

Transient absorption spectroelectrochemistry: accessing all oxidation states of catalytic metal centers in covalent dye-catalyst dyads

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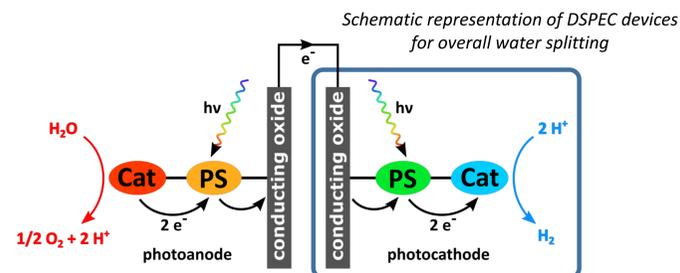
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Dye-sensitized Photoelectrochemical Cells

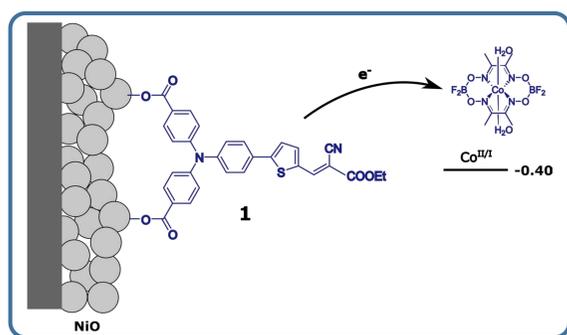
Solar fuels such as hydrogen (H₂) represent a promising alternative to the currently used fossil fuels. One approach to produce H₂ using solar energy and water relies on the dye-sensitized photoelectrochemical cells (DSPEC) technology. Such a device combines a photoanode where under visible light irradiation water oxidation occurs to supply the photoanode with H⁺ and e⁻, where H₂ is produced. Our groups is involved in the design and the H₂-evolving activity assessment of novel H₂-dye sensitized evolving photocathodes based on cobalt catalysts.

a) E. Gibson, *Chem. Soc. Rev.* **2017**, 46, 6194. b) A. G. Coutsolelos, F. Odobel and coworkers, *J. Mater. Chem. A*, **2017**, 5, 21077.



Excited-state processes and electron transfer Transient absorption spectroelectrochemistry (TA-SEC)

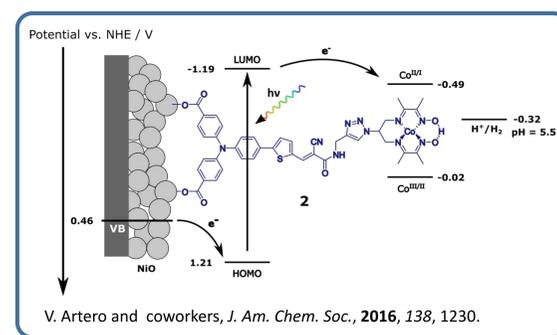
Catalyst in solution



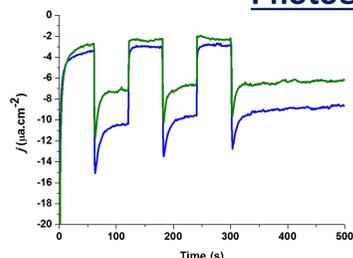
	Catalyst in solution	Dye-catalyst dyad
Faradaic yield	3%	8-10%
n(H ₂) / nmol·cm ⁻²	12 (6 h)	11 (4 h)

Ultrafast spectroscopic characterization:
Understanding the electron transfer dynamics
→ improvement of the molecular design

Covalent dye-catalyst assembly



Photoelectrochemistry



Chopped-light chronoamperometric measurements recorded in acetate buffer (0.1 M, pH 4.5) in the presence of [Co(dmgBF₂)₂(H₂O)] (1 mM) at an applied potential of 0.05 V vs RHE for NiO electrodes sensitized by **1** alone (blue line) or in the presence of CDCA as co-absorbent (green line).

	Without catalyst	With catalyst
Photocurrent density / μA·cm ⁻²	3	6
n(H ₂) after 4 h / nmol·cm ⁻²	3	12

Electron transfer to catalyst in solution

TA of **1** in ACN and on NiO

ACN:

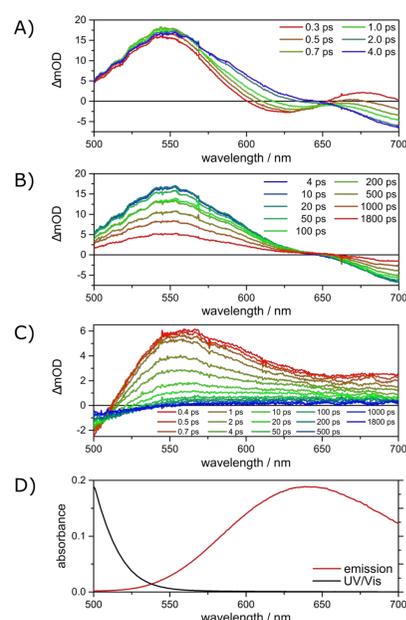
- Subpicosecond relaxation cascade to ICT' state
- Relaxation to the ground state with 132 and 1843 ps

NiO:

- Hole injection with 0.4 ps time constant
- Multieponential decay due to recombination
- Low-amplitude long-lived (>>1.8 ns) signal of charge-separated species

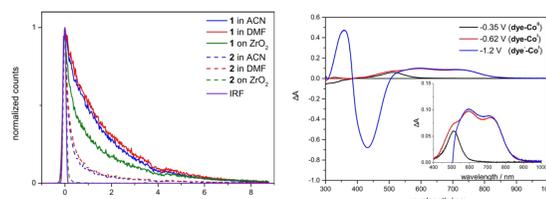
	solvent	τ ₁	τ ₂	τ ₃	τ ₄	τ ₅
1	ACN	0.2	0.9	132	1843	
	NiO	0.4	1.8	16	280	>>1800
2	ACN	0.3	1.1	82.6	467	
	DMF, OCP	0.7	2.6	67.7	351	
	DMF, Co ^{II}	0.7	2.9	57.2	290	
	DMF, Co ^I	0.6	2.0	22.3	173	

Lifetimes (in ps) obtained via a global fit of the TA data of **1** in ACN and on NiO as well as of **2** in ACN and DMF under different applied potentials.

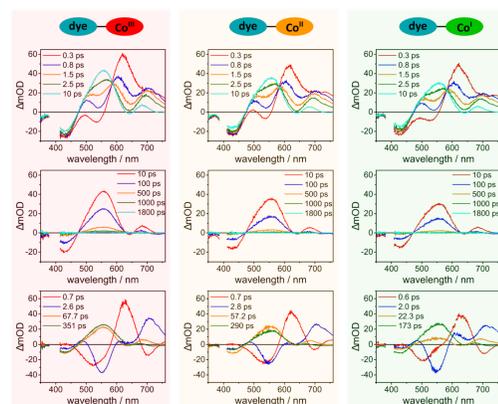


Transient absorption spectra of **1** in acetonitrile solution (A, B) and of a NiO film sensitized with **1** (C) at chosen delay times. The steady state absorption and emission (I_{ex} = 400 nm) spectra of **1** in ACN are given for comparison in the relevant spectral range (D).

Transient absorption spectroelectrochemistry

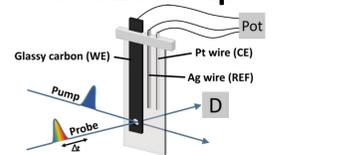


Left: Time-resolved emission spectra of the dye **1** and dye-catalyst assembly **2** in solution and on ZrO₂. Right: UV-Vis SEC differential spectra of **2** in DMF



TA spectra at OCP and reductive potentials. Upper graphs show short, middle graphs long delay times and bottom graphs decay-associated spectra. The spectra were recorded in DMF with 0.1M TBABF₄ as supporting electrolyte.

TA-SEC setup



The pump and probe beams were focused through a hole drilled in the glassy carbon working electrode. The working electrode thickness is close to the cuvette thickness to create a "microcuvette" in order to maximize the concentration of the reduced complex.

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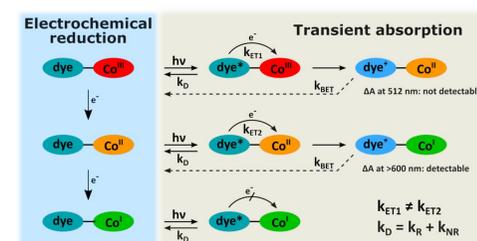
Emission quenching with catalyst → e⁻ transfer?

- Transient absorption (TA) spectroscopy to observe excited state processes
- Problem: Co^I state not spectrally observable (overlap with bleach). However, the Co^I state shows a stronger band at longer wavelengths and should be observable.
- Additionally, Co^I is the entry point to the catalytic cycle which adds to the interest of investigating the electron transfer leading to the Co^I state.

How to access the Co^I state with TA?

Combine TA with spectroelectrochemistry (SEC):

- Electrochemical reduction to Co^{II} or Co^I
- TA measurement



Possible observations in case of e⁻ transfer:

- Observation of Co^I band when starting from Co^{II}
- Change in decay rates due to different thermodynamic driving forces (from Co^{III} and Co^{II}) for electron transfer (k_{ET}) or impossibility of electron transfer when starting with Co^I state

None of these is observed when recording TA-SEC spectra in solution, so an oxidative quenching mechanism after excitation can be ruled out for this system. It seems that the excited state has to be reductively quenched before electron transfer can occur.

Perspectives

- TA-SEC measurements of dye-catalyst assembly on NiO
- Change linker structure to induce faster electron transfer
- rR-SEC on series of Co catalysts in solution
- rR-SEC of dye-catalyst assembly under operando conditions



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