

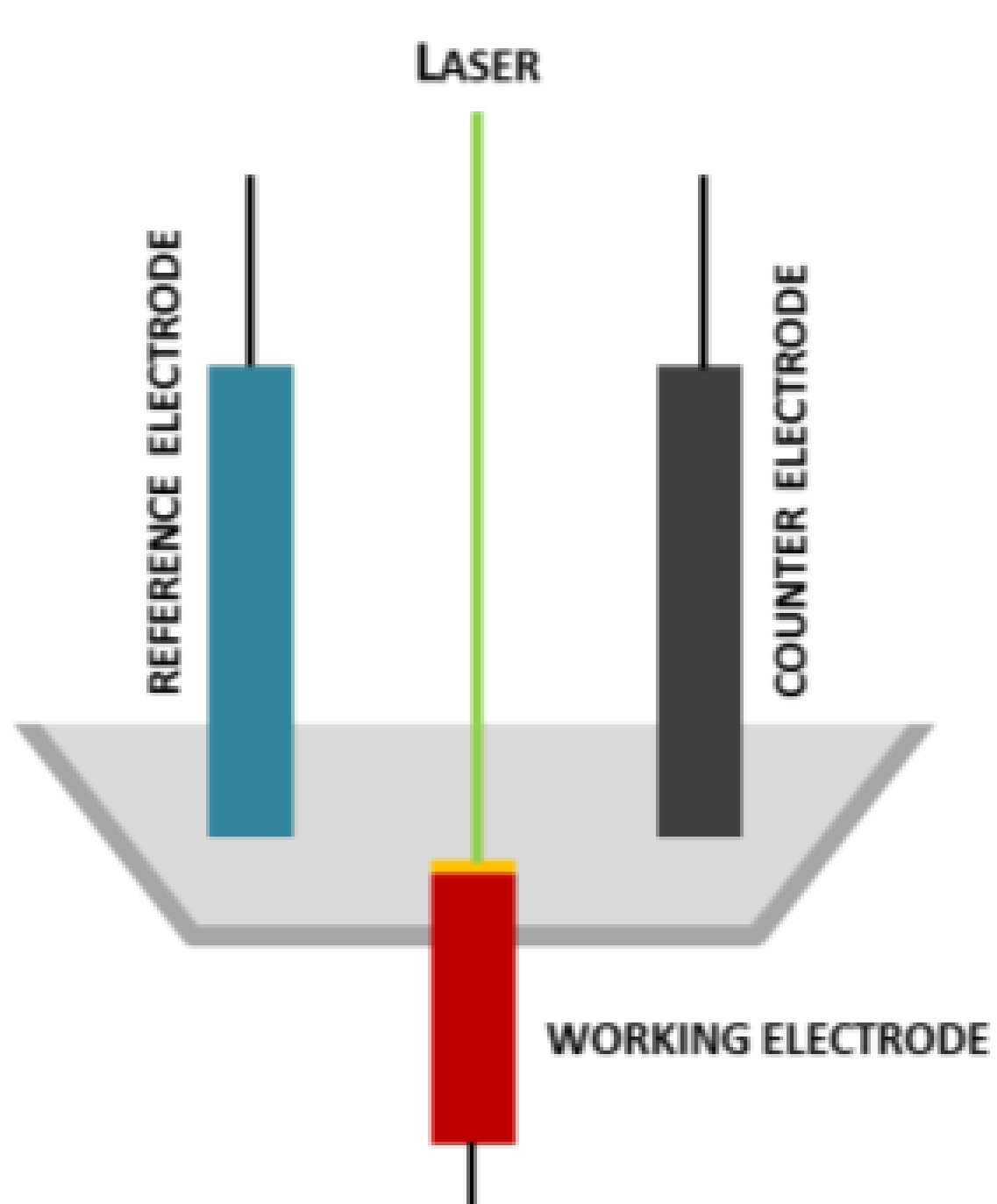
# Fading colors

## Understanding the cause of fading via (photo)electrochemistry

Understanding the reactivity of (semiconductor) pigments provides vital information on how to improve conservation strategies for works of art in order to avoid rapid degradation or discoloration of the pigments. Even more, the gained insights and strategies are easily transferable to all materials that capture light and suffer from discoloration (e.g. photovoltaics).

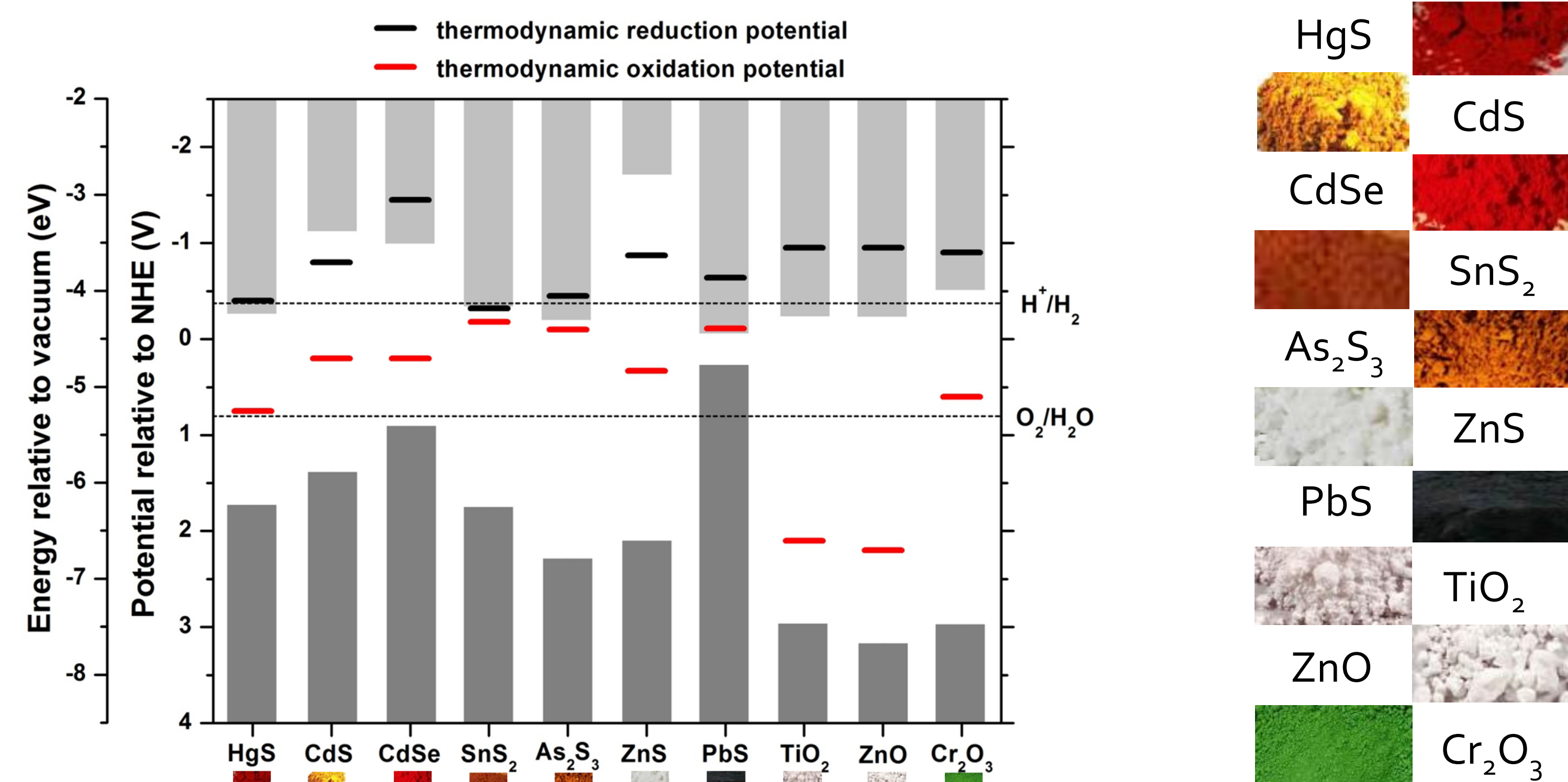
Fading has two main causes. Both physical (e.g. light, temperature) and chemical (e.g. salts/ambient chemical environment) parameters might induce deterioration. Lately (photo)electrochemistry is being used in our lab as a fast technique for identifying pigment degradation products and as a tool for monitoring pigment degradation processes in the aim of predicting harmful/favorable environmental conditions. This method does not require lengthy exposure of the pigments to (chemical or physical) degrading agents in an artificial ageing chamber.

## Concept – Experimental Setup

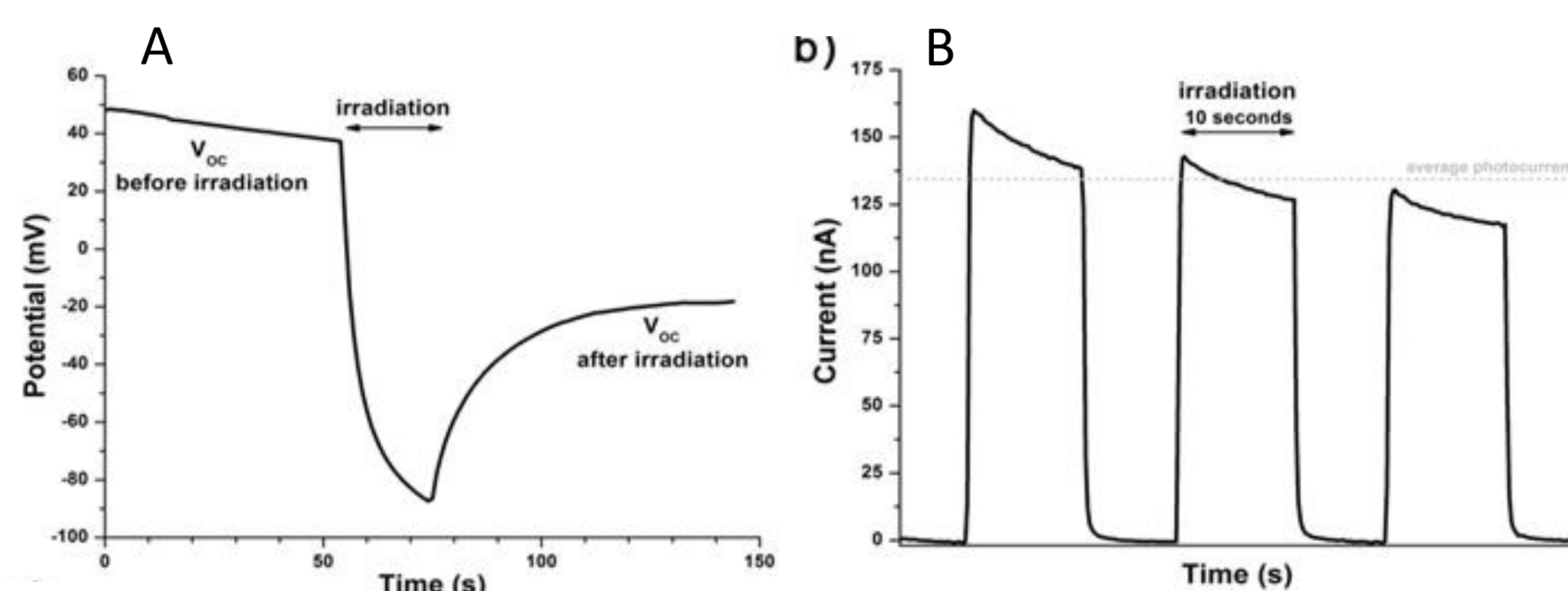
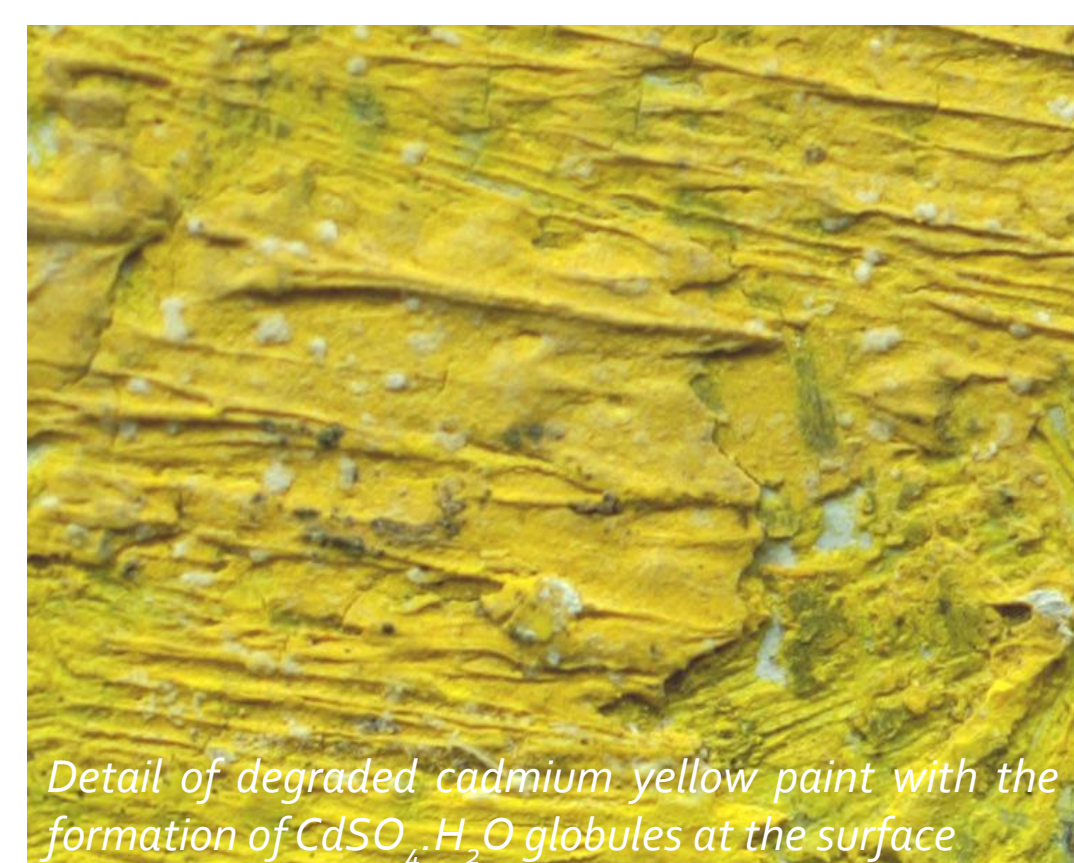


Pigment suspensions are dipped onto a graphite working electrode (C|pigment) mounting it in a three-electrode cell. Environmental conditions are mimicked by irradiating the electrode (pigment side oriented upward) with light of different wavelengths and intensity, while exposing the pigment to an electrolyte compound present in the atmosphere (e.g. an organic acid or water-soluble salts present in airborne particles). By application of an appropriate electrochemical method, details on the degradation process are gathered in a fast way by providing information on the changes in photocurrent intensity or in the oxidation state of the pigment.

## Thermodynamic prediction

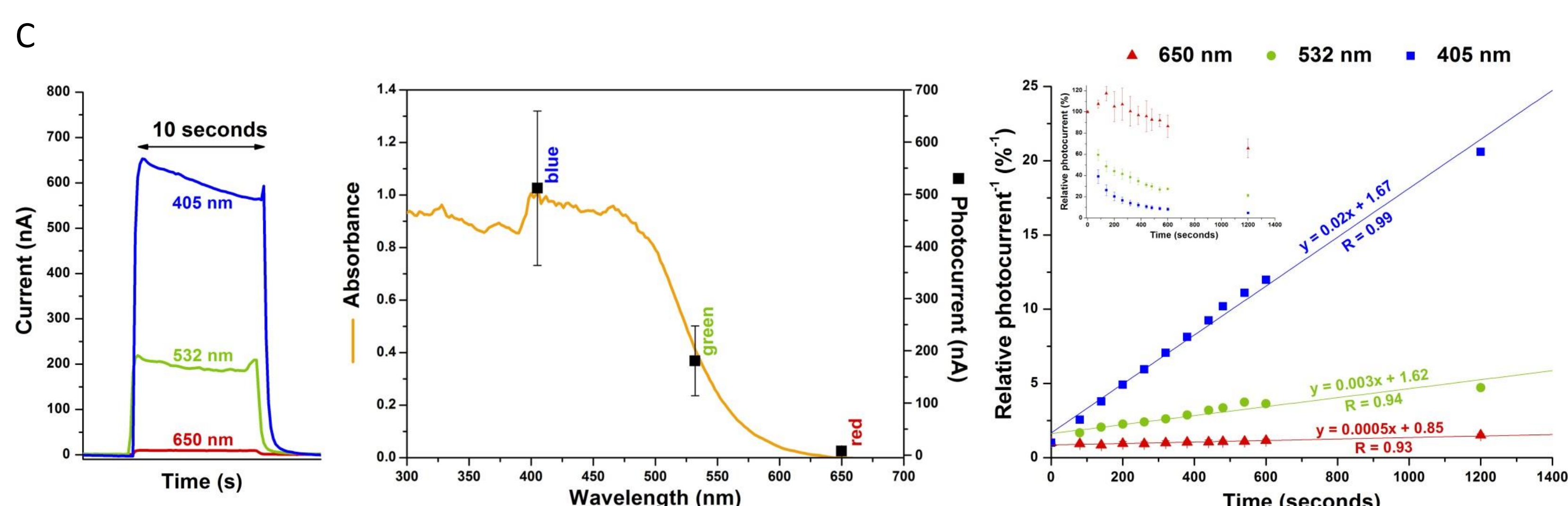


## Degradation of cadmium yellow



- ☐ n-type semiconductor (CdS)
- ☐ stable in the dark
- ☐ band gap of ~2.4 eV
- ☐ anodic photocurrent
- ☐ in the presence of water and oxygen,  $S^{2-}$  can be oxidized up to  $SO_4^{2-}$ , while  $Cd^{2+}$  is formed.
- ☐ water and oxygen may function as electron acceptor

Figure A represents the open circuit potential ( $V_{OC}$ ) before, during, and after illumination. Figure B shows the oxidative (photo)current of a C|CdS electrode in 1 mM NaCl, in the dark and under irradiation with green laser light (532 nm). The dependency of photoactivity on wavelength is illustrated in Figure C.



Further reading:

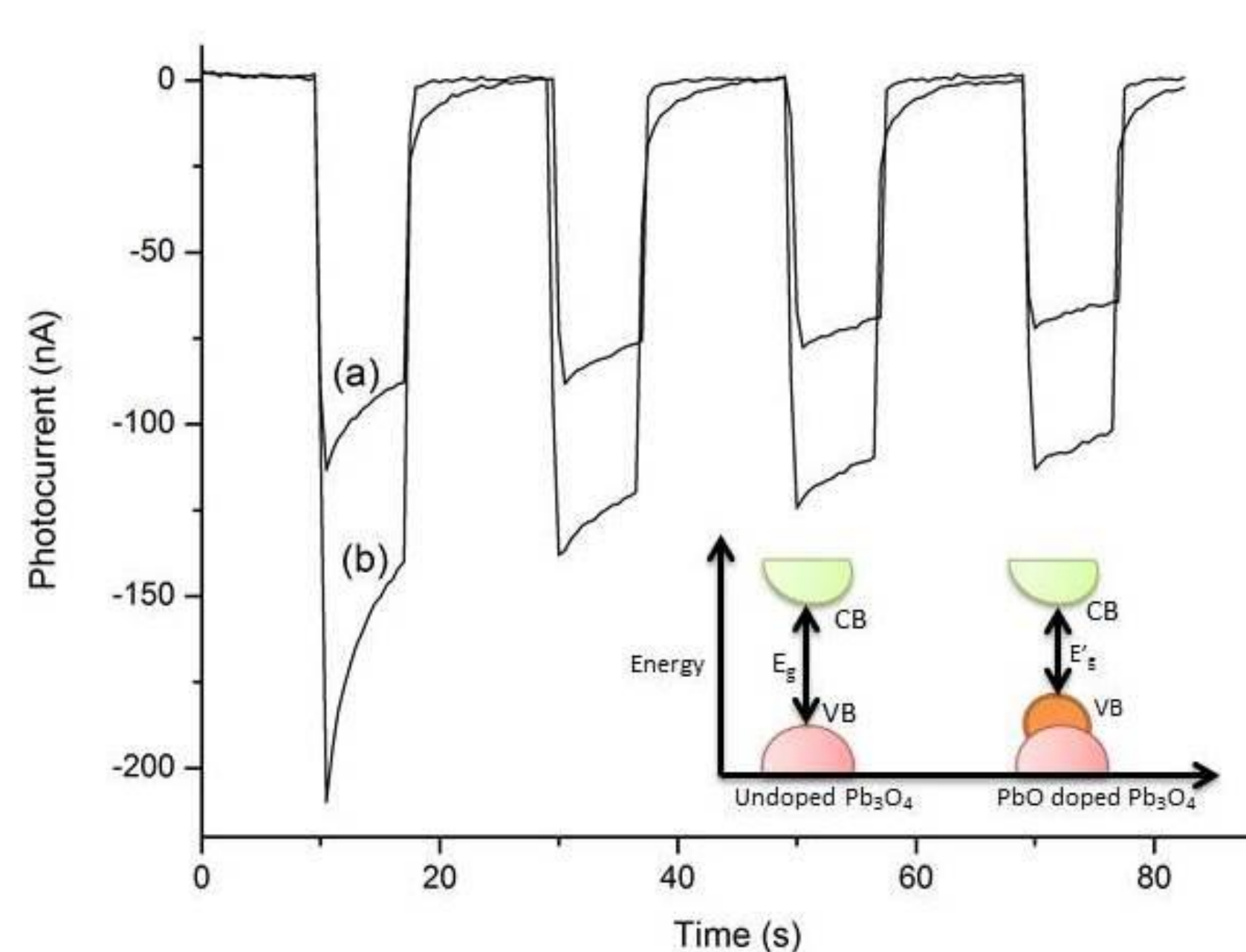
Dyes and pigments 113 (2015) 409-415

Analytical chemistry 86:19 (2014) 9742-9748

Angewandte Chemie: international edition in English 52:48 (2013) 12568-12571

- ☐ During exposure to light of appropriate energy, electrons are excited from valence to conduction band inducing conductivity.
- ☐ The photoactivity/degradation depends on the energy of the incoming light and the band gap energy of the semiconductor.
- ☐ The stability of the semiconductor pigment towards the environment can be predicted by considering the alignment of the thermodynamic oxidation and reduction potential towards the redox potentials of the environment.

## Degradation of minium



- ☐ p-type semiconductor ( $Pb_3O_4$ )
- ☐ stable in the dark
- ☐ red color fades away when exposed to light of wavelength below 605 nm (band gap ~2 eV)
- ☐ cathodic photocurrent
- ☐ photogenerated electrons are taken up by minium with conversion into lead oxides
- ☐ real samples of minium are doped with some litharge

C| $Pb_3O_4$  in a bicarbonate/carbonate solution:

higher photocurrent/activity compared to C| $Pb_3O_4$  in a NaCl solution as the subsequent reaction of lead oxides with bicarbonates, with formation of hydrocerussite, takes place. Identified by tandem analytical techniques.



C| $Pb_3O_4$  + litharge in a bicarbonate/carbonate solution:

enhancement of the photocurrent due to the introduction of new electronic states through  $PbO/Pb_3O_4$  interfacial bonds. The new states shift the valence band upward, inducing more efficient electron/hole separation and hence higher conductivity.

## Contact

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