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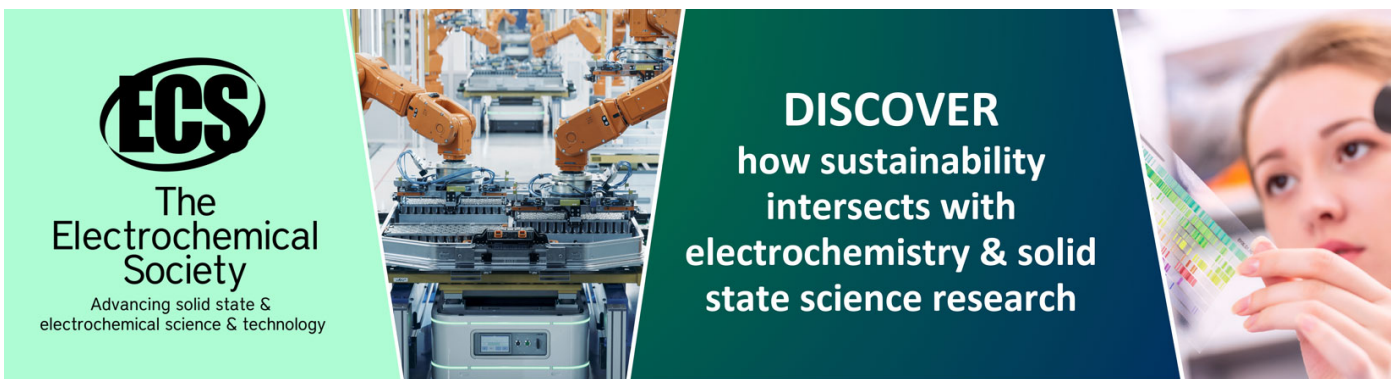
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# Time resolved XANES illustrates a substrate-mediated redox process in Prussian blue cultural heritage materials

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**Abstract.** The pigment Prussian blue is studied in heritage science because of its capricious fading behavior under light exposure. We show here that XANES can be used to study the photosensitivity of Prussian blue heritage materials despite X-ray radiation damage. We used an original approach based on X-ray photochemistry to investigate in depth the redox process of Prussian blue when it is associated with a cellulosic substrate, as in cyanotypes and watercolors. By modifying cation and proton contents of the paper substrate, we could tune both rate and extent of Prussian blue reduction. These results demonstrate that the photoreduction and fading of Prussian blue is principally mediated by the substrate and its interaction with the oxygen of the environment.

## 1. Introduction

Prussian blue (PB, iron(III) hexacyanoferrate(II)) is better known as electrochemically synthesized thin films, or as the original compound of a series of analogues where iron is substituted by other transitional metal atoms. However, before becoming a star compound in materials sciences, Prussian blue got an equal success as a pigment and dye. Thanks to its high tinting strength and its cheap and straightforward synthesis, it was used in various heritage artefacts, such as oil paintings, textiles, early-photographic processes or watercolors [1].

Despite this wide use, Prussian blue is still depicted as a problematic and mysterious pigment because of its capricious fading behavior under light exposure, which depends a lot on the object investigated. The fading is due to the photoreduction of Prussian blue, a process where the substrate, the environment, impurities, as well as the structure and chemical composition of Prussian blue play a role [2, 3]. Much remains to be done to understand the exact redox mechanism behind fading. For instance, the migration pathways of cations and electrons within the structure upon Prussian blue reduction remains unknown. In previous studies, we showed that X-ray absorption spectroscopies are particularly well dedicated to investigate the photoreduction of Prussian blue [2, 4, 5]. However, X-ray radiation damages were observed for Prussian blue embedded in a cellulosic paper, a model used to study cyanotypes and watercolors,



cultural heritage artefacts known to be very photosensitive [6]. X-ray radiation involves a reduction of the pigment, in a similar way than visible light does. We could recently put into profit this analogy to study by X-ray photochemistry the influence of the cellulosic substrate on the photosensitivity of Prussian blue in paper heritage materials [4].

Here, we further investigate the redox properties of those materials by investigating the impact of anoxia on the X-ray photoreduction kinetics of PB cellulosic model samples. These findings help us refining our understanding of the substrate-mediated redox process responsible for Prussian blue fading in paper heritage materials.

## 2. Experimental details

Prussian-blue paper model samples were prepared by immersion of a 100% cellulosic paper (Whatman) in a Prussian blue sol (synthesized as in [2]) and let dry in open air. KCl and HCl variantes were prepared by preliminary immersing the paper in KCl (1M) and HCl (1M) respectively. A section of approximately  $0.5\text{ cm} \times 0.5\text{ cm}$  was cut from the samples and inserted into a controlled atmosphere flow cell designed specifically for X-ray measurements in transmission geometry and to perform in-situ light fading of the samples [5]. A gas flow of nitrogen humidified at 50% RH was injected into the cell and kept flowing during the entire experiment, ensuring stable anoxic and relative humidity conditions around the sample ( $\text{N}_2$ -50%RH).

The Fe K-edge XAS spectra of the PB-paper samples were acquired by energy-dispersive X-ray absorption spectroscopy at the ODE beamline, SOLEIL synchrotron, Paris [7]. The X-ray beam was around  $30\mu\text{m} \times 35\mu\text{m}$  FWHM in size and the photon flux hitting the sample was  $1.1 \times 10^{11}$  photons/s. An oscillating movement of the sample over  $200\mu\text{m}$  in horizontal and vertical was performed during acquisition to take into account sample intrinsic heterogeneity (distribution of PB particles within fibers). XAS spectra were recorded over a range of 425 eV (7050–7475 eV). For each final XAS spectrum, up to 150 successive exposures (frames) were saved and averaged, with an exposure time to the CCD camera for each frame chosen from 5 to 25 ms depending on the pigment concentration into the sample. Each sample was continuously exposed to the beam during approximately one hour. The  $I_0$  was regularly recorded by exposing the direct beam onto the CCD camera. Energy calibration was based on the inflection point of the absorption edge at 7112 eV of a metallic iron foil regularly measured during the session.

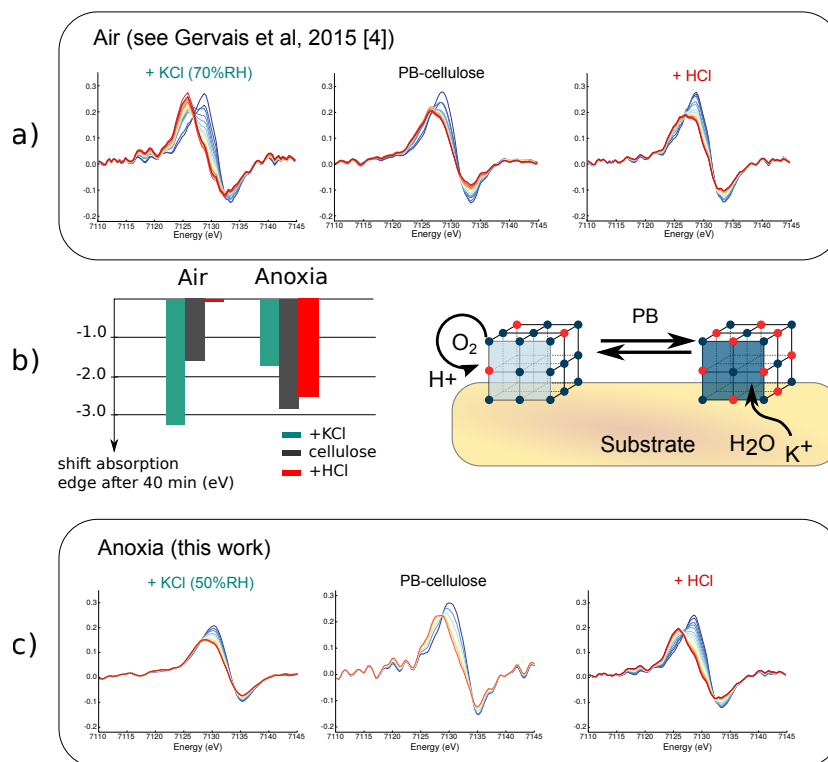
Data treatment was performed using the Iffefit 3.0.3 package with the computational code Larch [8]. The pre-edge range background was removed using an empirical polynomial function, and the absorption background was removed using a cubic spline with a normalization range between 40 and 220 eV after the edge.

Structural information was extracted from the XANES spectra by focusing on two features: On one hand, the maximum of the derivative of the XANES signal was chosen as the absorption edge and its variation upon time was monitored to estimate changes in the oxidation state of Prussian blue. On the other hand, the shape of the XANES derivatives was also investigated to estimate the amount of structural disorder generated during the redox process. The complete methodology is described in [4].

## 3. Results

During exposure of the Prussian blue paper samples to the X-ray beam, an absorption edge shift towards lower energies was systematically observed. This shift can be attributed to a reduction of iron(III) into iron(II) in Prussian blue and was associated with a visual discoloration of the pigment.

**Photochemistry of Prussian blue in air.** This X-ray photochemistry was recently put into profit to refine our understanding of the redox process between Prussian blue and a cellulosic



**Figure 1.** X-ray photochemistry of Prussian blue paper samples followed by Fe K-edge XANES. a) XANES derivatives in air in function of time (from [4]). (b) Left: Shift of the absorption edge after 40 minutes of continuous X-ray exposure. Right: Schematic overview of the redox process in these materials. (c) XANES derivatives in anoxia in function of time. In a) and c), colors of the spectra follow a rainbow code (from blue  $t = 0$ , to red  $t = 40$  min).

paper. The pH and alkali cation content of the paper substrate was modified and their influence on the X-ray photoreduction kinetics in air studied in [4]. Results are recalled Figure 1a).

Addition of KCl to the cellulosic paper and high relative humidity (70 %RH) promotes the reduction of Prussian blue and results in a clear and greater shift of the absorption edge in the XANES spectra (-3.2 eV compared to -1.6 eV for Prussian blue on a pure cellulosic substrate). These findings can be interpreted by considering that upon reduction, solvated cations are migrating into the Prussian blue crystal lattice in view of compensating the increase of charges induced by iron reduction.

To the contrary, acidification of the cellulosic paper leads to a very small shift of the absorption edge (almost 0 eV) as well as broader and less intense XANES derivatives. Protons brought into the system, together with the X-ray beam reductive effect, are reducing the oxygen contained in the air, which in turn leads to a re-oxidation of the photoreduced Prussian blue (Figure 1b, right). This dynamic, competitive redox process lead to defects in Prussian blue and a photoreduction which is ill-defined and small in extent.

**Photochemistry of Prussian blue in anoxia.** To further refine the role of the environment and particularly of the oxygen, we investigated in this work the X-ray photoreduction of the same three PB cellulosic samples, but this time in anoxia instead of air. Anoxic conditions were obtained with a flow of nitrogen humidified at 50% RH. Measurements in both works were performed during the same beamtime session on the same samples. Therefore, the photoreduction kinetics can be compared.

As shown Figure 1c, the photoreduction differs in amount and quality for the three samples. In general, anoxia increases the photoreduction and the redox process seems to be less sensitive to the substrate (see Figure 1b: -1.7 eV, -2.8 eV and -2.5 eV for KCl, cellulose and HCl samples respectively). In agreement with previous studies [5, 9], these results confirm that anoxic conditions are the driving factor of the reduction kinetics and not anymore the nature of the substrate. This latter plays a smaller role but leads nevertheless to interesting spectral variations.

For the acidified sample, anoxia induces a drastic increase of photoreduction compared to air. This can be explained by the fact that no re-oxidation of the photoreduced Prussian blue is possible. Protons added to the system are thus not anymore participating directly to the redox process, and the photoreduction looks similar in quality and extent to that of the Prussian blue pure cellulosic sample in anoxia.

For the sample loaded in cations, the photoreduction is still consequent in anoxia but lower than in air (Figure 1b: -3.2 eV in air and -1.7 eV in anoxia). The difference lies mainly in the shape of the XANES derivatives. While a clear shift of the absorption edge occurs in air, XANES derivatives are broad and loosely defined in anoxia, suggesting the creation of disorder and many oxidation regions in the photoreduced Prussian blue structure. One possible explanation lies in the multiple roles played by water. Water is necessary to solvate cations and allow them to migrate through the zeolite-like channels of the lattice, where the water molecular network acts as a cation carrier. The photoreduction kinetics in anoxia were recorded in a lower relative humidity environment (50%RH) than in air (70%RH), so that cations might be less readily solvated. As a consequence, the photoreduction might become limited by the low diffusion coefficients of the cations rather than by the anoxic environment. Another explanation lies in the water network present in the Prussian blue lattice, which might change in anoxic conditions.

#### 4. Conclusion

Thanks to an original approach based on X-ray photochemistry monitored by energy-dispersive XAS, we could refine the redox process of the Prussian blue in paper support and show that in fine, this one is controlled by the substrate content, structure and photosensitivity as well as its close interaction with the oxygen environment. Applied to Prussian blue in the context of heritage materials, the present approach could be interesting to investigate the photochemistry of novel multifunctional materials based on Prussian blue or Prussian blue analogues [10].

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