Pigment Discoloration

DOI: 10.1002/ange.201303977

Formation of Metallic Mercury During Photodegradation/Photodarkening of α-HgS: Electrochemical Evidence**

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Since antiquity, red mercury sulfide (α-HgS), called cinnabar in its natural form and vermilion in its synthetic form, has commonly been used as a pigment.[1] An undesirable phenomenon is the degradation of this bright-red material in the presence of light, chloride ions, and humidity,[2] causing it to turn black. This degradation phenomenon has been observed on the surface of frescoes at important heritage sites such as Pompeii, and of paintings from famous masters such as P. P. Rubens and P. Brueghel. An appropriate conservation of this valuable and irreplaceable heritage requires a profound knowledge on the degradation mechanism of the pigment. Several methods, such as X-ray diffraction (XRD), X-ray absorption near-edge spectroscopy (XANES), and secondary-ion mass spectrometry (SIMS) have been employed to identify the degradation products: $HgCl_2$, Hg_2Cl_2, $HgSO_4$, Hg_2SO_4, and $Hg_3S_2Cl_2$.[3–5] Yet, none of these compounds has a dark color that can explain the blackening of α-HgS in a convincing manner. Several hypotheses for the decomposition and discoloration have been proposed, some assuming the formation of black β-HgS[6,7] and others that of metallic mercury.[3,8–10] While volatile mercury has already been observed in photodegradation experiments on mercury ore,[9] neither β-HgS or metallic mercury as a deposit have been detected on naturally and artificially degraded HgS paint. Moreover, the role of chloride ions is not fully understood. This study presents the results of electrochemical experiments that demonstrate for the first time the formation of metallic mercury as a degradation product of HgS induced by the joint action of light and chloride ions. A degradation mechanism consistent with these findings is proposed.

First, cyclic voltammetry from −250 to 100 mV (scan rate: 50 $\mathrm{mV\,s^{-1}}$) in 0.1 M NaOH was employed to unravel the HgS redox transformation(s) (Figure 1). The behavior of a (red) α-HgS | Pt electrode, preconditioned for 20 seconds in a 1 M NaCl solution at a potential of −1750 mV (II), was compared to a non-pretreated equivalent (I). Additionally, another α-HgS | Pt electrode (III) was illuminated for 20 min with a blue laser (405 nm) in a 1 M NaCl solution. With electrode I, no oxidation or reduction processes are visible in the supporting 0.1 M NaOH electrolyte. The electrochemical pretreatment at −1750 mV induces the formation of metallic mercury at the surface of the α-HgS | Pt, which is due to the applied negative potential (preconditioning). The reoxidation becomes apparent during the first cyclic voltammetric scan (Figure 1, II) immediately obtained after the electrochemical pretreatment. The observed oxidation peaks at about −50 mV correspond to the oxidation of Hg^0 to Hg^{2+}.[11–13] The double peak is attributed to the underpotential deposition of mercury when applying strongly negative potentials.[14,15] The waves at about −100 and −200 mV are the corresponding reduction of Hg^{2+} formed during the previous oxidative sweep. After photodegradation of an α-HgS | Pt electrode in a Cl-rich environment that was not electrochemically pretreated at −1750 mV, an oxidation peak arises at a similar potential, indicating the presence of Hg^0 (Figure 1, III). The spot where the laser irradiated the electrode is clearly distinguishable by the disappearance of the red color (blackening; Figure 2).

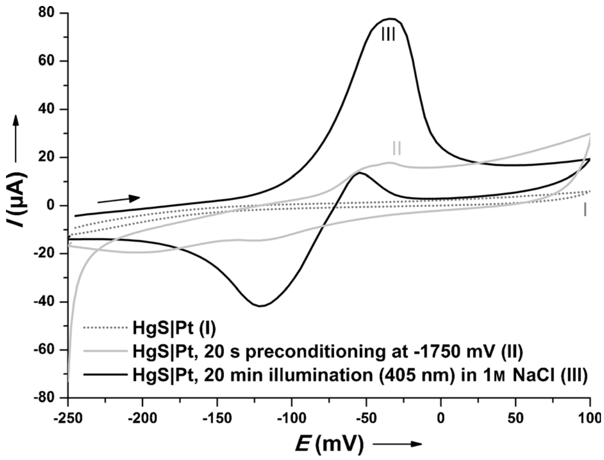

Figure 1. Cyclic voltammetric scans (first scans) of α-HgS | Pt electrodes (different pretreatments) in 0.1 M NaOH. I) Without pretreatment, II) electrochemical pretreatment in 1 M NaCl; III) illumination pretreatment in 1 M NaCl.

Secondly, the degradation behavior of α-HgS with and without chloride ions and with and without illumination was compared. To focus on the metallic mercury detection (the oxidation of Hg^0) at the surface of the degraded α-HgS | Pt electrodes, linear sweep voltammetric (LSV) experiments were performed in the −90 mV to 45 mV range, with 0.1 M NaOH as supporting electrolyte. In an initial experiment, an α-HgS | Pt electrode was pretreated by laser irradiation for 30 min, either in a 1 M NaCl solution or in deionized water, and subsequently measured with LSV. In deionized water, no

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[**] The authors acknowledge L. Klaassen for valuable discussions and providing samples. We acknowledge financial support from the SDD programme (S2-ART project) of the Belgian Federal Goverment.

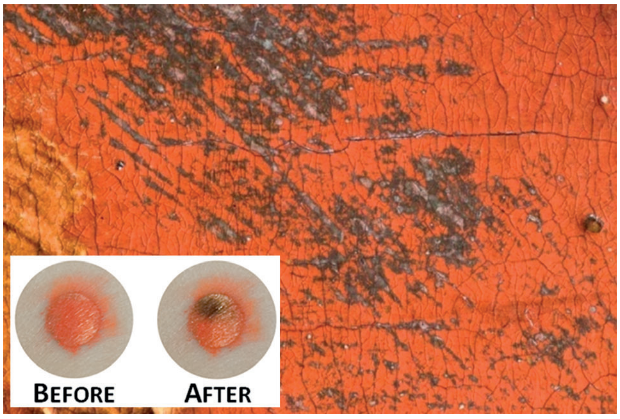

Figure 2. Visual alteration observed at Rubens' painting "The adoration of the Magi". Inset: an α-HgS|Pt electrode before and after 532 nm laser illumination (30 min irradiation in a 1 M NaCl solution, with the laser spot located in the upper half of the electrode).

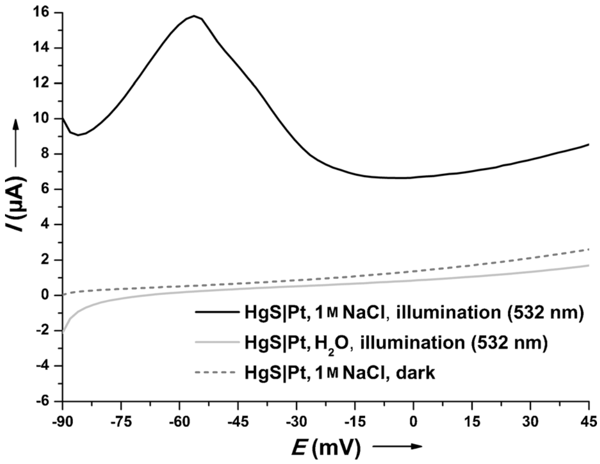

Figure 3. Linear sweep voltammetry of α-HgS|Pt electrodes from −90 to 45 mV (50 mV s^{-1}) in 0.1 M NaOH with different pretreatments: 30 min illumination in 1 M NaCl or H_2O, and 30 min immersion in 1 M NaCl in the dark.

significant amount of metallic mercury was detected, whereas in the 1M NaCl solution, a clear oxidation peak appears around −50 mV (Figure 3). To demonstrate the need of illumination in the process of metallic mercury formation, an α-HgS|Pt electrode was kept in the dark in a 1M NaCl solution for 30 min, and compared with a similar experiment under laser irradiation (30 min). Contrary to the experiment with illumination, no peak corresponding to Hg^0 oxidation appears in the dark. We conclude from the above that under the given circumstances, illumination of α-HgS in combination with chloride ions is required to induce the formation of metallic mercury.

To further unravel the degradation mechanism, an additional experiment with α-HgS suspensions was performed. The purpose was to monitor the release of protons and of SO_4^{2-} ions during photodegradation. After UV illumination of α-HgS in H_2O, a clear increase in SO_4^{2-} is observed, associated with a decrease in pH (Table 1) compared to the situation without light. A similar trend was observed by Okouchi and Sasaki.[9] In a 1M NaCl solution, larger numbers of SO_4^{2-}-ions and protons are released.

Table 1: SO_4^{2-} concentration and pH values for α-HgS-suspensions kept in darkness or illuminated for 500 h.

	SO_4^{2-} [mg L^{-1}][a]		pH	
	Dark	UV	Dark	UV
H_2O	21	111	4.6	3.2
1 M NaCl	22	215	4.8	2.8

[a] The initial SO_4^{2-} concentration is negligible.

The suggested degradation mechanism is based on the properties of α-HgS as a semiconductor having a band gap energy (E_g) of 2 eV. The energy positions of the valence and conduction band edges are respectively situated at 2.02 and 0.02 V vs. NHE (pH 2).[16] The thermodynamic oxidation ϕ^{ox} and reduction potential ϕ^{red} of HgS give an indication of the stability of the semiconductor against decomposition. These potentials can either be deduced from Pourbaix diagrams[17] or calculated.[18] For HgS, ϕ^{red} is situated at a potential as negative or more negative than the conduction band energy (that is, within the conduction band) for aqueous solutions with and without chloride ions, respectively.[19] Therefore, it can be assumed that photoinduced degradation will not decompose HgS directly to Hg^+ or Hg^0. Moreover, HgS behaves as an n-type semiconductor.[9,20] This corresponds to the fact that (oxidative) degradation mainly appears under the influence of light. Illumination with $h\nu > E_g$ will induce an increase in the minority charge carriers (that is, positive holes, h^+), making the oxidation of S^{2-} more probable. As ϕ^{ox} is more negative than the oxidation potential of H_2O, such an oxidation will effectively take place under illumination in aqueous solutions. When making abstraction of intermediate sulfur-containing species,[9,21] the following reaction is expected to take place:

$$\mathrm{HgS} + 4\,\mathrm{H_2O} + 8\,\mathrm{h^+} \rightleftharpoons \mathrm{Hg^{2+}} + \mathrm{SO_4^{2-}} + 8\,\mathrm{H^+} \tag{1}$$

This reaction explains the increased amount of sulfate and also the decrease in pH upon illumination that is experimentally observed (Table 1). A significant amount of the released Hg^{2+} is most probably adsorbed at the HgS surface, a phenomenon that has already been demonstrated in previous research.[20,21] In the presence of Cl^-, the photodegradation process is stimulated owing to the formation of more stable species such as the (1,4) coordination complex with Hg^{2+}:[19]

$$\mathrm{HgS} + 4\,\mathrm{Cl^-} + 4\,\mathrm{H_2O} + 8\,\mathrm{h^+} \rightleftharpoons \mathrm{HgCl_4^{2-}}_{(\mathrm{ads})} + \mathrm{SO_4^{2-}} + 8\,\mathrm{H^+} \tag{2}$$

Furthermore, these complexes can be reduced,[19] leading to the formation of metallic mercury:

$$\mathrm{HgCl_4^{2-}}_{(\mathrm{ads})} + 2\,\mathrm{e^-} \rightleftharpoons \mathrm{Hg}_{(\mathrm{ads})} + 4\,\mathrm{Cl^-} \tag{3}$$

The potential of reaction (3) is 0.48 V vs. NHE,[22] that is, situated in between the conduction and valence bands of HgS. This means that photoexcited electrons from the conduction band of HgS can be transferred towards adsorbed Hg^{2+} in the form of $HgCl_4^{2-}$ complexes, hereby reducing and forming adsorbed Hg^0.

To confirm Hg^{2+} adsorption at the HgS surface, an α-HgS | Pt electrode was immersed in an aqueous 0.1 M $HgCl_2$ solution for 20 min in darkness. Subsequently, cyclic voltammetric scans (not shown) were recorded in 0.1 M NaOH, starting at a potential of −75 mV. Initially, no oxidation peak is observed during the first scan. In the backward scan, however, a reduction peak appears around −120 mV, accompanied with a visual blackening of the α-HgS. In the subsequent reverse scan, an oxidation peak now appears around −50 mV. The appearance of the reduction and oxidation peak at the characteristic Hg^{2+}/Hg^0 potentials indicate the presence of adsorbed Hg^{2+} on the HgS surface. To test the ability of HgS to reduce this adsorbed Hg^{2+} under illumination (Figure 4), α-HgS | Pt and bare Pt electrodes were again immersed in 0.1 M $HgCl_2$ for 20 min and subsequently rinsed with water. Some of the electrodes were directly measured (no illumination) with linear sweep voltammetry in the −75 to 45 mV range (Figure 4, lower curve). Another batch was first illuminated for 30 min in a H_2O environment before analysis. To exclude the possible influence of Cl adsorption, a control α-HgS | Pt electrode was immersed in 0.1 M NaCl and subsequently illuminated for 30 min as well. Figure 4 confirms the hypothesis: only after Hg^{2+} adsorption combined with illumination, an oxidation peak of Hg^0 to Hg^{2+} appears.

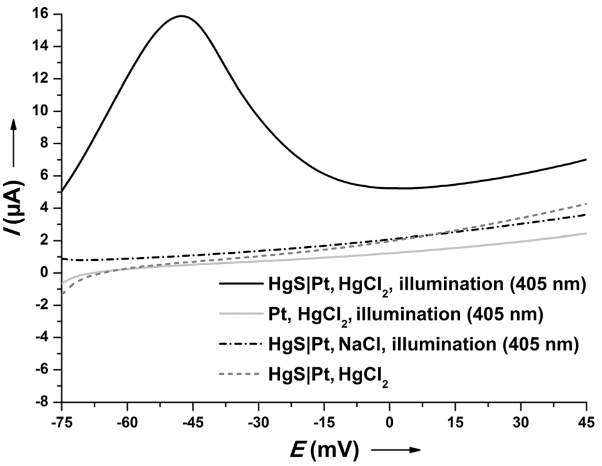

Figure 4. Linear sweep voltammetry of Pt and α-HgS | Pt electrodes from −75 to 45 mV (50 mVs^{-1}) in 0.1 M NaOH with different pretreatments: immersion for 20 min in 0.1 M $HgCl_2$ or 0.1 M NaCl with subsequent (optional) illumination in H_2O for 30 min.

In reaction (3), Cl^- is regenerated, acting as a catalyst in the degradation of HgS under the influence of light. In turn, the metallic mercury can react in various ways,[3] and form experimentally observed secondary products,[23] for example:

$$2\,Hg + 2\,Cl^- \rightleftharpoons Hg_2Cl_2 + 2\,e^- \qquad (4)$$

$$2\,Hg + SO_4^{2-} \rightleftharpoons Hg_2SO_4 + 2\,e^- \qquad (5)$$

The above set of experiments evidence the formation of metallic mercury as a degradation product of α-HgS induced by a joint action of light and chloride ions. Based on the electrochemical findings a possible degradation mechanism is suggested.

Experimental Section

Platinum and graphite electrodes were pretreated by mechanical polishing with a P320 SiC paper to obtain a rough surface. To remove any adherent SiC particles, the electrode was rinsed with deionized water and ethanol in an ultrasonic bath. Subsequently, 2 μL of an ethanol–HgS suspension (0.05 g α-HgS in 1 mL ethanol) was pipetted onto the electrode, relying on the VMP principle (voltammetry of microparticles).[24,25] The amount of HgS on the electrode surface is not well-controllable, but it is not of relevance as no quantitative results are provided. The electrode with the HgS side oriented upward was positioned in an open container. The latter was filled with 6 mL solution of interest (for example H_2O, NaCl solution). A low-power laser beam irradiated the HgS-modified electrode surface for a well-defined time period to induce HgS degradation. Lasers of 405 nm (blue) and 532 nm (green) were employed, both giving similar results. Afterwards, the electrode was gently rinsed with deionized water. Subsequently, electrochemical measurements were performed in a three-electrode system: a Ag/AgCl reference electrode, a Pt counter electrode, and the (degraded) HgS electrode. A 0.1 M aqueous NaOH solution was used as supporting electrolyte, as previous experiments had shown that it is most suitable for mercury detection.[26] Electrochemical experiments were performed with an Autolab PGSTAT101 potentiostat (Metrohm, the Netherlands) controlled by a PC using the NOVA 1.10 software. Only the results for α-HgS | Pt electrodes are shown here, but similar results were obtained for α-HgS | graphite electrodes. Thus, the underlying electrode material does not play a crucial role.

For the additional HgS suspension experiment, 0.5 g α-HgS powder was suspended either in 5 mL H_2O or in 5 mL 1 M NaCl. One set of both suspensions was illuminated for 500 h with UV fluorescence lamps; another set was kept in the dark for the same time period. Afterwards, the pH was measured with a pH electrode (Cyberscan pH510, Eutech Instruments, Nijkerk, the Netherlands) and the SO_4^{2-} concentration of the suspension (filtered and diluted) was determined by ion chromatography (IC, DX-120, Dionex, Sunnyvale, CA, U.S.A.).

Received: May 9, 2013
Published online: October 2, 2013

Keywords: degradation · electrochemistry · mercury sulfide · pigments · vermilion

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