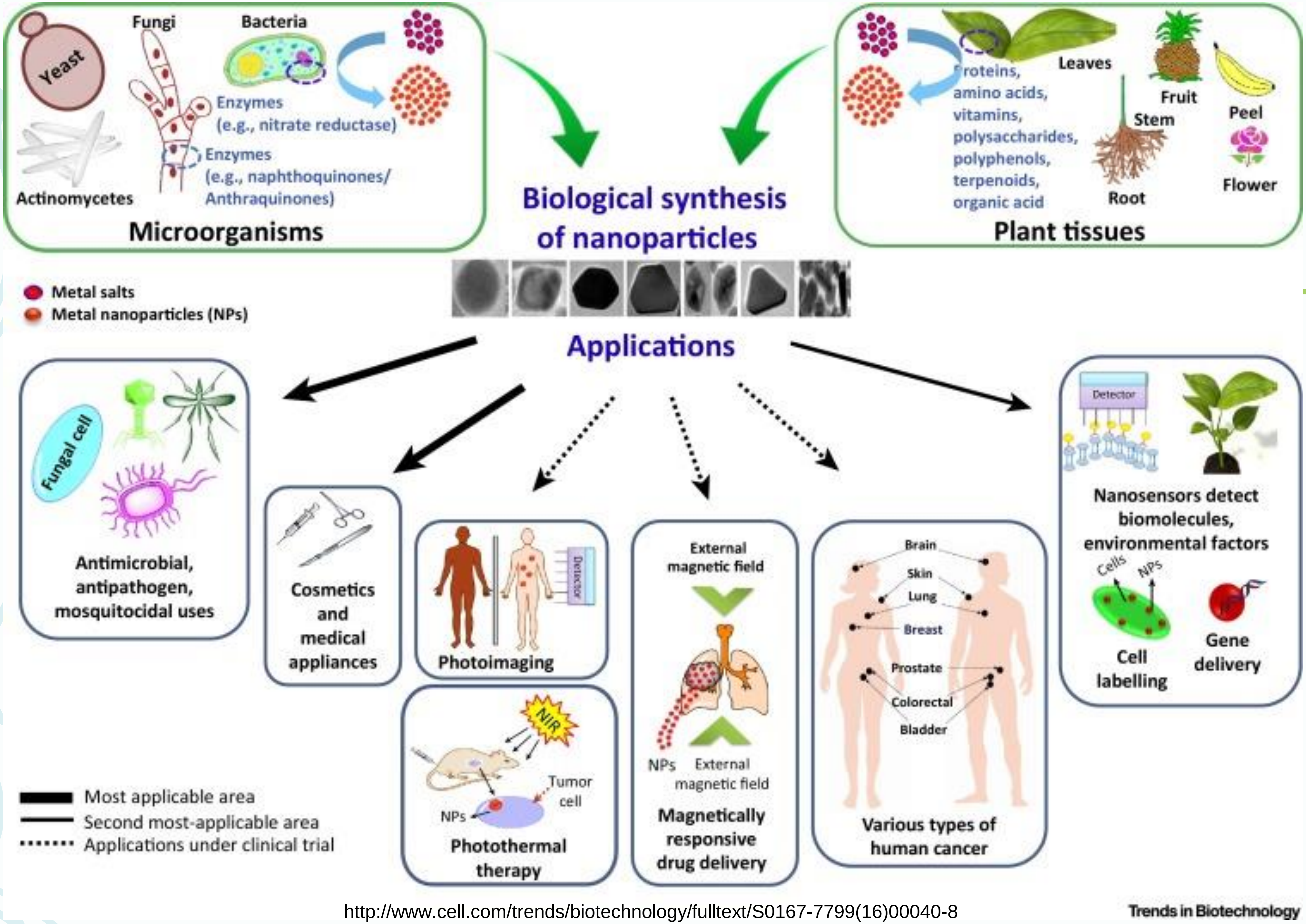


Ag and TiO_2 NPs

Any given method to obtain NPs

– **Advantages**

– **Disadvantages**



http://www.cell.com/trends/biotechnology/fulltext/S0167-7799(16)00040-8

Green Chemistry

- If NPs are intended for biomedical purposes
  - No toxic chemicals
  - If medicinal plants are used…….

DISADVANTAGES:

- **Available Resouce throughout the year**
- **Concentration of metabolites in the plant**
- **Modification of chemical structure of metabolites during the process**
- **Reproducibility**

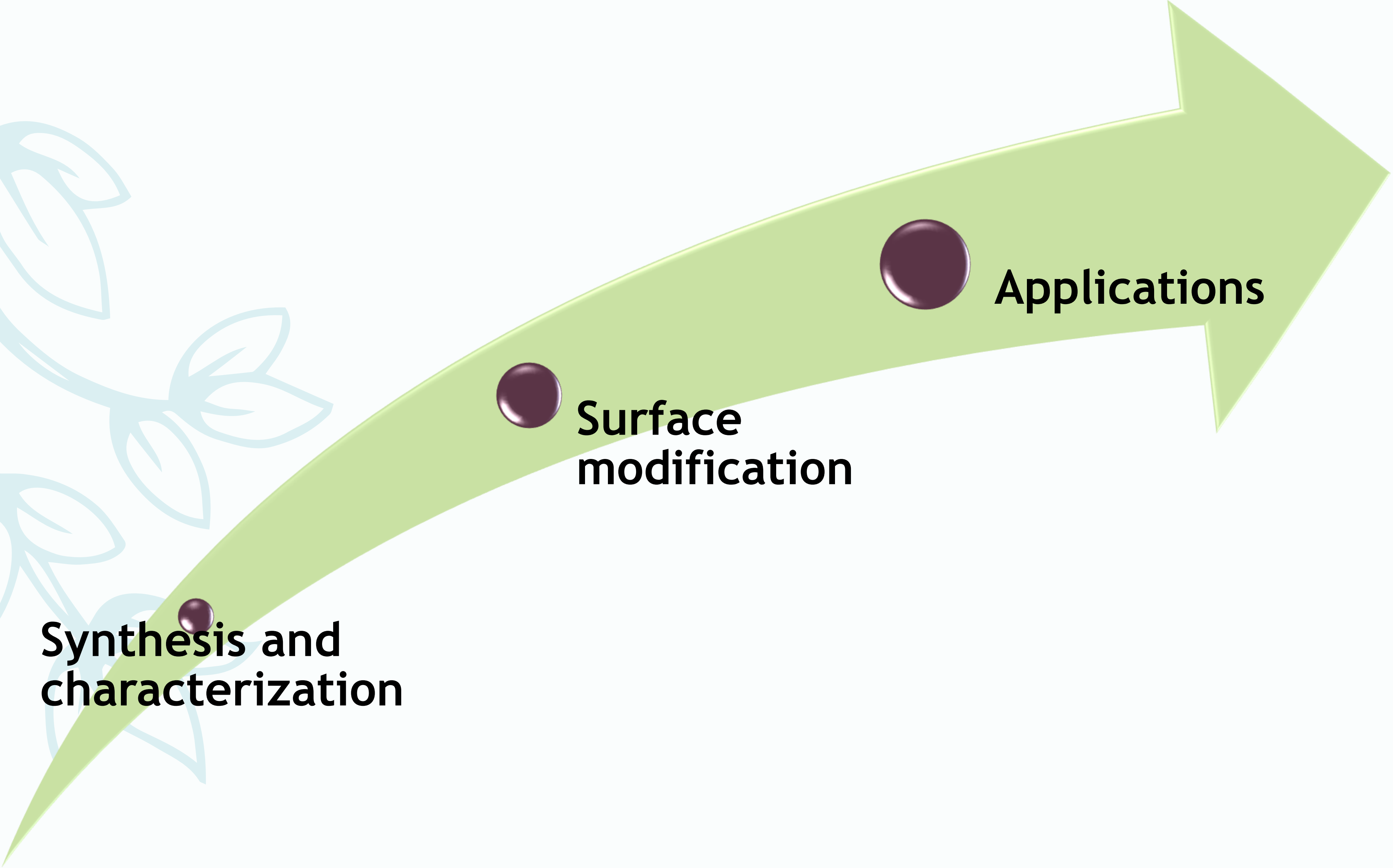
Using plant extracts:

Optimization Reproducibility

Target


Medicago Sativa

Nanoparticles



Objectives (NPs)

1. Ag
    1. Biosynthesis optimisation determining the most favorable conditions: pH, metabolite extractant, precursor concentration.
2. TiO_2
    1. Biosynthesis optimisation: pH, Relationship extractant/TIPO; Water/TIPO, using alfalfa extracts (isopropanol)
3. Potential applications

Ag NPs

- **Plant metabolite extractant**
  - **H_2O**
  - **Isopropanol**
  - **Methanol**
- **pH**
- **[Ag]**

ID	Solventes de extracción de metabolitos vegetales (PMES)	$[Ag^{+}]$ (mM)	pH
S01			10
S02	Agua	5.5	7
S03			3
S04		10.0	
S05	Isopropanol – Agua	5.5	7
S06		1.0	
S07		10.0	
S08	Metanol – Agua	5.5	7
S09		1.0	
S10		10.0	
S11	Agua	5.5	7
S12		1.0	

(a) pH = 10, $[Ag^+]$ = 5.5 mM and agua como PMES (S01);

(b) pH = 7, $[Ag^+]$ = 5.5 mM y agua como PMES (S02);

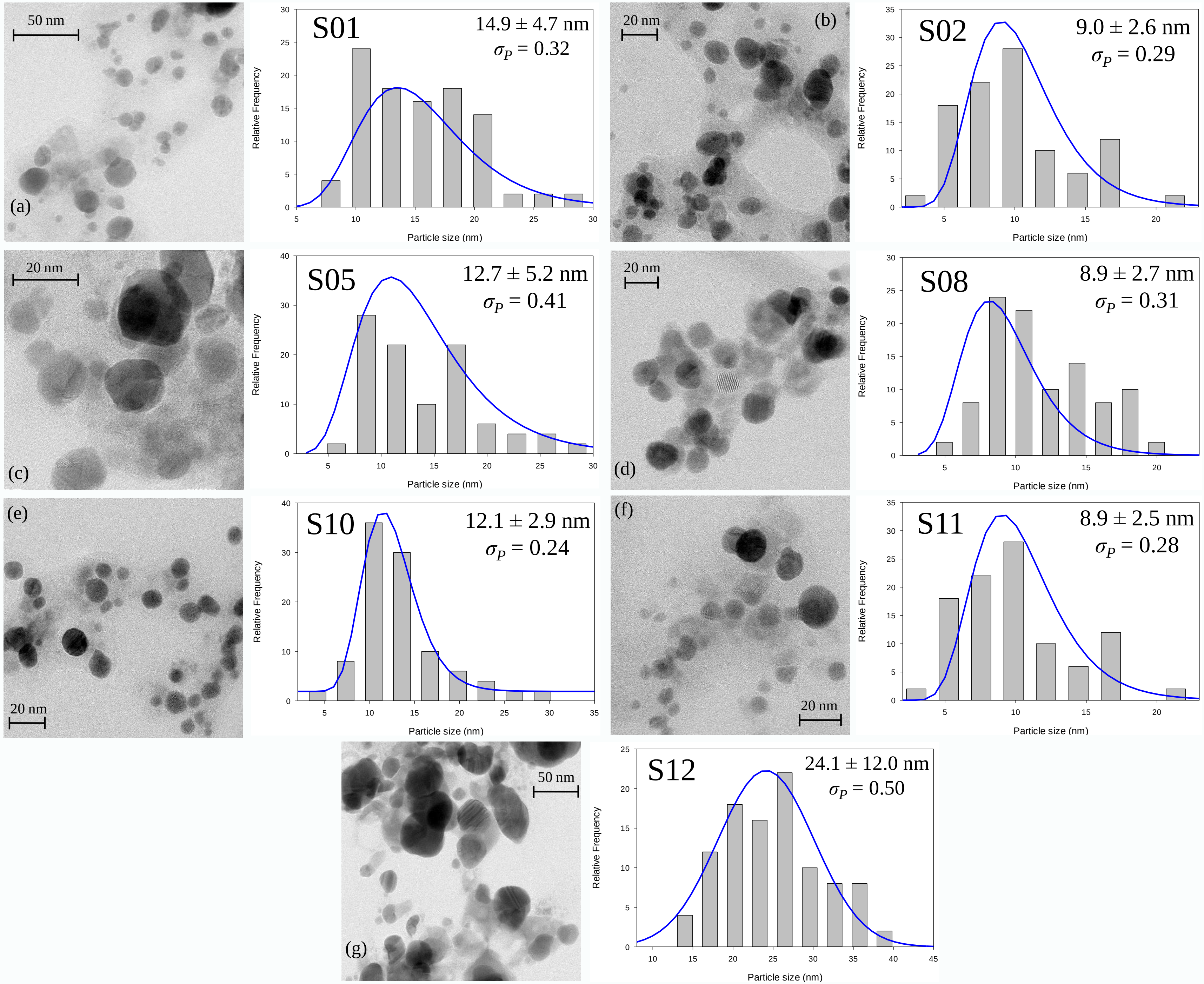
(c) pH = 7, $[Ag^+]$ = 5.5 mM e Isopropanol-Agua como PMES: (S05);

(d) pH = 7, $[Ag^+]$ = 5.5 mM, and Metanol-Agua como PMES (S08);

(e) pH = 7, $[Ag^+]$ = 10 mM y agua como PMES (S10);

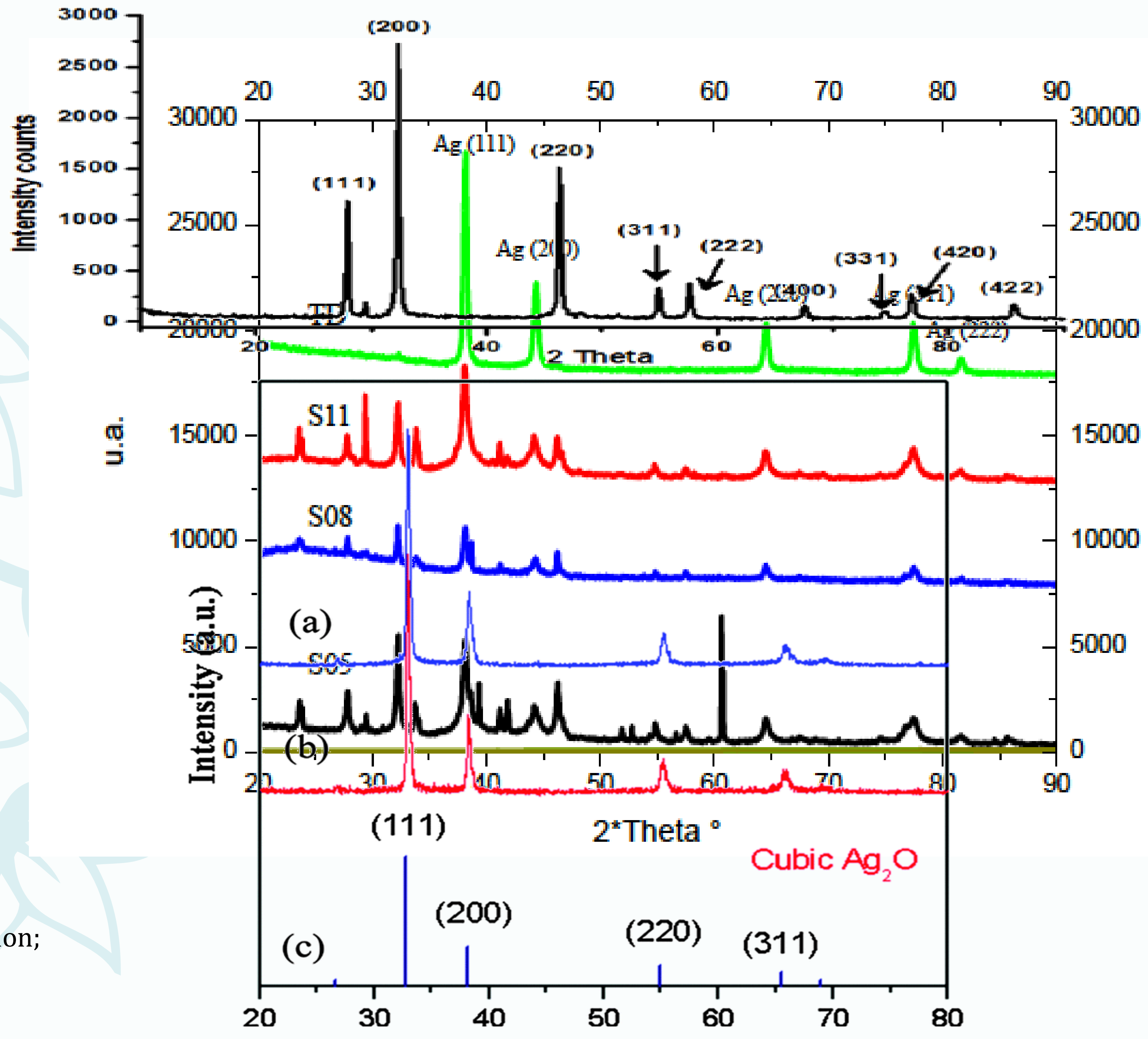
(f) pH = 7, $[Ag^+]$ = 5.5 mM y agua como PMES (S11);

(g) pH = 7, $[Ag^+]$ = 1 mM y agua como PMES (S12).



Ag NPs synthesis

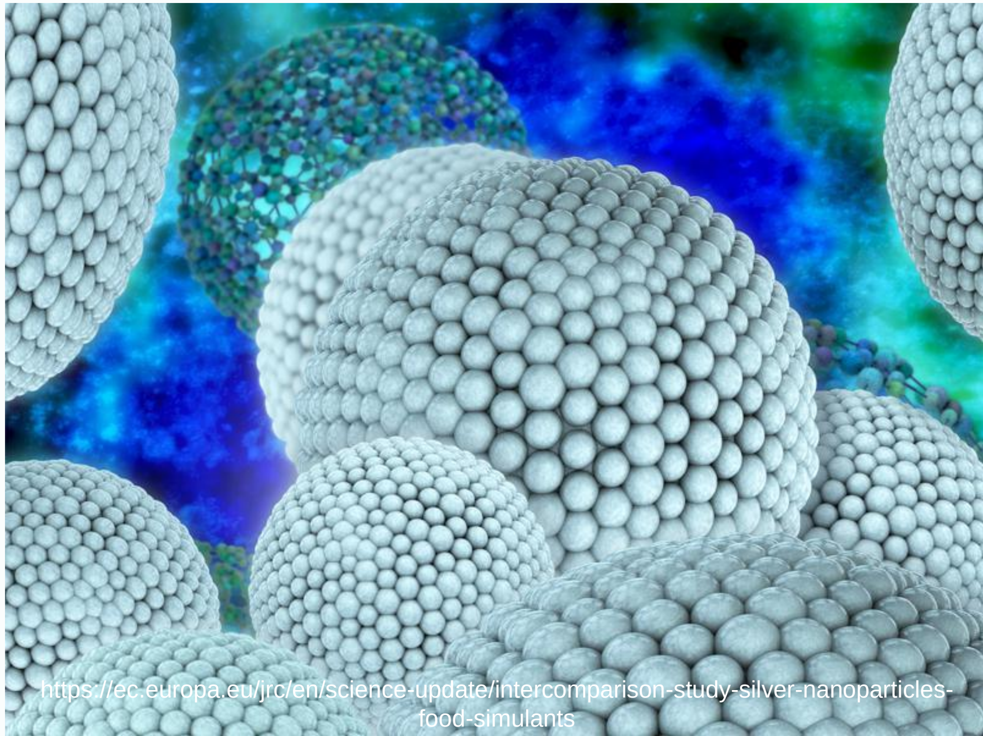
ID	D_{TEM} (nm)	σ_P (σ/D_{TEM})
S01	14.9 ± 4.7	0.32
S02	9.0 ± 2.6	0.29
S03	——	——
S04	8.6 ± 4.2	0.49
S05	12.7 ± 5.2	0.41
S06	20.6 ± 7.3	0.35
S07	18.4 ± 5.2	0.28
S08	8.9 ± 2.7	0.31
S09	7.2 ± 2.8	0.38
S10	12.1 ± 2.9	0.24
S11	8.9 ± 2.5	0.28
S12	24.1 ± 12.0	0.50



TD: Thermal decomposition;
S11: H_2O
S08: Methanol
S05: Isopropanol

18 Preliminary micro XAS/EXAFS

- Mixture AgCl, Ag, Ag_2O
- Different proportions
- Reproducibility to be determined



Ag NPs

- Leather fungi
- Cancer cells

TiO_2

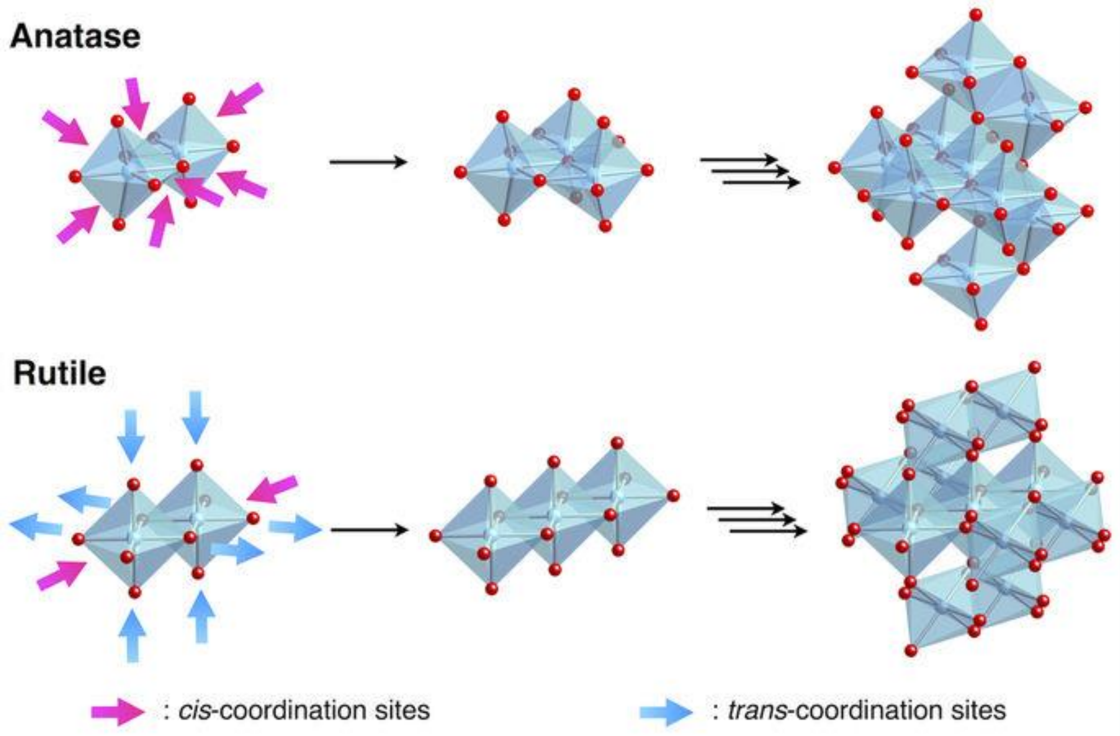
– **Anatase**

– **Patents:**

  – **$TiCl_4$**

  – **Ti hydroxide**

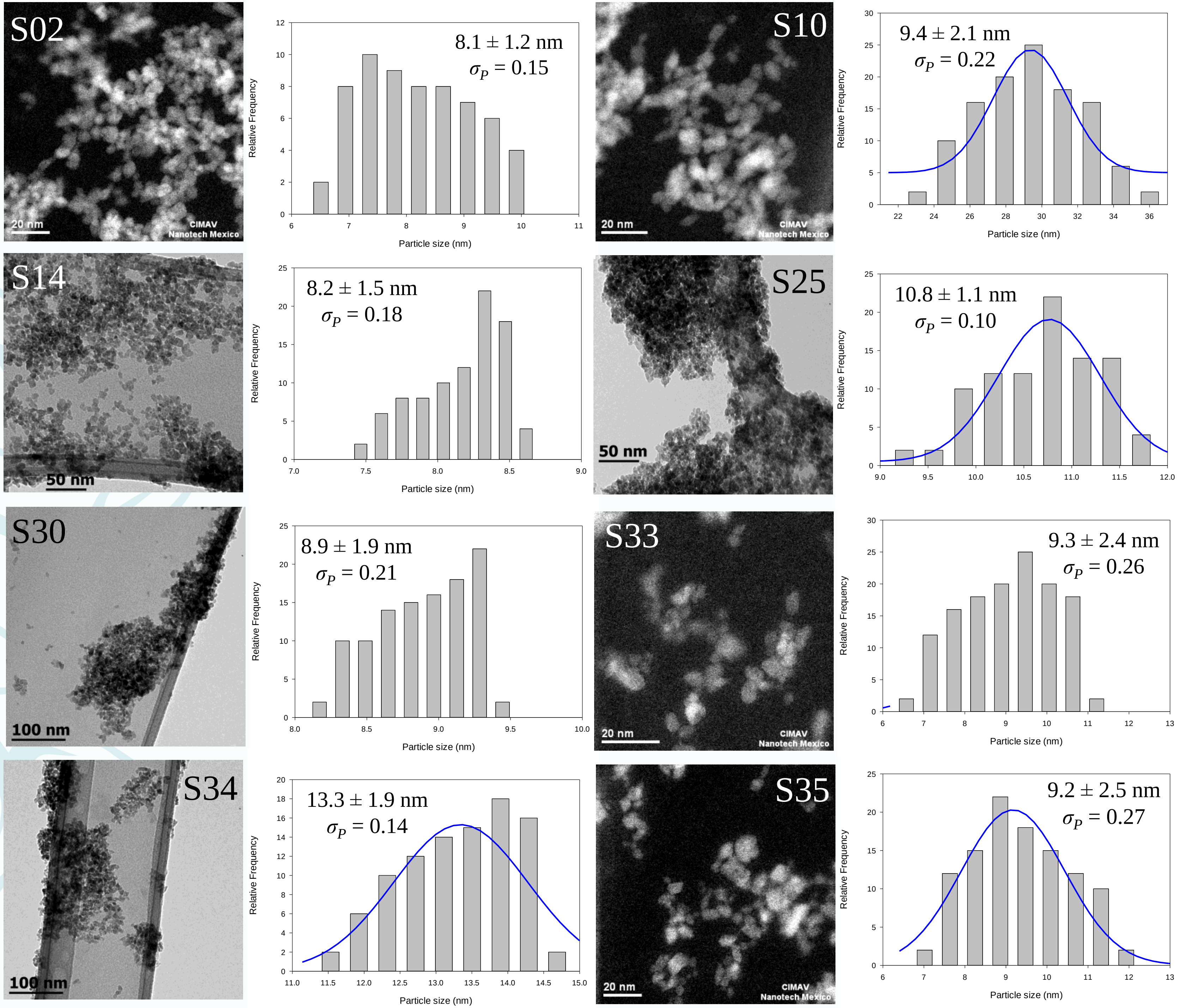
– **PMES, TIPO/H_2O**

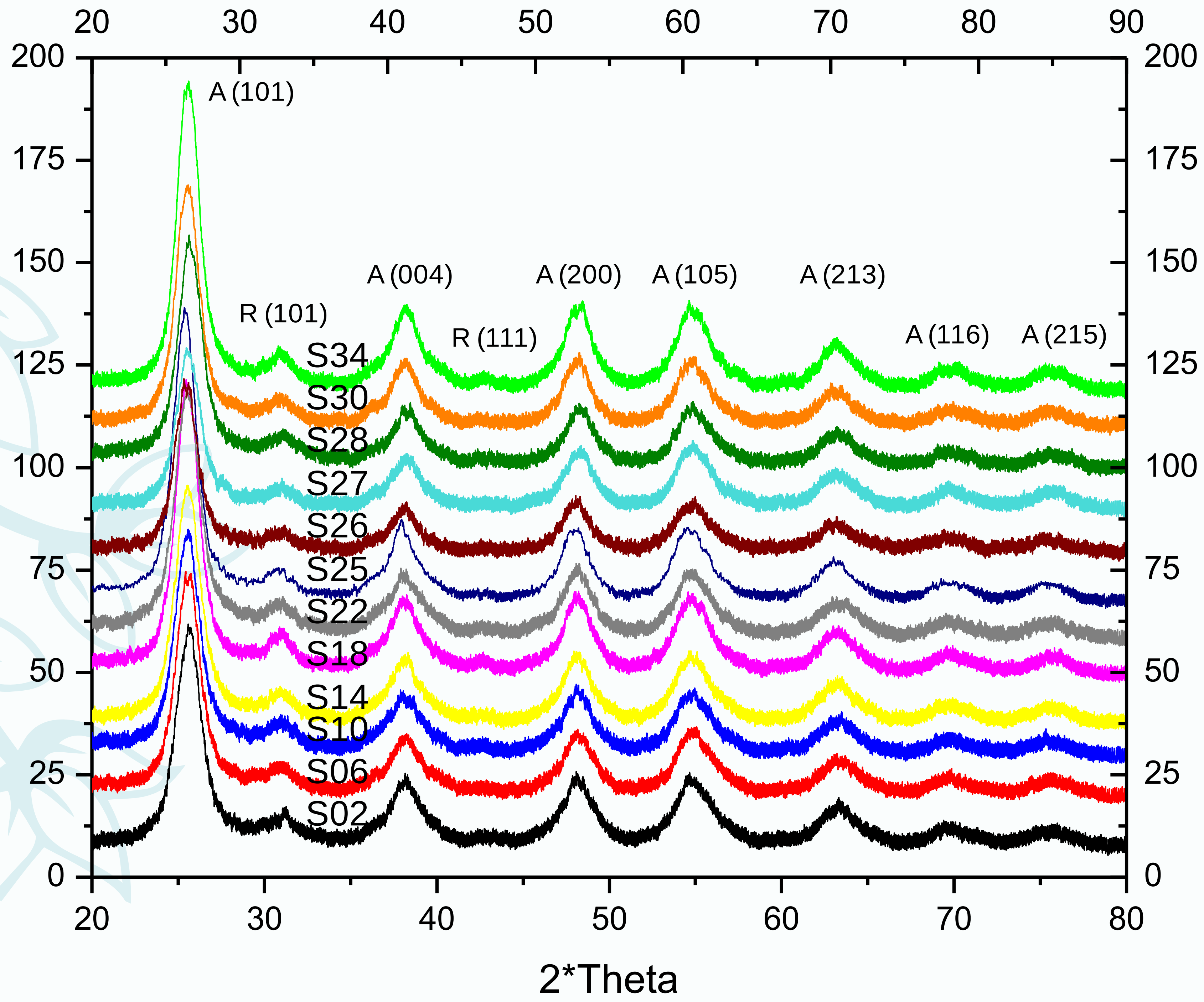


https://www.nature.com/articles/srep01959

21 Conditions

(a) pH: 1, 3, 6
(b) IsOH/ TIPO; 1.5:1
(c) Extract/ TIPO; 0.1, 0.2, 0.3
(d) TIPO
Reflux


S02
20 nm
CIMAV Nanotech Mexico
8.1 ± 1.2 nm
σ_P = 0.15
Relative Frequency
Particle size (nm)
S10
20 nm
CIMAV Nanotech Mexico
9.4 ± 2.1 nm
σ_P = 0.22
Relative Frequency
Particle size (nm)
S14
50 nm
8.2 ± 1.5 nm
σ_P = 0.18
Relative Frequency
Particle size (nm)
S25
50 nm
10.8 ± 1.1 nm
σ_P = 0.10
Relative Frequency
Particle size (nm)
S30
100 nm
8.9 ± 1.9 nm
σ_P = 0.21
Relative Frequency
Particle size (nm)
S33
20 nm
CIMAV Nanotech Mexico
9.3 ± 2.4 nm
σ_P = 0.26
Relative Frequency
Particle size (nm)
S34
100 nm
13.3 ± 1.9 nm
σ_P = 0.14
Relative Frequency
Particle size (nm)
S35
20 nm
CIMAV Nanotech Mexico
9.2 ± 2.5 nm
σ_P = 0.27
Relative Frequency
Particle size (nm)



A (101)
R (101)
A (004)
R (111)
A (200)
A (105)
A (213)
A (116)
A (215)
S34
S30
S28
S27
S26
S25
S22
S18
S14
S10
S06
S02
2*Theta

Yield

S02	97.58	S25	88.95
S06	95.75	S26	84.94
S10	99.67	S27	89.52
S14	**66.99**	S28	84.25
S18	95.37	S30	80.46
S22	**99.99**	S34	79.97

TiO_2 test


https://www.google.com/search?tbm=isch&q=tannery+industry&sa=X&ved=0ahUKEwjcreDuxqnXAhUF1WMKHe5MC6EQhyYIJg#imgrc=KIdYCJmlPlTWfM:

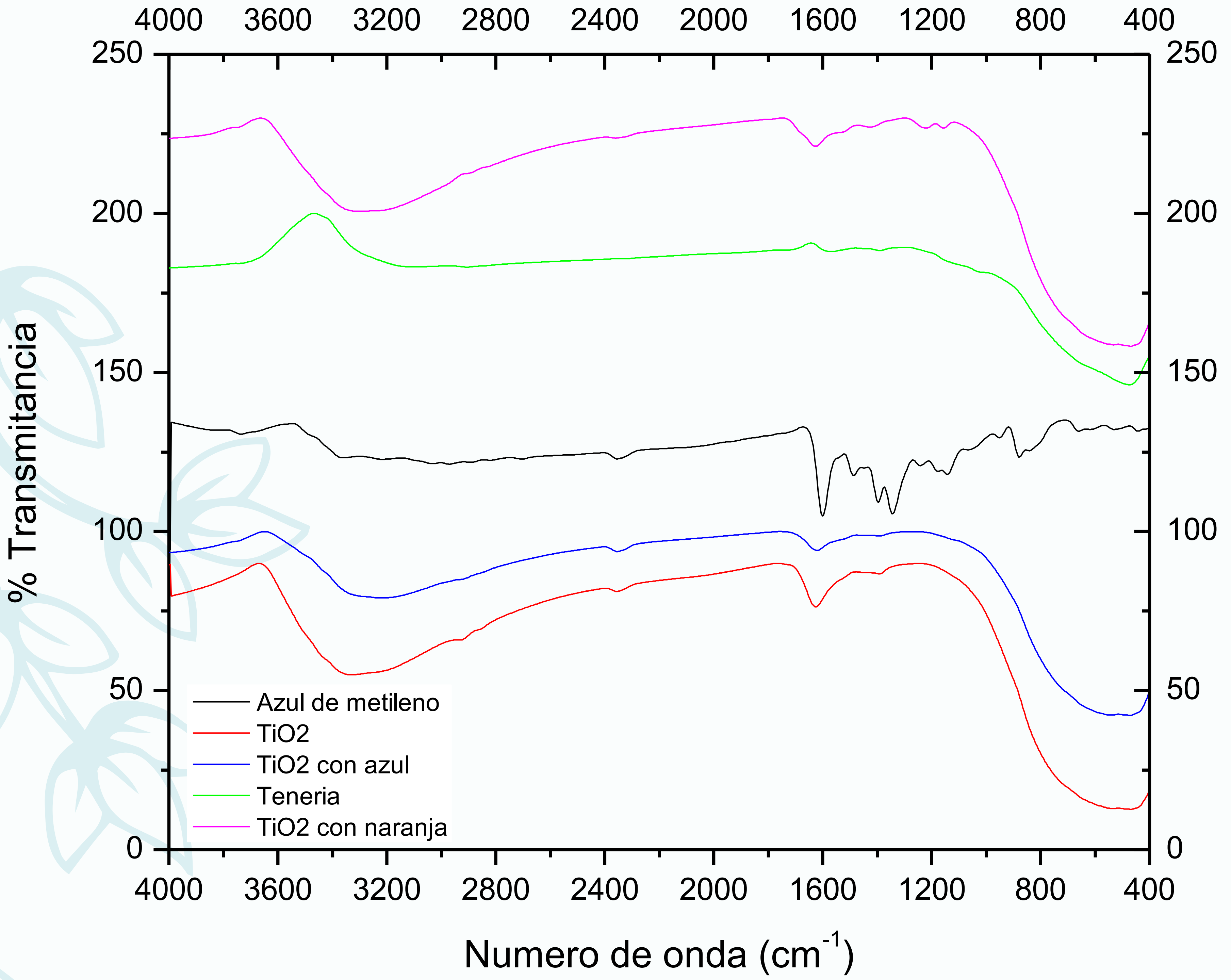
1. Removal of colorants in water using NPs de TiO_2
2. Tannery effluent treatment
3. Kinetic studies

NP size (nm)	Concentration (mg/L)			
	500		1500	
	Average	SD	Average	SD
300	97.9967	0.4179	95.2967	0.2701
560	95.7267	1.1091	93.2833	0.6035
WTHT NPs	3.7633	0.6258		

% orange methyl removal

% removal methylene blue

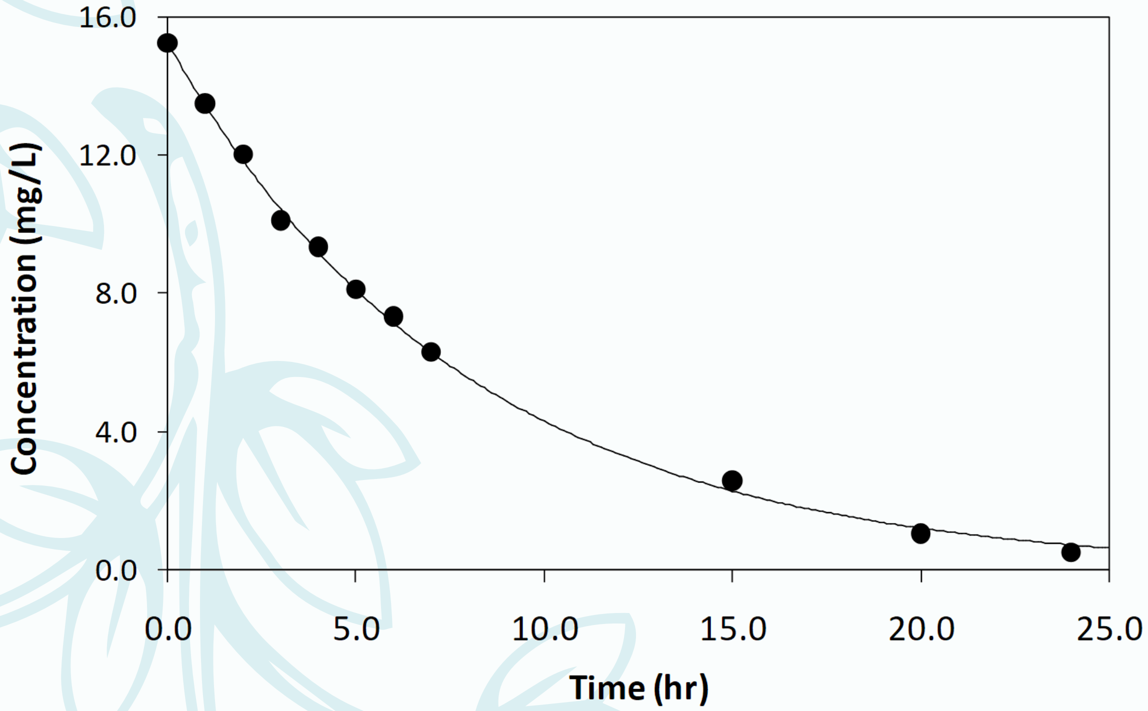
NP size (nm)	Concentration (mg/L)			
	500		1500	
	Average	SD	Average	SD
300	97.7300	0.4004	97.7533	0.4315
560	55.4367	1.4981	95.2367	0.1274
Wtht NPs	5.6300	3.2509		



Before and after degradation

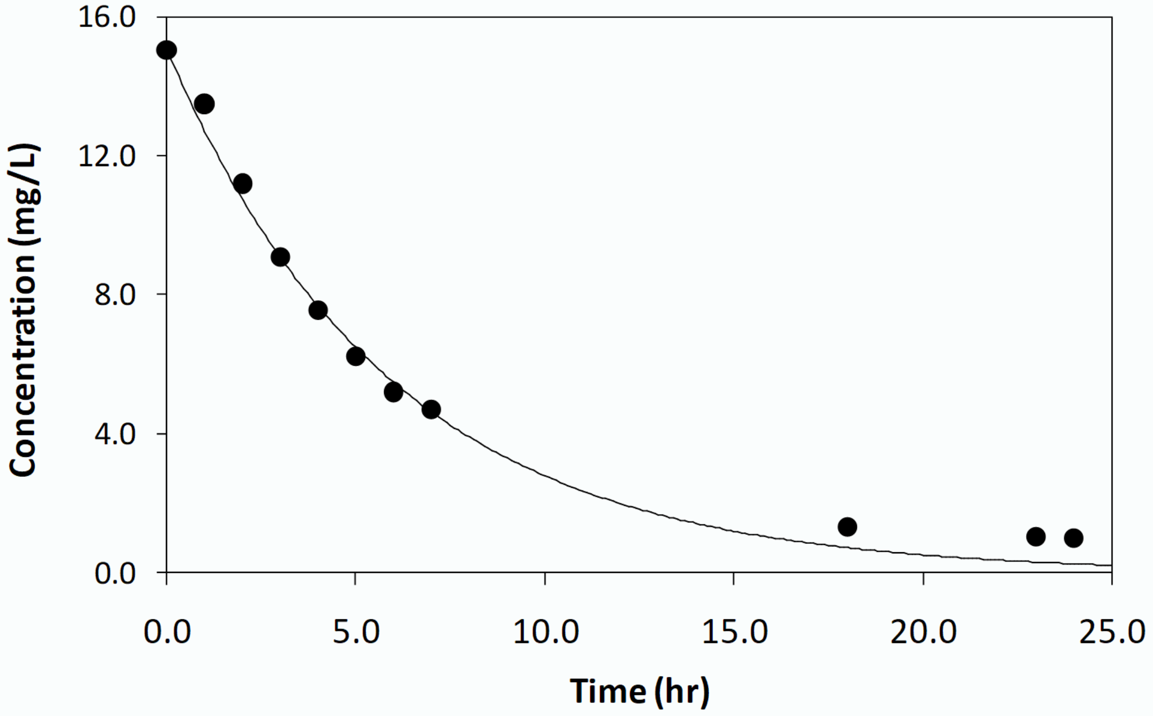
Methyl orange

$$k = 0.1262 \ \text{hr}^{-1}$$



Methylene blue

$$k = 0.1682 \ \text{hr}^{-1}$$



Summary of findings, Ag

- Size and size distribution depend on pH, PMES, and initial Ag concentration

- best numbers were obtained when PMES was water, pH 7 (8.9 ± 2.5 nm, σ_P = 0.28)

- Kinetics indicated a complex reaction

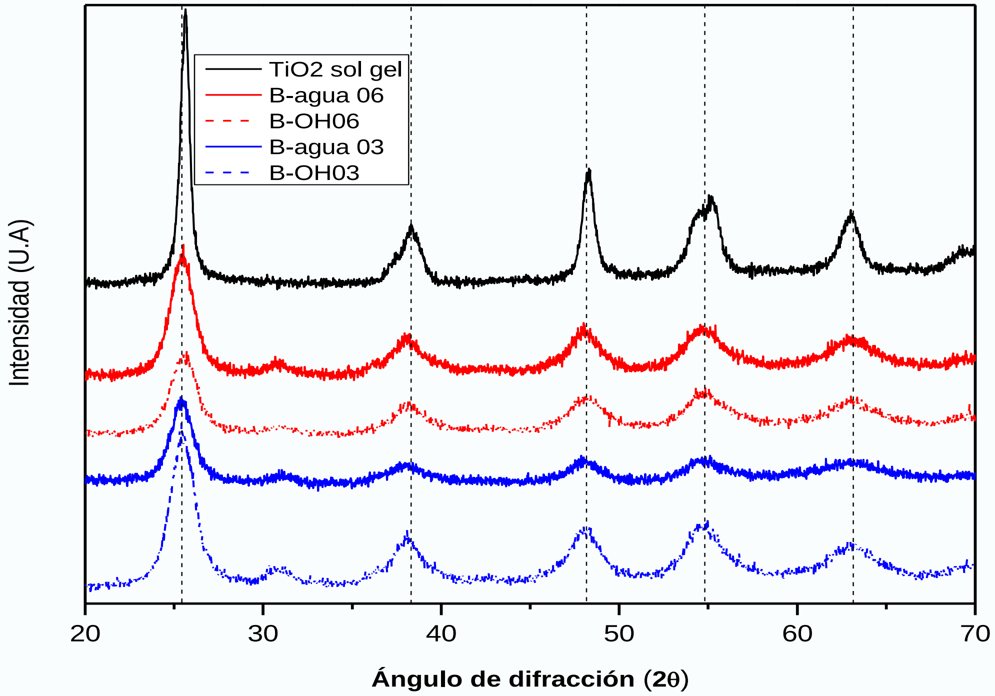
- NPs contain a mixture of Ag, AgCl, Ag_2O

- **Summary of findings, TiO_2**
- Size and size distribution depend on pH, H2O/TIPO, Extracts/TIPO
- Crystal phase may be controled (mostly, anatase is obtained)
- Best conditions to obtain anatase are pH 6, hydrolisis ratio 500, Extract/TIPO ratio of 0.1
- Colorant degradation depends on particle size

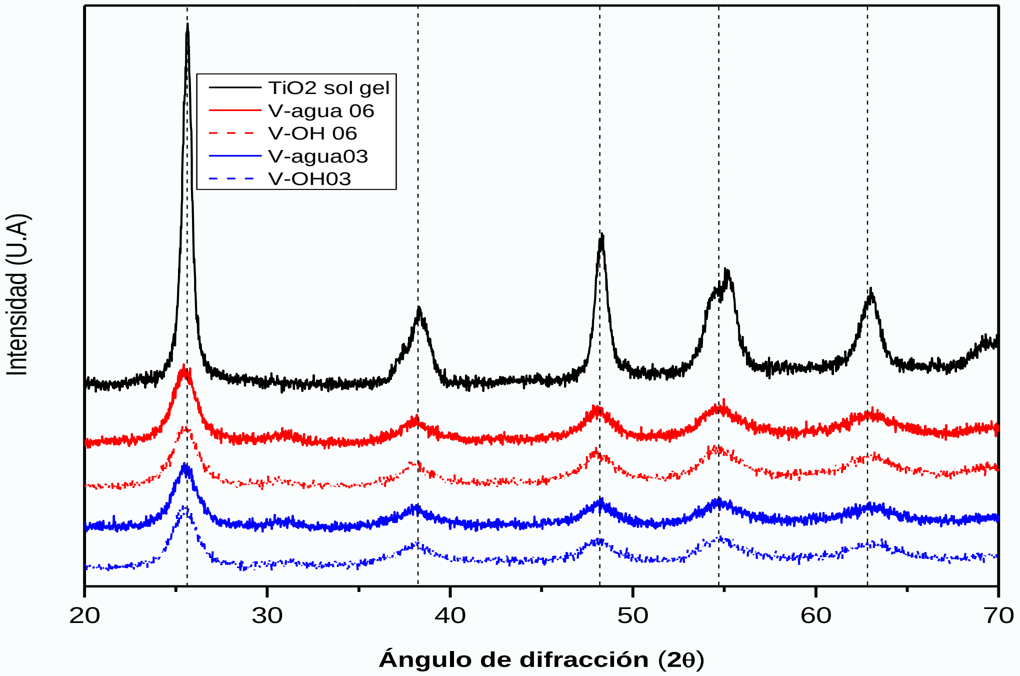
What are we up to?

- Bouganvillea
- Vainillin
- guayacol

Bouganvillea

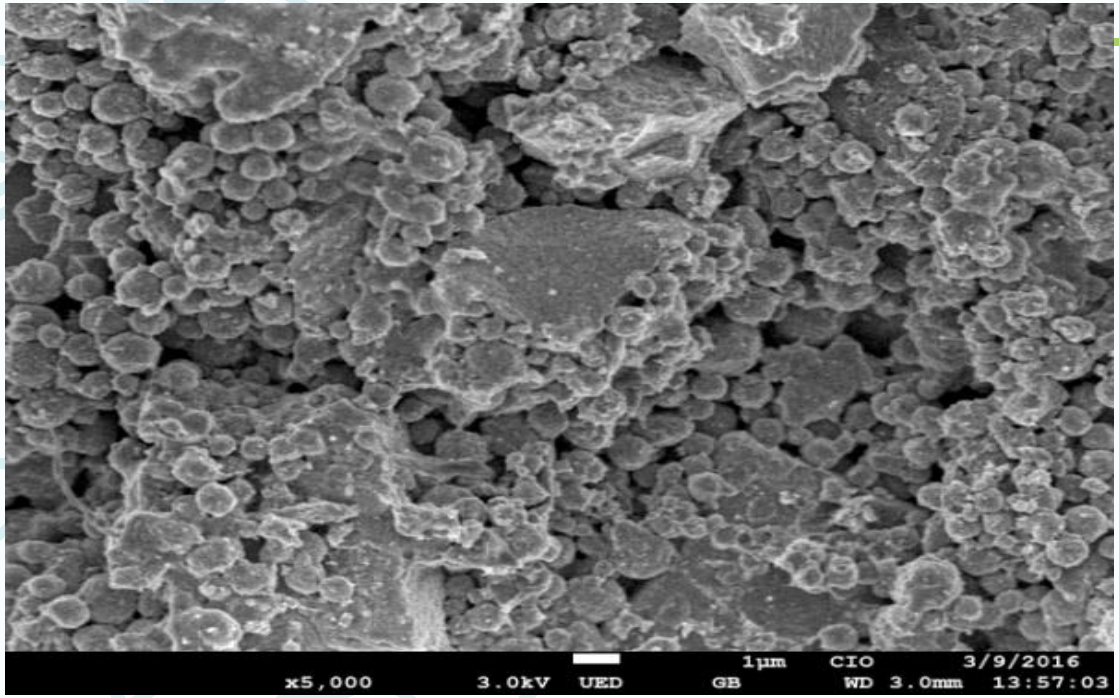


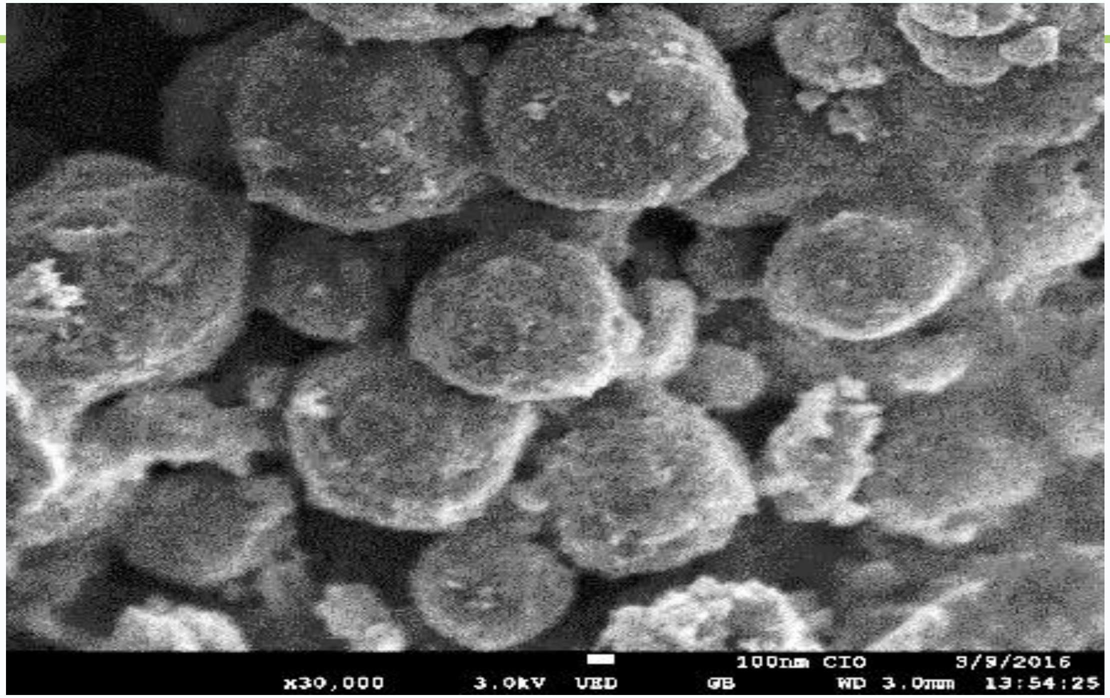
Vainillin



R. Vijayalakshmi and V. Rajendran. Arch.Appl.Sci.Res; 2012, 4(2): 1183-1190

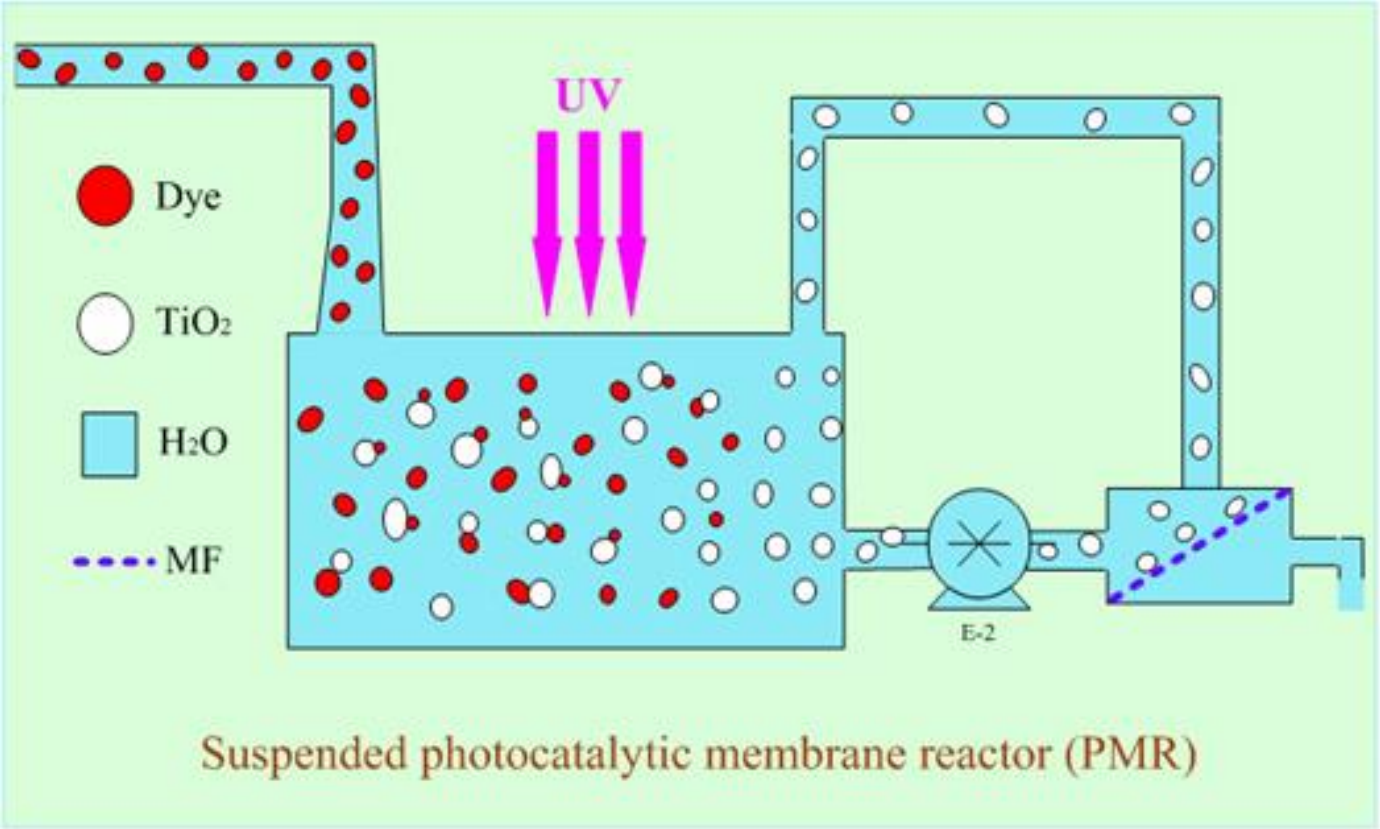
SEM





VANILLIN

35 Tannery effluent



ZHANG Hui;ZHANG Guoliang*;YANG Zhihong;CHEN Jinyuan;NI Lijia; Degradation of Azo Dye Wastewater in a TiO2 Photocatalysis and Membrane Separation Hybrid System ; Chinese J of Catalysis, 2009

J. Jesús Ibarra
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IAEA
International Atomic Energy Agency

Universidad Autónoma de Coahuila

RedTULS
Red Temática Usuarios de Luz Sincrotrón

IJS

Univerza v Ljubljani
Biotehniška fakulteta

ICTP
The Abdus Salam International Centre for Theoretical Physics

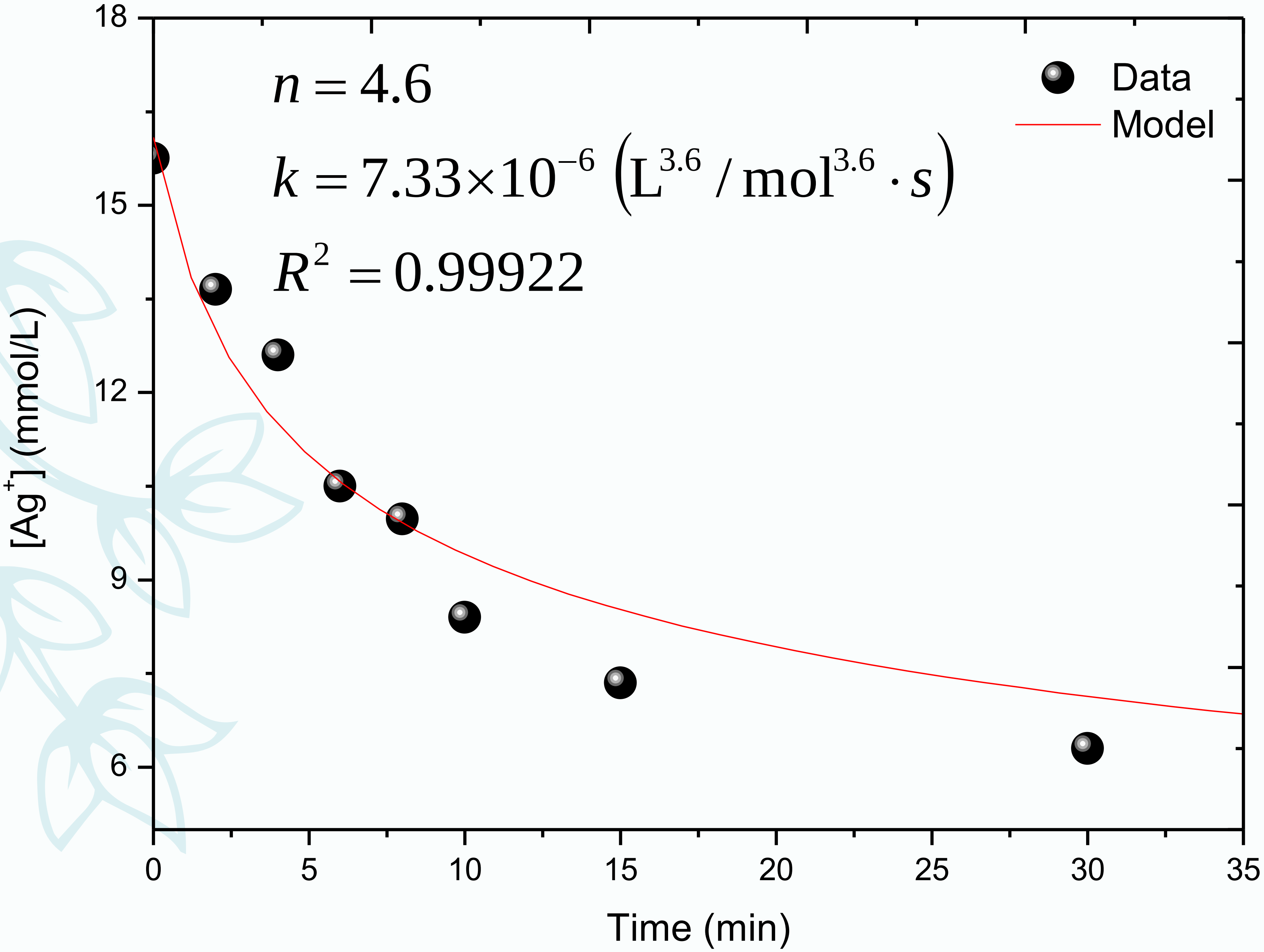
CONACYT

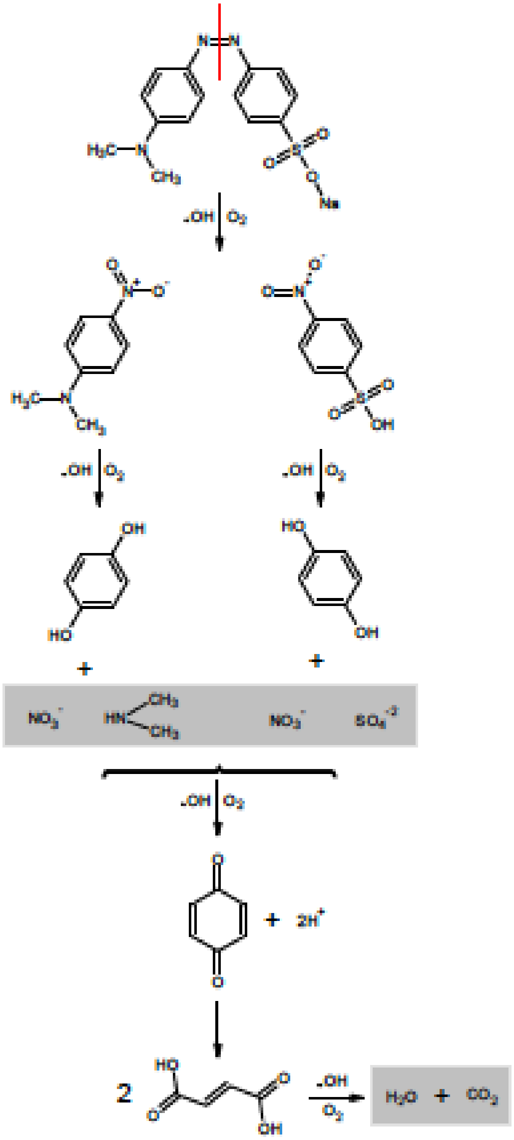
ESRF
The European Synchrotron

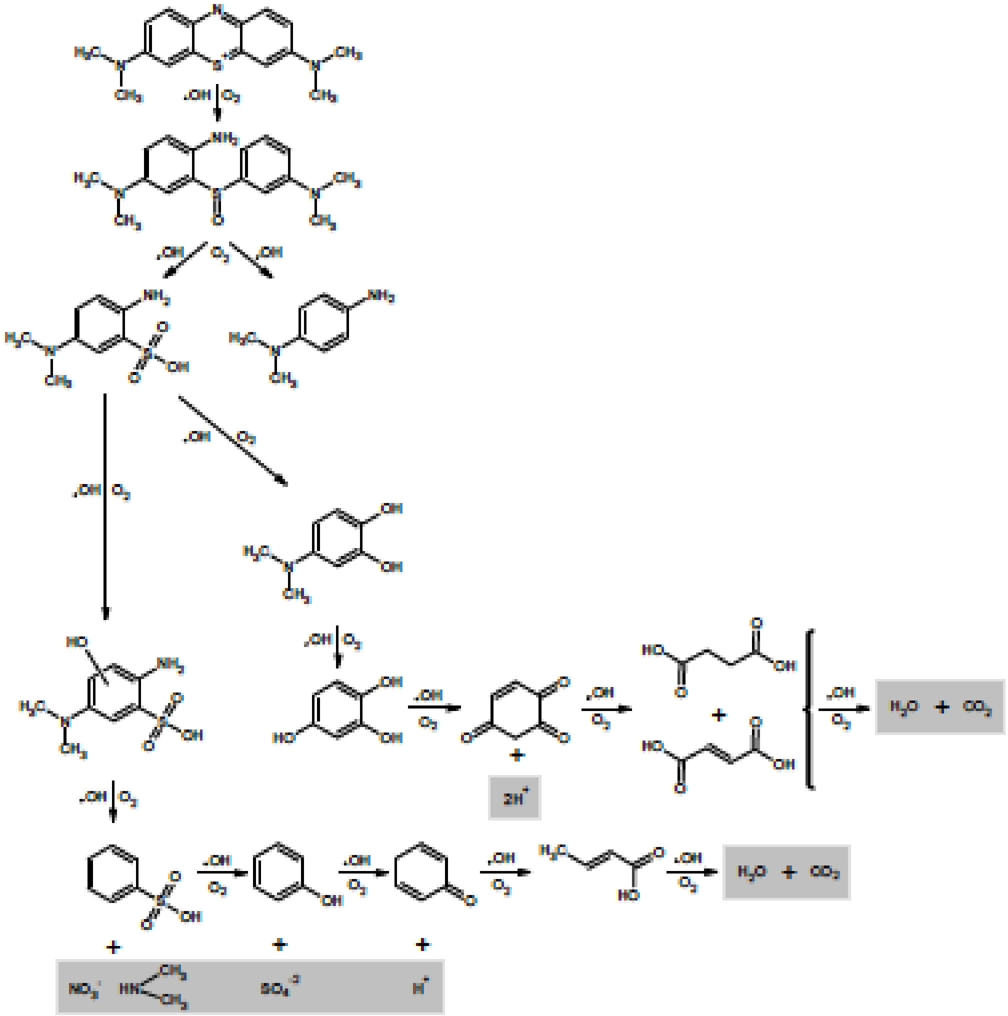
QUESTIONS?

Tabla 2.5. Costo de las SNPs para diversas rutas de síntesis.

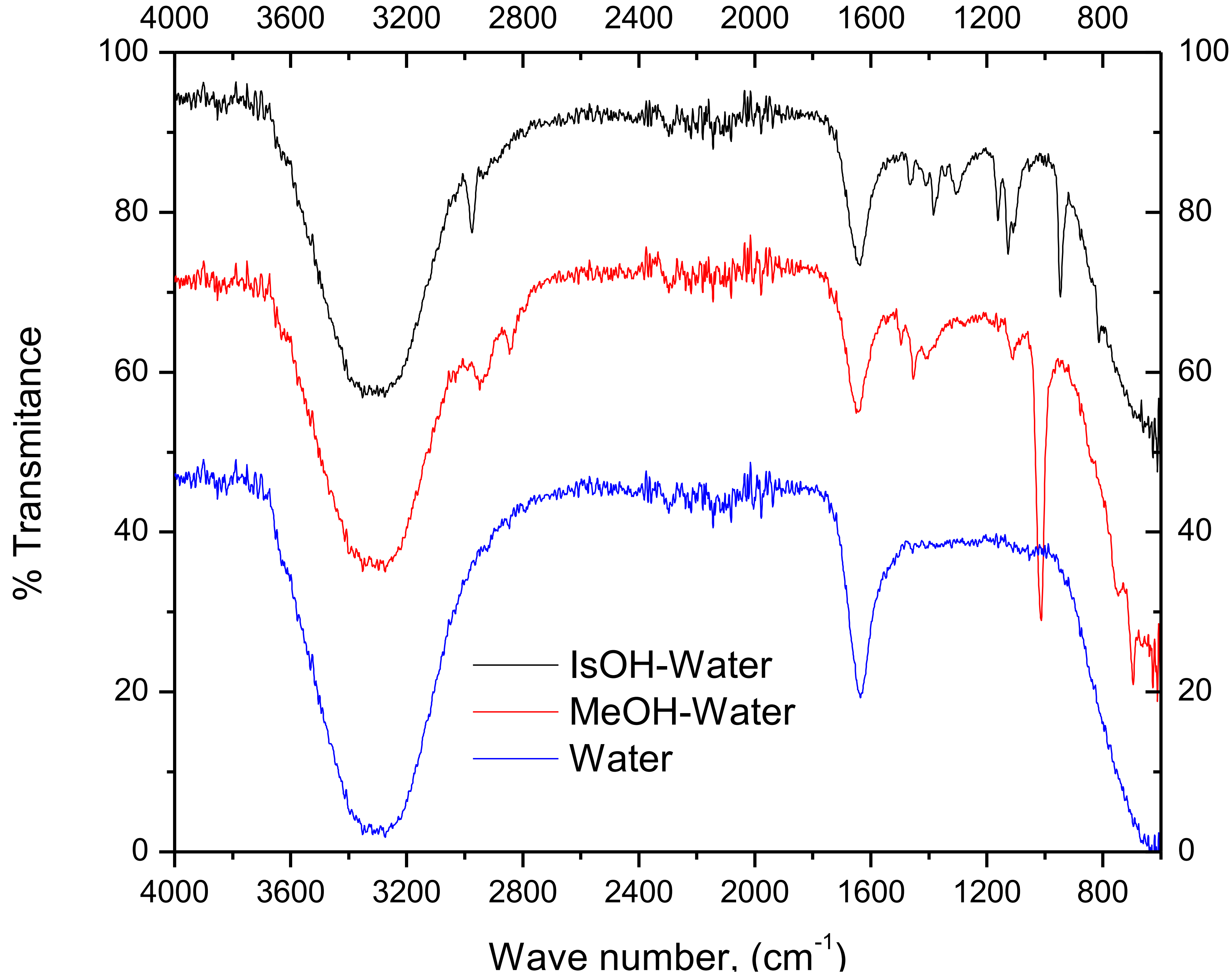
Reductor	**Costo ($ (pesos)/g de Ag)**
Alfalfa	279.762
Sacarosa	7948.374
Maltosa	23090.326
Azúcar morena	340.606
Citrato de sodio	1457.806
Ted Pella®	680000.00
Descomposición térmica	562.982

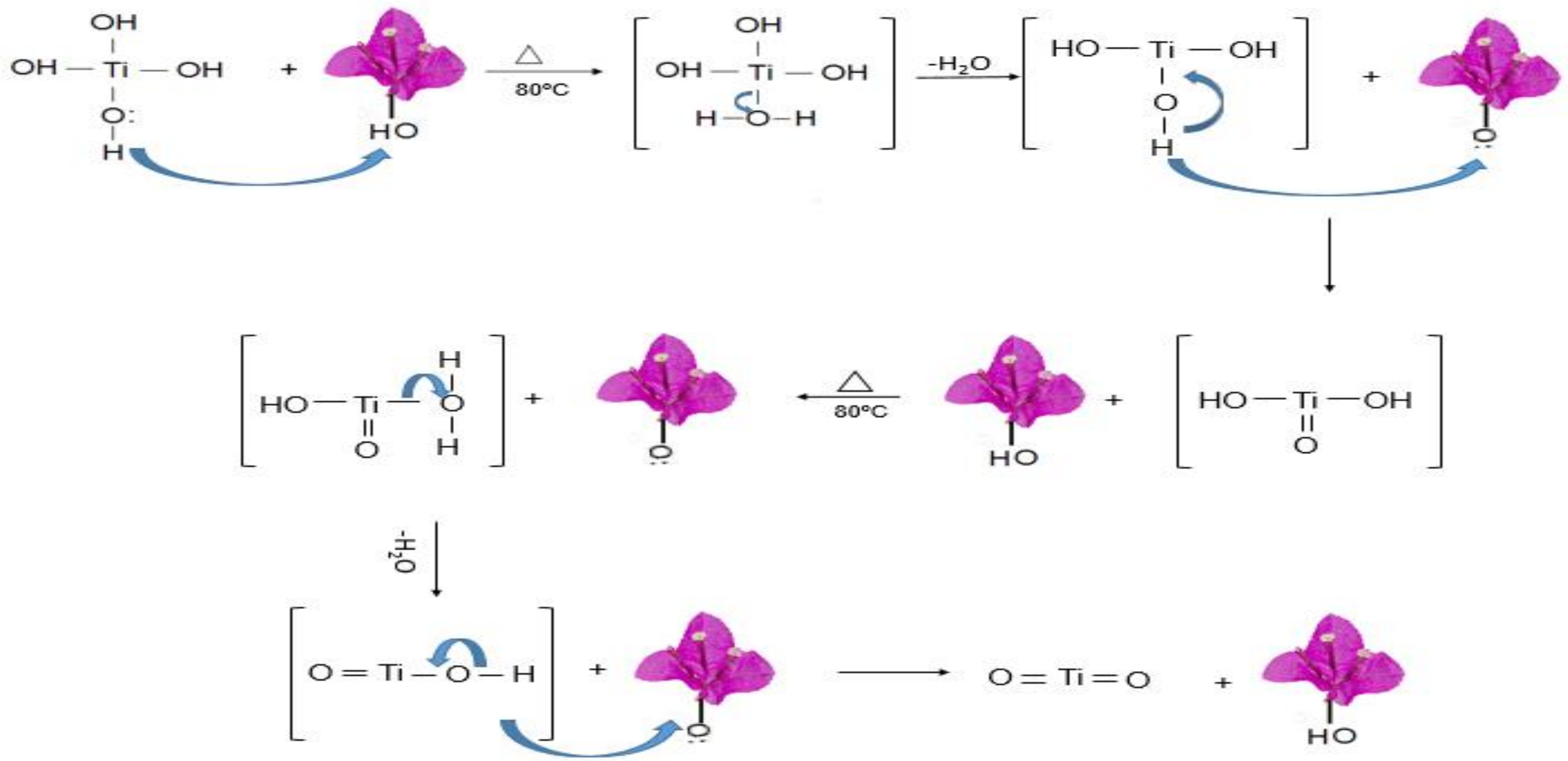

$n = 4.6$
$k = 7.33\times10^{-6}\ \left(L^{3.6}/mol^{3.6}\cdot s\right)$
$R^2 = 0.99922$
Data
Model
18
15
12
9
6
0
5
10
15
20
25
30
35
$[Ag^+]$ (mmol/L)
Time (min)





Espectros de IR para los distintos extractos




OH
OH — Ti — OH
O:
H
+
HO
80°C
OH
OH — Ti — OH
H — O — H
-H₂O
HO — Ti — OH
O
H
+
O:
HO — Ti — OH
O
+
HO
80°C
+
O:
H
HO — Ti — O
O
H
-H₂O
O = Ti — O — H
+
O:
O = Ti = O
+
HO