

Photomagnetic Prussian Blue analogue as 5 nm-particles: Structural and electronic effects of size reduction

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Photoswitchable molecular compounds containing transition metals are appealing candidates for the future of electronic and high-density data storage. Since their integration into real applications requires a nanoprocessing step, our group developed an original bottom-up approach based on the use of well-defined ordered porosity of mesoporous silica as a nanoreactor to control the size, shape and spatial organisation of functional object. We applied this strategy to the well-known photomagnetic $\text{Rb}_2\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.3}$ PBA (**RbCoFe**), which present a $\text{Co}^{\text{III}}(\text{LS})\text{Fe}^{\text{II}} \rightarrow \text{Co}^{\text{II}}(\text{HS})\text{Fe}^{\text{III}*}$ charge-transfer at 10K under light irradiation. We managed to synthesize single-crystalline 5-nm particles (**nanoRbCoFe**). First results from X-ray Diffraction, infrared spectroscopy and SQUID magnetometry showed the existence of a photomagnetic effect in **nanoRbCoFe** but also revealed several unexplained differences with the free powder.

Therefore we undertook a detailed investigation of the local environment and oxidation states of the Co and Fe ions in **RbCoFe** and **nanoRbCoFe** by in situ Fe/Co K-edge XAS. These compounds were compared to a non-photomagnetic reference $\text{Co}_4[\text{Fe}(\text{CN})_6]_{2.7}$ PBA (**CoFe**) and its 5-nm derivative (**nanoCoFe**), synthesized exactly the same way than **nanoRbCoFe**. The measurements were performed in the transmission mode on the SAMBA beamline (SOLEIL, France) at room temperature and, for **RbCoFe** and **nanoRbCoFe**, at 10K with x-ray irradiation.

These XAS experiments confirmed the conservation of the photomagnetism observed for **RbCoFe** at the nanoscale, since the $\text{Co}^{\text{III}}(\text{LS})\text{Fe}^{\text{II}} \rightarrow \text{Co}^{\text{II}}(\text{HS})\text{Fe}^{\text{III}*}$ charge-transfer could be unambiguously established from the variation of the white line energy at both edges in the XANES spectra. Few differences were observed between the powder and nanocompounds in the photoexcited state, which suggests a similar local environment and oxidation state for Co and Fe whatever the size of the particle. However, striking features were observed for the ground state. First, on the contrary to **nanoCoFe** which contains only $\text{Co}^{\text{II}}\text{-Fe}^{\text{III}}$ pairs as **CoFe**, the XANES spectrum of **nanoRbCoFe** displays a double white line, from which we deduced a $\text{Co}^{\text{II}}:\text{Co}^{\text{III}}$ ratio of 60:40 (%). This is a first major effect of the size reduction, because it is well-known that $\text{Co}^{\text{II}}:\text{Co}^{\text{III}}=20:80$ (%) in **RbCoFe**. Then the comparative analysis of the 4 compounds spectra revealed a core-shell structure of the nanoparticles, the core of **nanoRbCoFe** (resp. **nanoCoFe**) corresponding to **RbCoFe** (resp. **CoFe**). Unexpectedly, the spectrum of the shell is identical between the two nanocompounds (whatever the core) and indicates the presence of only Co^{II} and Fe^{III} ions; we managed to establish the thickness of the shell for both **nanoCoFe** (0.9 nm) and **nanoRbCoFe** (1.1 nm). This $\text{Co}^{\text{II}}\text{-Fe}^{\text{III}}$ shell thus indicates for **NanoRbCoFe** that only the core of the nanoparticle carries the photomagnetism, which is a completely new piece of information.

To conclude, these in situ experiments enables to get three main results: (i) the coexistence of two oxidation states for Co and Fe in **nanoRbCoFe** in different proportions than in **RbCoFe**, (ii) a core-shell structure of the nanoparticle, with an identical shell in both **nanoCoFe** and **nanoRbCoFe**, and (iii) the preservation of the photomagnetic property of the **RbCoFe** at the nanoscale. This knowledge is crucial for the deep understanding of the effect of size reduction on the nanoparticles properties and on their control.