



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.

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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 (α -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,

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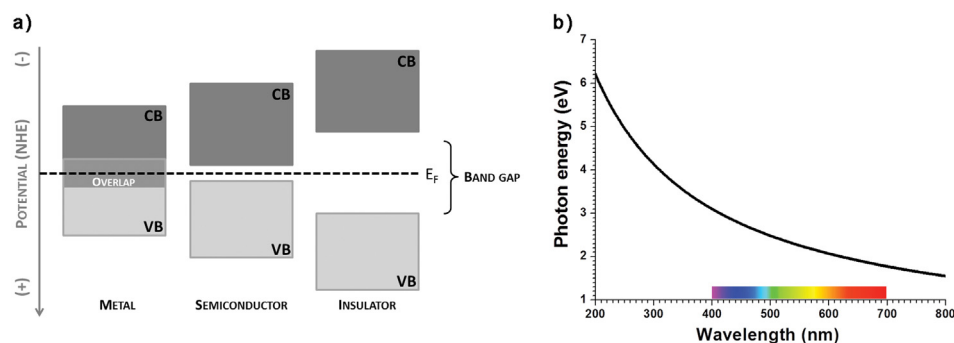


Fig. 1. (a) Schematic overview of the position of the valence and conduction band for the bulk of metals, semiconductors and insulators. Indication of the Fermi energy and the band gap. (b) Photon energy (band gap) to wavelength and color dependence. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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: $\lambda(\text{nm}) \leq 1241/E_g(\text{eV})$ (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

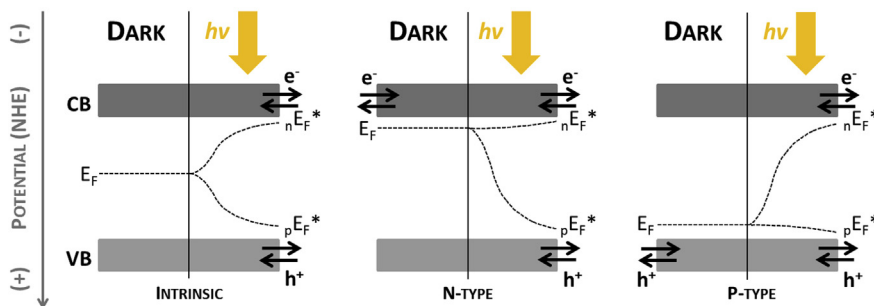


Fig. 2. Schematic overview of the Fermi level (E_F) in the dark, and the quasi-Fermi levels pE_F^* and nE_F^* under illumination for an intrinsic, n-type and p-type semiconductor (adapted from Ref. [11]). Band bending was not considered in the simplified scheme.

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