Università Ca'Foscari Venezia

DEPARTMENT OF MOLECULAR SCIENCE AND NANOSYSTEMS
Seminars of the PhD PROGRAMME IN CHEMISTRY

Fading colors: please mind the gap! Understanding the (in)stability of semiconducting pigments

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Abstract

Several artists' pigments are semiconductors. Examples of such colorful 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), minium (Pb_3O_4) or titanium dioxide white (TiO_2). Some of these materials appear stable over time, whereas others already show remarkable signs of degradation after limited time periods, sometimes triggered by physical or chemical parameters. In this study, the stability of semiconductor pigments is thermodynamically predicted, based on literature data. A starting approach to predict the photostability of semiconductor pigments, is based on thermodynamics. Gerischer [1] already introduced the concept of thermodynamic oxidation and reduction potentials of the semiconductor (ϕ_{ox} and ϕ_{red}). 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 degradation in an aqueous/humid environment. This theoretical approach can be used as a fast and easy screening, and corresponds well to experimental data describing pigment permanence and degradation phenomena. Apart from studying degradation products, a new electrochemical approach is developed for the real-time monitoring of pigment degradation processes and the prediction of (environmental) harmful conditions. 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, water-soluble salts present in airborne particles, etc.). By applying 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. In combination with spectroscopic techniques such as raman, we recently gained new insight in different degradation processes [2-5].

[1] Gerischer, H. On the stability of semiconductor electrodes against photodecomposition.J Electroanal Chem. 82 (1977) 133-43.§
[2] Anaf, W.; Janssens, K., De Wael, K. Formation of metallic mercury during photodegradation/photodarkening of α -hgs : electrochemical evidence. Angewandte Chemie: international edition in english 52:48 (2013) 12568-12571.
[3] Anaf, W.; Trashin, S.; Schalm, O.; Van Dorp, D.; Janssens, K., De Wael, K. Electrochemical photodegradation study of semiconductor pigments: influence of environmental parameters. Analytical Chemistry 86:19 (2014) 9742-9748.
[4]Anaf, W.; Schalm, O.; Janssens, K., De Wael, K. Understanding the (in)stability of semiconductor pigments by a thermodynamic approach. Dyes and Pigments 113 (2015) 409-415
[5] Ayalew, E.; Janssens, K.; De Wael, K. Unraveling the reactivity of minium towards bicarbonate and the role of lead oxides therein. Analytical Chemistry 88:3 (2016) 1564-1569.

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