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# Electrochemical Photodegradation Study of Semiconductor Pigments: Influence of Environmental Parameters

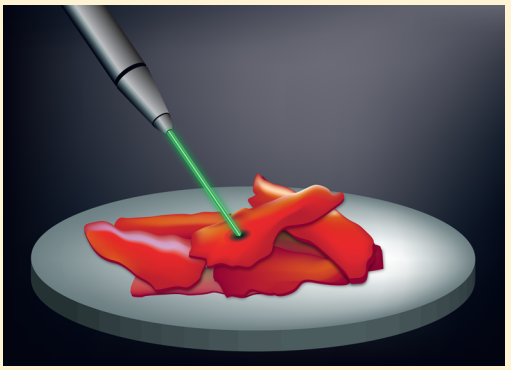
Willemien Anaf,[†] Stanislav Trashin,[†] Olivier Schalm,[‡] Dennis van Dorp,[§] Koen Janssens,[†] and Karolien De Wael*[,†]

[†]AXES, Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerpen, Belgium

[‡]Conservation Studies, University of Antwerp, Blindestraat 9, 2000 Antwerpen, Belgium

[§]IMEC, Kapeldreef 75, 3001 Leuven, Belgium

**ABSTRACT:** Chemical transformations in paintings often induce discolorations, disturbing the appearance of the image. For an appropriate conservation of such valuable and irreplaceable heritage objects, it is important to have a good know-how on the degradation processes of the (historical) materials: which pigments have been discolored, what are the responsible processes, and which (environmental) conditions have the highest impact on the pigment degradation and should be mitigated. Pigment degradation is already widely studied, either by analyzing historical samples or by accelerated weathering experiments on dummies. However, in historic samples several processes may have taken place, increasing the complexity of the current state, while aging experiments are time-consuming due to the often extended aging period. An alternative method is proposed for a fast monitoring of degradation processes of semiconductor pigments, using an electrochemical setup mimicking the real environment and allowing the identification of harmful environmental parameters for each pigment. Examples are given for the pigments cadmium yellow (CdS) and vermilion ($\alpha$-HgS).



In the second half of the 19th century, numerous new pigments have been introduced in the painter's palette such as cadmium yellow (CdS), titanium white ($TiO_2$), or viridian green ($Cr_2O_3 \cdot 2H_2O$). In some cases, these "modern" pigments already show remarkable signs of degradation and unstable behavior. An example is cadmium yellow.[1] Characteristic is the fading of the yellow color, probably caused by photoinduced oxidation of cadmium sulfide (CdS) to hydrated cadmium sulfate ($CdSO_4 \cdot xH_2O$), observed in, for example, *Still Life with Coffeepot, Cabbages and Mask* by Ensor.[2] The presence of other compounds such as cadmium carbonate ($CdCO_3$) has been established, either originating from the pigment manufacturing process or forming in a secondary reaction between $CdSO_4 \cdot xH_2O$ and atmospheric $CO_2$. This occurred for example in the painting *Le Bonheur de Vivre* by Matisse.[3] More complex secondary reactions were observed in *Flowers in a Blue Vase* by Van Gogh, where the degraded CdS paint was covered with a varnish containing lead-based driers and oxalate ions.[4] Only recently, one starts to understand that the 19th century inorganic pigments are more prone to deterioration than was ever expected. Moreover, only the pigments most sensitive to transformations have been investigated. Such pigments do not show pronounced deterioration yet. Though, to improve the environmental conditions in which the paintings are stored and housed, the prediction of their sensitivity to the most important environmental parameters, well before actual deterioration takes place, is crucial.

On the other hand, pigments that were introduced centuries ago often already show a well-pronounced degradation due to the extended natural aging times. An example is the red pigment $\alpha$-HgS, used since antiquity. It is called cinnabar in its natural form and vermilion in its synthetic form. Degradation can induce a black discoloration of the initial bright red pigment, which was recently related to the formation of metallic mercury.[5] Examples are the Pompeian wall paintings[6] and the 17th century painting *Adoration of the Magi* by Rubens.[7] Although it is known that a combination of light, chlorine, and humidity influences the blackening, detailed knowledge on the exact conditions and the blackening capacity of other environmental compounds is lacking.

Thus, to counteract future degradation of both historic and modern pigments, insight into the chemical reactions that cause the degradation is essential for an appropriate conservation and preservation of valuable and irreplaceable paintings.

Studies on pigment degradation mainly focus on chemical analyses of historical paint samples using specialized techniques such as scanning electron microscopy (SEM), $\mu$-X-ray diffraction (XRD), and X-ray absorption near-edge structure (XANES) analysis (e.g., refs 2, 4, 6, 8, and 9). Such investigations are complemented with monitoring studies of

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model samples aged under specific conditions (e.g., refs 7 and 10−12). Although aging experiments often result in indispensable information on the degradation process, these are usually time-consuming: model samples for the complete painter's palette need to be exposed to degrading agents such as light, moisture, and gases for days up to months to mimic the natural degradation during decades to centuries. However, during such a time period, the single chemical transformations such as the oxidation of a pigment is accompanied by other unwanted slower transformations, for example, the sulfates formed in situ from sulfidic pigments may dissolve in small volumes of moisture present in the paint, migrating to the surface and precipitating there together with any present counterion.

To reduce the time needed to extract information on the (photo)degradation of pigments, an alternative approach is proposed, on the basis of electrochemical methods of detection. In the heritage sector, the use of electrochemical methods is already well-established in the branch of metal conservation and restoration, and is applied for cleaning, stabilization, and consolidation.[13,14] Moreover, metal coupons or thin metal sensors are used in the evaluation and monitoring of environmental corrosivity, relating the formed corrosion layer with the atmospheric conditions by using electrochemical methods.[15,16] In the past decade, electrochemistry has also been introduced in the analysis, mainly identification, of other heritage materials such as pigments and dyes[17−20] and ceramic materials.[21] However, electrochemical methods did not yet find their general use in the study of pigment degradation processes. Apart from studying degradation products,[5] a new electrochemical approach is developed for the real-time monitoring of pigment degradation processes and the prediction of (environmental) harmful conditions. The general concept consists of depositing the pigment of interest on the surface of a graphite electrode, mounting it in a three-electrode cell and monitoring the degradation processes electrochemically. In the cell, environmental conditions are mimicked by irradiating the electrode with light of different wavelengths and intensity, while exposing the pigment to an electrolyte compound present in the atmosphere (e.g., an organic acid and water-soluble salts present in airborne particles). By application of an appropriate electrochemical method such as amperometry or linear sweep voltammetry, details on the degradation process can be gathered in a fast way by providing information on the changes in photocurrent intensity or in the oxidation state of the metal ions present. Effects of environmental parameters (light, air aggressiveness, etc.) on the redox properties of the pigments are not yet described in the literature. This work discusses how the sensitivity toward such parameters can be estimated for sulfide semiconductor pigments (e.g., orpiment ($As_2S_3$), vermilion/cinnabar ($\alpha$-HgS), mosaic gold ($SnS_2$), and cadmium yellow (CdS)). Experimental results for CdS and $\alpha$-HgS are discussed, with main focus on the influence of wavelength on the degradation process. In the future, the approach could be extended with more advanced techniques such as simultaneous (synchrotron-based) XRD, X-ray absorption spectroscopy (XAS), or XANES analyses. Such techniques help in the better understanding of the degradation reactions, and the characterization of (insoluble) degradation products in situ by using a special cell. Synchrotron spectroelectrochemistry has already been described for the corrosion monitoring of metal-based heritage objects.[22−24]

## EXPERIMENTAL SECTION

Graphite working electrodes (⌀ = 3 mm) were pretreated by mechanical polishing with a P400 SiC paper to obtain a rough surface. To remove any adherent SiC particles, the electrodes were rinsed with deionized water and ethanol in an ultrasonic bath for 15 s each. Subsequently, a 1 $\mu$L drop of either an isopropanol−CdS suspension (0.05 g of CdS in 1 mL of isopropanol) or an ethanol−HgS suspension (0.05 g of $\alpha$-HgS in 1 mL of ethanol) was deposited onto the electrode surface using a micropipette, relying on the VMP principle (voltammetry of microparticles).[13,25] The choice of solvent is related to the most stable suspension of pigment grains in solution. After solvent evaporation, a thin layer of the respective pigment is left at the electrode surface. The modified electrodes are denoted as C|CdS and C|$\alpha$-HgS. A silver−silver chloride (Ag|AgCl) electrode and a platinum (Pt) electrode were used as the reference and counter electrode, respectively. The electrodes were mounted in an open container, with the pigment-modified side of the working electrode oriented upward, enabling pigment irradiation using 30 mW lasers of 405 nm (blue), 532 nm (green), and 650 nm (red) pointing downward (Figure 1). The Ag|AgCl reference electrode was

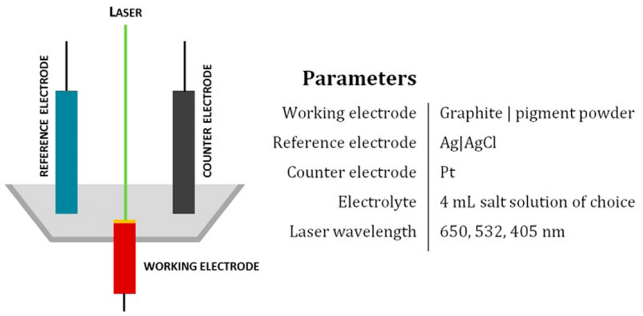


**Figure 1.** Electrochemical setup of a pigment-modified electrode with irradiation possibility.

protected from light illumination by covering it with aluminum foil. The open container was filled with 4 mL of an electrolyte of choice, providing approximately 0.5 cm of solution layer above the electrode. To be sure that the laser beam was not obstructed or significantly absorbed by the electrolyte, the absorbance of the different electrolyte solutions was controlled by UV−vis spectrophotometry (Cary 100 Dual Beam, Agilent Technologies). Electrochemical experiments were performed with an Autolab PGSTAT101 potentiostat (Metrohm, The Netherlands) controlled by NOVA 1.10 software.

The experiments in the electrochemical cell were carried out in two modes: (1) passive mode for long-term light irradiation (up to 60 min), where the open circuit potential was measured without applying any potential or current, and (2) active mode in which amperometry at a constant potential was used when short-term irradiation (few seconds) was applied to record the photocurrent. This current was used to characterize the pigment layer. Electrodes with freshly deposited pigments showed noticeable well-detectable photocurrents while a bare graphite electrode showed no photocurrents.

Absorption spectra of CdS and $\alpha$-HgS were measured with diffuse reflectance UV−vis spectrophotometry (DR−UV−vis) (Evolution 500 UV−vis double-beam spectrophotometer with RSA-UC-40 DR-UV integrated sphere, Thermo Electron Corporation, Waltham, MA). The pigment powders were


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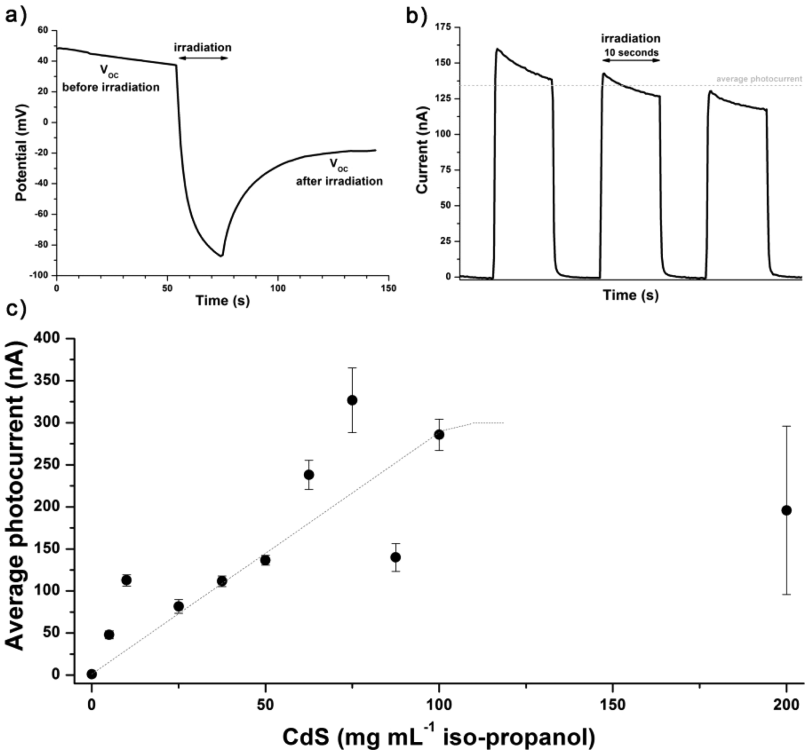


**Figure 2.** ClCdS electrode in 0.001 M NaCl, irradiation with green laser light (532 nm). (a) Open circuit potential ($V_{OC}$) before, during, and after illumination, (b) measured (photo)current in the dark and under illumination conditions, and (c) average CdS photocurrent vs CdS concentration in isopropanol suspension (error bars indicate the standard deviation).

mixed and crushed with KBr dried at 200 °C (0.02 g of CdS in 0.98 g of KBr and 0.015 g of HgS in 0.985 g of KBr). The mixtures were homogeneous and positioned in the DR−UV−vis cell for measuring in the 250−800 nm range.

## ■ RESULTS AND DISCUSSION

**Cadmium Yellow.** CdS is a semiconductor with a band gap energy ($E_g$) of ∼2.4 eV. Upon illumination with supra band gap light, electrons are excited from the valence band into the conduction band. In an electrochemical cell, this results in a potential drop of the working electrode and a rise of "photocurrent" that originates from the ejection of excited electrons from the CdS and the activation of oxidation processes at the CdS working electrode (e.g., oxidation of sulfide to sulfate). This is a typical behavior of an n-type semiconductor.[26,27] In the case of CdS in the presence of water and oxygen, $S^{2-}$ can be oxidized up to $SO_4^{2-}$, while $Cd^{2+}$ is formed (eq eq 1).[28] Water and oxygen may function as electron acceptor.

$$CdS_{(s)} + 4H_2O + 8h^+ \rightarrow Cd^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 8H^+{}_{(aq)} \quad \text{(eq 1)}$$

In a first experiment, the relationship between the amount of CdS deposited on the electrode and the photocurrent was studied by preparing different ratios of CdS−isopropanol suspensions. First, the open circuit potential $V_{OC}$ was determined for each ClCdS electrode, using a 0.001 M NaCl solution as electrolyte. The potential between electrode surface and solution was clearly different for the period before, during, and after illumination. As shown in Figure 2a, illumination causes a sudden decrease in $V_{OC}$. Since thermodynamically the potential is directly proportional to Gibbs free energy ($\Delta G^0 = -nF(E_{reduction} + E_{oxidation})$),[29] this indicates that CdS becomes more prone to chemical oxidation reactions upon illumination due to the change in Fermi energy ($E_F$) and band bending.[30,31] After irradiation, $V_{OC}$ slowly stabilizes. This $V_{OC}$ was subsequently taken as the potential for amperometric measurements and allows the electrode to be near the equilibrium in the dark. In this way, the background was not influenced by any overpotential and resembled most to a "natural" environment. Because of the formation of degradation products and a change in the initial state of the surface, the $V_{OC}$ in the dark slightly changes over the experiment.

During the amperometric measurement, four alternating cycles of darkness (∼10 s) and illumination (10 s) with a green laser (532 nm) were used (Figure 2b). The photocurrent was calculated as the average of the last three illumination cycles, with a correction for the (mostly negligible) dark current. The small decrease in photocurrent observed during each cycle is due to the oxidation of the CdS pigments grains, dissolving $Cd^{2+}$ and $SO_4^{2-}$. For every concentration ratio, the experiment was repeated for at least three different electrodes.

A clear trend is observed: the more CdS is present, the higher the photocurrent (Figure 2c). Since higher amounts of CdS result in a lower fraction of pigment particles to be in direct contact with the graphite electrode, while a thicker pigment layer partially blocks illumination of the CdS in contact with the electrode, the linearity of the response is limited. Therefore, with very high amounts of CdS (>200 mg mL$^{-1}$ isopropanol), the photocurrent does not increase anymore and larger deviations appear.

The ClCdS electrode preparation procedure does not allow for perfect control of the amount and distribution of CdS on the electrode. A clearly better reproducibility is obtained at lower CdS concentrations. Therefore, subsequent experiments


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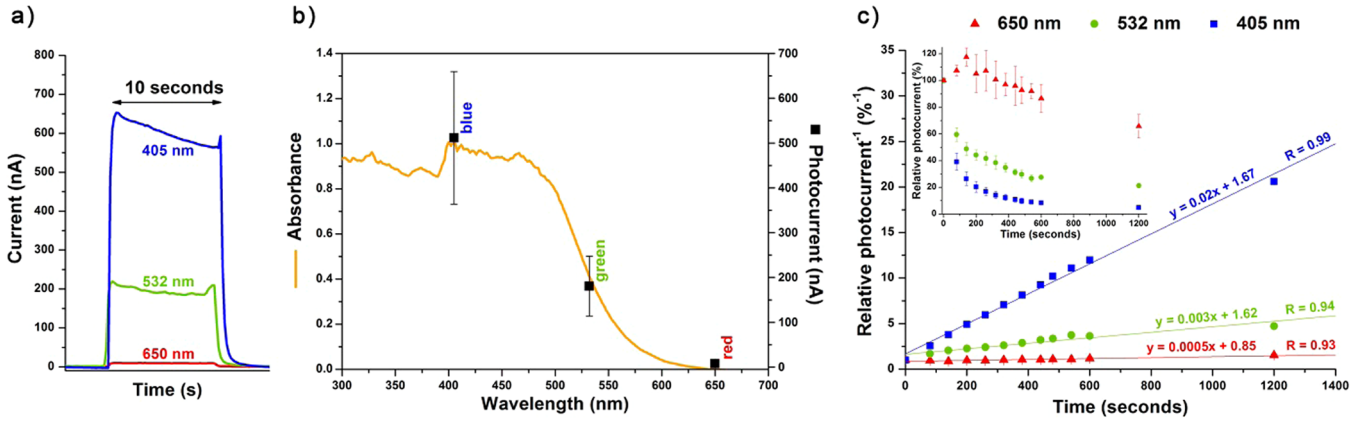


**Figure 3.** (a) ClCdS electrode, subsequently illuminated with 650, 532, and 405 nm wavelengths. (b) CdS absorption spectrum with photocurrents for irradiation with 650, 532, and 405 nm wavelengths. (c) Degradation kinetics of CdS in a 0.001 M NaCl solution and irradiation (405, 532, and 650 nm wavelengths).

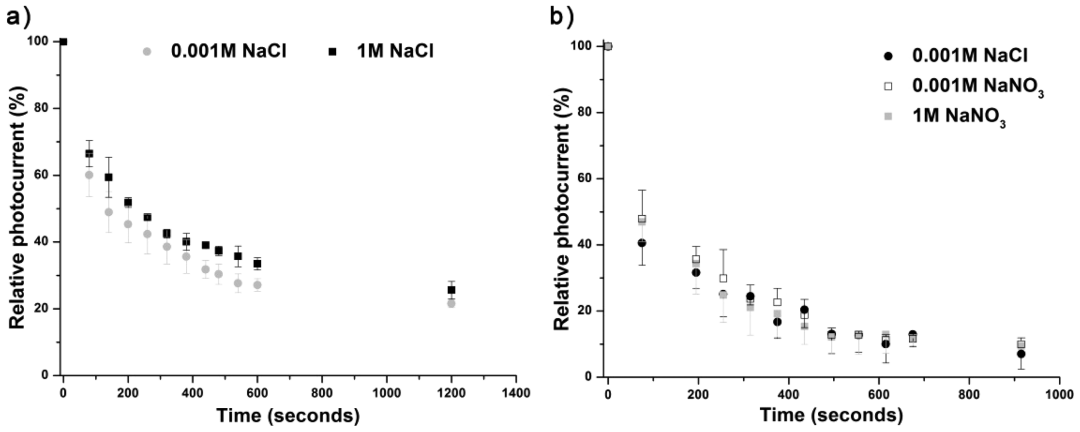


**Figure 4.** (a) Degradation kinetics of CdS in 0.001 and 1 M NaCl solution (irradiation with 532 nm wavelength). (b) Degradation kinetics of CdS in 0.001 M NaCl, and 0.001 and 1 M $NaNO_3$ solution (irradiation with 405 nm wavelength).

were performed with a 50 mg $mL^{-1}$ isopropanol suspension of CdS.

Figure 3a shows the photocurrent for a single ClCdS electrode, subsequently illuminated with red, green, and blue lasers. For each wavelength, three illumination cycles of 10 s were applied. Figure 3a only shows one illumination cycle. The experiment was repeated for five different electrodes. Although illumination of each electrode was limited to 30 s per wavelength, the sequence of red, green, and blue laser illumination was varied to eliminate the influence of previous degradation. However, no significant difference was observed. For each wavelength, the average photocurrent of the five electrodes was subsequently plotted onto the absorption spectrum of the CdS powder (Figure 3b). The pseudoabsorbance spectrum shows a typical shape for a semiconductor material, exhibiting an absorption edge near 564 nm, corresponding to a band gap of 2.2 eV. Since the red laser has an energy below the CdS absorbance band ($h\nu < E_g$), only a very small photocurrent (~5 nA) is observed. The wavelength of the green laser is situated in the middle of the absorption edge, inducing a partial excitation of the CdS. The blue laser light, in contrast, is fully absorbed, generating the highest photocurrent.

Since the photocurrent is dependent on the amount of CdS on the electrode (Figure 2c), a gradual decrease in photocurrent is expected when the CdS pigment becomes more degraded by photoinduced oxidation. Indeed, as the expected oxidation product $CdSO_4 \cdot xH_2O$ is water-soluble and does not possess semiconductor properties, it will not contribute to the measured photocurrent. In this manner, the setup provides the possibility to electrochemically monitor the degradation of CdS versus time under different conditions. As an example, the degradation kinetics of CdS were measured during illumination with red, green, and blue lasers in a 0.001 M NaCl electrolyte. Analogous to the previous experiment, the stabilized $V_{OC}$ was first determined, and subsequently used as the fixed potential during amperometric measurements (i.e., the active mode). Then the electrodes were illuminated for a certain time interval without any electrochemical intervention (i.e., in passive mode). Afterward, the next amperometric measurement was performed. This sequence was continued up to 20 min light irradiation. For each wavelength, the experiment was repeated for three different electrodes. For both the green and blue laser light, a clear solubilization of the CdS occurred, visible by a disappearance of the bright colored powder in the area where the laser irradiated the electrode. Figure 3c represents the degradation kinetics at the three wavelengths as the relative photocurrent (inset) and as the inverse of the relative photocurrent. For both the green and blue laser a clear photocurrent decay (hyperbolic trend) is followed, strongly suggesting a second-order decay reaction. This could indicate that the degradation involves more complicated reactions. Also


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pigment grain size could be a factor of influence. More research is needed to clarify this trend. The photocurrent decay depends on the excitation wavelength used: after 20 min of illumination, a decay of 79 ± 1% (green laser) and 95 ± 1% (blue laser) is observed. The large error observed for the red laser is related to the very low photocurrents measured, and should be considered with caution. Nevertheless, a small decrease in photocurrent is observed, corresponding to a decay of ∼34 ± 9% after 20 min of irradiation. This is attributed to defect states in the CdS structure, creating energy levels in the band gap, and assisting in the light absorption process (trap-to-band transitions). The limited photocurrent (Figure 3a) indicates that this process is not efficient and only a small amount of CdS is oxidized compared to the green and blue laser.

Since it is generally advised not to use highly diluted electrolytes to avoid effects of increased solution resistance, ion migration, and unclear surface charge at the electrode−solution interface,[32] the irradiation experiment with the green laser was repeated for a 1 M NaCl electrolyte (Figure 4a). An upward shift of 3% relative photocurrent was observed for the 1 M NaCl compared to the 0.001 M NaCl, lying within the experimental error. The same experiment with 0.001 M NaCl, 0.001 M $NaNO_3$, and 1 M $NaNO_3$ (blue laser irradiation) also results in similar degradation kinetics (Figure 4b). Therefore, the presence or absence of these salts does not significantly influence the degradation of the CdS powder.

With adjustment of the experimental setup, different light sources and hazardous environmental compounds could now be tested on their damaging effects toward CdS. Light source such as LED, halogen, and glass fibers with varying temperature color could be evaluated for their photo-oxidizing capacity. In conservation practice, light sensitivity of materials is commonly expressed in illuminance (lux). Also, the influence of this parameter could be easily evaluated by varying the amount of light that strikes the electrode per surface area.

**Vermilion.** $\alpha$-HgS is an n-type semiconductor with $E_g$ ∼2 eV. However, its degradation appears more complex compared to that of CdS. Figure 5 shows the photocurrent versus time

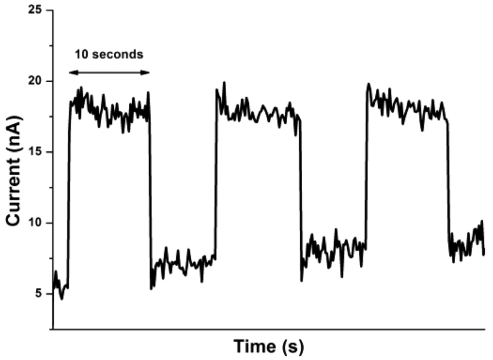


**Figure 5.** Amperometry of a Cl$\alpha$-HgS electrode in 0.001 M NaCl with alternating dark-illumination cycles (green laser).

during alternating cycles of darkness and illumination with 532 nm light in 0.001 M NaCl. The potential used is determined in a manner analogous to that for CdS. The positive photocurrent suggests an oxidation process as expected for an n-type semiconductor. Since the photocurrent is remarkably lower compared to that for CdS, fewer oxidation products are formed.

For the real-time monitoring of the degradation process, amperometric measurements were performed during continuous illumination, following up the change in photocurrent. The experimental setup was employed to evaluate the effect of light with different wavelengths on the degradation of $\alpha$-HgS. Cl$\alpha$-HgS electrodes were monitored during a 1 h illumination in 1 M NaCl (Figure 6a). Under the conditions used, after around 6 and 12 min of illumination with the blue and green laser, respectively, the photocurrent starts to increase instead of decreasing as was the case for CdS (Figure 3c). Afterward, the current decreased again, but even after 60 min of illumination, it is still significantly higher compared to the initial current recorded. For the red laser, the current increase is negligible.

A photocurrent increase for $\alpha$-HgS has already been observed by Davidson and Willsher[33] and corresponds to a slight blackening of the electrode, visible with the naked eye. Also, in the experiments performed in the current study, the photocurrent increase is related to the blackening of $\alpha$-HgS. Previous research assigned this discoloration to the formation of $Hg^0$.[5] To confirm the presence or absence of $Hg^0$ after the amperometric monitoring, additional control with linear sweep voltammetry from −200 to 75 mV was performed, using 0.1 M NaOH as electrolyte. The $Hg^0/Hg^{2+}$ oxidation peak is situated around −50 mV, whereas $\alpha$-HgS does not show any redox transformation in the applied potential range.[5] The voltammetric control measurement confirms the formation of $Hg^0$ for the blue and green laser, while after red light illumination, no $Hg^0$ is formed. Since red light does not have enough energy to excite electrons from the valence band into the conduction band of $\alpha$-HgS, the absence of $Hg^0$ with red light illustrates that electron excitation is mandatory to induce blackening of $\alpha$-HgS.

The photocurrent increase may be attributed to a catalytic effect of the (discontinuous) film of metallic mercury (nano)particles that is formed in situ,[5] changing the energetics of the electron-transfer process at the semiconductor surface.[31] If metallic mercury is formed at the surface of the $\alpha$-HgS particles, a superior electric contact between semiconductor and graphite electrode is formed. $Hg^0$ can facilitate the transport of excited electrons toward adsorbed $Hg^{2+}$ species, inducing a faster formation of $Hg^0$. In addition, $Hg^0$ can cause a larger fraction of the pigment to be in contact with the electrode due to the increase of the conductive surface, possibly improving the kinetics of the sulfide oxidation. The faster increase in photocurrent for the blue laser suggests a faster $Hg^0$ production. After some period of time, the photocurrent starts to drop. This can have different causes such as a decreasing amount of $\alpha$-HgS that can participate in the oxidation reaction, a preferential oxidation of $Hg^0$ compared to the semiconductor, and/or the formation of a continuous $Hg^0$ film which partly blocks the amount of light that can be absorbed by the underlying $\alpha$-HgS.[31]

The harmful effect of chlorides on the blackening of $\alpha$-HgS is a well-known phenomenon.[1,19,5,26] The setup was also used to identify the blackening capacity of other environmental compounds by using them as the electrolyte. In this way, additional experiments with green laser illumination proved the deleterious effects of organic acids such as formic and acetic acid and ammonium-rich compounds such as $NH_4NO_3$ and $(NH_4)_2SO_4$, both present in airborne particulate matter (Figure 7). However, the degradation kinetics are slower compared to when NaCl is present: the increase in photocurrent appears later and/or shows a less steep increase. Other compounds such as $NaNO_3$ and $Na_2SO_4$ showed a negligible increase in photocurrent within the tested time span. Analogous to the experiment shown in Figure 6b, linear sweep voltammetry was


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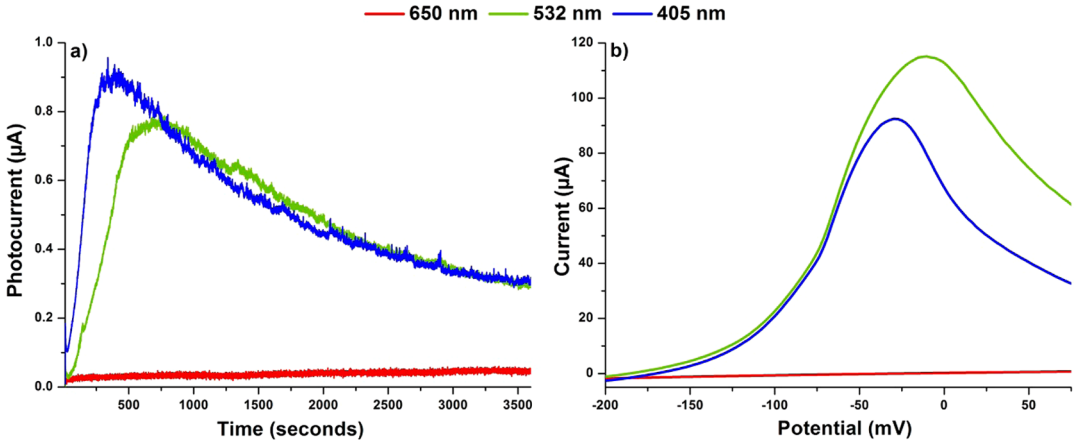


**Figure 6.** Comparison of three different wavelengths on the degradation capacity of $\alpha$-HgS. (a) Chronoamperometric measurement during 1 h illumination in 1 M NaCl, illustrating the catalyzing effect of the degradation product. (b) Linear sweep voltammograms in 0.1 M NaOH after 1 h of illumination, confirming the in situ formation of $Hg^0$ in case of the green and blue lasers, and the absence of $Hg^0$ with the red laser.

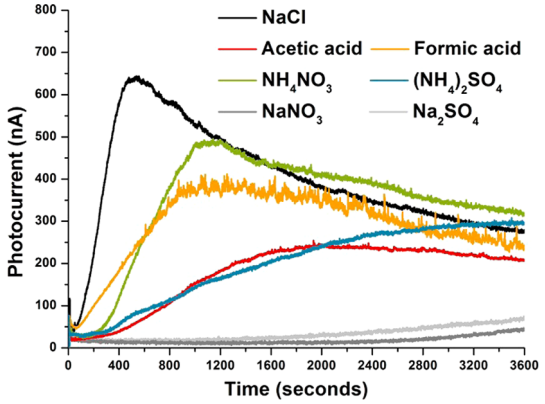


**Figure 7.** Comparison of different environmental compounds on the degradation capacity of $\alpha$-HgS. Chronoamperometric measurements during 1 h illumination (green laser) in 1 M solutions.

performed after the chronoamperometric measurement to confirm the formation of $Hg^0$. A $Hg^0/Hg^{2+}$ peak appeared for acetic and formic acid, and $NH_4NO_3$ and $(NH_4)_2SO_4$. No $Hg^0$ was detected for $NaNO_3$ and $Na_2SO_4$, both showing a negligible photocurrent increase. Therefore, these compounds can be considered as harmless regarding $\alpha$-HgS blackening.

## CONCLUSION

The proposed electrochemical method for a fast and real time monitoring of pigment degradation gives interesting and promising results for semiconductor pigments such as CdS and $\alpha$-HgS. By using amperometry at the open circuit potential ($V_{OC}$), the degradation can be followed up and evaluated under various conditions. The conditions can be varied in (1) the type of sample (i.e., pigment), (2) the type of irradiation, and (3) the type of electrolyte.

Different light sources can be tested on their damaging effects toward semiconductor pigments. The experimental setup can easily be adjusted, taking into account the type of light, illuminance, and color temperature. In addition, the influence of different types of hazardous environmental compounds can be evaluated, provided that they can serve as (aqueous) electrolyte (e.g., organic acids and salts occurring in airborne particles). Results of such experiments help in the identification of environmental hazards, for example, to draw up a risk assessment though, in the current study, the pigments were used in their pure form, without taking into account combinations of materials typically present in paintings (e.g., binding medium and mixtures with other (inorganic) pigments). Also, the influence of the semiconductor grain size toward their environmental stability could be studied. Such more complex conditions are the obvious step in understanding the degradation phenomena in real paintings. However, they present challenges. To study pigment mixtures and grain sizes, it is necessary to exactly control the amount of semiconductor deposited onto the electrode, and to ensure a homogeneous dispersion. Binding media such as oil (partially) block the contact between the pigment and the graphite electrode. However, electrochemical experiments require a contact interface between the electrode material and the pigment. This hinders mimicking a more realistic paint situation in which most pigment grains are initially well encapsulated in the binding medium. At this moment, experiments are ongoing to overcome these challenges.

For both CdS and $\alpha$-HgS, illumination with supra band gap light induces an oxidative degradation, though CdS appeared more prone to oxidation compared to $\alpha$-HgS, based on its remarkable higher photocurrent. Where the electrolyte composition is of less importance for CdS, it has a major influence for $\alpha$-HgS: certain compounds such as chlorides induce secondary reactions, forming $Hg^0$. This alteration product induces an increase in photocurrent, catalyzing the degradation process. Apart from semiconductor pigments, the electrochemical approach could also be used for other pigments exhibiting redox reactions as part of their degradation behavior (e.g., chrome yellow).

The electrochemical experiments are presented as an alternative to classical time-consuming accelerated aging experiments. However, not all natural aging phenomena can be reproduced in the electrochemical experiments. A main reason is the liquid environment in the electrochemical cell. Processes such as dissolution−recrystallization cycles of soluble degradation products (e.g., cadmium sulfates) due to variations in ambient relative humidity do not occur in the electrochemical cell. Also, secondary reactions with pigment degradation products and their environment can be hindered by the liquid environment. It is for example hypothesized that $Hg^0$, the black degradation product of $\alpha$-HgS, further reacts


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with $Cl^-$ to form $HgCl_2$ or $Hg_2Cl_2$.[5,9] Such reactions are (partially) hindered in large volumes of water in which $Cl^-$ easily dissolves. Despite this disadvantage, the electrochemical monitoring experiments are very useful to speed up the degradation reactions, dissociate different steps in complex degradation phenomena, and study degradation kinetics in various environments. The proposed methodology could be applied to study all redox-active substances that react under a physical stimulus such as light, or interact with a chemical reagent.

## AUTHOR INFORMATION


### Corresponding Author

*E-mail: Karolien.DeWael@uantwerpen.be.


### Notes

The authors declare no competing financial interest.

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