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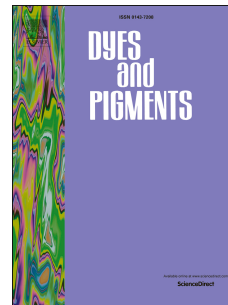
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Understanding the (in)stability of semiconductor pigments by a thermodynamic approach

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Abstract

Several artists' pigments are semiconductors. Some of these materials appear stable over time, whereas others already show remarkable signs of degradation after limited time periods. The (in)stability of these pigments can be understood using a thermodynamic approach. For several pigment-related materials, the thermodynamic oxidation and reduction potential (ϕ^{ox} and ϕ^{red}) were determined and evaluated considering the absolute energy positions of the valence and conduction band edges and the water redox potentials. The positions of ϕ^{ox} and ϕ^{red} can be used in a fast screening of the stability of semiconductor pigments towards photoinduced corrosion in an aqueous/humid environment. This theoretical approach corresponds well with experimental data on pigment permanence and degradation phenomena found in literature.

1. Background

1.1 Introduction

Many compounds used as artists' pigments or adulterations can be classified as semiconductors. Examples of such materials are the ancient pigments vermilion ($\alpha\text{-HgS}$), orpiment (As_2S_3) or mosaic gold (SnS_2), and the modern pigments cadmium yellow (CdS), cadmium red (CdSe), titanium dioxide white (TiO_2), zinc white (ZnO) or chromium oxide green (Cr_2O_3). Moreover, some pigment degradation products can also be classified as semiconductor materials, e.g., PbS as the black degradation product of lead white ($2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$) [1] or $\text{Cr}_2\text{O}_3\cdot 2\text{H}_2\text{O}$ formed after photoreduction of chrome yellow ($\text{PbCr}_{1-x}\text{S}_x\text{O}_4$) [2]. Some of these materials appear stable over time, whereas others already show remarkable signs of degradation after limited time periods, triggered by physical or chemical parameters. In the current study, the stability of semiconductor pigments is thermodynamically predicted, based on literature data. In order to get a better insight in their stability and degradation behavior, some general semiconductor properties are treated first. By predicting the stability of pigments, it becomes possible to slow down the degradation processes by taking mitigation measures before they have any visual impact.

1.2 Built-in semiconductor characteristics

Semiconductor materials consist of atoms containing core electrons located in the atomic orbitals and electrons located in the molecular orbitals. For this type of material, the molecular

orbitals form a valence band (VB), which is the energetically highest occupied electronic band, and the conduction band (CB), which is the first subsequent empty band. A gap between VB and CB, with E_g the energy difference between the bands, governs the electron transitions. The presence of this band gap, with typical values ranging between a few meV up to 4 eV, distinguishes semiconductors from conductor materials (metals). On the other hand, the gap is not as large as for insulators (> 4 eV) [3] (Fig. 1a). In between the valence and conduction band, the Fermi level E_F is defined. This level is considered as a hypothetical electron energy level, describing a state with a 50 % probability of being occupied by an electron [4]. In a perfect crystal lattice, there are no allowed energy levels within the band gap. For such intrinsic semiconductors, the concentration of holes and electrons is equally large and E_F lies just in between the VB and CB. However, intrinsic semiconductors hardly exist since real crystals contain imperfections such as impurities, deviations in stoichiometry, surface defects, etc. Such lattice defects represent an excess of electric charge, creating occupied energy levels in the forbidden zone. An excess of negative charge carriers implies that the electrons that do not participate in a covalent bond, are only weakly bound in the crystal lattice. These electrons are located on donor energy levels (E_D) close to the conduction band, with E_F lying in between E_D and the CB. This type of semiconductors is classified as 'n-type', referring to the (negative) electrons as majority charge carriers. In p-type semiconductors, the majority carriers are (positive) holes, located on acceptor energy levels (E_A) close to the valence band. In this case, E_F is defined close to the VB. Thermal excitation at room temperature is sometimes already sufficient to excite electrons into the CB (n-type) or create holes in the VB (p-type) [5-7].

Several characteristics of semiconductor pigments are related to their semiconductor properties. An example is their color. Wavelengths with energy higher than the band gap energy are absorbed by the semiconductor, the others are reflected. Since the wavelength region of the visible light is situated in between 400 nm (i.e., 3.1 eV) and 700 nm (i.e., 1.8 eV), semiconductors with a band gap energy $E_g < 1.8$ eV are black, with $E_g > 3.1$ eV are colorless or white and with 1.8 eV $> E_g > 3.1$ eV are colored. Clear examples are black PbS ($E_g = 0.4$ eV), yellow CdS ($E_g = 2.4$ eV) and white ZnO ($E_g = 3.4$ eV). For the conversion of wavelength to band gap energy, the following relation is valid: λ (nm) $\leq \frac{1241}{E_g$ (eV) (Fig. 1b). The particle size of the pigment grains also influences the color. Usually, E_g increases with decreasing particle size [4, 8]. For CdS, for example, it is known that smaller particles have a more yellowish shade, whereas larger particles appear orange [9].

1.3 Semiconductor-environment characteristics

When the semiconductor comes into contact with an aqueous environment (e.g., humid atmosphere forming a thin water layer at the pigment surface), the Fermi level of the semiconductor and the Fermi level of the aqueous environment (i.e., the redox potential) will equilibrate. Electrons are exchanged between the two phases and the transfer continues up to the point that the Fermi levels are aligned. When E_F of the environment is more positive than E_F of the semiconductor (vs. NHE), often the case for n-type semiconductors, some electrons from the semiconductor will be transferred to the environment, leaving a positive charge behind. Since the charges repel each other, they will be located at the surface of the solid. For metals, the charges are concentrated in a surface skin, but for semiconductors, the charges are located in a diffuse space charge layer just beneath the surface. An electrical Helmholtz double layer is formed between the semiconductor and the environment with a positive space charge layer at the semiconductor side, surrounded by negative ions at the environment side. The positive space charge layer results in an upward bending of the band edges ('depletion layer'). On the other hand, when the E_F of the environment is initially at a more negative potential than that of the semiconductor, electrons will flow from the environment to the semiconductor, causing downward band bending which is most common for p-type semiconductors ('accumulation layer', negative surface charge) [7, 10].

In the dark and at sufficiently low temperature, no charge transfer is expected for intrinsic semiconductors in contact with an aqueous environment. For n- and p-type semiconductors charge transfer is possible with the CB or VB, respectively, upon the availability of electrons (e^-) or holes (h^+) (Fig. 2, situation in the dark). Light, however, changes the entire situation, increasing the semiconductor reactivity. Upon illumination with supra band gap light ($h\nu > E_g$), an electron in the VB absorbs a photon with $E > E_g$ and is transferred to the CB. This leads to an electron concentration in the CB, leaving holes in the VB. The concentration of each charge carrier (e^- and h^+) is now displaced from equilibrium. For this non-equilibrium situation, new Fermi energies have to be described separately for holes and electrons by the quasi-Fermi level ${}_pE_F^*$ and ${}_nE_F^*$, respectively (Fig. 2, situation under illumination). With increasing light intensities, the quasi-Fermi levels become closer to the band edges [11]. In intrinsic semiconductors, the concentration of electrons as well as holes will increase in equal measure and the split of ${}_pE_F^*$ and ${}_nE_F^*$ will occur in a symmetric manner. For n-type/p-type semiconductors, the concentration of the majority carriers (e^-/h^+) will not alter much, but the concentration of minority carriers (h^+/e^-) will strongly increase. Therefore, for an n-type semiconductor, ${}_nE_F^*$ changes only slightly, while ${}_pE_F^*$ increases drastically. For p-type semiconductors, the opposite is the case. As indicated in Fig. 2, upon illumination ($h\nu > E_g$), charge transfer is possible with the valence as well as the conduction band for all semiconductor

types [11, 12]. However, since most of the pigments are stable in the dark, it is assumed that their photodecomposition is caused by reactions of minority carriers, i.e., h^+ for n-type semiconductors and e^- for p-type semiconductors. Upon illumination, charge separation is promoted in the presence of band bending, inhibiting electron-hole pair recombination at the surface due to the existing electric field (Fig. 3a). Defects at the surface, on the other hand, create intermediate energy levels within the band gap, promoting recombination reactions.

Due to the limited penetration depth of the light inside an opaque solid, the generation of photoinduced electron-hole pairs occurs mostly just beneath the surface. Thus, the non-equilibrium situation with the distinction in quasi-Fermi levels is often very superficial [13]. Moreover, the electron transfer from semiconductor to environment is influenced by the wavelength, in addition to band bending. Shorter wavelengths (with $h\nu > E_g$, known to be more harmful for paintings) are absorbed closer to the semiconductor surface, exciting electrons in the very superficial region. Longer wavelengths, on the other hand, will penetrate deeper into the semiconductor (Fig. 3a). Additionally, when the interface semiconductor-environment is subjected to band bending, the present electric field will prevent electron-hole recombination (Fig. 3b). Excited electrons further away from the interface, as is the case for the deeper penetration of longer wavelengths, do not encounter any influence of the electric field, and easily recombine.

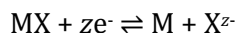
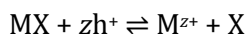
In general, three possible transformations might occur with the photogenerated electron-hole pairs: (1) recombination of the electron-hole pairs, (2) alteration of environmental compounds (e.g., pigments catalyze the decomposition of the binding medium), or (3) transformation of the semiconductor materials themselves (e.g., the degradation of pigments). Such decomposition reactions occur exclusively at the surface, i.e., at the interface semiconductor-environment. Whether the environment (2) or the semiconductor itself (3) is degraded, can be thermodynamically predicted, as discussed in the next section.

2. Results and discussion

2.1 Semiconductor degradation

A starting approach to predict the photostability of semiconductor pigments, is based on thermodynamics. Already in 1977, Gerischer [11] introduced the concept of thermodynamic oxidation (ϕ^{ox}) and reduction (ϕ^{red}) potentials of semiconductors under illumination. These potentials describe the energy that is required to make oxidation or reduction happen from a

thermodynamic point of view. They are defined by the following reactions, consuming either photogenerated holes or electrons [14]:



Depending on the levels of the quasi-Fermi energies, one of these reactions may occur, inducing the decomposition of the semiconductor. A semiconductor is considered as thermodynamically stable when ϕ^{ox} is more positive than the VB maximum and ϕ^{red} more negative than the CB minimum. When this condition is only valid for either ϕ^{ox} or ϕ^{red} , photodecomposition is controlled by both thermodynamic and kinetic criteria. For such cases, the stability of the semiconductor pigment towards the environment can be predicted by considering the alignment of ϕ^{ox} and/or ϕ^{red} towards the redox potentials of the environment. As an example, the stability of semiconductors in aqueous or humid environment is illustrated (Fig. 4). When ϕ^{ox} is more negative than $\phi^{(\text{O}_2/\text{H}_2\text{O})}$, the semiconductor is unstable against oxidation in water and can decompose (Fig. 4, B and C). On the other hand, when ϕ^{red} is more positive than $\phi^{(\text{H}^+/\text{H}_2)}$, the semiconductor is unstable against reduction in water (Fig. 4, A and D) [11, 14]. The concept is comparable to the corrosion of metals. However, even when thermodynamics predict the decomposition of the semiconductor, the kinetics of the competing redox reactions can highly influence the actual stability [15]. Therefore, the stability prediction on the base of ϕ^{ox} and ϕ^{red} should be considered as an initial tool for a fast screening of the pigment stability. Nevertheless, until now, literature and experimental data indicate a good correspondence of the theoretical approach to pigment permanence and experimentally observed pigment degradation phenomena [9, 16-23].

To evaluate the stability of the semiconductor pigments, (1) the energy positions of the valence and conduction band were plotted together with (2) their respective thermodynamic oxidation and reduction potential in aqueous environment.

The absolute energy position of the conduction (E_{CB}) and valence (E_{VB}) band edges, indicated as bars in Fig. 5, were taken from Chen & Wang [14] (CdS, CdSe, ZnS, TiO₂ and ZnO) and Xu & Schoonen [4] (HgS, SnS₂, As₂S₃, PbS and Cr₂O₃). In these publications, most energies are given at extreme pH-values (pH 0-2), which are not realistic considering heritage pigments. Since the band edge positions of many semiconductors are subjected to pH, recalculation for pH 7 was performed. For metal oxide semiconductors, the band edge positions mostly follow a Nernstian behavior as for water redox potentials [14]. Therefore, a fraction of -0.059 V was

counted for each pH increase of 1. For metal sulfide semiconductors, the pH-dependence is not yet fully clear. The band edges for ZnS, for example, are probably pH-independent [14]. However, apart from ZnS, all band edge energies were adjusted using the Nernstian relation.

The semiconductor oxidation (ϕ^{ox}) and reduction (ϕ^{red}) potentials were deduced from Pourbaix diagrams of the respective compounds in aqueous environment [24-28] or adopted from Chen & Wang [14]. All ϕ^{ox} and ϕ^{red} were determined for pH 7, except for ZnO which dissolves at a pH < 8.5 (ϕ^{ox} and ϕ^{red} at pH 8.5). More information on the procedure how to deduce ϕ^{ox} and ϕ^{red} from Pourbaix diagrams can be found in Park & Barber [26]. Since ϕ^{ox} and ϕ^{red} are independent of the exact energy positions of the valence and conduction band, small errors or deviations in the absolute energy positions of the latter are not problematic [14]. Both ZnO and TiO₂ appeared stable against oxidative decomposition in the range of the consulted Pourbaix diagram (> 2.0 eV) at the pH of interest. Therefore, ϕ^{ox} was set at the upper limit of the Pourbaix diagram.

Fig. 5 reveals the stability of the pigments in the presence of water, showing a clear trend: most of the semiconductor pigments are prone to oxidation under light illumination in aqueous environment. Exceptions are the metal oxide pigments TiO₂ and ZnO. TiO₂ is stable over a wide pH range, whereas ZnO is only stable in the 8.5 to 12 range [24]. More acidic environments will induce dissolution/decomposition. Other publications such as Chen & Wang [14] indicate the unstable behavior for ZnO against photo-oxidation, however, with the remark that it is stable in alkaline solution. Cr₂O₃, another oxide semiconductor, is prone to oxidation since chromium is not in its highest valence and can be further oxidized (Cr³⁺ to Cr⁶⁺). On the other hand, most of the pigments are stable against the reductive decomposition. Only SnS₂ could be sensitive to photoreduction, which, under certain conditions, has indeed been proven [29].

Fig. 5 indicates the stability at a pH of 7. For most of the pigments, the stability predictions would be similar for more acidic or basic environments. However, based on the Pourbaix diagrams, some pigments show greater unstable behavior. As₂S₃ only exists at pH-values < 10.5. As illustrated in Fig. 5, it shows the tendency to oxidize upon illumination in aqueous environment at pH 7. From pH-values slightly higher than 8, the pigment also shows the ability towards reductive decomposition, forming AsS or As⁰. Another example is SnS₂, which is only stable in the neutral to acid pH ranges. Its tendency towards reductive decomposition disappears from pH-values smaller than ~3. The conversion of Fig. 5 to different pH conditions

is useful when for example considering pigments in wall paintings, which are known for their alkaline environment.

To compare the expected stability results deduced from Fig. 5 with real situations, three pigment degradation studies are exemplified. (1) The bright yellow pigment CdS is subjected to fading, due to its oxidation to $\text{CdSO}_4 \cdot 2\text{H}_2\text{O}$ [16, 30]. A study on an Ensor painting clearly showed the protective capacity of the frame, shielding the underlying paint from light and other environmental compounds [16]. (2) Another clear example is the light-induced oxidation of the black lead white degradation product PbS to white PbSO_4 , an old restoration treatment proposed in the 17th century by Norgate in his "*Miniatura or the Art of Limning*": 'bleaching' (i.e., formation of white PbSO_4) is induced by exposure to strong natural light. In the 20th century, an acceleration of the bleaching process was remarked when the object was damp [17]. Thus, light in the presence of water is able to oxidize PbS, as expected from Fig. 5. (3) The red pigment α -HgS (vermilion/cinnabar) has the tendency to turn black. Recent research hypothesized that the blackening process is preceded by an oxidation reaction of the sulfide [18]. In previous studies, scientists indeed identified mercury sulfates at degraded paint surfaces [31]. To explore whether the SO_4^{2-} is indeed originating from the pigment degradation, an additional experiment was performed. 0.5 g α -HgS-pigment was suspended in 5 mL H_2O or 1 M NaCl solution and kept in a closed glass vial. Subsequently, the suspensions were illuminated with UV-fluorescence lamps with a central wavelength of 370 nm during a period of 500 hours. A control was kept in the dark for the same time span. The suspensions were filtered up to 0.2 μm and the leachate was analyzed with ion chromatography (IC, model Dionex DC-120, Dionex, Sunnyvale, CA, USA) [18]. Compared to the samples kept in the dark, a significantly higher SO_4^{2-} concentration was detected for the illuminated samples (> 110 mg L^{-1} vs. $\sim 20 \text{ mg L}^{-1}$). As illustrated in Fig. 5 for H_2O , ϕ^{ox} ($\sim 0.8 \text{ V}$) is situated in close proximity of $\phi^{(\text{O}_2/\text{H}_2\text{O})}$. Therefore, competition probably exists between these two processes. However, when deducing ϕ^{ox} for a Hg-S-Cl- H_2O system, there is a significant shift towards a more negative potential ($\phi^{\text{ox}} \sim 0.0 \text{ V}$). This increases the potential difference between the oxidation potential of the semiconductor and that for the aqueous Cl⁻-rich environment. This thermodynamic more favorable situation could be a possible explanation for the higher amount of SO_4^{2-} formed in a 1 M NaCl solution compared to H_2O (215 mg L^{-1} vs. 111 mg L^{-1}). The current experiment used UV-illumination. Such short wavelengths are mostly blocked from indoor museum environments. However, other experiments performed by the authors have demonstrated the oxidative decomposition of α -HgS at longer wavelengths as well (405 and 532 nm) [18, 32].

Fig. 4 and 5 predicts the semiconductor stability towards aqueous environments. However, few pigments are exposed to wet conditions, and thin adsorbed water layers behave differently compared to water in the liquid (condensed) phase. Nevertheless, several conditions can induce sufficient water at the paint surface to induce the suggested semiconductor pigment decomposition at ambient relative humidity (RH). As is often the case for (historic) metal objects, corrosion is not only influenced by ambient humidity: it is caused by a combination of ambient humidity and atmospheric constituents. Examples are polluting gases such as NO_x and SO_2 , and airborne particles (particulate matter, PM) such as NaCl , NaNO_3 , NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$. The latter are hygroscopic salts: from a certain ambient RH, they absorb water, creating small droplet-like (electrochemical) cells. Therefore, once deposited, they increase the water content at the (paint) surface. The harmful impact of hygroscopic airborne particles on metal corrosion was already proven for indoor environments and electronic devices in specific (e.g., [33, 34]).

Many of the hygroscopic airborne salts show deliquescence behavior: their phases remain unchanged until the deliquescence relative humidity (DRH) is reached. At that point, the salt crystals at once form a saturated salt droplet. For many pure salts, the DRH is higher than the museum target conditions (often $55 \pm 5\%$). As an example, the DRH for NaCl is around 75% [35]. However, not all paint collections are conserved in 'ideal' museum environments: also churches and other uncontrolled heritage buildings often house paintings. In such buildings, the RH can easily reach high values, closely corresponding to the outdoor RH. Moreover, once hygroscopic particles are deliquesced, they will not recrystallize at the DRH. They become highly supersaturated until the crystallization relative humidity (CRH) is reached. This delayed recrystallization is called 'hysteresis' [36]. For NaCl , the CRH is around 45% [37]. Thus, once the DRH is reached, even for short time spans, deposited particles keep water at the (paint) surface.

The DRH and CRH highly depend on the exact chemical composition of the particles. PM-particles are rarely pure salts, but mixtures, which show different deliquescence behavior [38]. Highly hygroscopic magnesium and potassium salts, present in sea salt particles, already show deliquescence behavior at RH 30-40%, partly dissolving the multicomponent sea salt particles [39]. Moreover, volatile organic compounds (VOC's) which are known to adsorb on atmospheric particles, often behave as a surfactant coating for inorganic airborne particles, affecting their water uptake as well as their deliquescence behavior [40].

Analogous to metal corrosion, some of the formed corrosion products are hygroscopic and promote advanced water uptake at the material surface. An example is $\text{CdSO}_4 \cdot x\text{H}_2\text{O}$ as a degradation product of the pigment cadmium yellow (CdS). Earlier research on the Ensor

painting “*Still Life with Coffeepot, Cabbages and Mask*” has shown that the $\text{CdSO}_4 \cdot x\text{H}_2\text{O}$ degradation product formed globules, probably due to a process of recurring moistening and drying of the paint surface, e.g., by fluctuating climatologic conditions [16]. Thus, the $\text{CdSO}_4 \cdot x\text{H}_2\text{O}$ (globule) formation suggests that (1) sufficient water content was present at the historical paint surface to induce oxidative decomposition of the semiconductor pigment, and (2) the degradation product shows hygroscopic properties.

2.2 Degradation of the environment

So far, only pure pigment powders were considered. In paintings, ideally all pigment grains are encapsulated in the binding medium which protects the pigment from the (humid) environment. Varnishes provide an additional protection. Unfortunately, ideal circumstances do not exist. Initial imperfections exist and the binding medium around the pigment particles weakens or disappears over time because of chemical degradation, cracks, or other defects. In these circumstances, the pigment grains can be attacked by environmental agents.

Fig. 6a schematically shows oil breakdown in the presence of a non-photoactive pigment (e.g., the green copper acetate ‘verdigris’). Since oil is sensitive to photoinduced oxidative degradation [41], the oil binding medium degrades upon light exposure. Since the pigment particles locally protect the medium from irradiation, they create ‘pillars of medium’ [19].

In the presence of a semiconductor pigment, also the pigment itself can destroy the binding medium upon illumination. The medium erodes around the pigment particles, creating holes in the paint film as illustrated in Fig. 6b. Breakdown of the binding medium is expected when the oxidation potential of the medium (ϕ^{med}) is more negative compared to ϕ^{ox} of the semiconductor pigment. This assumption is based on an analogous argumentation as in Fig. 4, considering ϕ^{med} instead of $\phi^{(\text{O}_2/\text{H}_2\text{O})}$.

The pigment induced oil breakdown increases the contact area between the pigment grains and the environment. Depending on the pigment semiconductor properties, the breakdown has at least two possible consequences. (1) When unstable in aqueous environment, the semiconductor pigment decomposes due to atmospheric humidity and light exposure. Thus, by inducing oil breakdown, the pigment increases its own sensitivity towards the environment. (2) When stable in aqueous environment, the semiconductor pigment decomposes the aqueous environment upon light exposure. Reactive hydroxyl and hydroperoxyl groups can be formed,

which further promote the breakdown of the surrounding organic materials [19]. Thus, the pigment induces an advanced degradation of the binding medium.

Literature indicates that vermilion (α -HgS), cadmium yellow (CdS) and titanium white (TiO_2) attack their (oil) binding medium [19, 42, 43]. Both α -HgS and CdS are examples of situation (1) as mentioned above: upon illumination, the pigment first attacks the oil. Once in contact with the aqueous environment, the pigment decomposes (Fig. 5). Rasti & Scott [42] studied the effect of different pigments, such as α -HgS, on the photo-oxidation of linseed oil. Pigment-oil mixtures showed generally higher oil oxidation at shorter wavelengths. However, α -HgS appeared also effective in causing oil degradation at longer wavelengths. Increased amounts of dicarboxylic acids, typical oil degradation products, were formed. Thus, α -HgS accelerates the oil oxidation process. For CdS, no specific research was found on its catalyzing effect on linseed oil degradation. However, the photo-oxidation of other polymers such as polyethylene is promoted in the presence of CdS [43]. For historic paintings, several experts and authors mentioned the poor quality of CdS oil paint [16, 30]. Leone et al. [44] even mentioned that in extreme cases, the binding medium almost completely disappears at the surface.

TiO_2 is an example of situation (2): upon illumination, the pigment first attacks the oil. Once in contact with the aqueous environment, the pigment promotes further oil breakdown (Fig. 5). Laver [19] discusses some studies on photoinduced medium degradation in the presence of TiO_2 . The author made a distinction between the anatase and the less reactive rutile form of TiO_2 . The latter is mentioned as the pigment of choice for artists and conservators.

Next to the binding medium, the semiconductor pigments also influence the stability of other pigments or dyes, when in contact and upon illumination. Examples are the fading of Prussian blue, madder lake and azo dyes when mixed with TiO_2 [19, 45].

3. Conclusion

For semiconductors, illumination is a prerequisite for electron transitions between valence and conduction band. Such transitions enhance electron transfer to the environment, which includes: binding medium, water layers caused by air humidity and surrounding pigments. To easily and quickly screen semiconductor photostability, a thermodynamic approach was applied. It evaluates the positions of thermodynamic oxidation (ϕ^{ox}) and reduction (ϕ^{red}) potentials of the semiconductor relative to the redox potentials of the environment. The semiconductor is prone

to oxidative decomposition if ϕ^{ox} is more negative than the oxidation potential of the environment. On the other hand, the semiconductor is prone to reductive decomposition if ϕ^{red} is more positive than the reduction potential of the environment. The theoretical predictions correspond well to experimental data describing pigment permanence and degradation phenomena. However, when a pigment is thermodynamically unstable comparing the potentials, it does not mean that the pigment degrades easily. The kinetics of the decomposition reaction also play a role: with very slow kinetics, the pigment will appear quasi-stable, whereas fast kinetics confirm the pigment instability.

To delay further degradation, some measures can be considered. Most semiconductor pigments are prone to photo-oxidative degradation in aqueous environments. Therefore, degradation can be hindered by blocking them from any water, e.g., by encapsulating the pigment grains into binding medium and/or protecting them with a varnish layer. By reducing the light intensity, less electron-hole pairs are generated which can participate in decomposition reactions. For some pigments, the pH of the environment is crucial towards their stability. This can be deduced from Pourbaix diagrams. As_2O_3 , SnS_2 and ZnO , for example, can only exist in a specific pH-range. Also ϕ^{ox} and ϕ^{red} can be pH-dependent.

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Figure captions

Fig. 1: (a) Schematic overview of the position of the valence and conduction band for the bulk of metals, semiconductors and insulators. Indication of the Fermi energy and the band gap.

(b) Photon energy (band gap) to wavelength and color dependence.

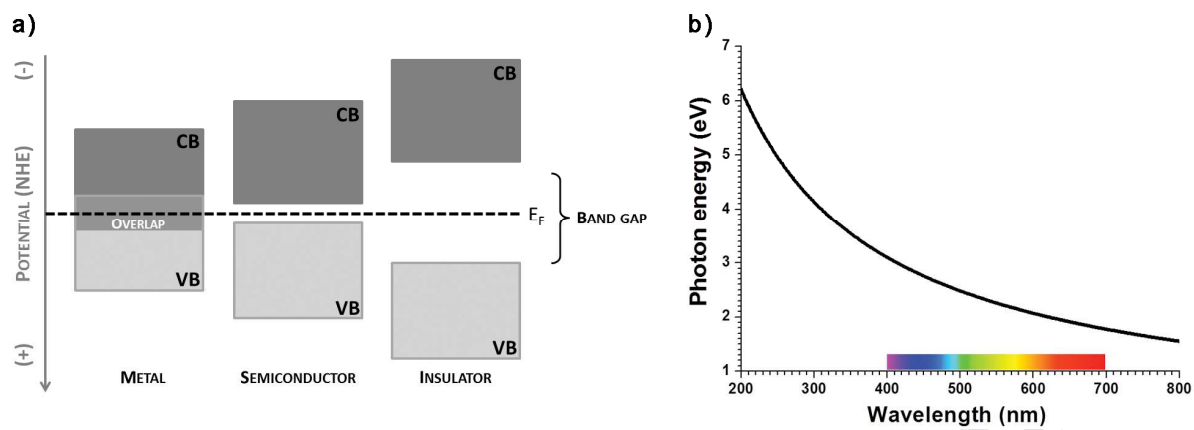
Fig. 2: Schematic overview of the Fermi level (E_F) in the dark, and the quasi-Fermi levels ${}_pE_F^$ and ${}_nE_F^*$ under illumination for an intrinsic, n-type and p-type semiconductor (adapted from [11]). Band bending was not considered in the simplified scheme.*

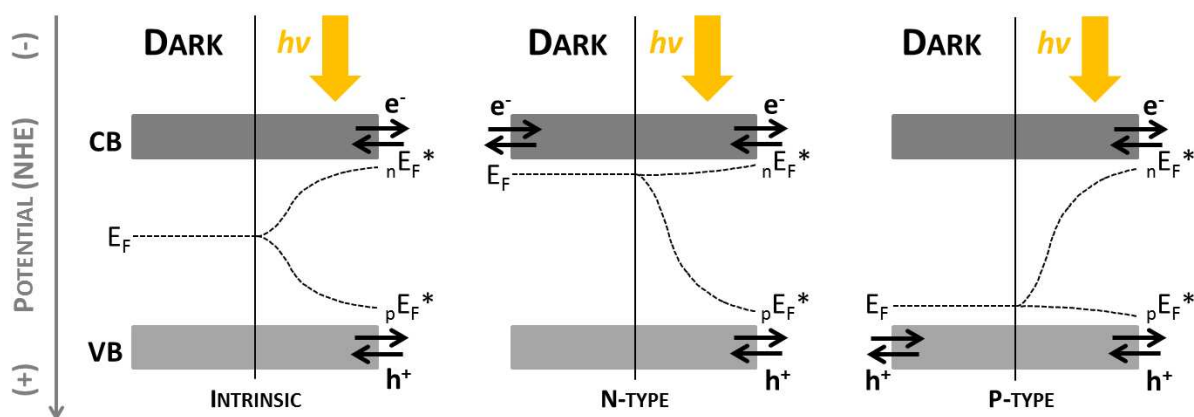
Fig. 3: (a) Indication of the penetration depth of blue (~450 nm), green (~510 nm) and red (~650 nm) light. (b) Band bending for n-type semiconductors under illumination: accumulation layer (negative surface charge), flat band potential and depletion layer (positive surface charge, most common for n-type semiconductors). The arrows indicate either recombination of the generated electron-hole pairs, or charge separation in the presence of an electric field induced by band bending.

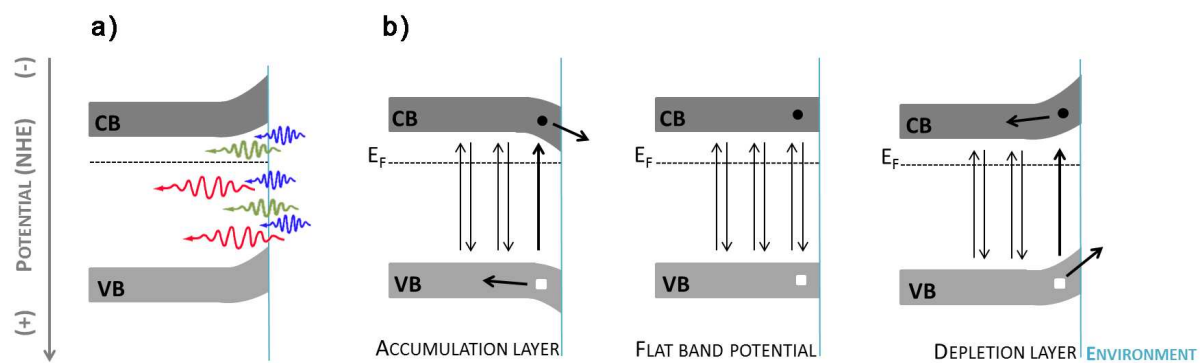
Fig. 4: Schematic overview on the stability of semiconductors in water. Oxidation and reduction potentials of a semiconductor relative to the oxidation and reduction potential of H_2O .

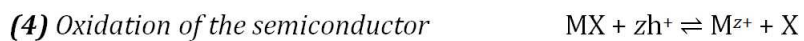
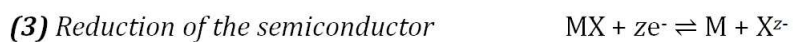
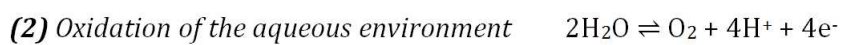
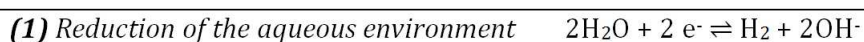
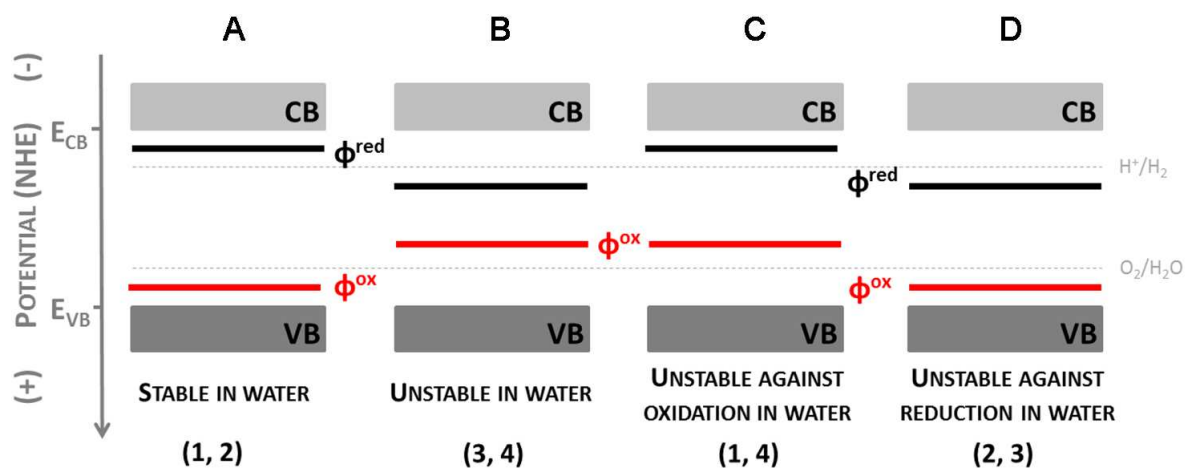
Fig. 5: Oxidation and reduction potentials relative to the NHE and vacuum level for relevant semiconductor pigments or pigment degradation products in aqueous solution at pH 7 (pH 8.5 for ZnO), plotted versus the valence (dark grey columns) and conduction (light grey columns) band edge positions at pH 7.

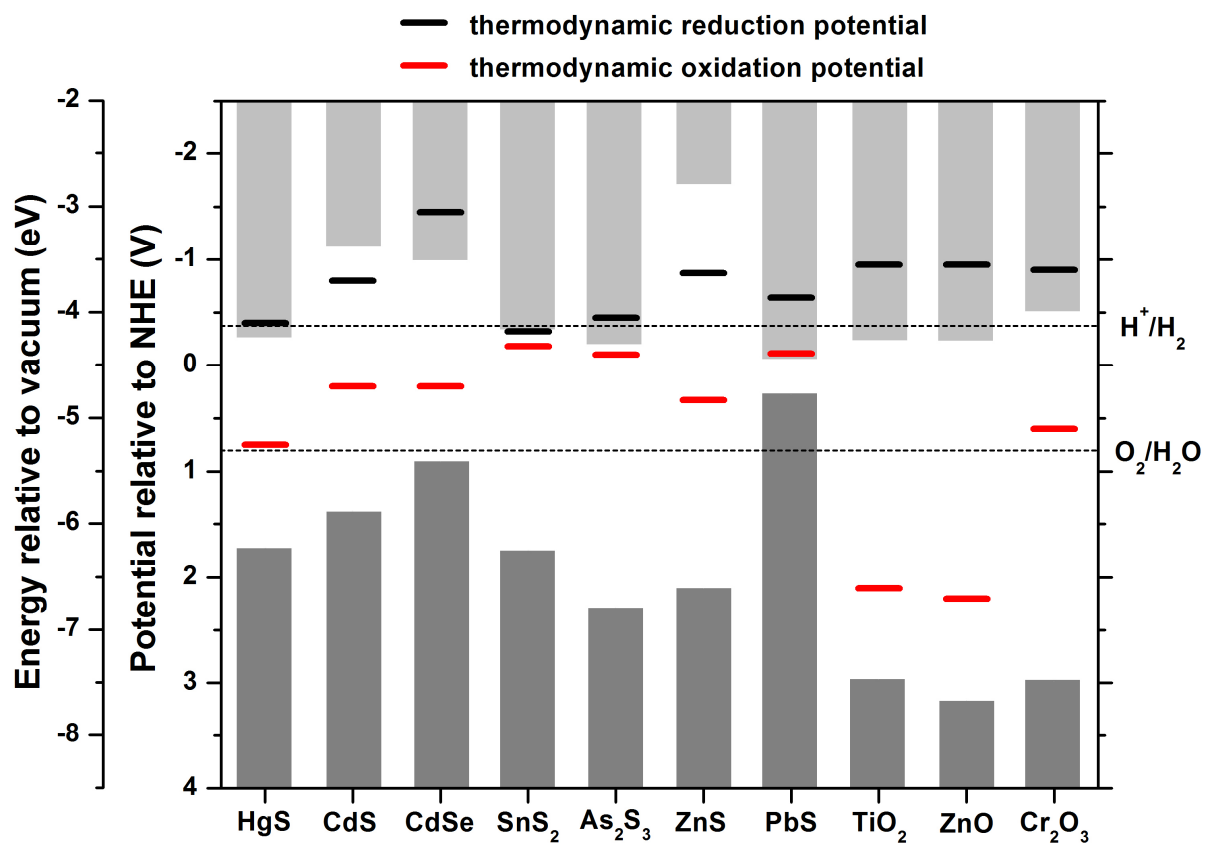
Fig. 6: Typical morphology of oil breakdown in the presence of a (a) non-photoactive and (b) photoactive pigment. After illumination, underbound particles are exposed at the surface (adapted from [19]).

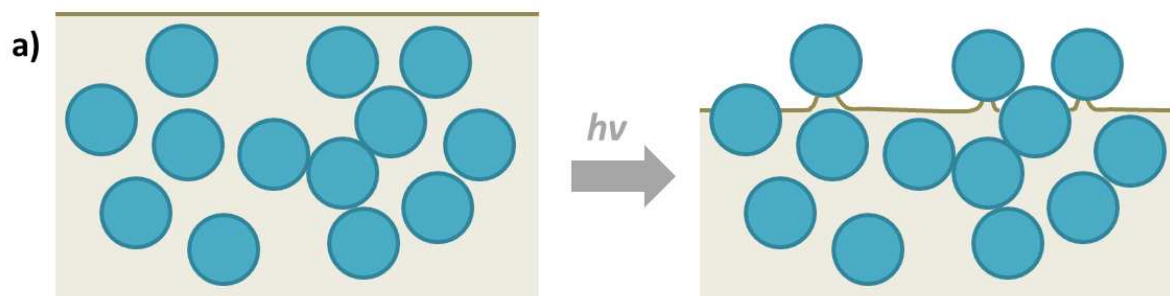
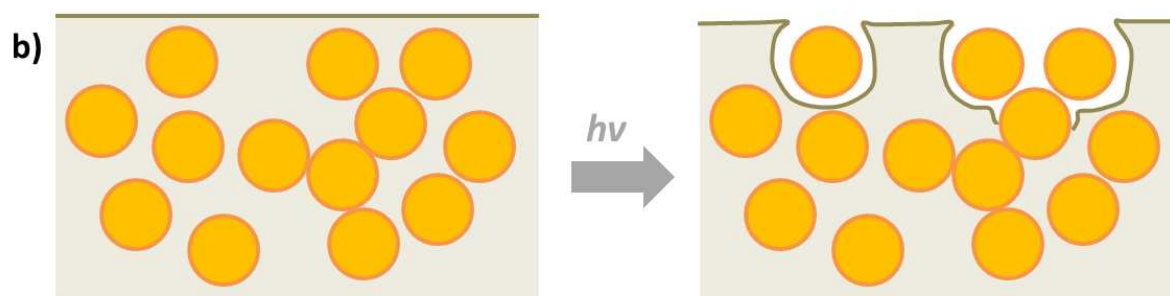










OIL BREAKDOWN**NON-PHOTOACTIVE PIGMENT****SEMICONDUCTOR PIGMENT**

ACCEPTED MANUSCRIPT

- Several historical artists' pigments were considered as semiconductors.
- The (in)stability of the pigments was theoretically predicted using a thermodynamic approach.
- The approach easily and quickly screens semiconductor photostability.
- Theoretical predictions correspond to experimental data.

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