

# Catalysis in Switzerland

Swiss Federal Institute of Technology Lausanne (EPFL)

*Chimia* 50 (1996) 47–49  
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ISSN 0009–4293

## Hetero-Supramolecular Modification of Nanocrystalline TiO<sub>2</sub>-Film Electrodes: Photoassisted Electrocatalysis at B<sub>12</sub>-on-TiO<sub>2</sub>

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**Abstract.** Nanocrystalline TiO<sub>2</sub>-film electrodes exhibit a unique set of intrinsic properties (transparency for visible light, electric conductivity in the doped state, semiconductor properties, large surface area, surface affinity towards organic anchoring groups). These can be combined with those of TiO<sub>2</sub>-surface-anchored molecular subunits such as light emitters or absorbers, redoxactive – possibly electrochromic – compounds, and electroactive molecular hosts or catalysts. The number of macroscopic devices resulting from such a hetero-supramolecular architecture includes photovoltaic cells, erasable photochromic devices, electrochromic displays and filters, and electrocatalytically active surfaces. The principals behind these applications are reviewed with special emphasis on a new type of photoassisted electrocatalysis using vitamin B<sub>12</sub>-modified TiO<sub>2</sub>.

### 1. Introduction

The intrinsic properties of thin, nanocrystalline TiO<sub>2</sub> films (a few μm thick) on transparent conducting glass are:

1. transparency for VIS light,
2. electronic conductivity in the doped state,
3. semiconductor properties,
4. large surface area, and
5. surface affinity towards organic anchoring groups (carboxylates, salicylates, phosphonates).

These properties can be combined with those of appropriate molecular building blocks connected tightly to the semiconductor surface *via* anchoring groups and linkers (*cf.* Fig. 1, I). Most obvious are molecular functions that can be directly coupled to the inherent properties of TiO<sub>2</sub>, *i.e.*, electron acceptors/donors (Fig. 1, II) and photon emitters/absorbers (Fig. 1, III). As will be shown, interesting new function in the field of sensors and electrocatalysis can be achieved by surface modifi-

ers that interact with solution species (S) (Fig. 1, IV).

The macroscopic devices that result from such hetero-supramolecular architectures are immense and include – among others – the well-known photovoltaic cell, developed in Lausanne (Fig. 2, A) [1–3], electrochemically erasable, sensitized photochromics (Fig. 2, B) [4], as well as electrochromic displays and filters (Fig. 2, C) [5][6]. It is worthwhile to have a closer look at the recently discovered erasable, redox-type photochromic phenomenon, in order to demonstrate, how complex macroscopic functions can be realized by the hetero-supramolecular approach [7]. The surface modifier consists of a photon absorber (sensitizer, bis(terpyridyl)ruthenium complex), equipped with an anchoring group (phosphonate), and an electrochromic redoxactive subunit (triarylamine). Coloration upon visible-light illumination involves injection of an electron into the conduction band of the semiconductor that is logically related to the oxidation of the triarylamine subunit pointing into the solution. Decolorization can be achieved by stepping the *Fermi* level negative of the flatband potential of TiO<sub>2</sub> ( $\Delta E$ ). Notably, in all examples shown in Fig. 2 the surface roughness of nanocrystalline TiO<sub>2</sub> leads to amplification of the phenomena by a factor in the order of 1000.

### 2. Photoassisted Electrocatalysis

The concept of photo-electrocatalysis *via* band gap excitation of TiO<sub>2</sub> electrodes has early been recognized by *Fujishima* and *Honda* and quantum yields up to 0.85 have been reported for water oxidation [8][9]. Anodic reactions at TiO<sub>2</sub> electrodes of organic compounds include oxalic acid and *p*-aminophenol [10][11]. However, the oxidizing power of the semiconductor holes is difficult to adjust and too positive for many synthetically interesting reactions, and the reductive power of conduction band electrons does not show up because of kinetic limitations. One way to

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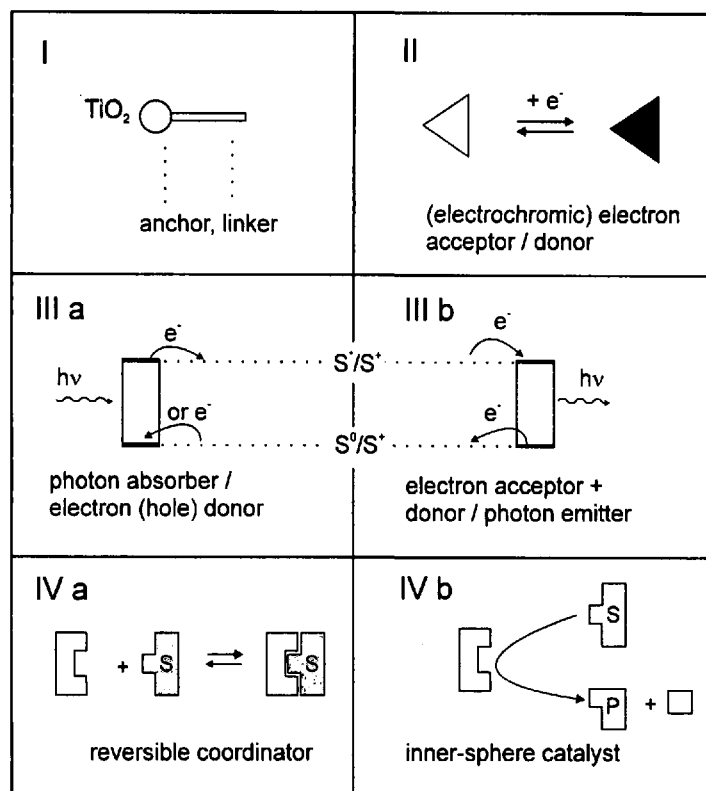


Fig. 1. Anchoring group, linkers, and functional building blocks used as  $TiO_2$  surface modifiers. I)  $TiO_2$  Anchor connected to a linker, II) reversible redoxactive compounds (possibly with electrochromic properties), IIIa) photon absorbers undergoing light-induced electron transfer or IIIb) electron/hole acceptors undergoing electron-transfer-induced light emission, IVa) reversible substrate (S) coordinators, and IVb) inner-sphere catalysts.

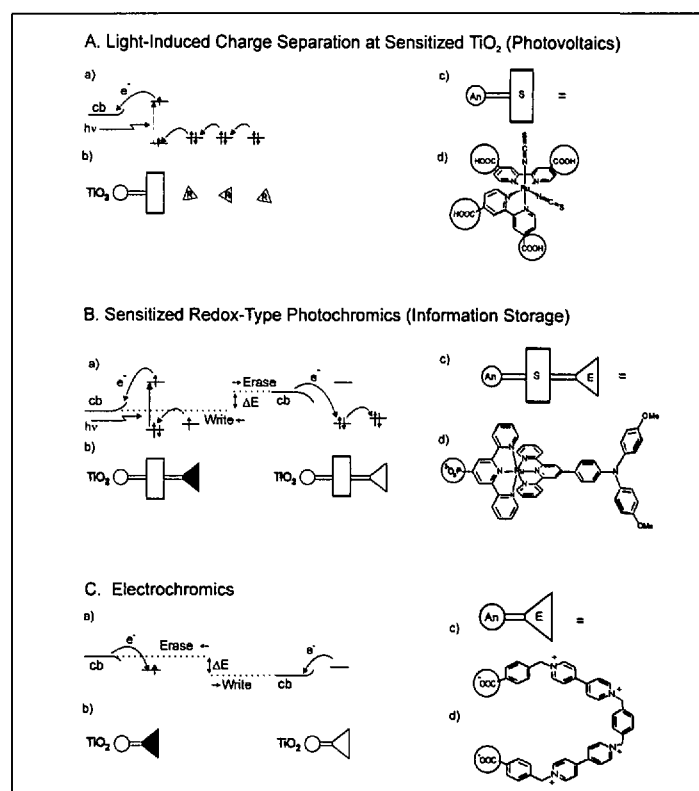


Fig. 2. Macroscopic functions achieved by heterosupramolecular modification of nanocrystalline  $TiO_2$ -film electrodes: A) photovoltaics; B) sensitized redox-type photochromics; C) electrochromics. a) Electron transfer and excitation; b) schematic surface architecture; c) surface modifier in terms of functional building blocks; d) surface modifier (structure); S: sensitizer, R: reversible redox system; An:  $TiO_2$ -anchoring group, E: electrochromic subunit, cb: conduction band,  $\Delta E$ : potential necessary to switch between write and erase function.

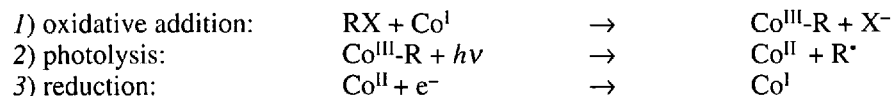
circumvent this problem is to use an electrocatalyst tightly bound to the  $TiO_2$  surface allowing fast electron transfer from  $TiO_2$  to a given substrate.

Principally, catalysts for electrosynthesis could be used in conjunction with  $TiO_2$  electrodes in four different variations,

- i) anodic processes driven by band gap excitation,
- ii) anodic processes driven by dye-sensitized hole formation, as well as
- iii) non-light-dependent cathodic processes, and
- iiii) sensitized cathodic processes.

Recently, we found a very interesting representative of group *iiii*: Photoassisted electrocatalysis of alkyl-halide reduction is feasible on surface-modified thin-film nanocrystalline  $TiO_2$  electrodes using appropriately modified vitamin  $B_{12}$  derivatives such as **1** (Fig. 3) [12]. The EDTA side chain on **1** has been introduced for tight attachment on  $TiO_2$ .

Photoelectrocatalysis of  $B_{12}$ -on- $TiO_2$  is based on the sequence of reaction 1–3 [13]:



The overall reaction – driven by visible light and electrochemical energy – corresponds to the formation of alkyl radicals

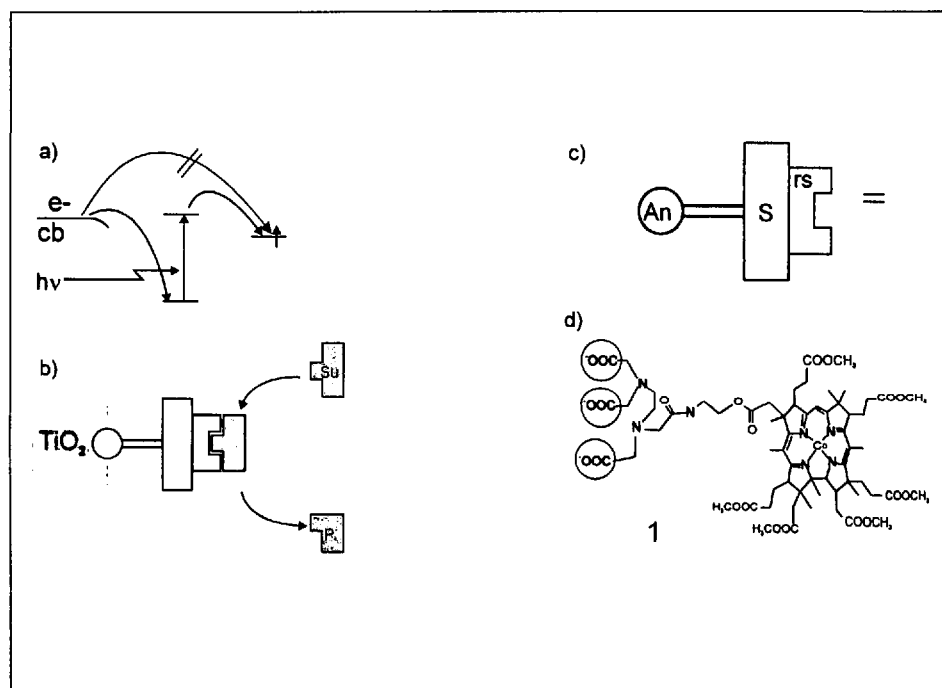


Fig. 3. Photoassisted electrocatalysis by vitamin  $B_{12}$ -modified nanocrystalline  $TiO_2$ -film electrodes. a) Electron transfers and excitation; b) schematic surface architecture; c) surface modifier (functional aspects); d) surface modifier (structure); An:  $TiO_2$ -anchoring group; RS: reaction site; S: sensitizer, Su: substrate, P: product.

Scheme. *Radical-Type Ring Closure Catalyzed by B<sub>12</sub>-on-TiO<sub>2</sub> (3 μm thick)*. B<sub>12</sub> surface concentration: 5 · 10<sup>-8</sup> mol/cm<sup>2</sup>. After 20 h the catalyst showed ca. 3300 turn-over and ca. 60% of the starting material was consumed.

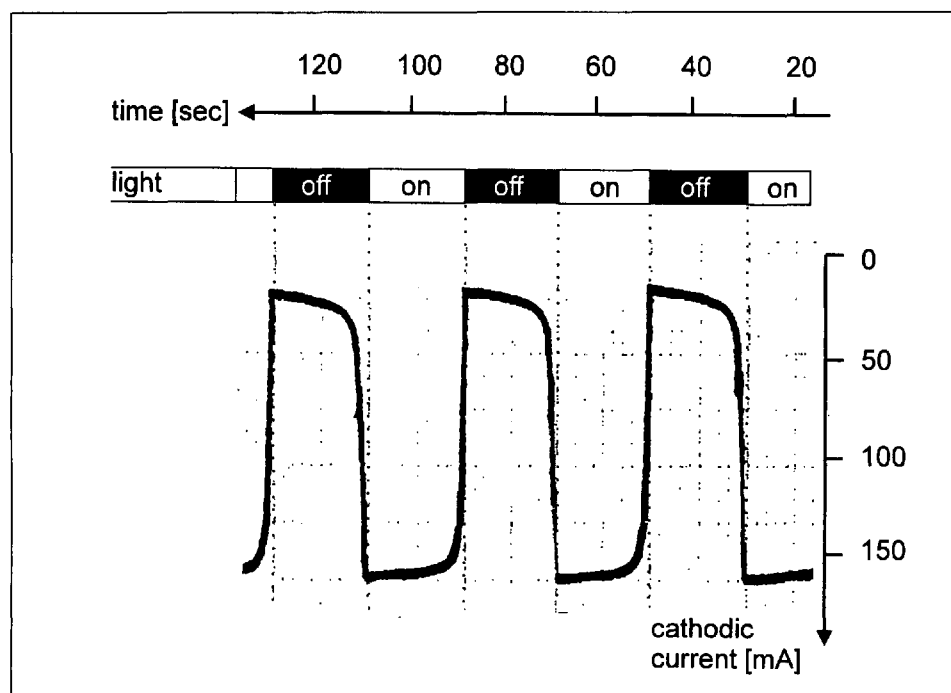
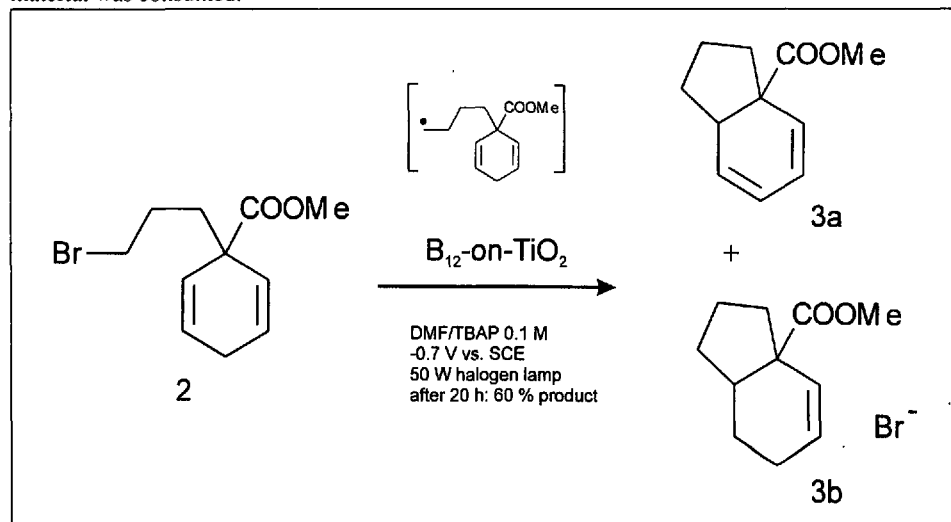


Fig. 4. Cathodic photocurrent observed on a B<sub>12</sub>-on-TiO<sub>2</sub> electrode under chopped light conditions. Polarization: -0.7 V vs. SCE in propylene carbonate/TPAP 0.25M in presence of propyl iodide and acrylonitrile, light source: 50 W halogen lamp with cut-off filter 400 nm.

R<sup>•</sup> from alkyl halides (RX). R<sup>•</sup> can be trapped by a synthetically interesting partner. It was possible to induce radical-type cyclization of methyl [3-(3-bromopropyl)cyclohexa-1,4-diene-3-yl]carboxylate (**2**) via intermediate radical formation at a mild potential of -0.7 V vs. SCE and visible-light illumination of the modified TiO<sub>2</sub> electrode to the bicyclic compounds **3a** and **3b** (Scheme).

The catalyst underwent more than 3000 turn-over in this reaction, a number that compares well with our earlier attempts to use polymeric vitamin B<sub>12</sub> on carbon electrodes as an electrocatalytic electrode.

The product formation is accompanied by a cathodic photocurrent that can be chopped in the time domain of one second (cf. Fig. 4). The current depends on

1. light intensity (at 1 sun white light up to 1 mA/cm<sup>2</sup>);
2. electrode potential (*E* must be negative of *E*<sup>0</sup>(Co<sup>II</sup>/Co<sup>I</sup>));
3. type and concentration of RX (because of the bimolecular reaction between catalyst and substrate);
4. type of chemical follow-up reaction of R (one- or two-electron process).

Received: January 16, 1996

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