



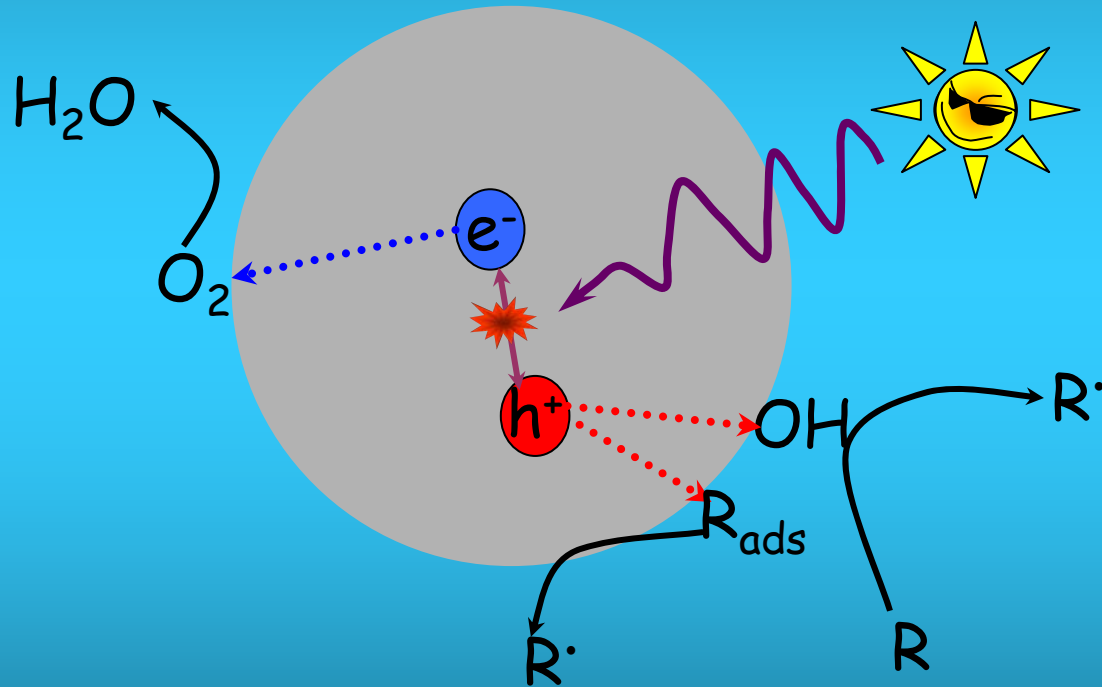
TiO₂: microestructura, fotocatálisis y fotoelectrocatalisis

Mauricio Calvo, Roberto Candal, Sara Aldabe Bilmes

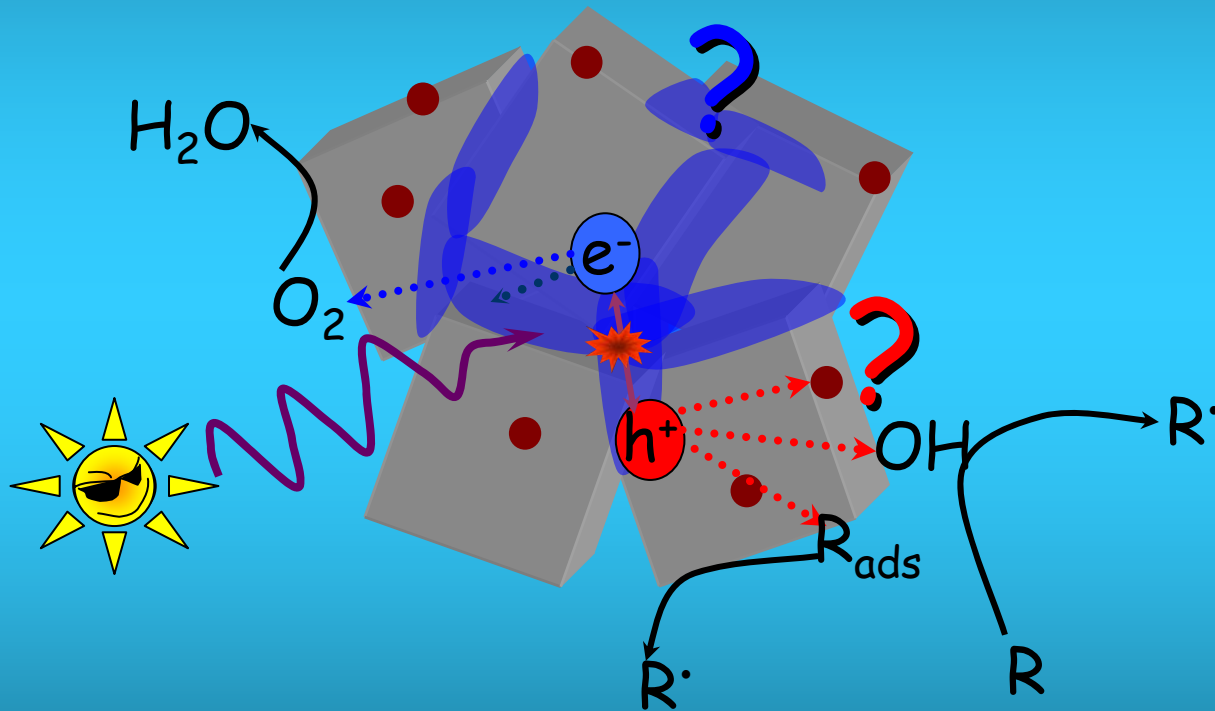
recorrido

1. introducción: cristalinidad, trampas de huecos y electrones
2. síntesis y tratamiento térmico: sintonía de cristalinidad y trampas
3. fotocatalisis y fotoelectrocatalisis
4. medición de la concentración de trampas
5. relación entre degradación y trampas

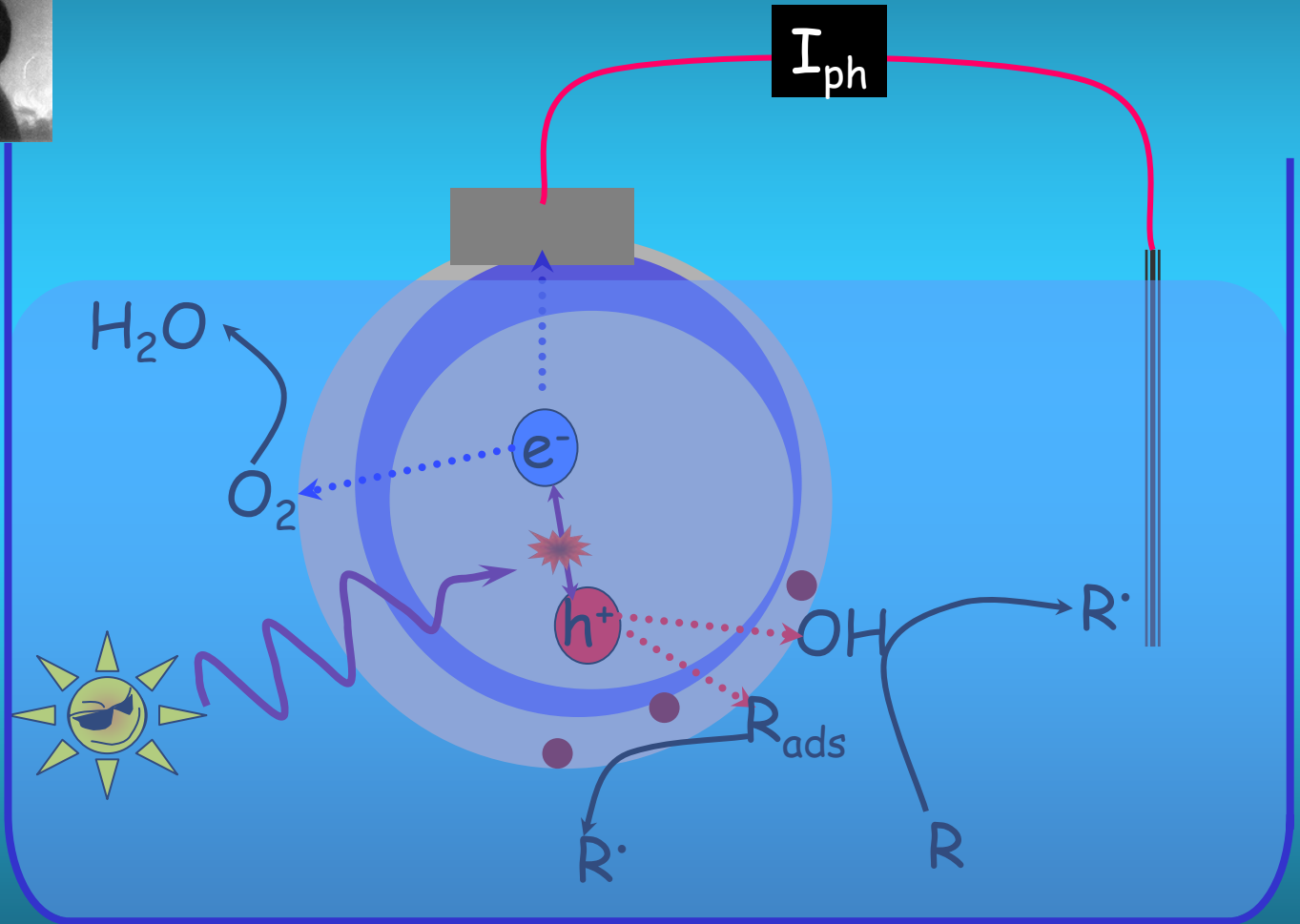
introducción



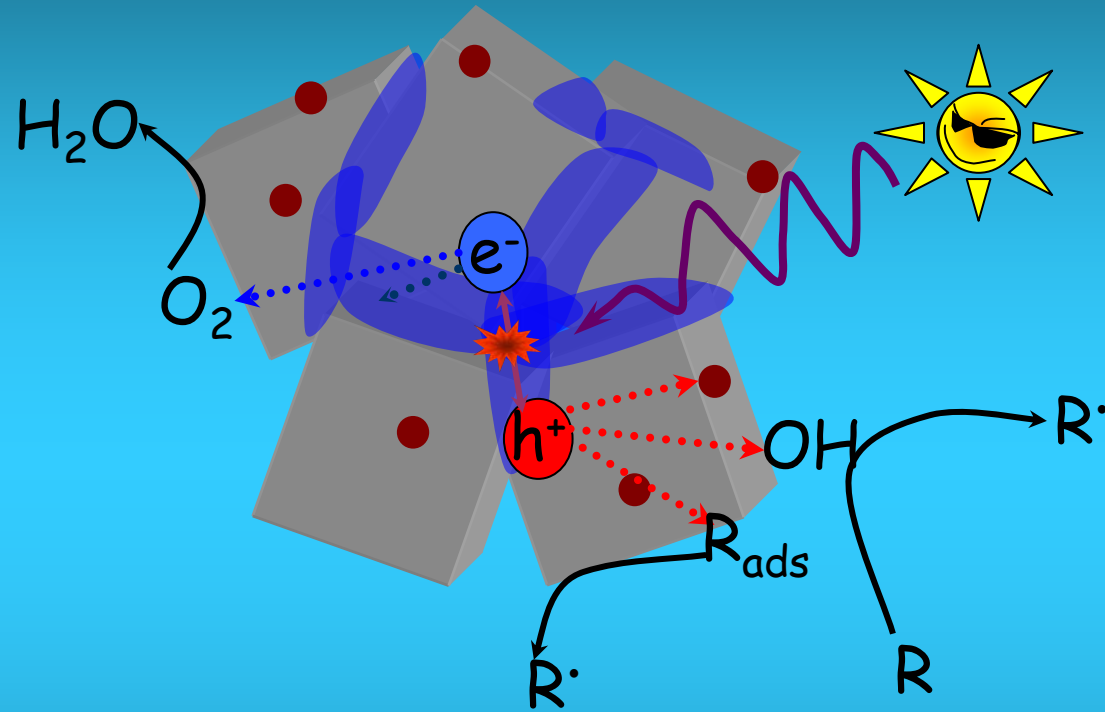
introducción



introducción

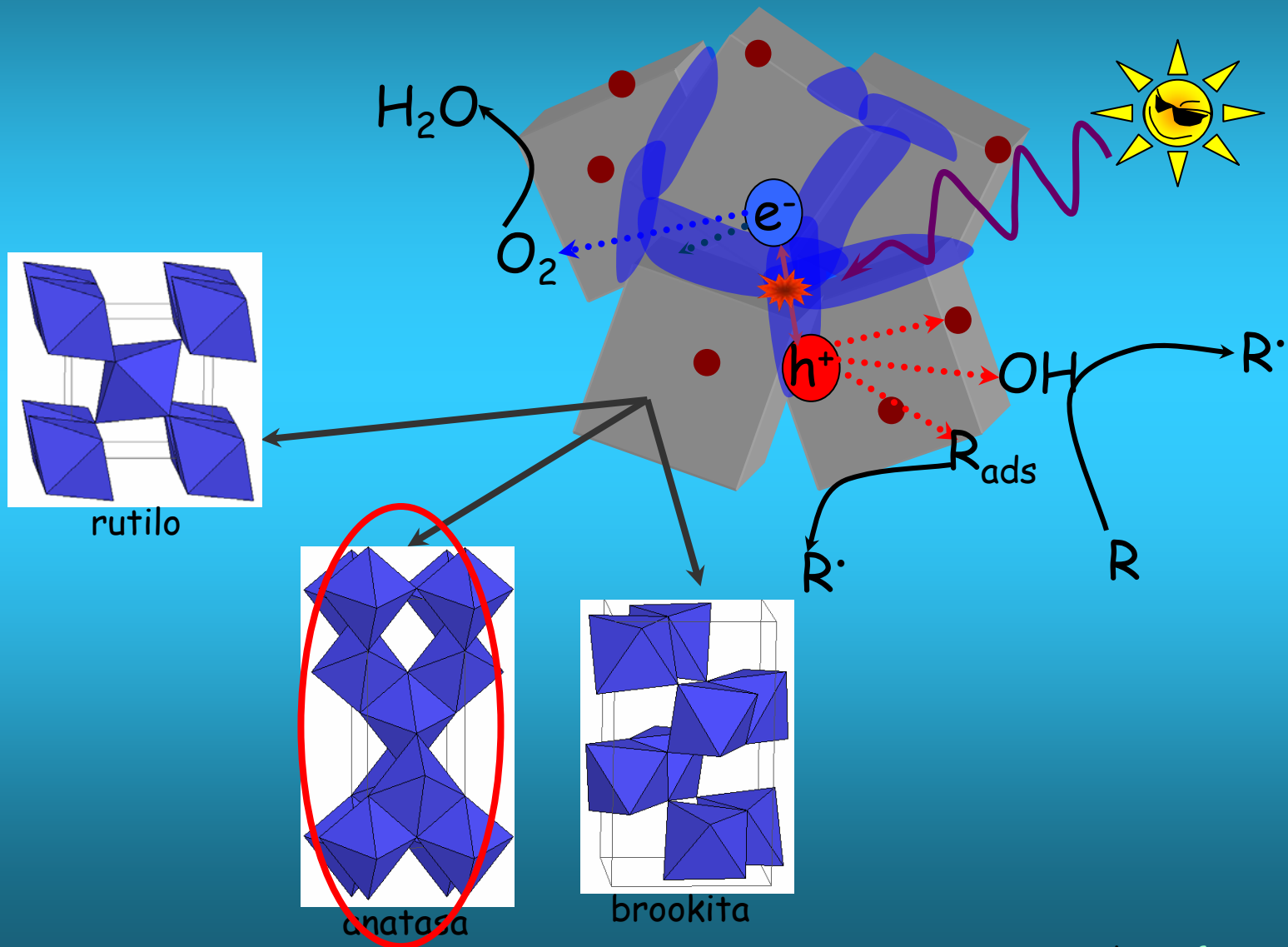


marketing

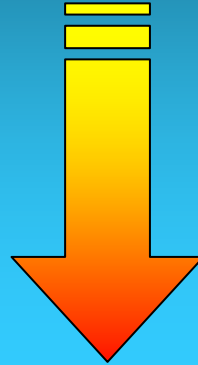


- cristalino, 80-90% anatasa
- área alta
- mínimo de trampas

cristalinidad



nuevos fotocatalizadores
restringir prueba y error



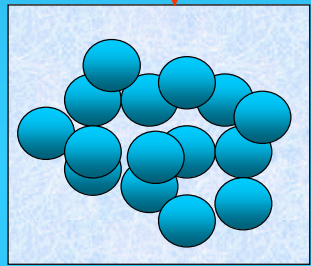
hechar mano a la síntesis

desarrollar experimentos para
determinar concentración de trampas

hechando mano a la síntesis

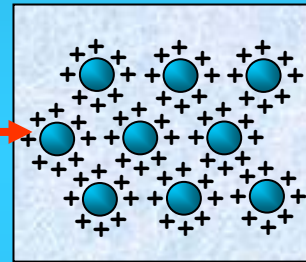


síntesis: sol-gel particulado



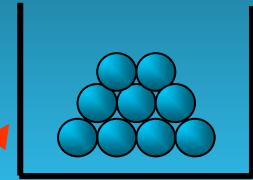
precipitado

peptización (t, T, R)

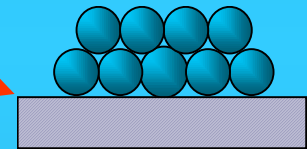


sol particulado

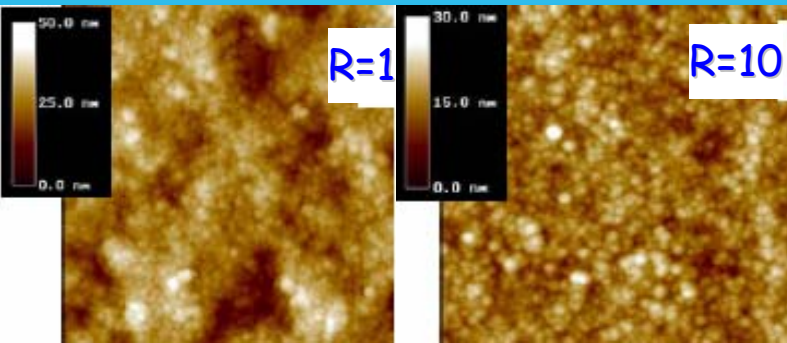
HNO_3
 TEAOH



membranas

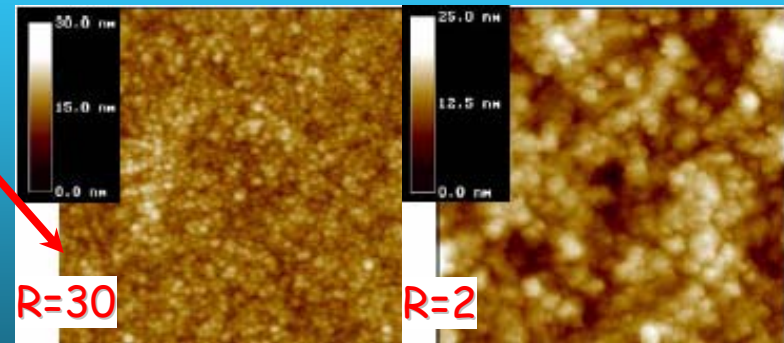


films



$1\mu\text{m}$

$$R = \frac{[\text{Ti}]}{[\text{pept}]}$$



$1\mu\text{m}$

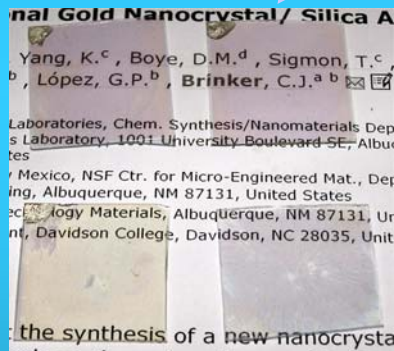
films, 4 capas, 400°C

simposio solar safe water - iguazu 2005

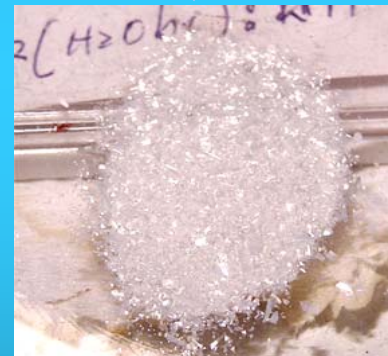
síntesis: sol-gel particulado



$T_{\text{calcination}} = 400^{\circ}\text{C}$



películas

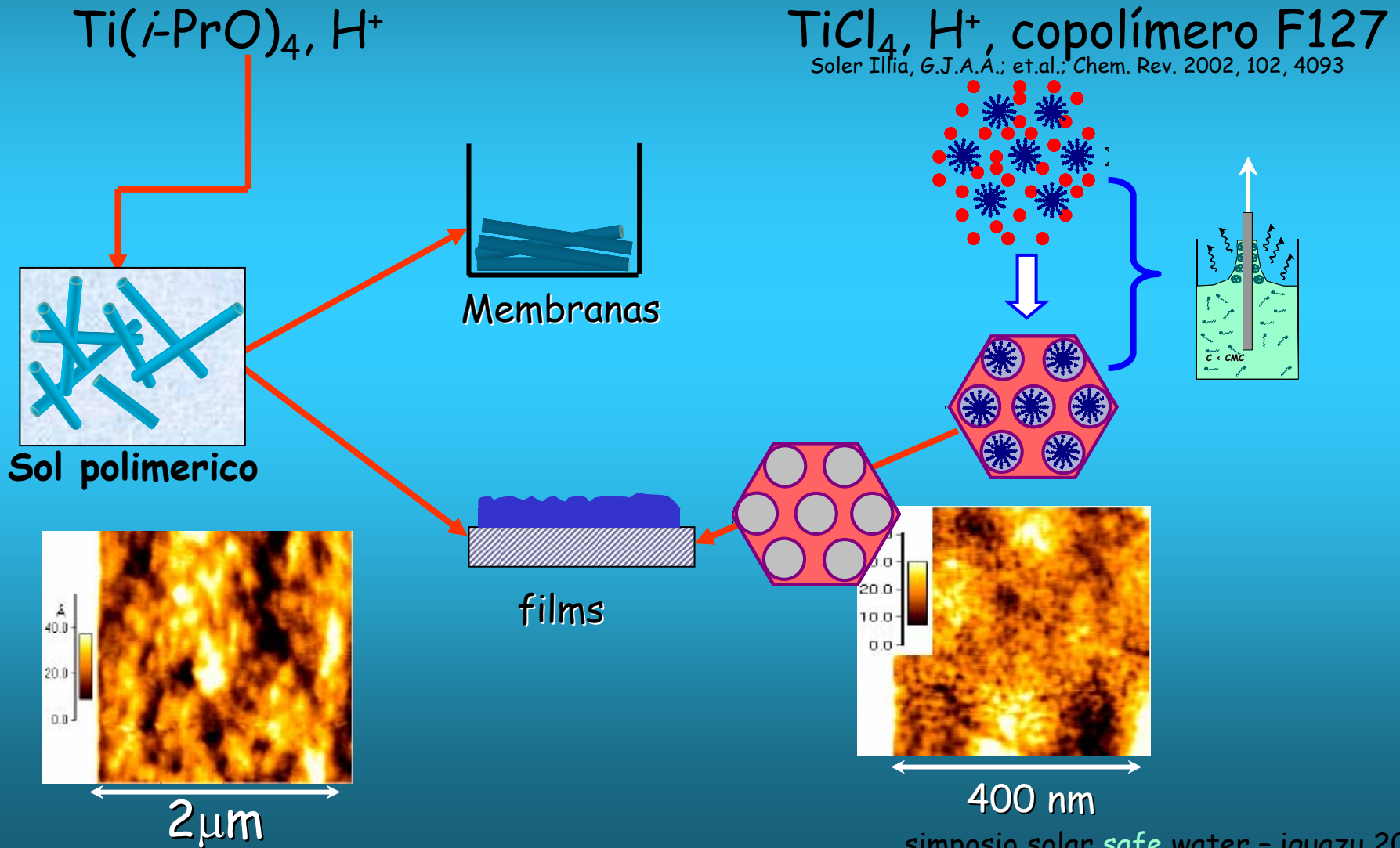


membranas

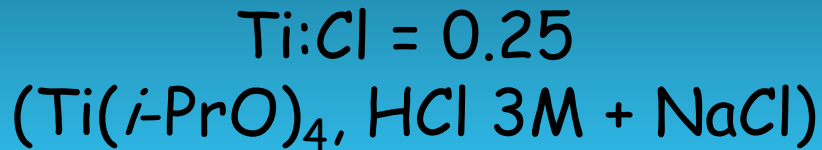
films, 4 capas, 400°C

síntesis: sol-gel polimerico

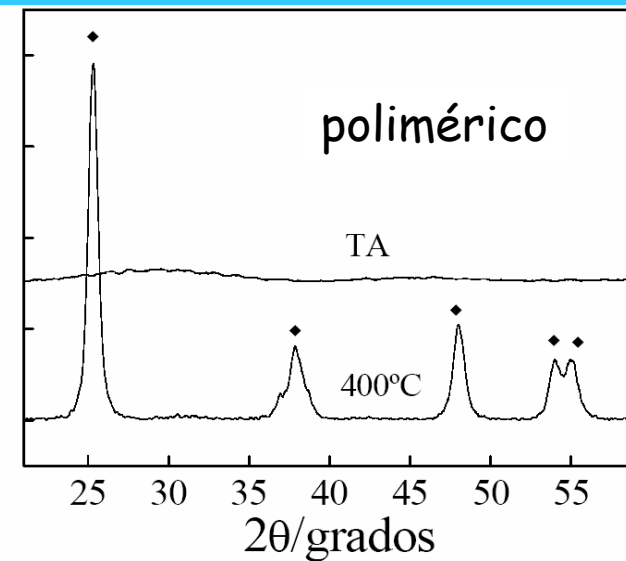
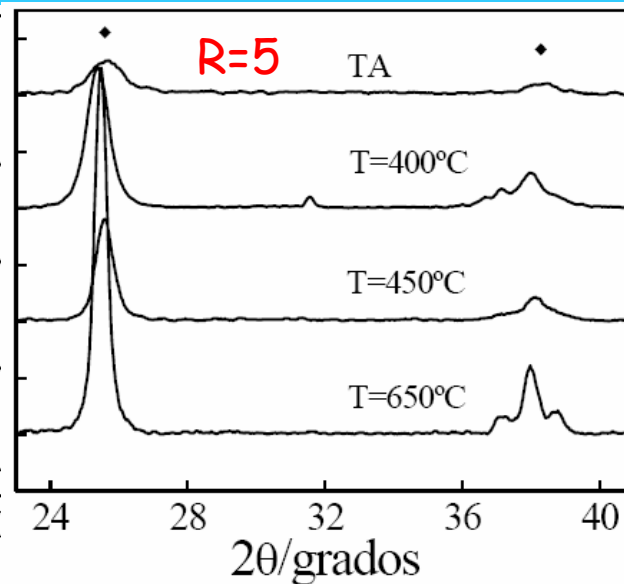
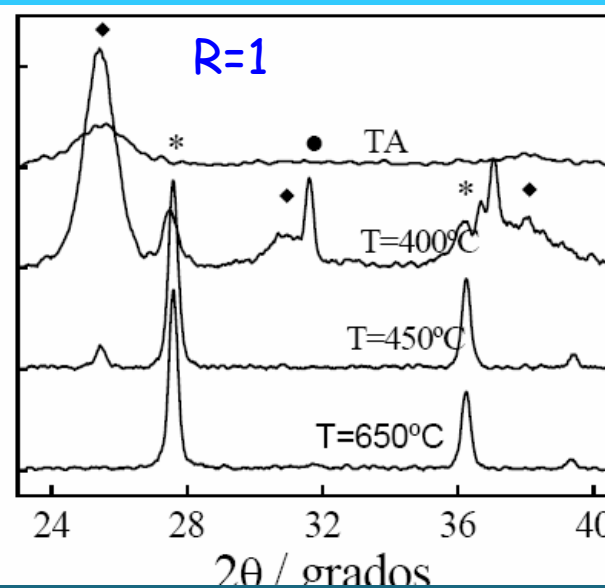
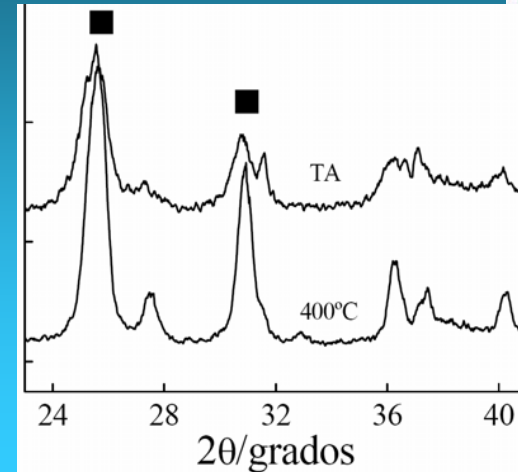
medio alcohólico, relación estequiométrica Ti : H₂O



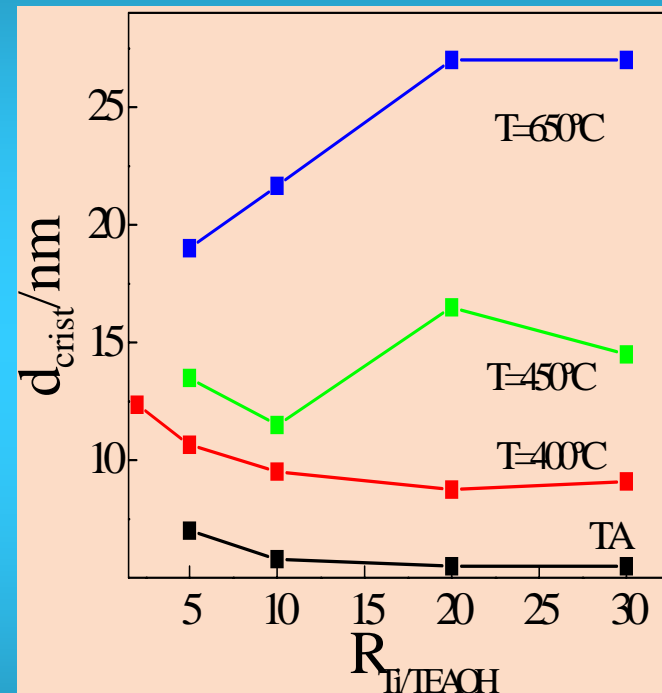
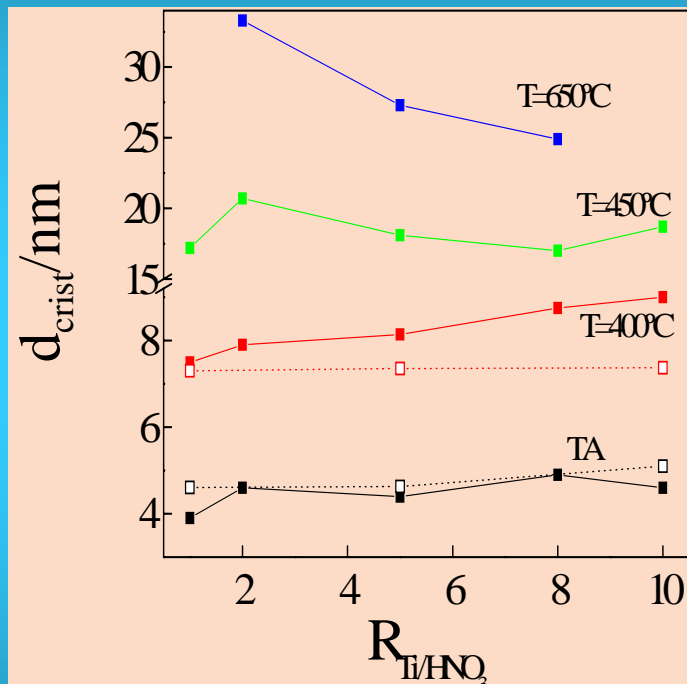
síntesis: sol de brookita



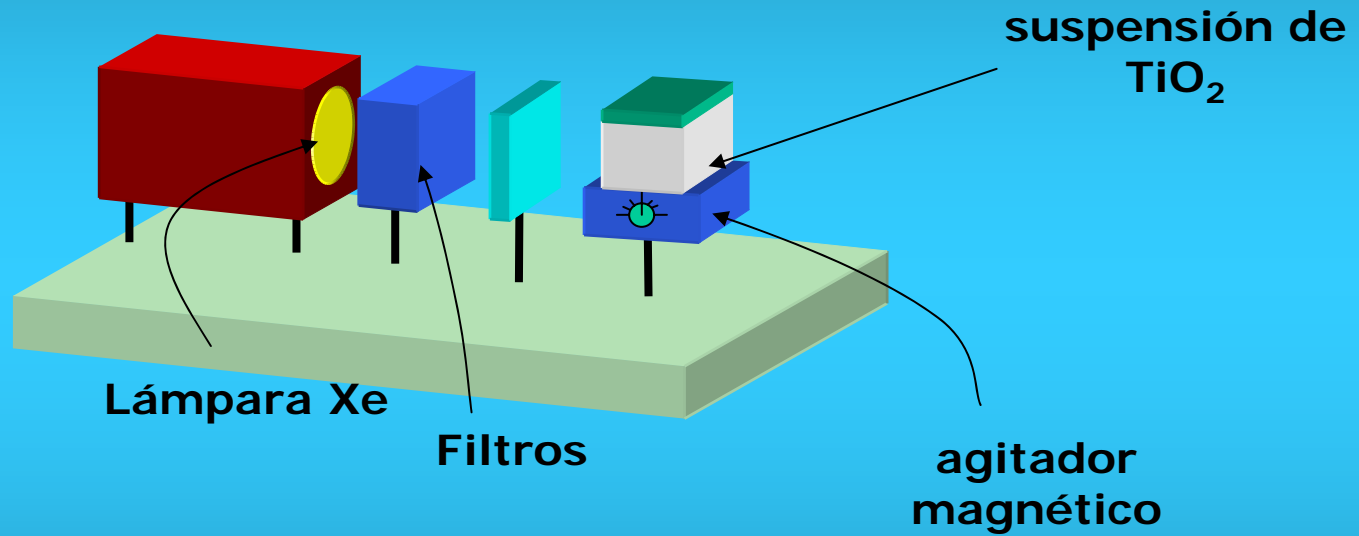
Pottier, A; Chanéac, C; Tronc, E; Mazerolles, L; Jolivet, J.-P; J. Mater. Chem. 2001,11,1116



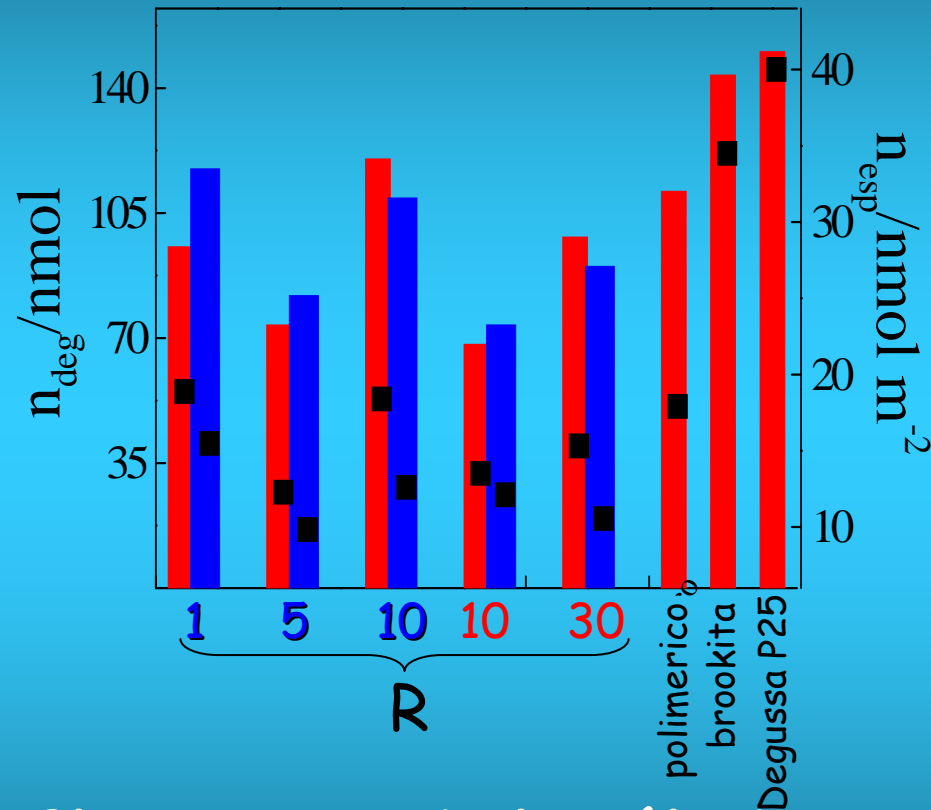
sintonia cristalina: T y R



fotocatálisis



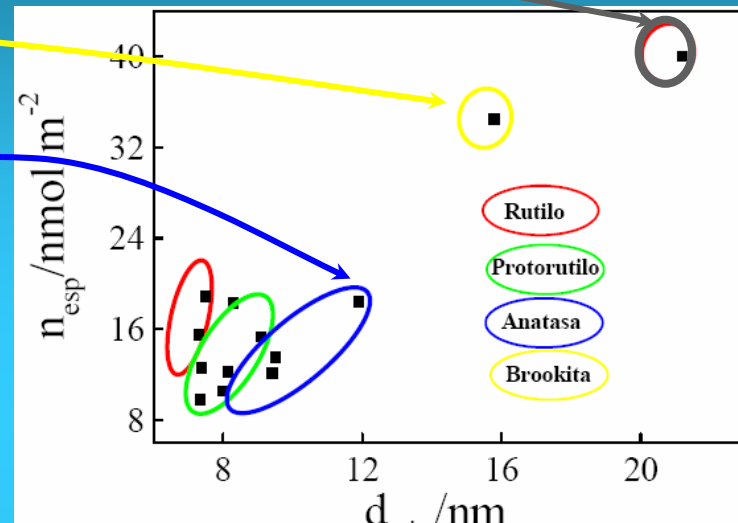
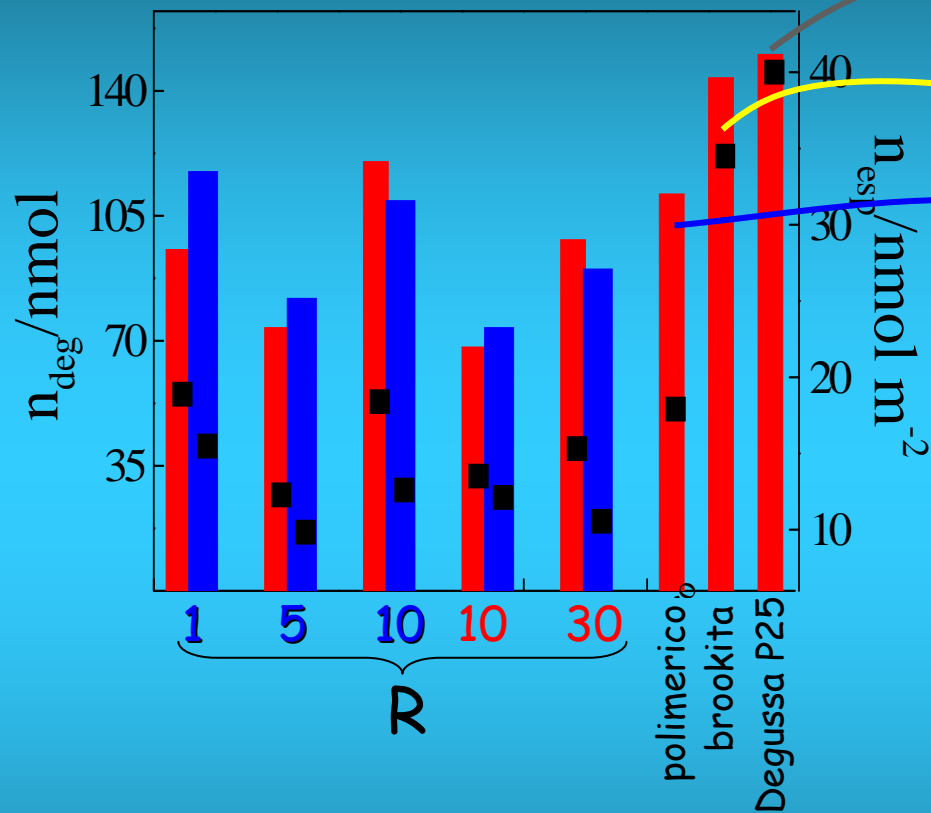
fotocatálisis



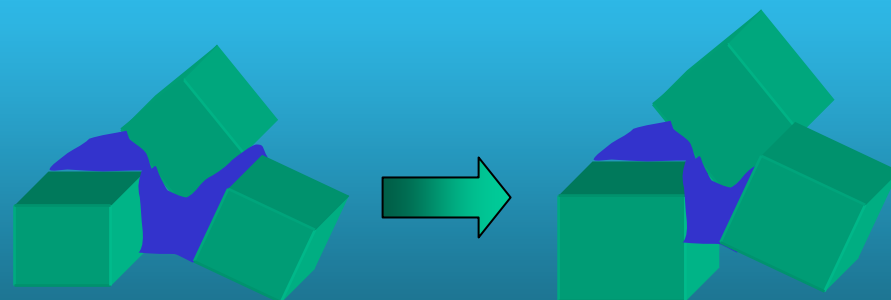
mayor influencia del sólido que del área

films calcinados a 400°C

fotocatálisis

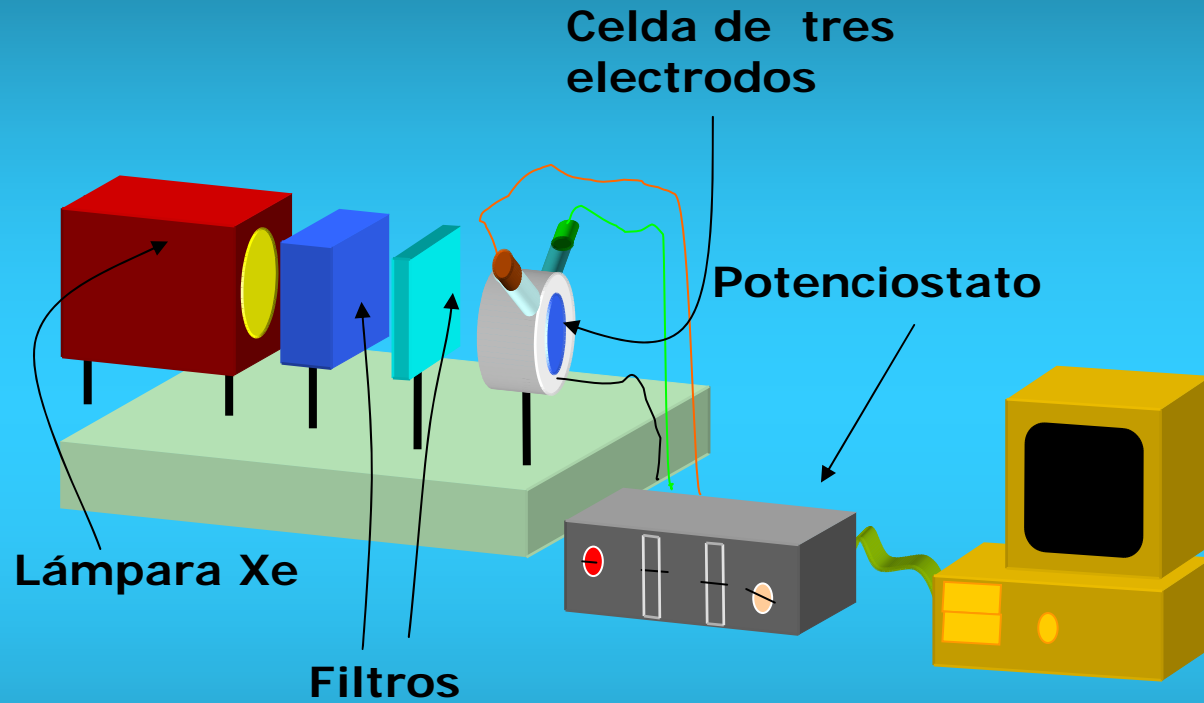


anatasa a 400°C



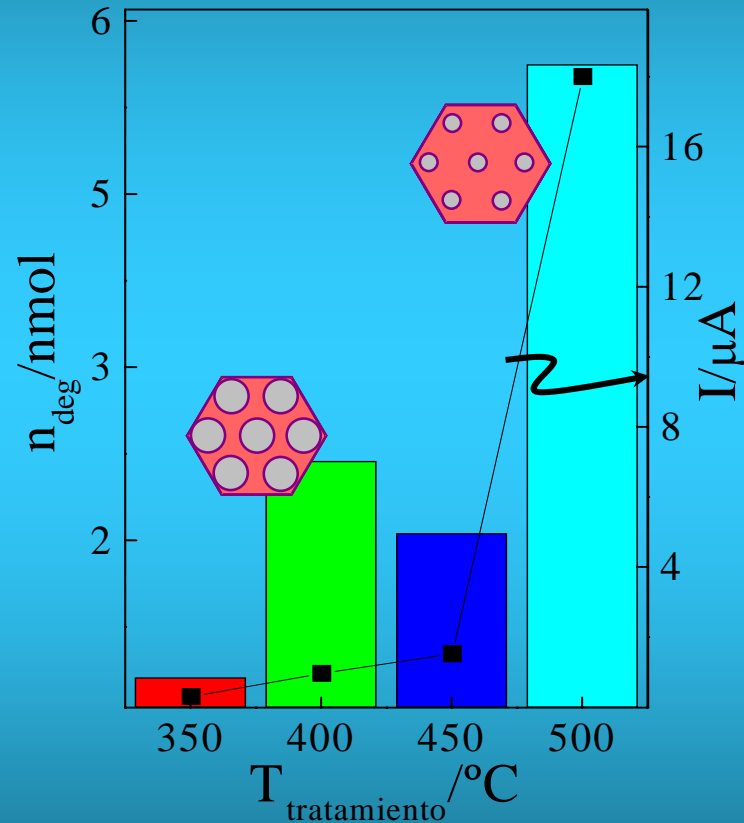
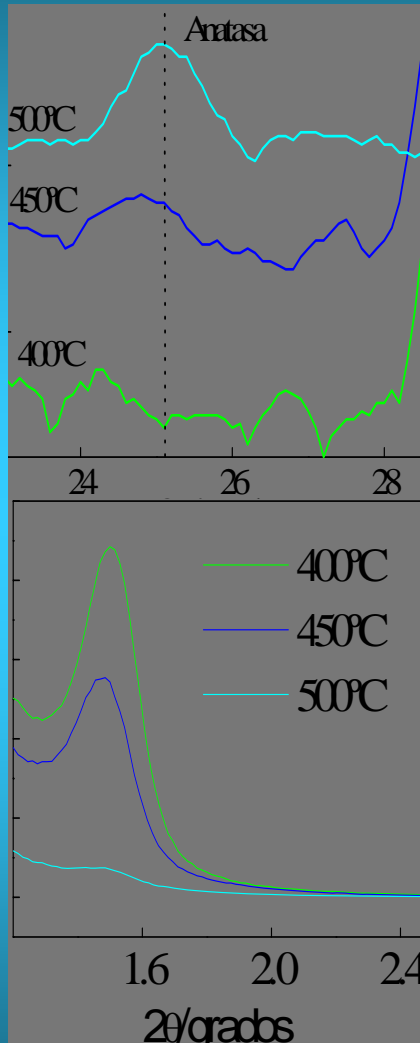
$$[\Omega] \propto \frac{1}{d}$$

fotoelectrocatalisis



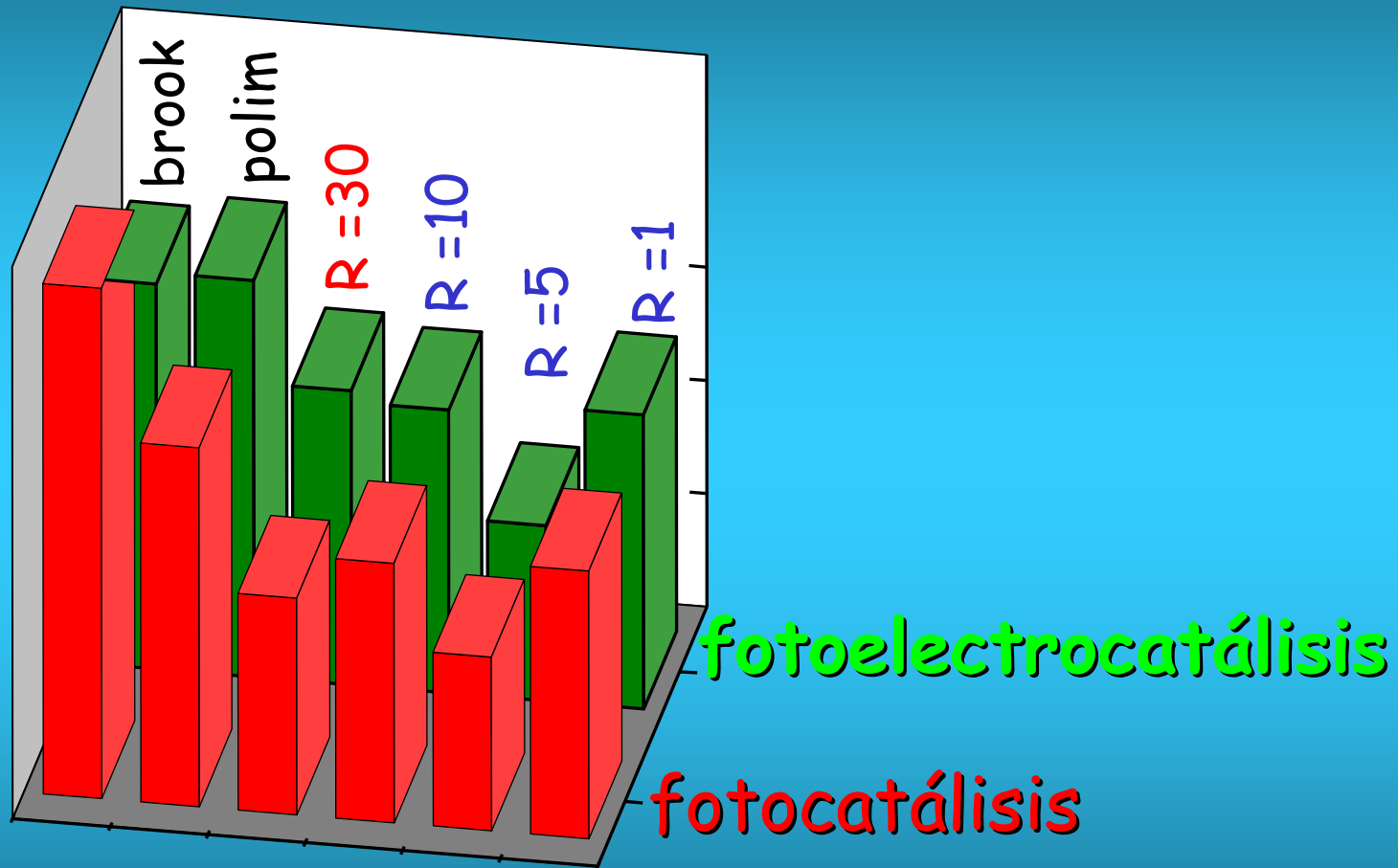
fotoelectrocatalisis

Films Mesoporosos



n_{deg} mas vale sólido cristalino que área grande

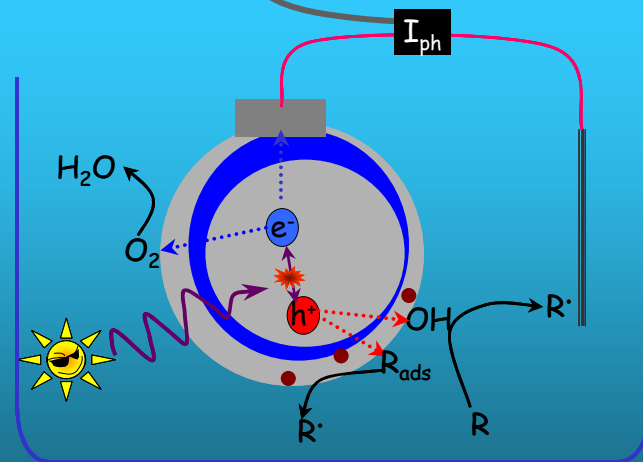
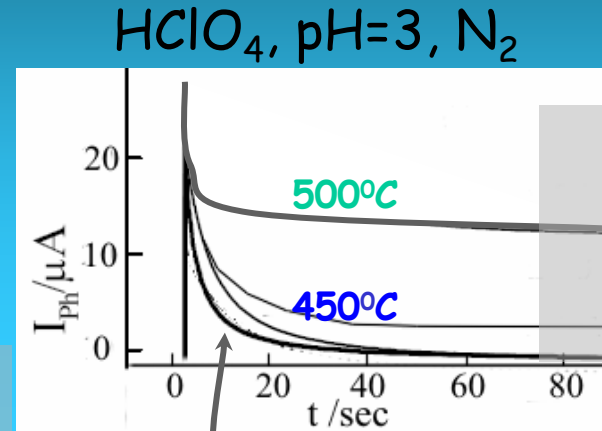
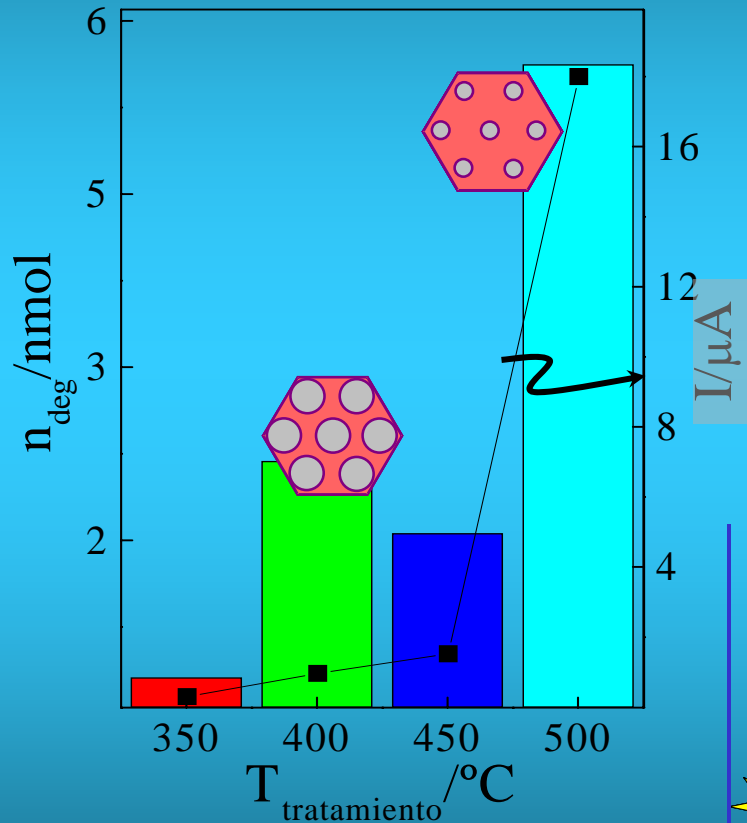
fotocatálisis vs. fotoelectrocatalisis



T=400°C

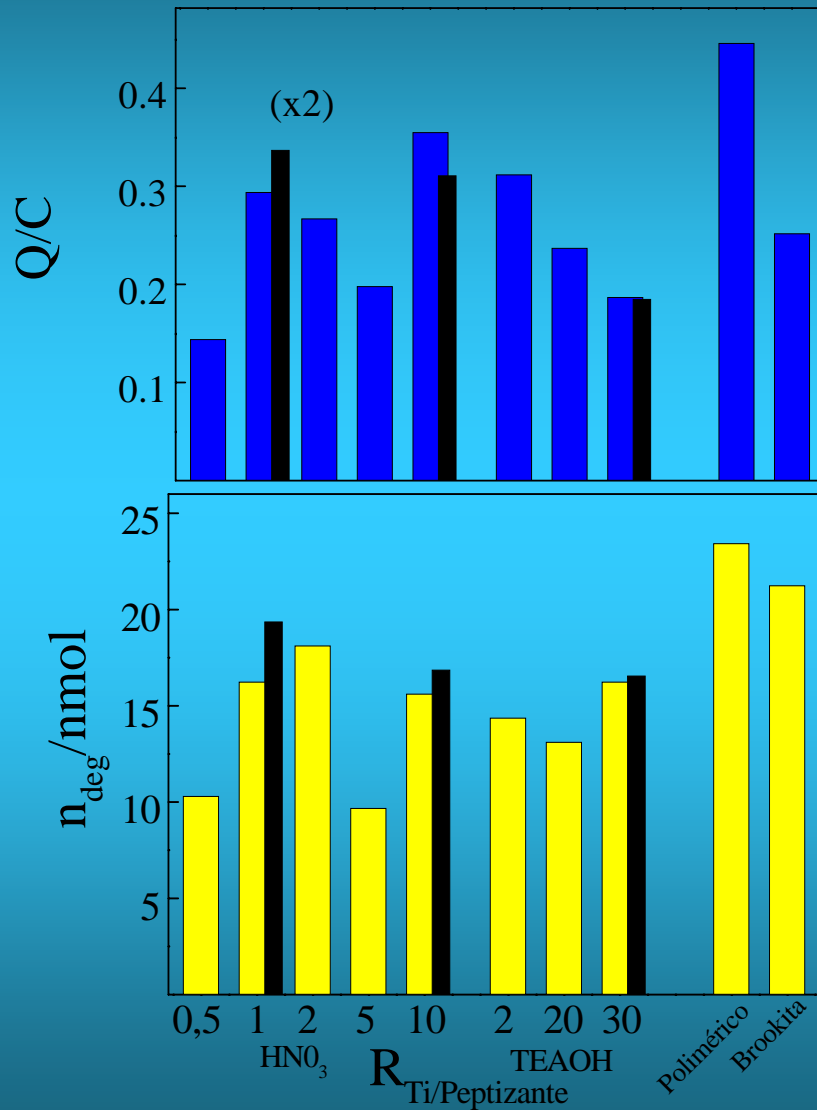
fotoelectrocatalisis

Films Mesoporosos



I_{ph} : mas vale sólido cristalino que área grande

films: carga y moles degradados



trampas de huecos: Ti(III)

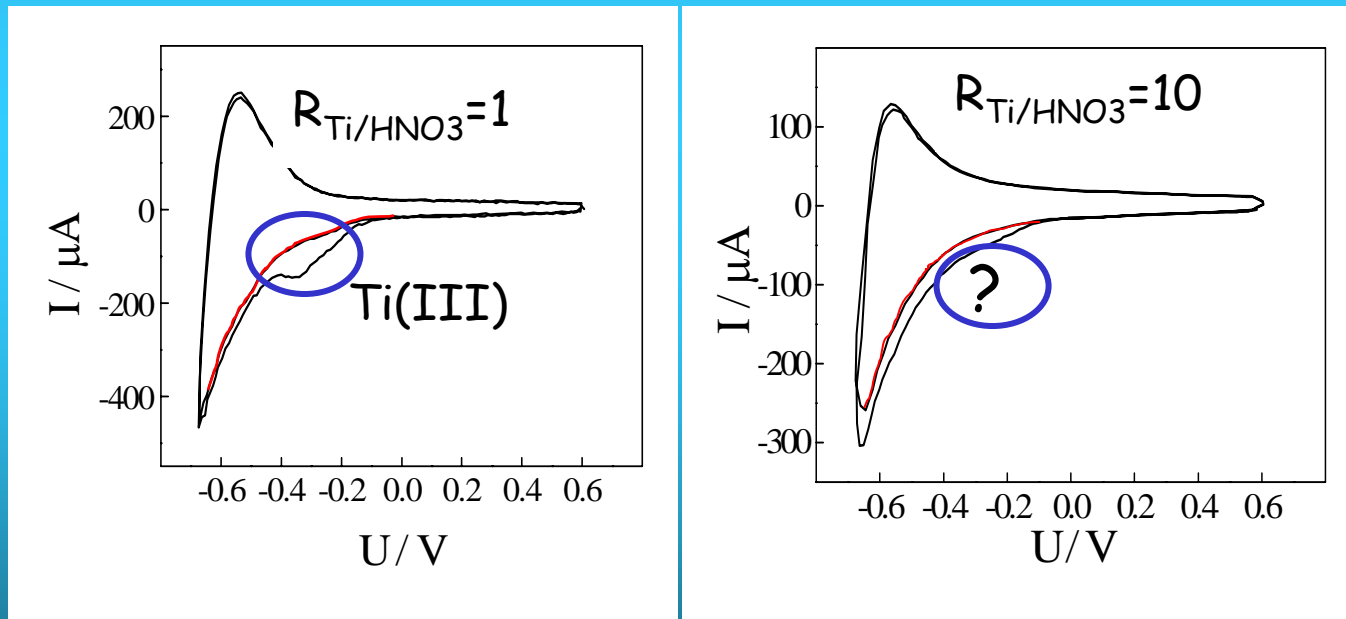
Estudios Previos

Partículas: FTIR Hoffmann, M. et al. J. Phys Chem B 2002

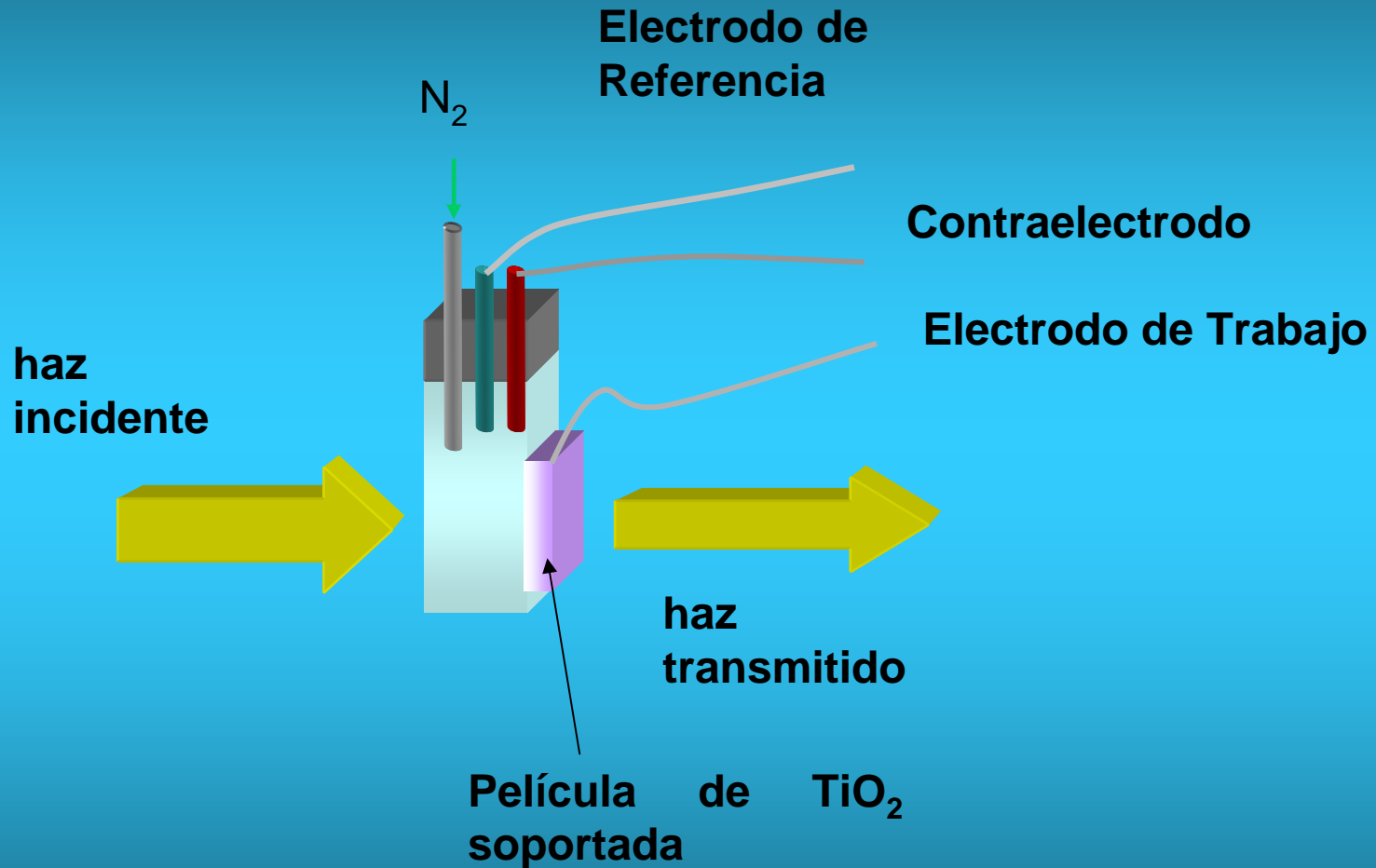
EPR Thurnauer, M; et al J. Phys Chem B. 2002

Películas: UPS, XPS, PDS varios

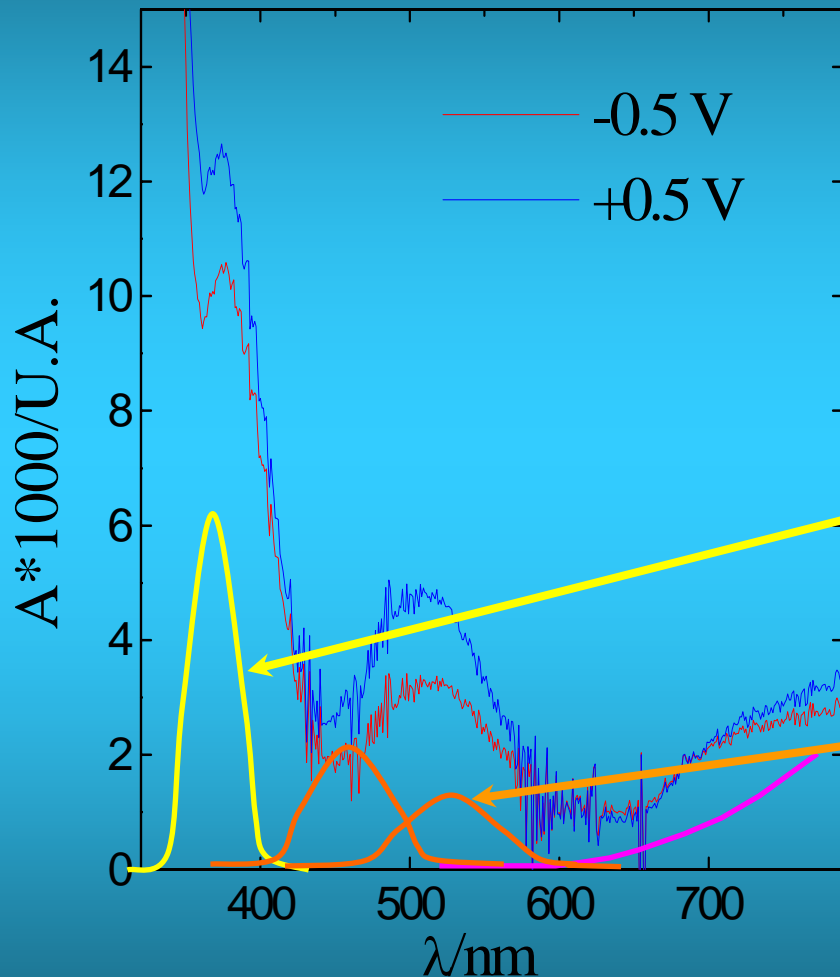
voltametría cíclica in-situ Lindquist, S. et al; J. Phys Chem. B 2001



trampas de huecos: Ti(III)



trampas de huecos: Ti(III)

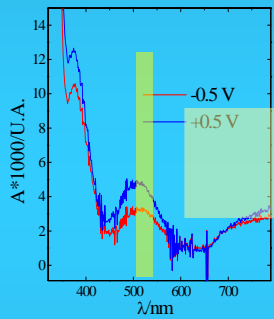


[SA] = 10^{-3} M pH=3

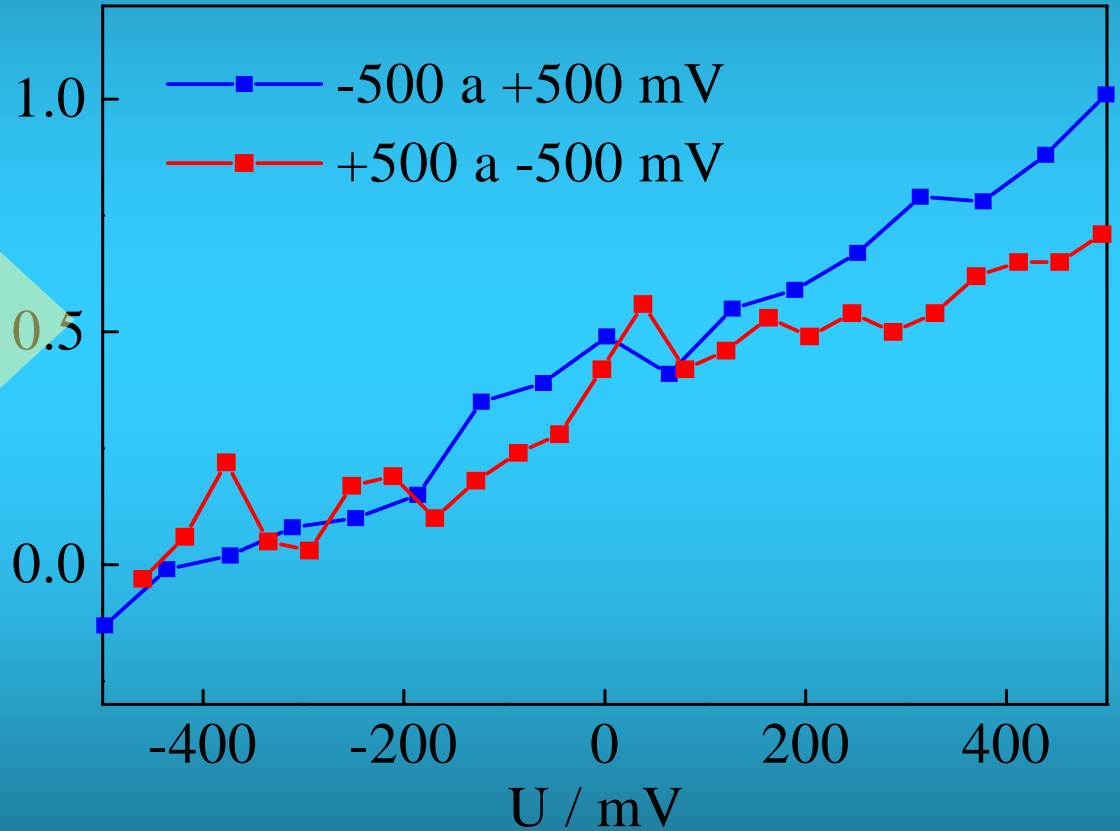
TCLM [SA-Ti^{IV}]

transiciones d-d Ti^{III}
 ${}^2T_{2g} \rightarrow {}^2E_g$ permitidas por spin
prohibidas por simetría

trampas de huecos: Ti(III)



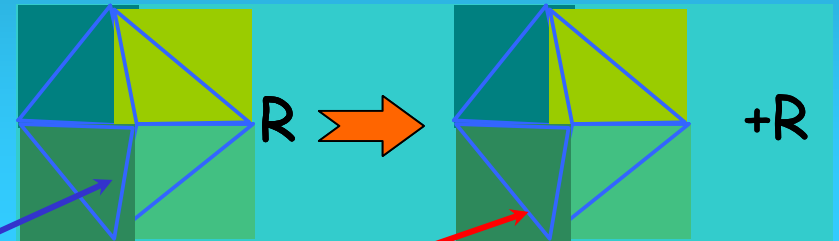
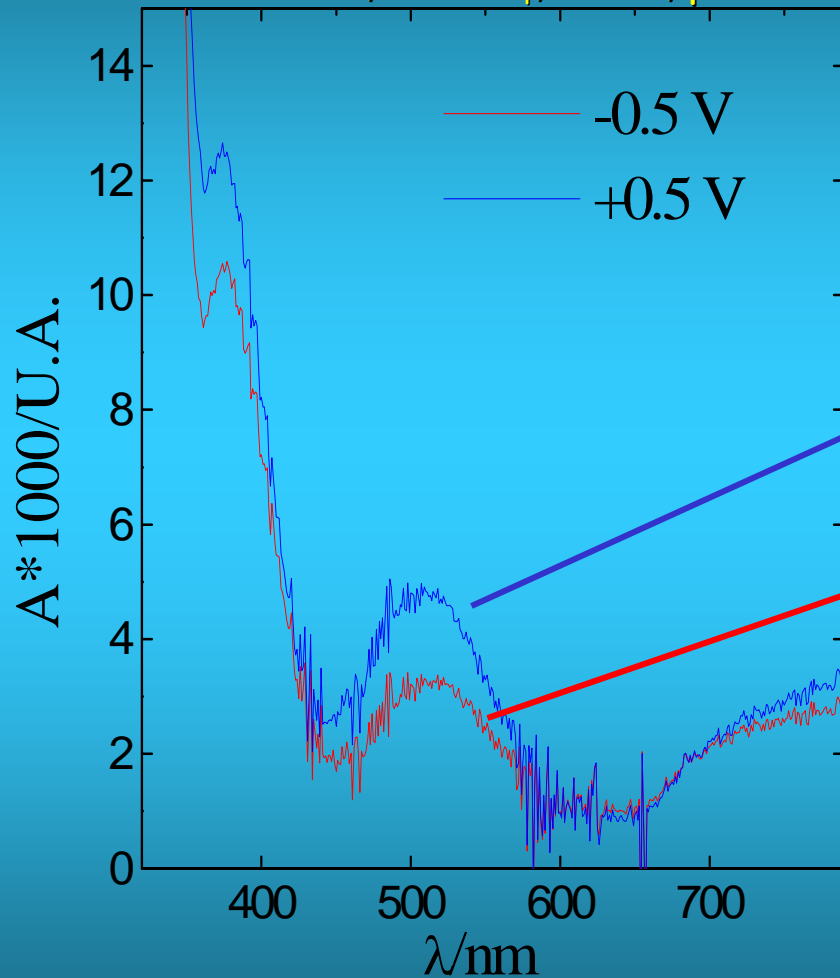
$A_{530 \text{ nm}} \cdot 1000 / \text{U.A.}$



salicilato, NaClO_4 , 0.1M, pH=3

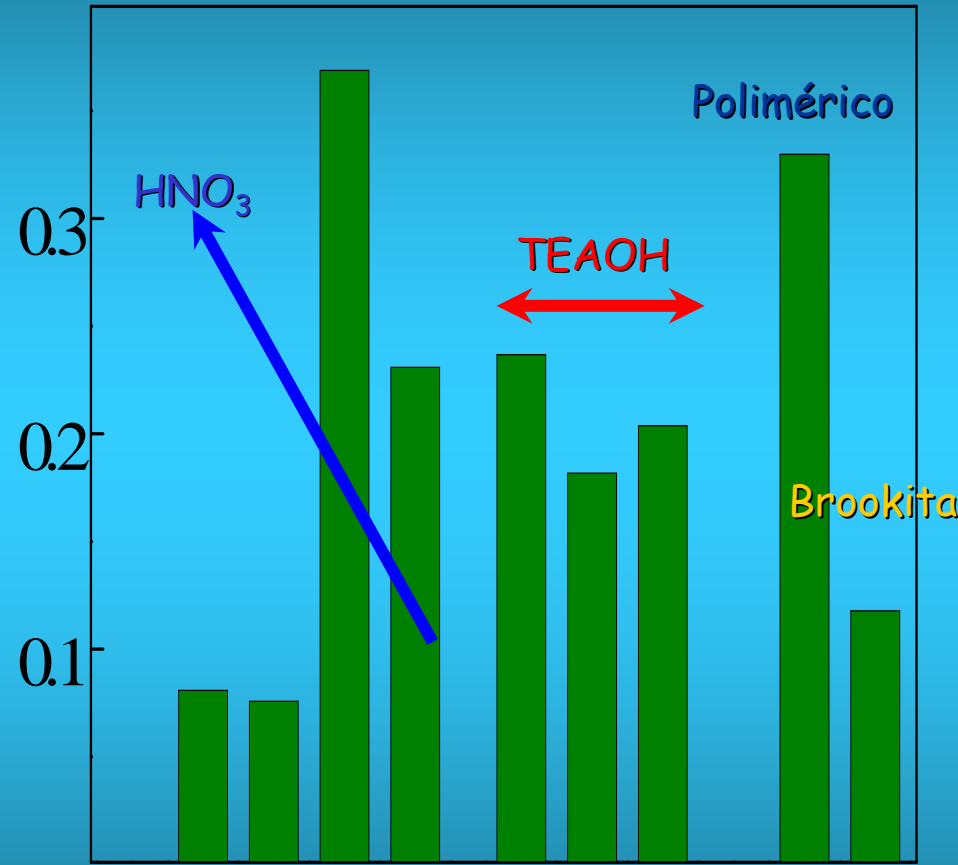
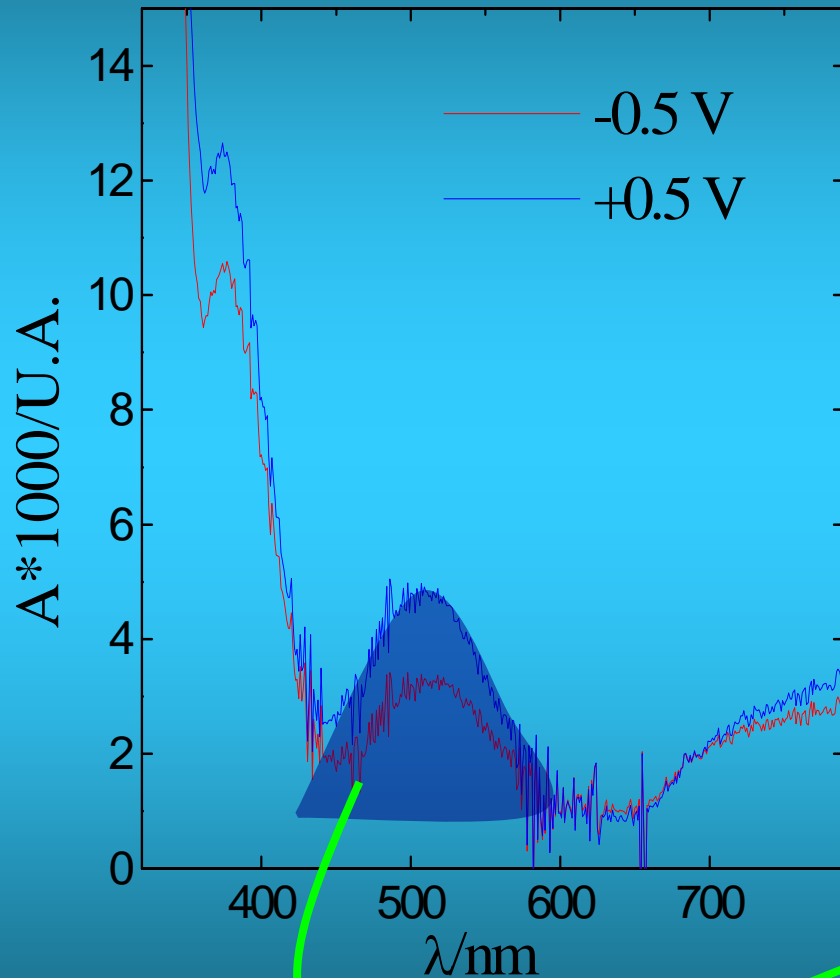
trampas de huecos: Ti(III)

salicilato, NaClO_4 , 0.1M, pH=3



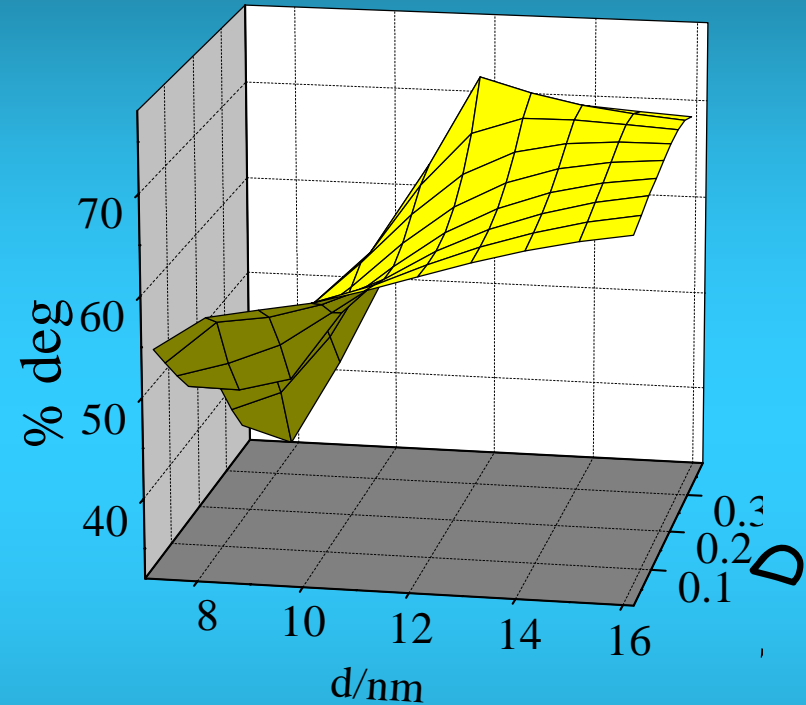
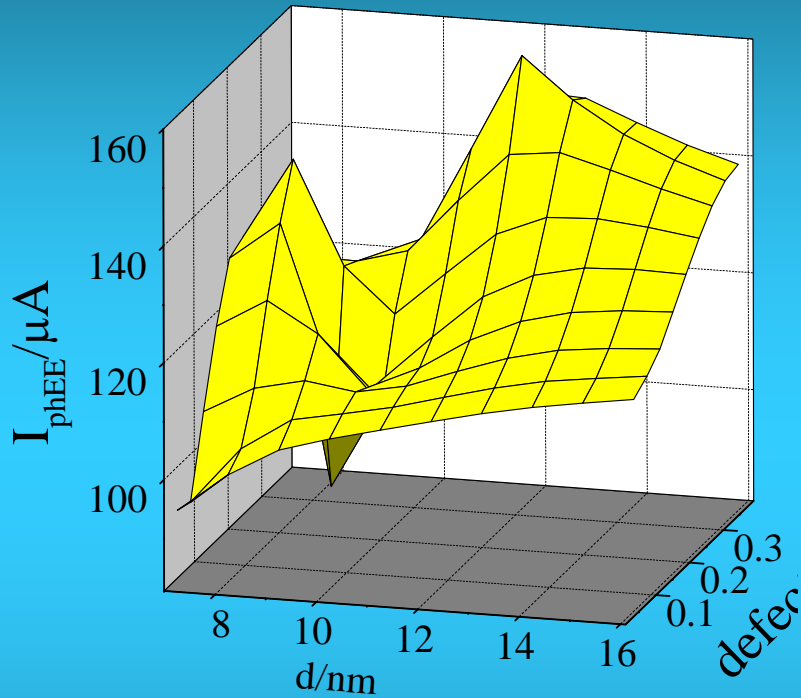
desorción verificada por FTIR
verificado para otros adsorbatos

trampas de huecos: Ti(III)



$$D \propto [\text{Ti(III)}]$$

trampas de huecos y electrones



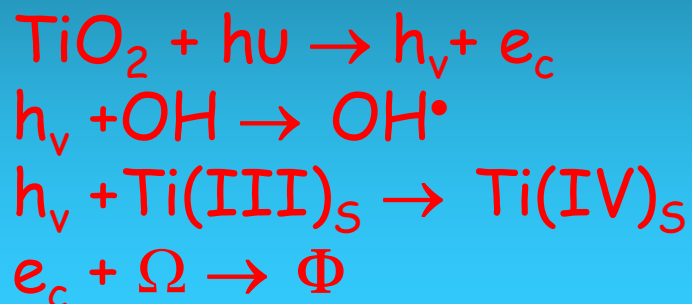
$$I_{phEE} = f([\text{Ti(III)}_s], [\Omega])$$

$$n_{deg} = f([\text{Ti(III)}_s], [\Omega])$$

D

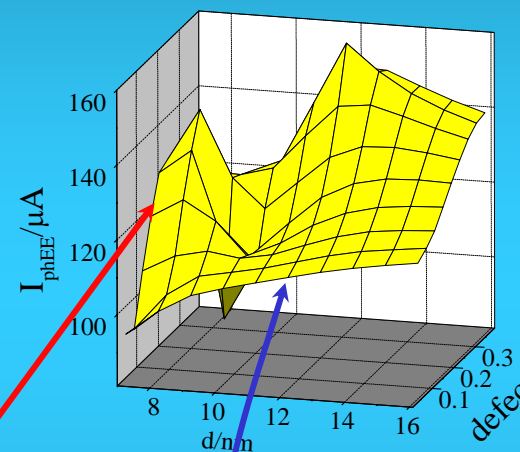
$\frac{1}{d}$

rol de trampas de huecos y electrones



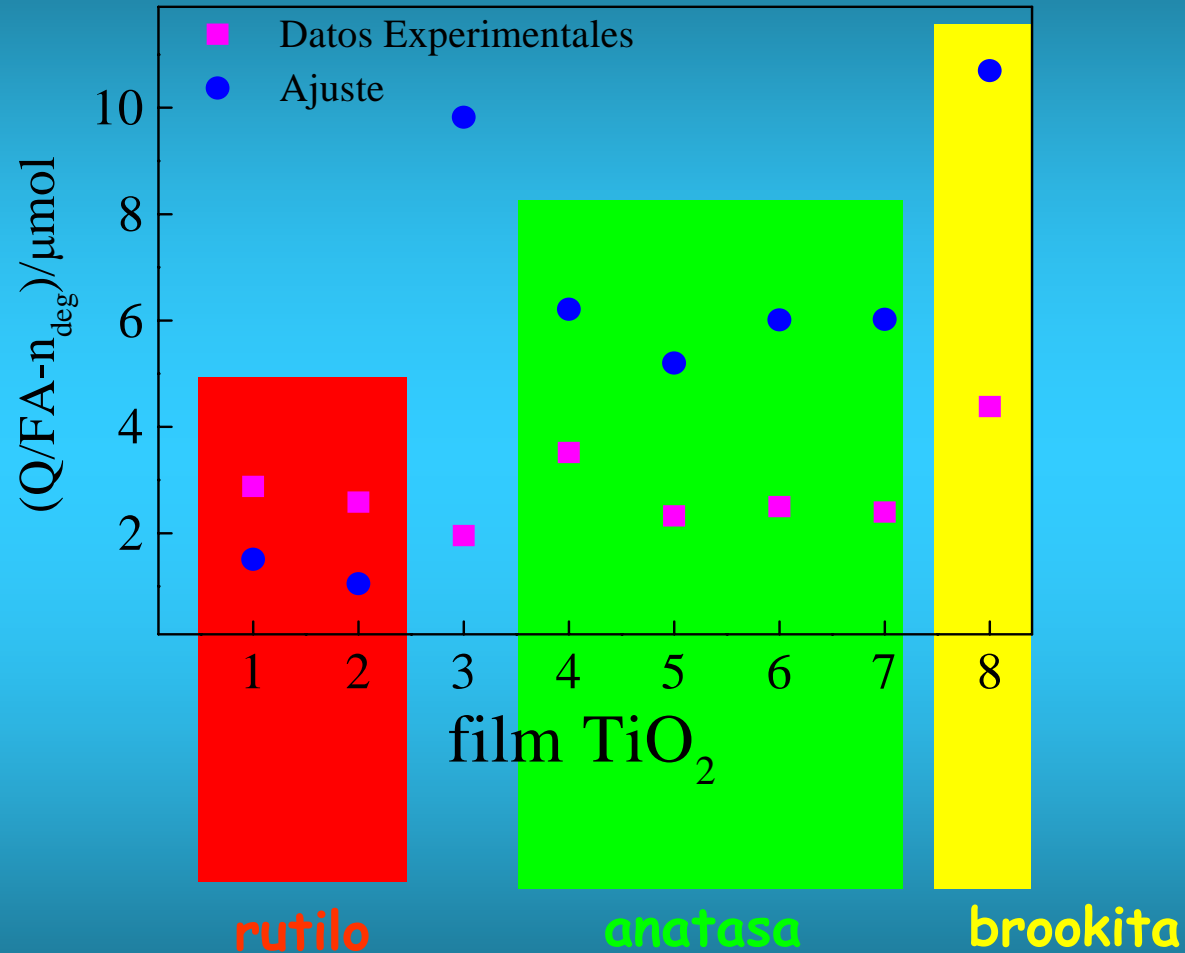
$$\frac{\partial(h_\nu)}{\partial t} = \frac{\partial(e_c)}{\partial t}$$

$$\frac{I_{\text{phEE}}}{FA} = k_2(h_\nu)(\text{OH}) + k_3(h_\nu)[\text{Ti(III)}_S] - k_5(e_c)[\Omega]$$



rol de trampas de huecos y electrones

Carga, moles degradados y microestructura



$$\frac{Q_d}{FA} - n_{deg} = A + B[Ti(III)_s] - C[\Omega]$$

conclusiones

SÍNTESIS

Sitios de recombinación Ω

Cristalinidad

Defectos Ti(III)

Absorbancia

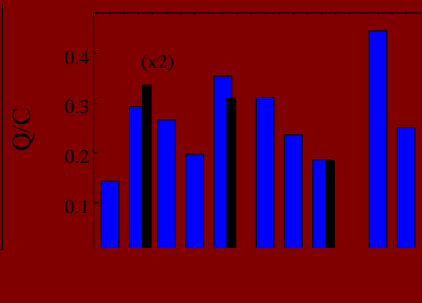
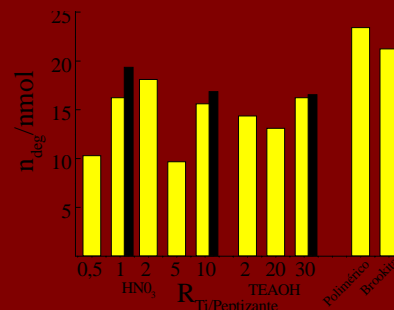


ACTIVIDAD CATALÍTICA

Fotoelectroquímica

SA, O₂

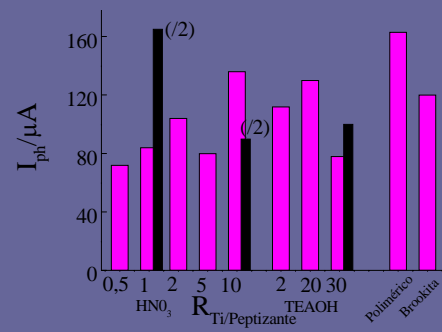
n_{deg}, Q_d



+

$I_{ph, EE}$

NaClO₄, N₂



With a little help of my friends

Roberto Candal
Matias Jobbagy
Claudia Marchi
Mauricio Calvo
Mercedes Perullini
Eugenio Otal
Carolina
Valeria DellaSavia



Galo Soler-Illia
Paula Angelome
Elsa Sileo

gracias a: UBA, anpcyt, conicet por \$\$

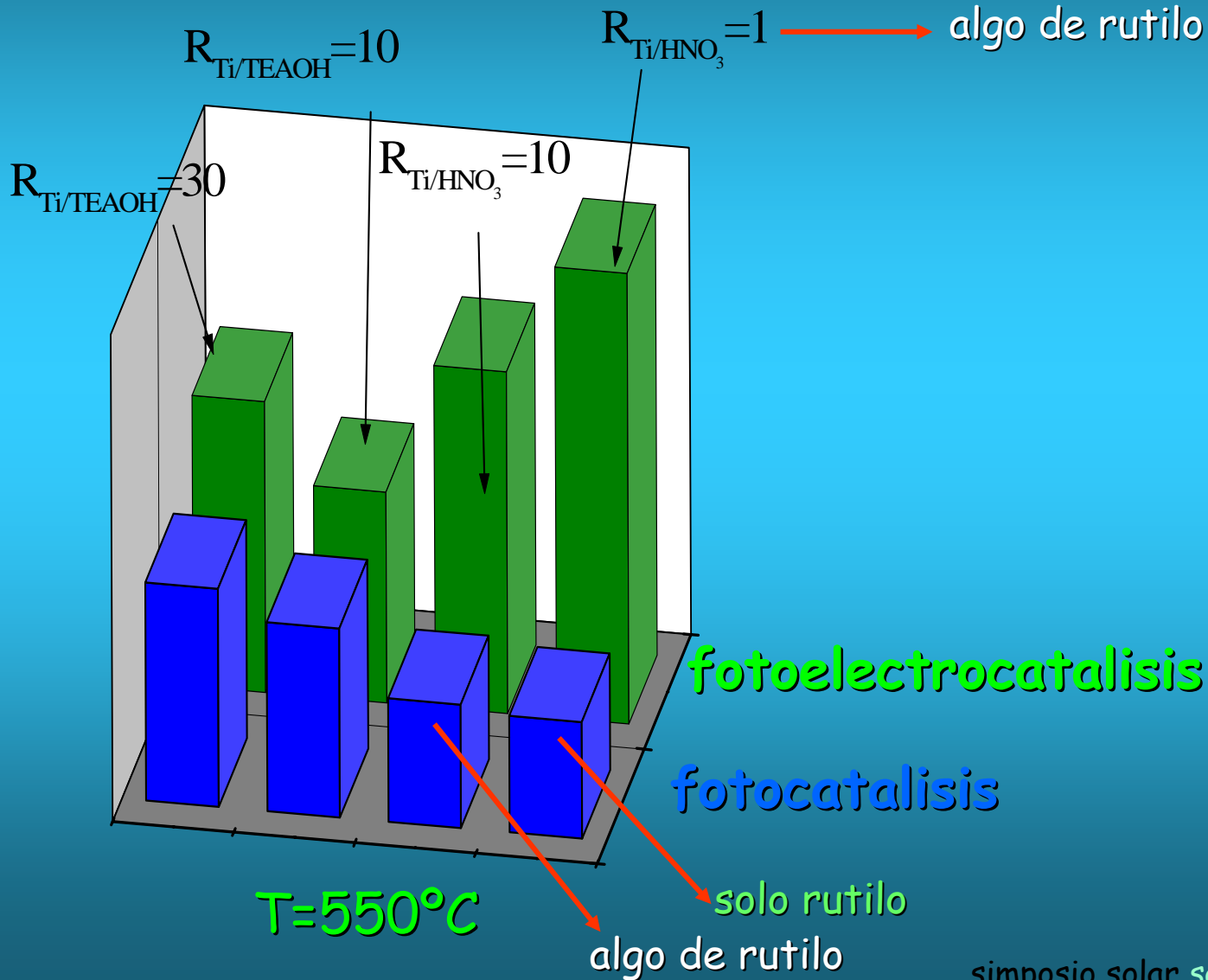
Irene, Andres, Raul

propiedades films

Tabla 4.3. Espesor e índice de refracción obtenido para películas de 1 y 4 capas tratadas a 400°C

Película	Espesor (nm) 1 capa	n 1 capa	Espesor (nm) (4 capas)	n 4 capas	Porosidad 4 capas (%)
$R_{Ti/HNO_3}=1$	84	2.11	256	2.09	30
$R_{Ti/HNO_3}=5$	45	1.85	261	1.92	45
$R_{Ti/HNO_3}=10$	54	1.76	275	1.89	50
$R_{Ti/TEAOH}=20$	85	1.72	295	1.81	56
$R_{Ti/TEAOH}=30$	104	1.78	324	1.85	54
Polimérico	77	1.85	242	2.18	24
Polimérico + F127 (400°C)	250	1.66			72
Brookita			320	1.74	65

fotocatalisis vs fotoelectrocatalisis



celda

