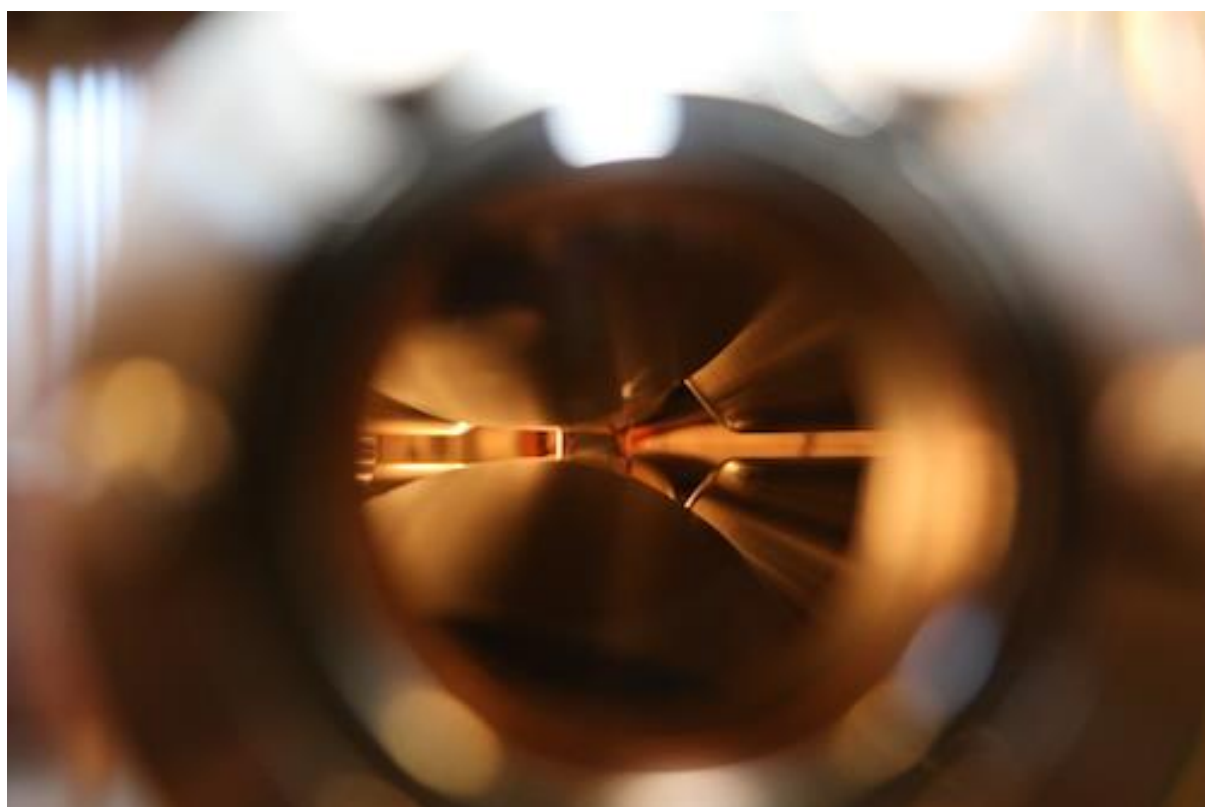


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XAS–XES measurements on protonated amino acid–montmorillonite and deprotonated amino acid–layered double hydroxide bionanocomposites

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Clays exhibit many profitable features (such as low cost, wide range of preparation variables, ease of set-up and work-up, gain in yield and/or selectivity, etc.), which may be useful tools in the move towards establishing environmentally friendly technologies [1]. In addition to ceramics, including building materials, clays are also used as paper coatings and fillings, drilling muds, foundry moulds, pharmaceuticals, cat litters, etc. Furthermore, clays can be used as adsorbents, catalysts or catalyst supports, ion exchangers, decolorising agents, etc., depending on their specific properties. Studies on both natural and synthetic clay minerals including layered double hydroxides (LDHs) for biological applications are extensively carried out. Among them, the research on novel nano-biohybrids that combine efficient and safe transport carriers for biological molecules provides a new paradigm. Clay minerals possess excellent properties, such as low or zero toxicity, good biocompatibility, and promise for controlled release, thus give rise to interest in their development for biological purposes, for example, pharmaceutical, cosmetic, and even medical ones [2, 3].

Amino acids are components of enzymes and natural proteins. If enzymes and proteins can be immobilised in the interlayer space of clays, new type of catalytically active materials with high selectivities and reactivities, and carriers for drug delivery may be expected. Amino acids have a close relationship with mineral clays once they penetrated into the interlayer space of layered materials [4].

Clays may be divided into two broad groups: cationic clays, widespread in nature, and layered double hydroxides rarer in nature, but relatively simple and inexpensive to synthesise. The cationic clays have negatively charged aluminosilicate layers having cations in the interlayer space to balance the charge, while the anionic clays, also known as layered double hydroxides, have positively charged metal hydroxide layers with charge-balancing anions and water molecules located interstitially. Similarly to natural mineral clays, such as montmorillonite and kaolinite, layered double hydroxides possess a clear hierarchical structure of positive and negative charges.

Amino acids can be considered as zwitterions in solution, because of involving -NH_2 and -COOH groups. The specific ionised state largely depends on the pH. When protonated (acidic pH) the cationic form can be introduced between the layers of montmorillonite, when deprotonated (basic pH) the anion can enter the interlayer space of layered double hydroxides.

In this work, L-proline and L-cystine were intercalated in the appropriate ionic forms into montmorillonite with ion-exchange and into Ca–Fe layered double hydroxides with the dehydration-rehydration method utilising the memory effect of the layered double hydroxides.

The materials were characterised by X-ray diffractometry (XRD), infrared (IR) spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) measurements. X-ray absorption–X-ray emission (XAS–XES) measurements were performed in Max-Lab at the I511-3 beamline.

Information obtained from the combined analysis of the relevant X-ray diffractograms, IR spectra, SEM images and the SEM–EDX elemental maps revealed that intercalation occurred, indeed.

The X-ray absorption spectra of the pristine CaFe-LDH, montmorillonite as well as the amino acid intercalated samples were registered at and around the Ca1s, Fe2p, O1s and N1s absorption edges. The samples were inserted in a high-vacuum chamber (the pressure was lower than 3.4×10^{-8} mbar), and the spectra were recorded at 0.05 eV steps around the absorption edges. Measurements were performed in the total fluorescence yield (TFY) mode and at various spots of the samples to avoid radiation damage.

The XAS spectra of the pristine CaFe-LDH, and, as an example, the proline-intercalated nanocomposite at the various absorption edges are seen in Figure 1.

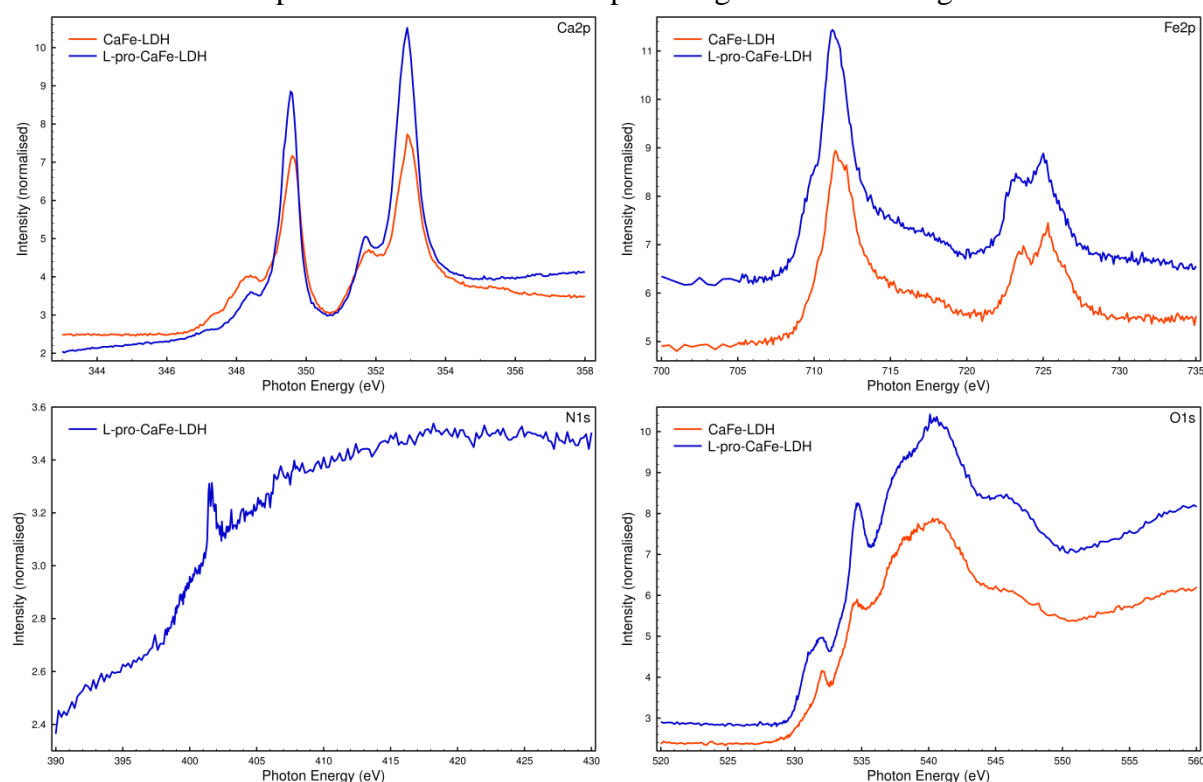


Figure 1 The X-ray absorption spectra of the pristine CaFe-LDH and the L-proline–CaFe samples at and around the Ca2p, Fe2p, N1s and O1s absorption edges.

It is to be observed that the intercalated proline does not perturb the structure of the LDH. One may think that it is not even intercalated, however, the N1s X-ray absorption spectra clearly verifies its presence. Moreover, the shoulder at 531 eV and the intensified peak around 547 eV the $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ transitions of its carboxylate bond.

The XES spectra are still in the stage of evaluation.

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