Template-assisted electrodeposition of TiO_2 on transparent conductive oxide substrates

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Electrochemical deposition of semiconductors

Electrochemical synthesis is cheap, scalable, controllable, and affords relatively good control of the synthesis conditions. **Semiconductor thin-film electrodeposition** has matured and offers several advantages over other deposition techniques.

- Good control of deposition parameters,
- cheap,
- widely used in many industrial settings,
- solution chemistry opens up many possibilities.

At the same time, ironically, the main disadvantages are related to solution chemistry:

- product contains residual electrolyte,
- sample handling may be complicated.

Preparation of $TiCl_4$–HCl aqueous solution

$TiCl_4$ (liquid) was transferred into a 10 ml plastic syringe. The syringe was inserted into a three-neck round bottom flask (under dry nitrogen atmosphere) and the $TiCl_4$ was slowly added to an ice-cold 37 % HCl solution while stirring.

Titanium hydrolysis and deposition reactions

$TiCl_4$ hydrolyzes immediately upon contact with moisture,

$$TiCl_4 + 2\,H_2O \rightarrow TiO_2 + 4\,HCl$$

and forms titanium dioxide and acidic vapours.
In fact, several species are present in aqueous solution:

$$Ti(OH)_2^{2+} + Ti(OH)_3^{+} + Ti(OH)_4 + 3\,OH^- \leftrightarrow 3\,TiO_2 + 6\,H_2O$$

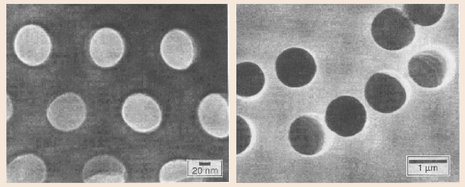
Deposition of titanium oxide presumably occurs via a peroxocomplex in solution.

$$[Ti(O_2)(OH)_{n\text{-}2}]^{(4-n)+} + mOH^- + kH_2O \rightarrow TiO_3(H_2O)_x$$
$$2\,TiO_3(H_2O)_x \rightarrow 2\,TiO_2 + O_2 + 2\,xH_2O$$

The product usually requires firing above 450 °C to crystallise.

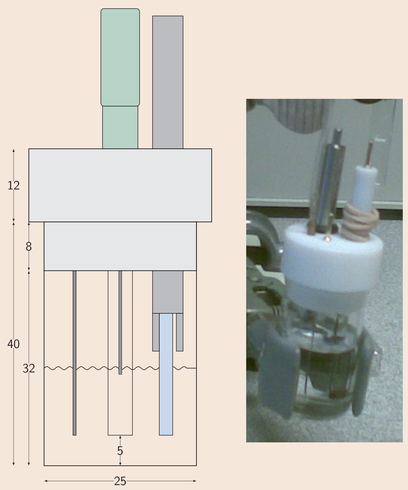
Solid porous templates

Below left: an anodized aluminium oxide membrane with evenly spaced and uniformly sized pores.
Below right: a track-etched polycarbonate membrane with uniformly sized pores.



The polycarbonate membrane is easy to work with and easy to remove, but has lower pore density and the pores may be tilted away from the substrate plane normal. The aluminium oxide membrane has better pore properties, but is more cumbersome to work with and harder to remove without damaging the deposit.

Electrodeposition cell configuration



Net water splitting reaction

$$\mathbf{H_2O(liq) + 2h\nu \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)}$$

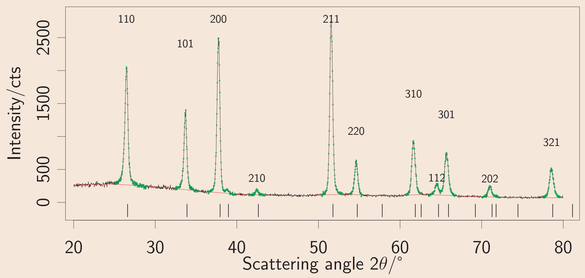
Water splitting is an uphill reaction with $\Delta G° = +237.2\,kJ/mol$, corresponding to a minimum energy of 1.229 eV per photon, or a photon wavelength of 1010 nm.

Earth receives a vast amount of solar energy

The Earth is constantly irradiated by sunlight. In fact, solar energy provides more energy to the Earth in one hour than humanity transforms in a year. Averaged over a year, sunlight with a total energy of 100 000 TW hits the Earth. Humanity transforms about 13 TW yearly for its needs (in 2001). In 2050, human energy transformation is projected to reach 27 TW.
Clearly, solar energy could supply all of humanity's energy needs for the foreseeable future. Even though technical estimates put the amount of solar energy that could be converted to just 600 TW, that is clearly still much more than current energy requirements.

Transparent conductive oxide glass

- A transparent substrate greatly simplifies device construction.
- Glass can withstand large temperature variations.
- Depending on composition, oxide layer may also withstand high temperatures.



TEC7 fluorine-doped tin oxide substrates from Pilkington. Cu Kα X-ray diffractometry indicates it is well-crystallised. The sheet resistance of TEC7 is 7 Ω/□ and the optical transmittance is 81 %. Haziness 5 %.

Bibliography

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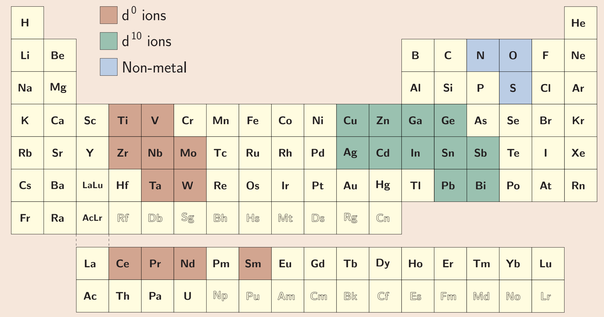
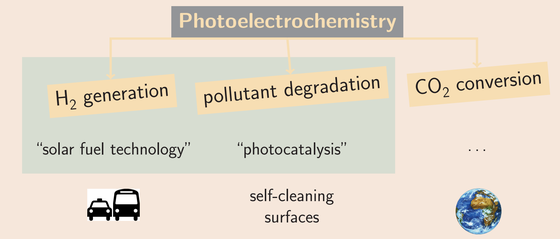
What is a photocatalyst made of?



Photoelectrochemical applications



What does a photoelectrochemical cell do?

A photoelectrochemical cell can perform all three functions of an energy-conversion and storage system:

- capture the incident light by way of absorption,
- convert it into an electron-hole pair,
- store that energy by reducing some compound, e.g. H_2O, producing a fuel in the process, e.g. H_2.

Absolute band gap positions