Electrodeposited zinc oxide nanorods ALD-coated with iron oxide

Photocatalytic and photoelectrochemical properties

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Combining two semiconductors to make one photoanode

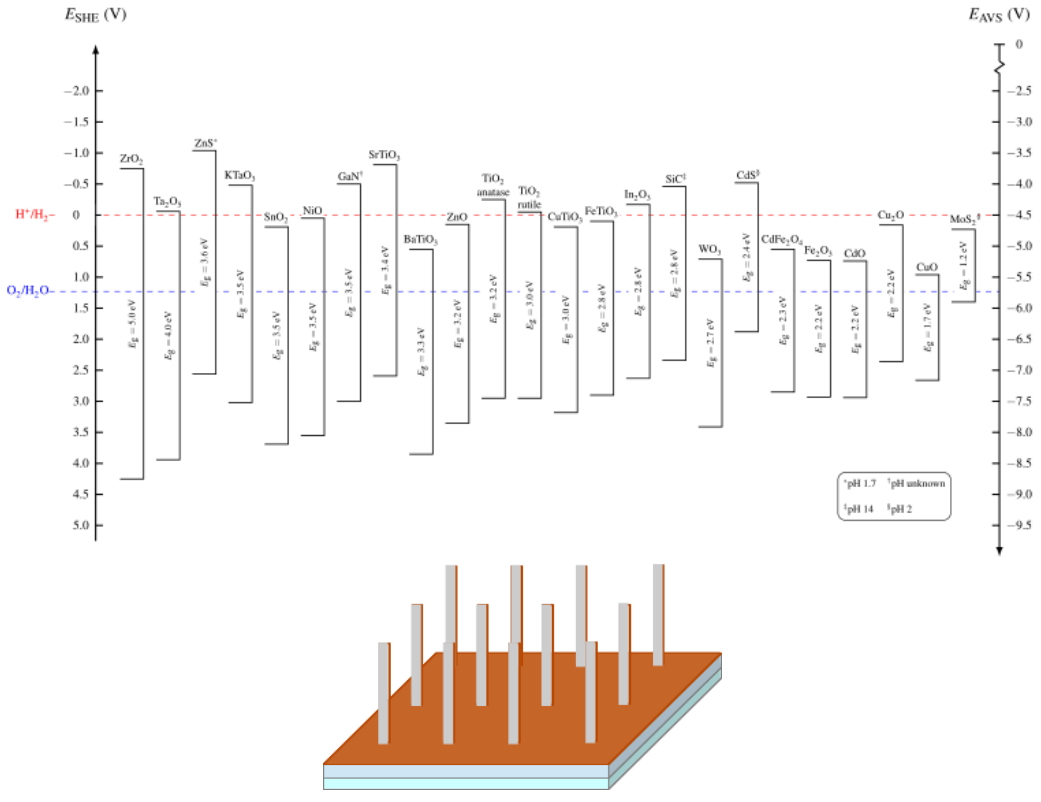
Combining two semiconductors. . .

to absorb more light and more colours,
to better separate photoexcited electron-hole pairs

. . . ZnO nanorods coated with varying thickness of iron oxide

nanorods cause increased surface area,
ZnO is white, iron oxide commonly red,
band edges fairly well matched

Tailoring morphology and electronic band structure



Electrodeposition of zinc oxide, ALD of iron oxide

Electrodeposition

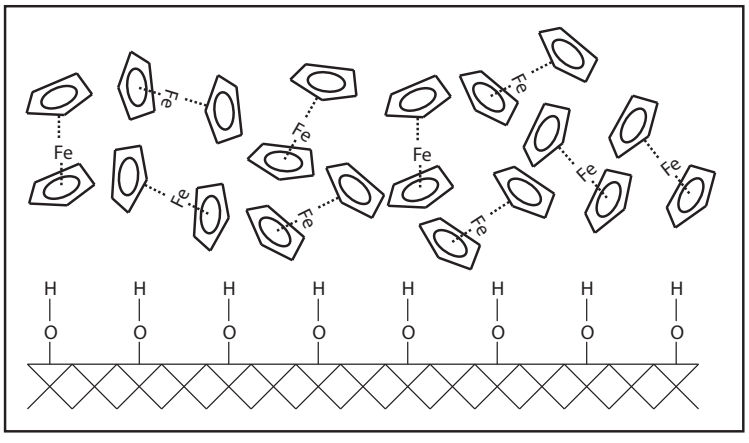
Potentiostatic cathodic deposition for 1.5 h in $ZnCl_2$(aq), three-electrode cell, Ag/AgCl RE, Pt-wire CE

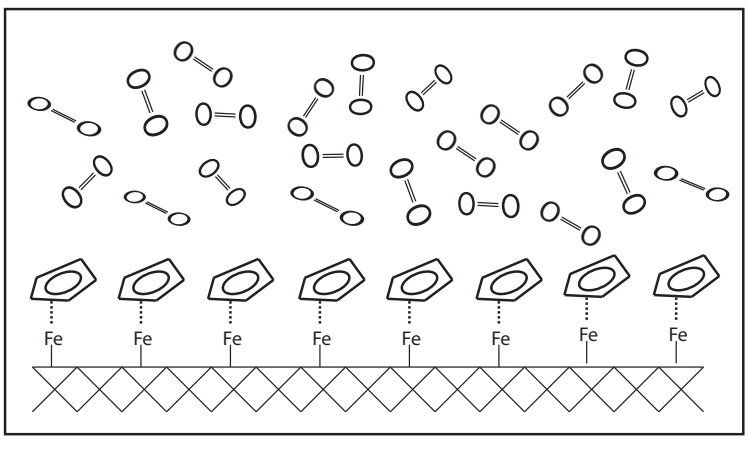
Atomic-layer deposition

Cycles of ferrocene and oxygen gas, using Picosun ALD reactor at 450 °C,
conditions targeted for hematite formation,
Number of cycles varied between 35 to 100 (< 25 nm)

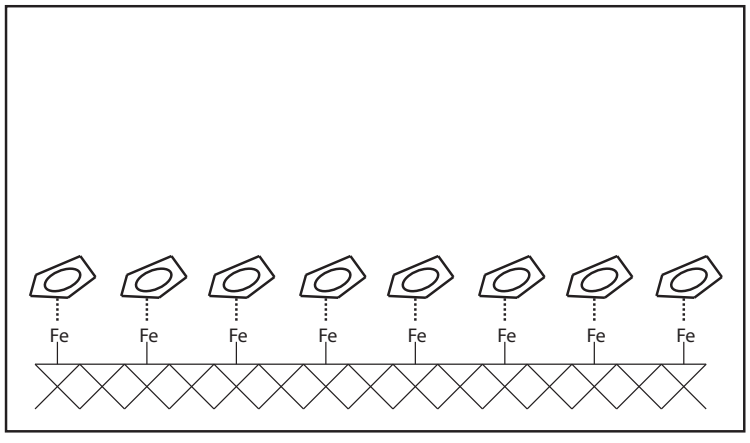
Atomic-layer deposition mechanism

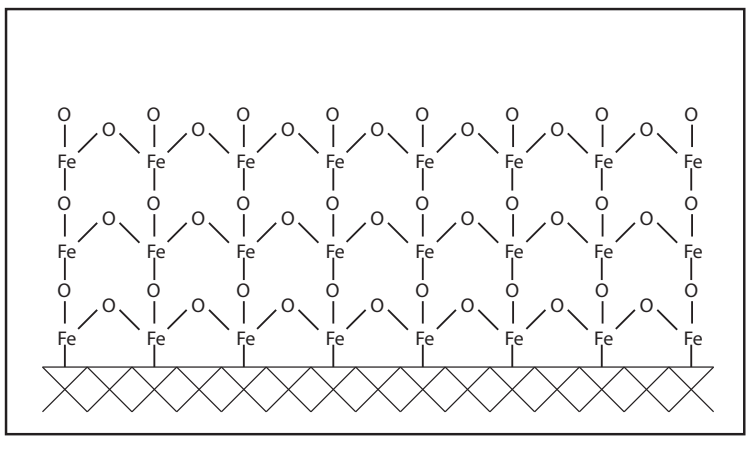
Reactive cycle





Inert cycle

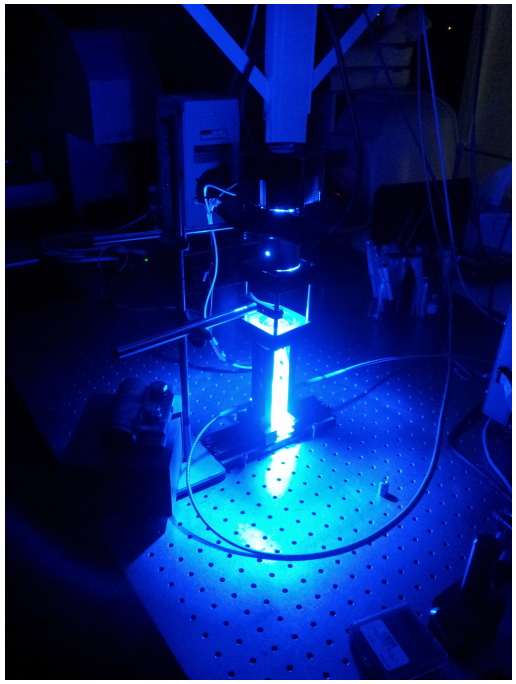


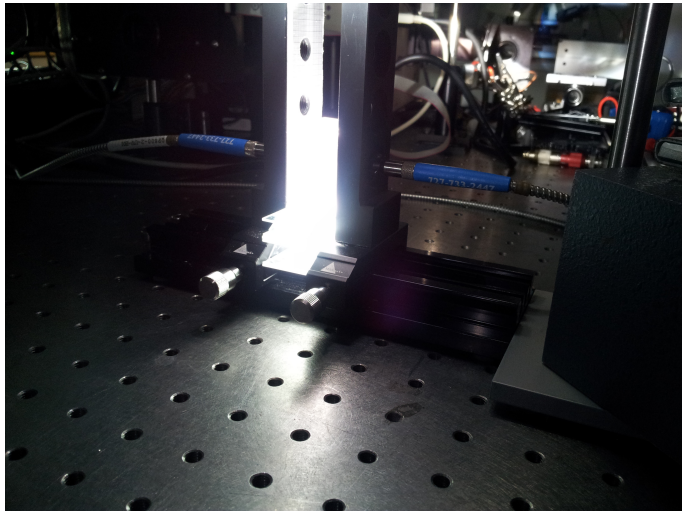


In-situ tracking of dye degradation

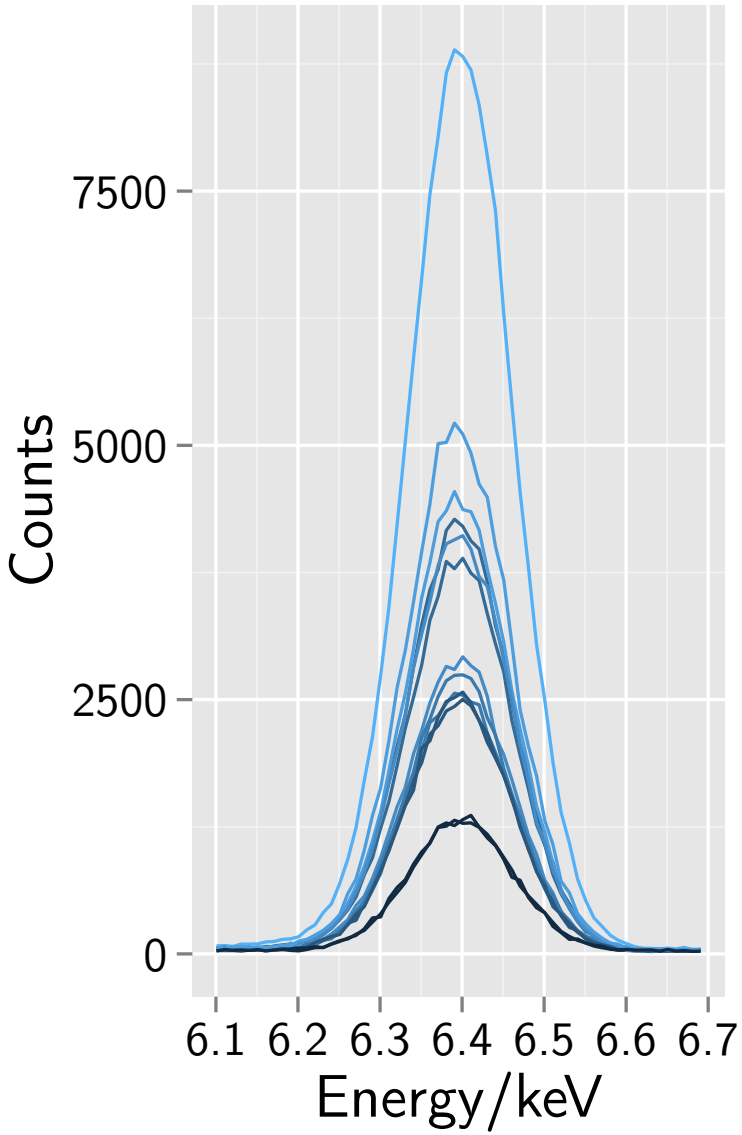
Degradation of azo dye in aqueous soln. under visible-light

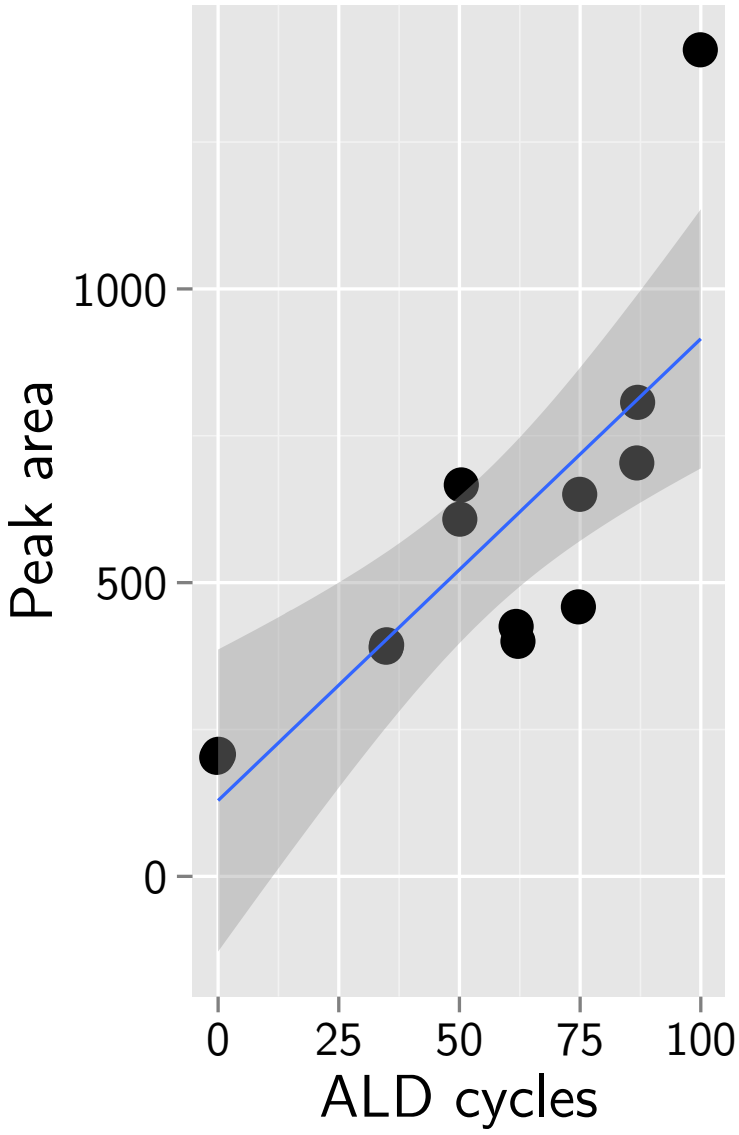
Dye: eriochrome black T, 5 mg l^{-1}.
Light source: 50 W 450 nm LED.





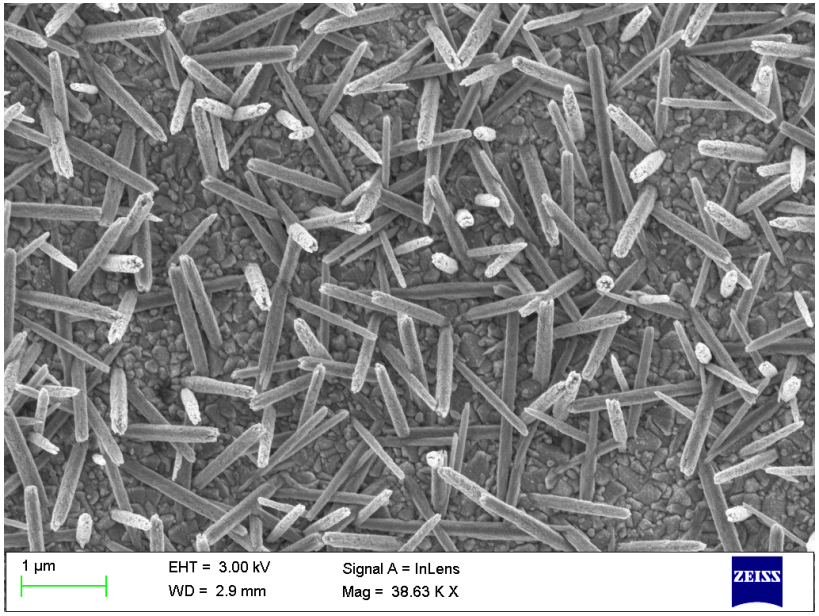
XRF: Fe KL_3 transition increases with ALD cycles



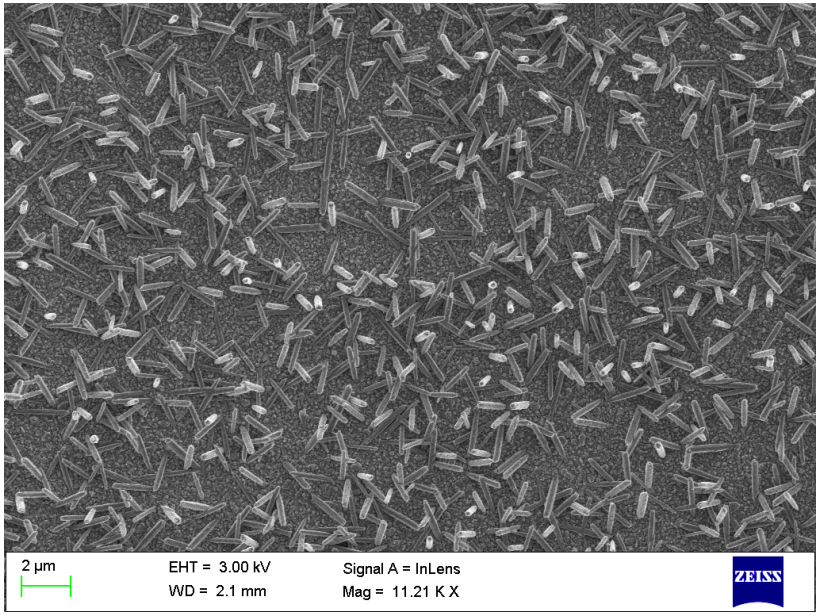


Iron-phase is so thin that it does not affect morphology

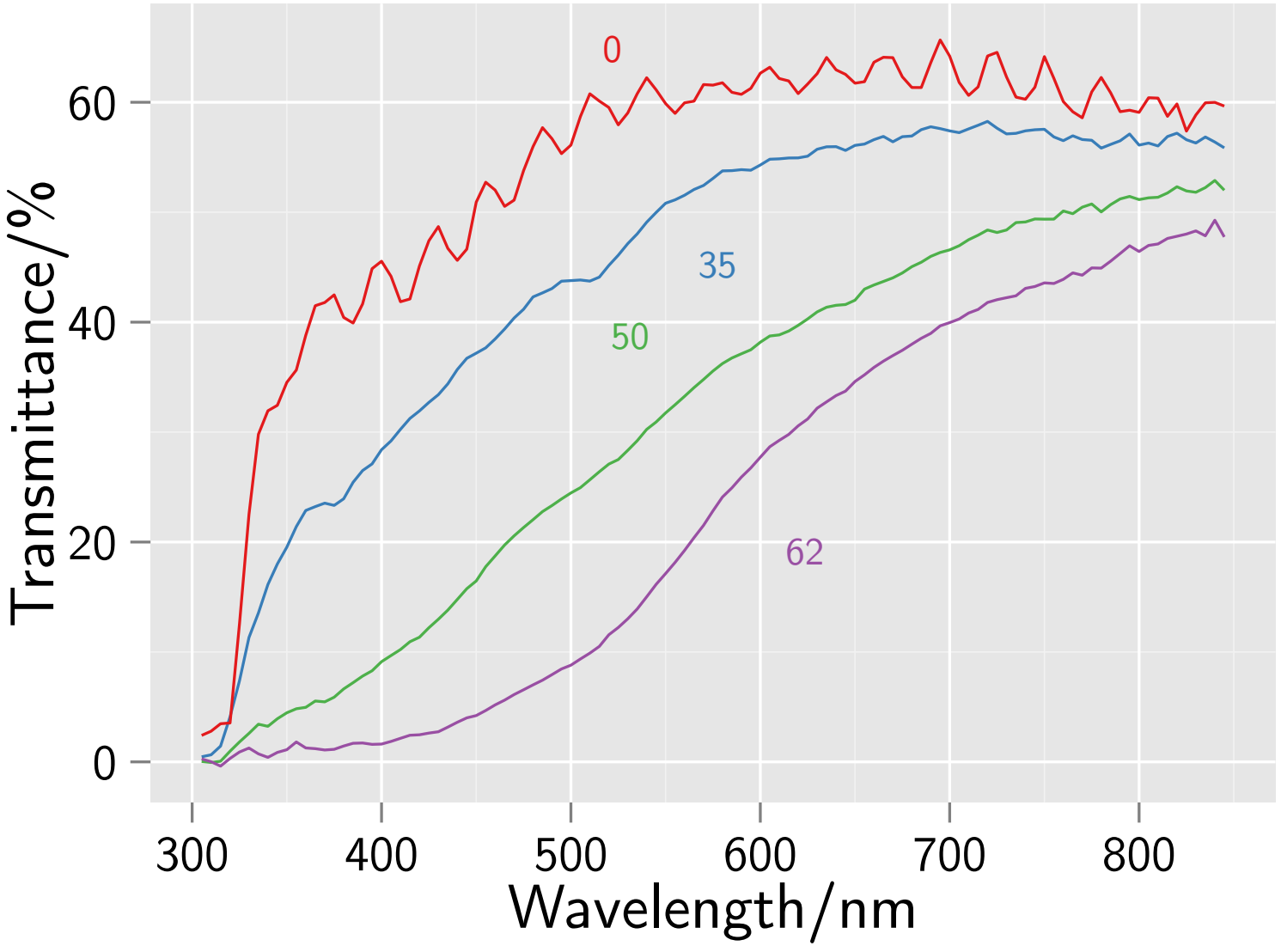
Before



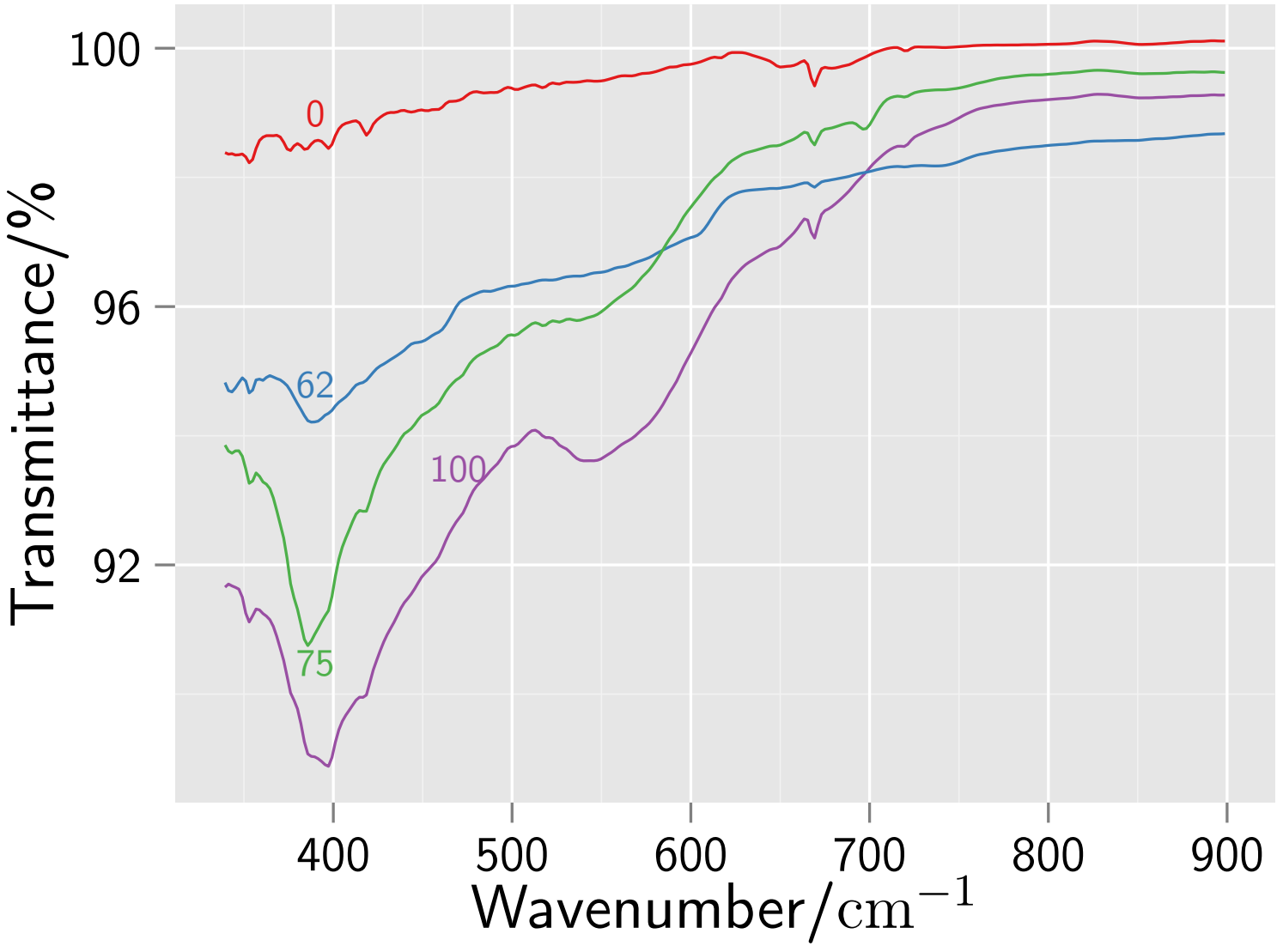
After



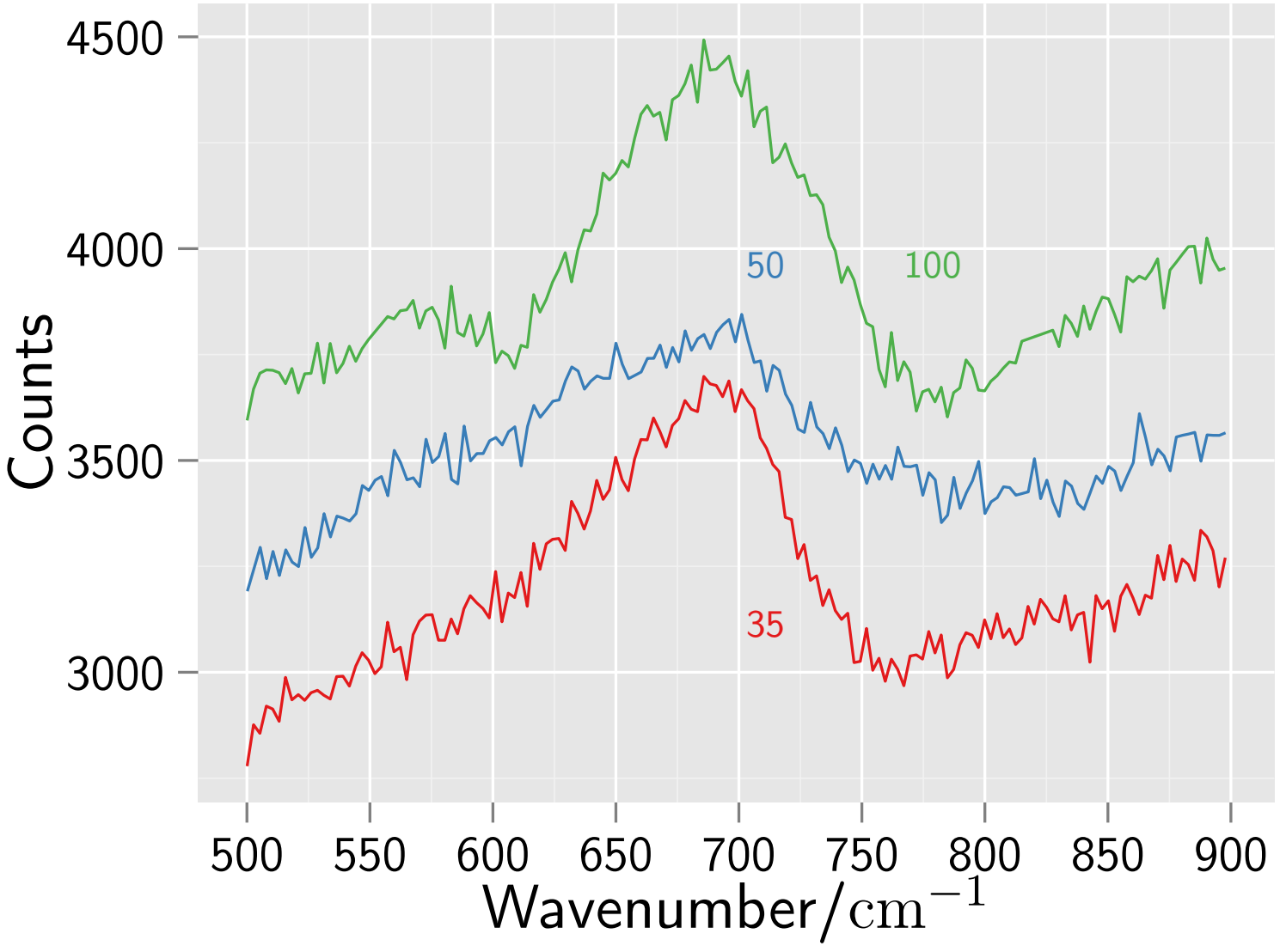
Optical spectroscopy: overall absorption increases



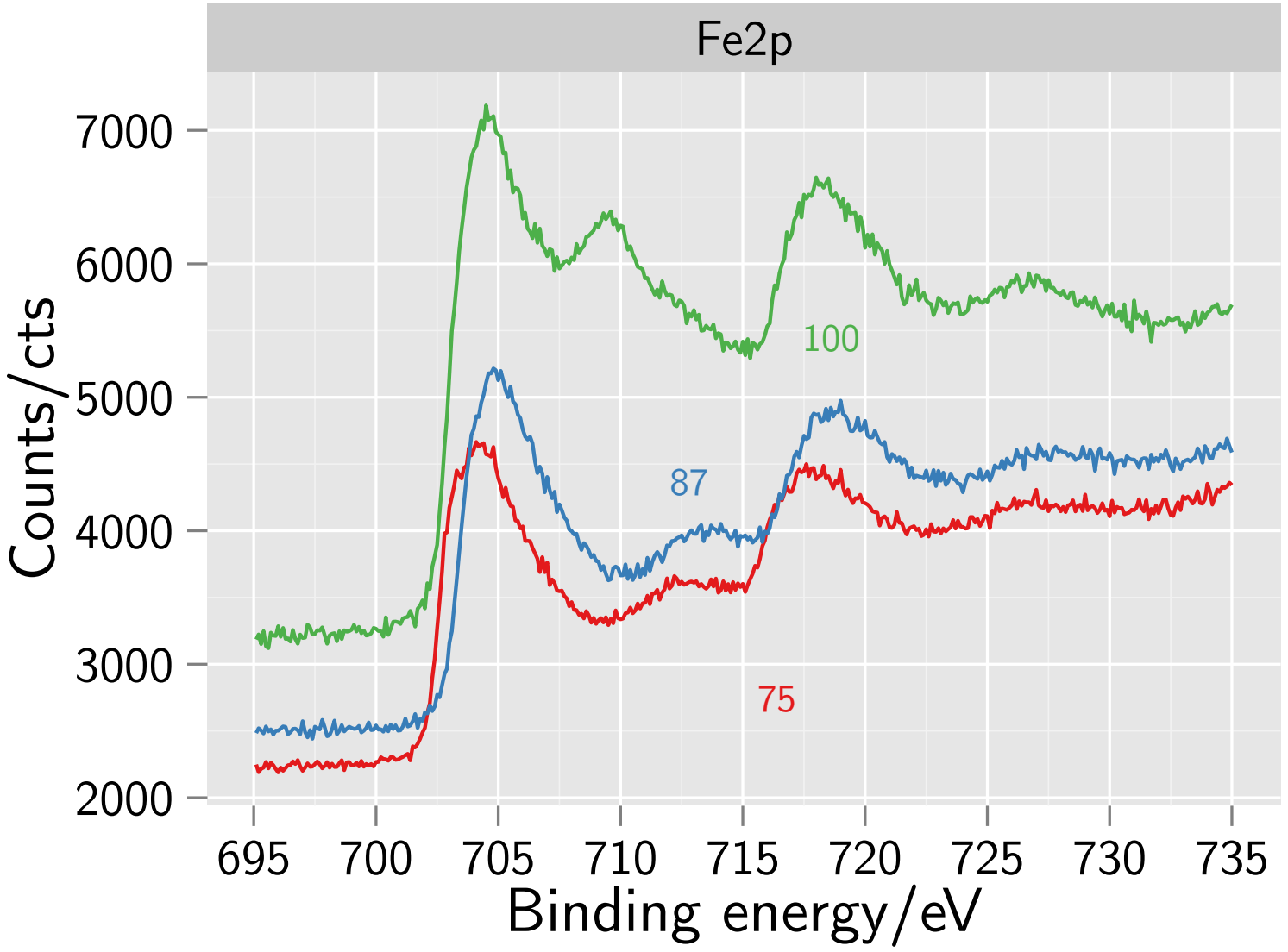
ATR-FTIR spectroscopy: hard-to-interpret weak signal



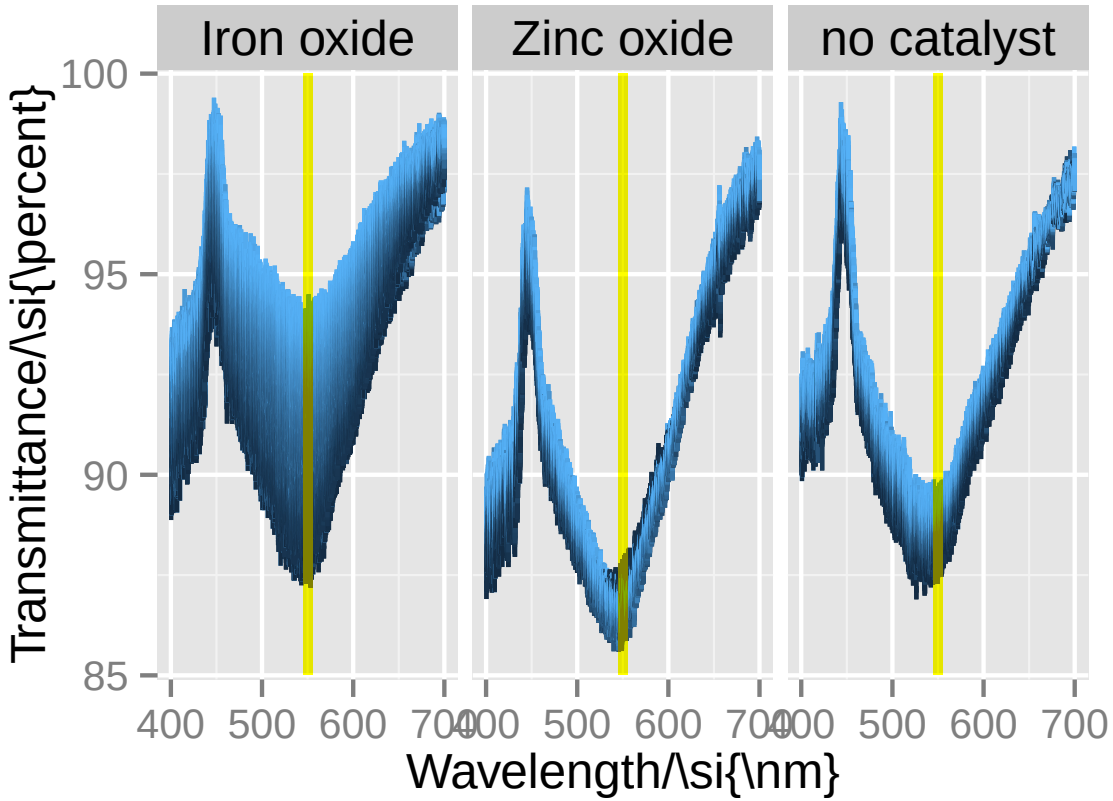
Raman spectroscopy: perhaps not pure hematite...



XPS: . . . hematite after all?



Photocatalytic effect improves with thickness



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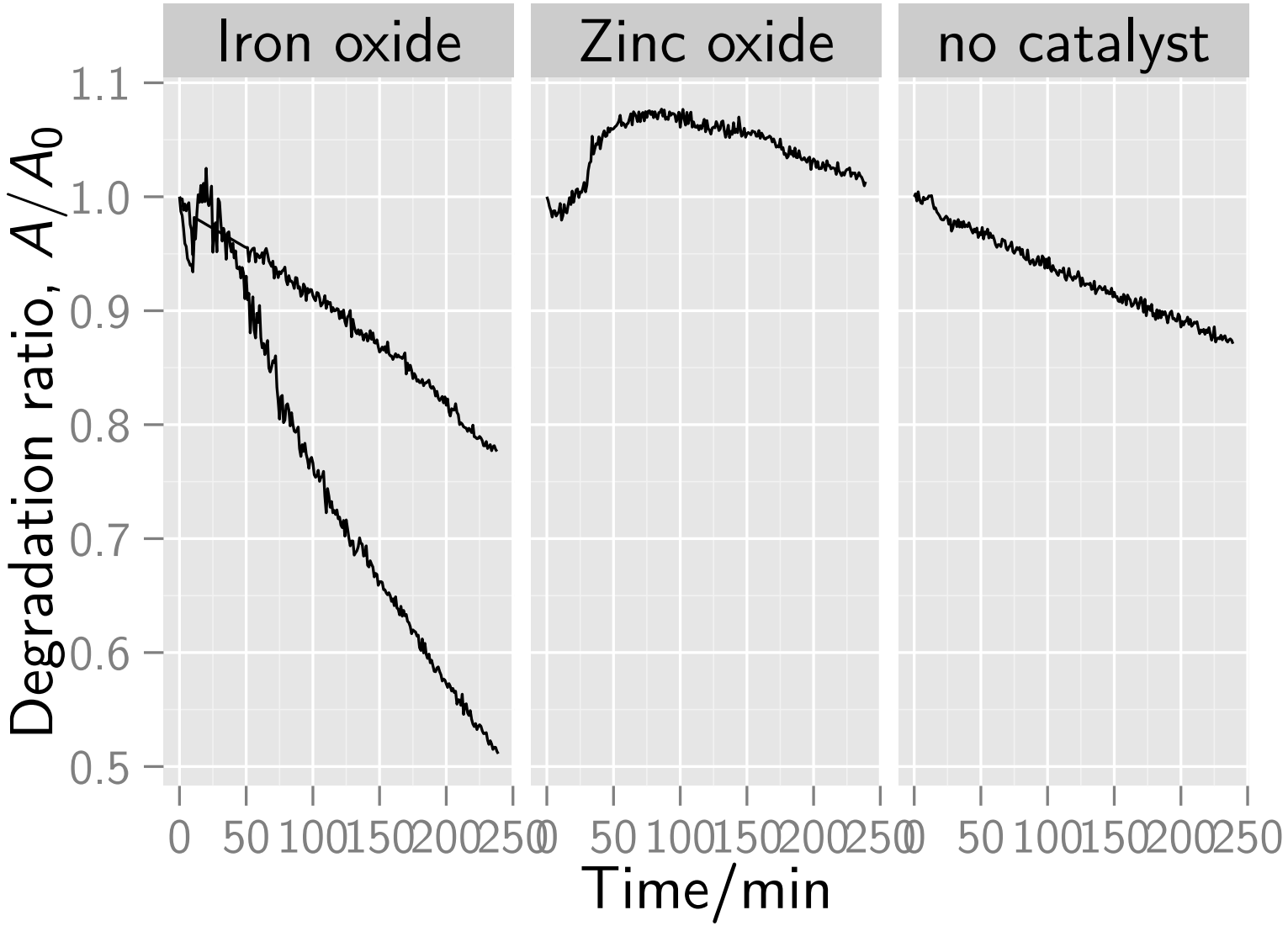


Conclusions

Photocatalytic activity improves with increasing thickness

but even our 'thickest' coating is really thin. Perhaps the biggest gain is that the samples show very good stability under irradiation. This is due to the iron oxide coating.

Iron oxide phase

XPS strongly indicates hematite,
but poor crystallinity and very thin iron oxide layer complicates analysis.

Conclusions

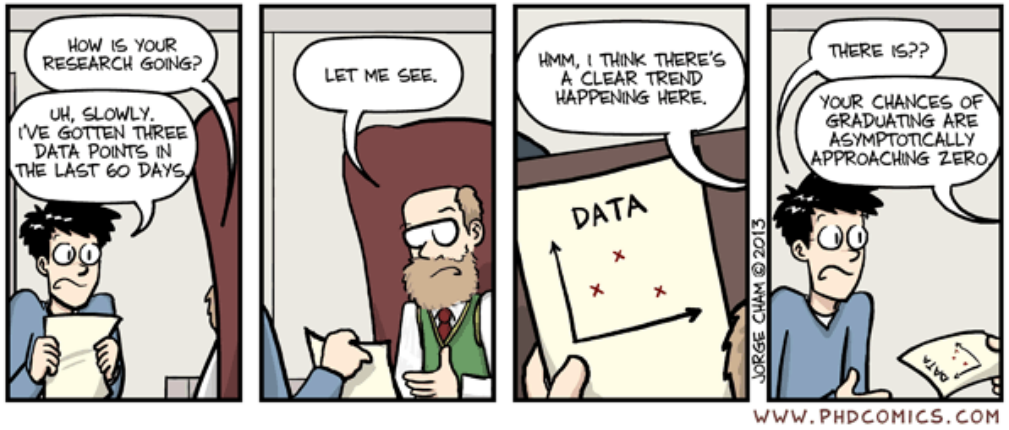
Simple preparation gives 3D-nanostructure

Addition of ultrathin conformal iron oxide layer improves stability greatly, and makes the photoanode active in visible light.

Low PC activity thought to be partly due

to small amount of visible-light-active catalyst on each sample.

Trending


HOW IS YOUR RESEARCH GOING?
UH, SLOWLY. I'VE GOTTEN THREE DATA POINTS IN THE LAST 60 DAYS.
LET ME SEE.
HMM, I THINK THERE'S A CLEAR TREND HAPPENING HERE.
DATA
THERE IS??
YOUR CHANCES OF GRADUATING ARE ASYMPTOTICALLY APPROACHING ZERO.
DATA
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Electrodeposition

Electrodeposition of zinc oxide

$$\frac{1}{2}\,\mathrm{O_2} + \mathrm{H_2O} + 2\,\mathrm{e^-} \longleftrightarrow 2\,\mathrm{OH^-} \quad (1)$$

$$\mathrm{Zn^{2+}} + 2\,\mathrm{OH^-} \longrightarrow \mathrm{ZnO} + \mathrm{H_2O} \quad (2)$$

Dissolved oxygen in the electrolyte is reduced to hydroxide ions, local pH increase at the electrode's surface precipitates zinc hydroxide, zinc oxyhydroxide, and zinc oxide (temperature dependent).

Other oxygen-sources have been used, e.g., nitrate ions in solution, water. Bubbling oxygen allows easy control of O_2 concentration, and leaves no by-products.

Electrodeposition

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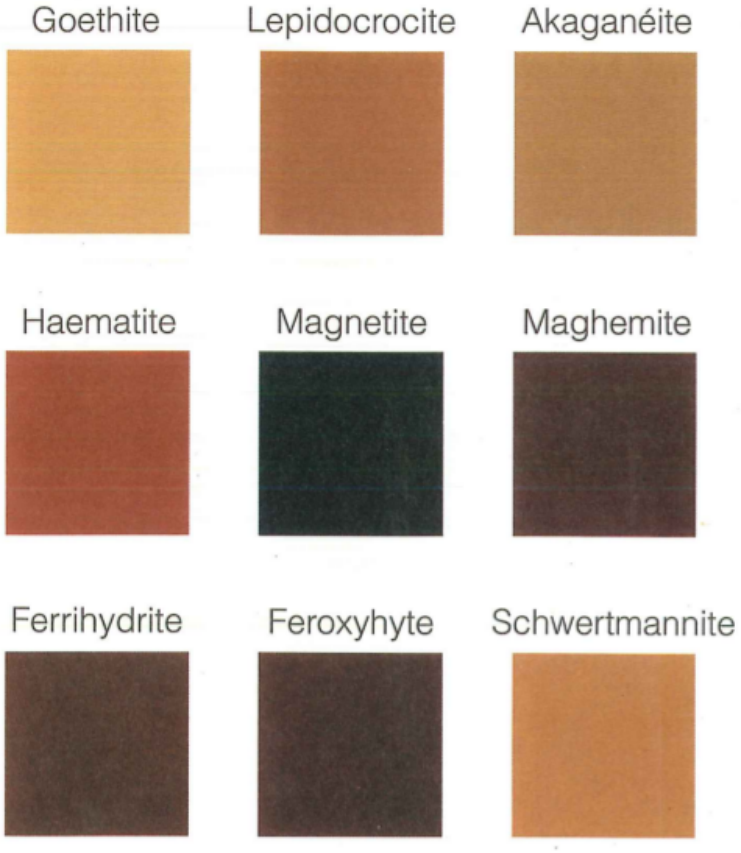
Iron oxide comes in a variety of structures and compositions

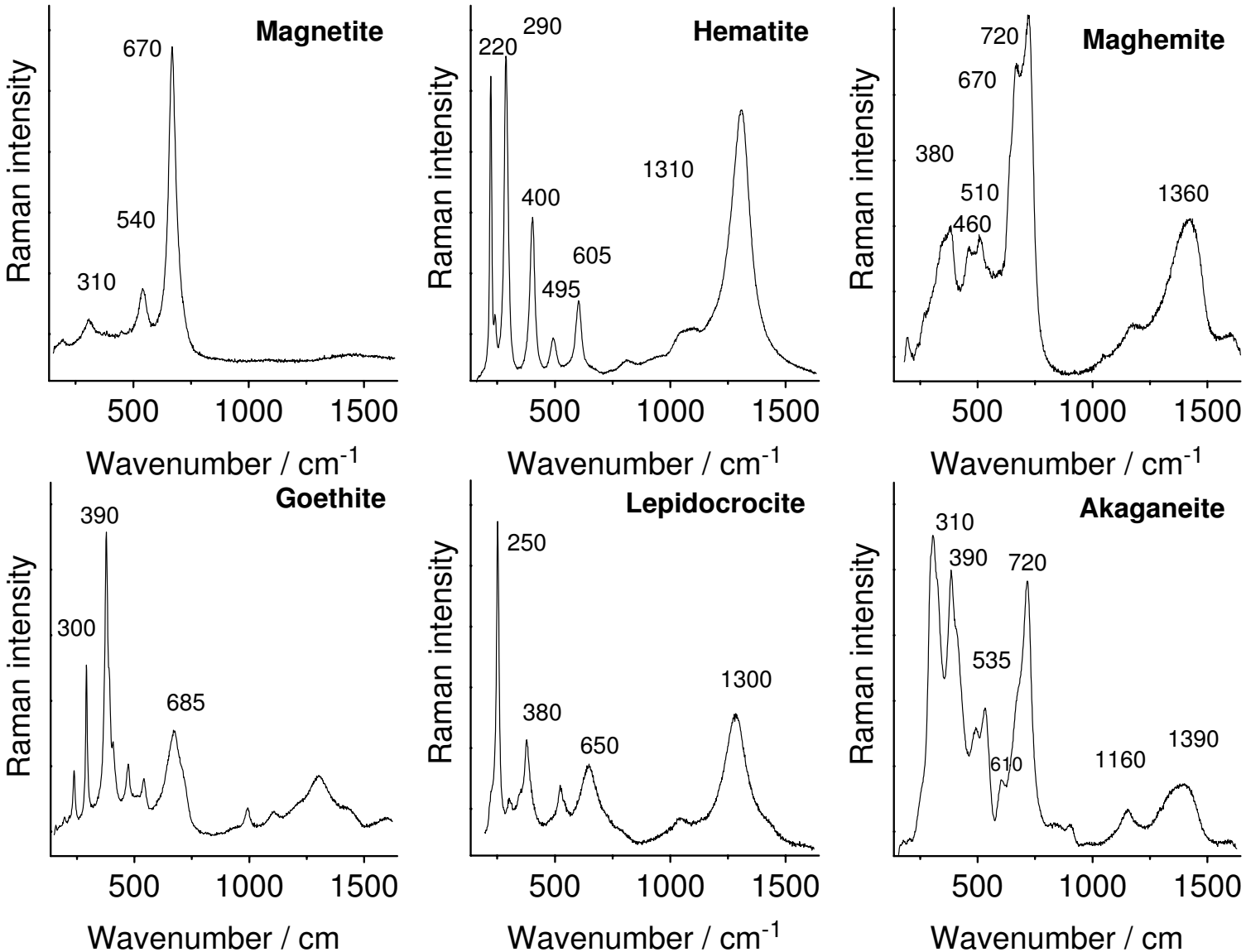


Cornell & Schwertmann. The Iron Oxides. Wiley-VCH Verlag (2003)

Iron oxide polymorphs (a selection)

Polymorph	Type	Symmetry	Spacegroup	Density/g cm^{-3}
Wustite, FeO		cubic	$Fm3m$	6
Magnetite, Fe_3O_4	spinel	cubic	$Fd\bar{3}m$	5.18
Hematite, α-Fe_2O_3	corundum	trigonal	$R\bar{3}c$	5.23
Maghemite, γ-Fe_2O_3	spinel	cubic	$P4_332$	4.87
Goethite, α-FeOOH			$2/m2/m2/m$	3.7
Lepidocrocite, γ-FeOOH			$Cmcm$	4

Each polymorph shows a characteristic Raman spectrum...



Colomban et al. Journal of Raman Spectroscopy 39, 881–886 (2008) 10.1002/jrs.1927

. . . but IR is more open to interpretation

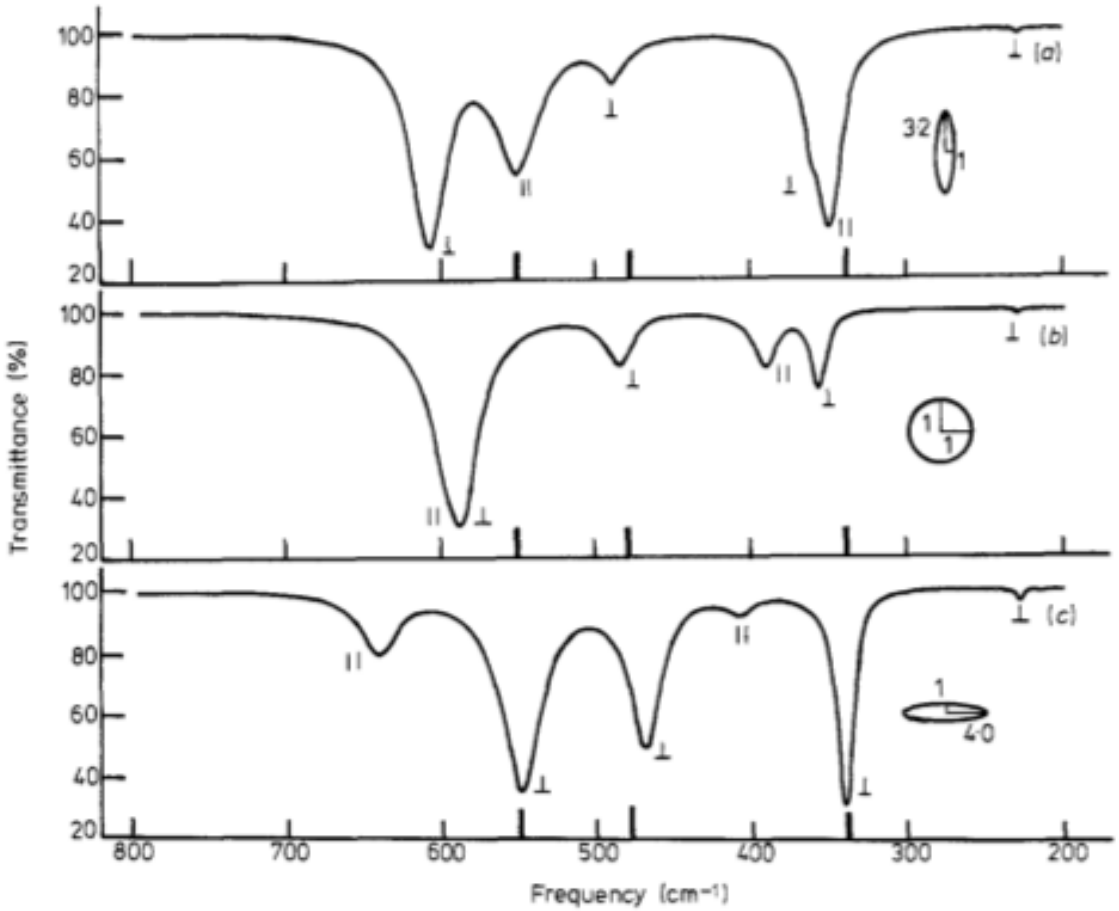


Figure 3. Calculated transmission spectra corresponding to three different particle shapes; (*a*) long prolate with $L_\perp = 0{\cdot}45$ and $L_\parallel = 0{\cdot}10$; (*b*) sphere with $L_\perp = L_\parallel = \frac{1}{3}$; (*c*) the flat oblate with $L_\perp = 0{\cdot}15$ and $L_\parallel = 0{\cdot}70$. Thick vertical bars on the abscissae indicate the observed peak frequencies.

Hayashi & Kanamori. Journal of Physics C: Solid State Physics 13, 1529–1538 (1980)

Hematite IR/Raman peaks (literature)

TABLE 9: Calculated and Observed Wavenumbers for Hematite

obs[26,27]/cm^{-1}	calcd/cm^{-1}	sym species	activity	ions involved
225	228	A_{1g}	Raman	Fe,O
229	290	Eu	IR	Fe,O
247	200	E_g	Raman	Fe,O
293	294	E_g	Raman	Fe,O
299	327	E_g	Raman	Fe,O
310−335	310	E_u	IR	Fe,O
310−335	339	A_{2u}	IR	Fe,O
380−400	368	E_u	IR	Fe,O
380−400	378	A_{2u}	IR	Fe,O
412	391	E_g	Raman	Fe,O
440−470	454	E_u	IR	Fe,O
498	447	A_{1g}	Raman	Fe,O
613	466	E_g	Raman	Fe,O

Chamritski & Burns The Journal of Physical Chemistry B 109, 4965–4968 (2005)