

Supporting Information

Fully Controlled Precipitation of Photomagnetic CoFe PBA Nanoparticles within the Ordered Mesoporosity of Silica Monoliths.

Giulia Fornasieri, Merwen Aouadi, Pierrick Durand, Patricia Beaunier, Eric Rivière and Anne
Bleuzen*

This file includes:

Figs. S1 to S8

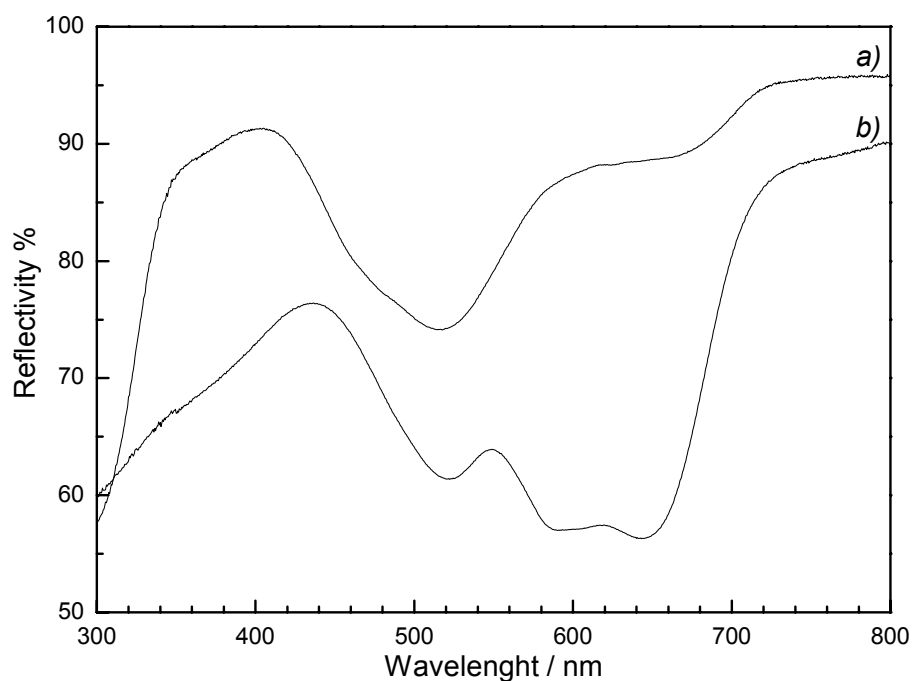


Figure S1. UV-visible spectra of **a)** the as-synthesized Co^{2+} -containing silica monolith. The ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transition (520 nm) is the signature of an octahedral complex such as $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, and **b)** the Co^{2+} -containing silica monolith after thermal treatment at 500°C . The multiple band around 585 nm is assigned to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ transition of a Co^{2+} ion in tetrahedral environment.

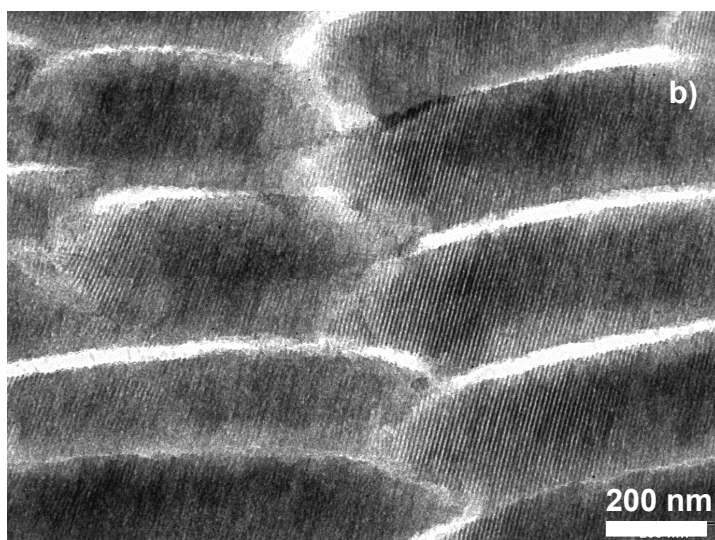
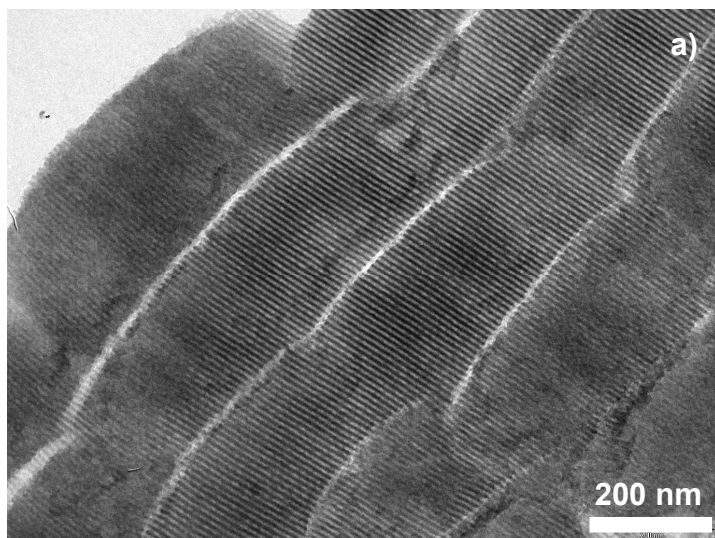


Figure S2. TEM micrographs of: **a)** Co^{2+} -containing silica mesoporous monolith (microtomed sample) with 2D-hexagonal structure (longitudinal section) and **b)** CoFe PBA-containing silica monolith (microtomed sample) with 2D-hexagonal structure (longitudinal section).

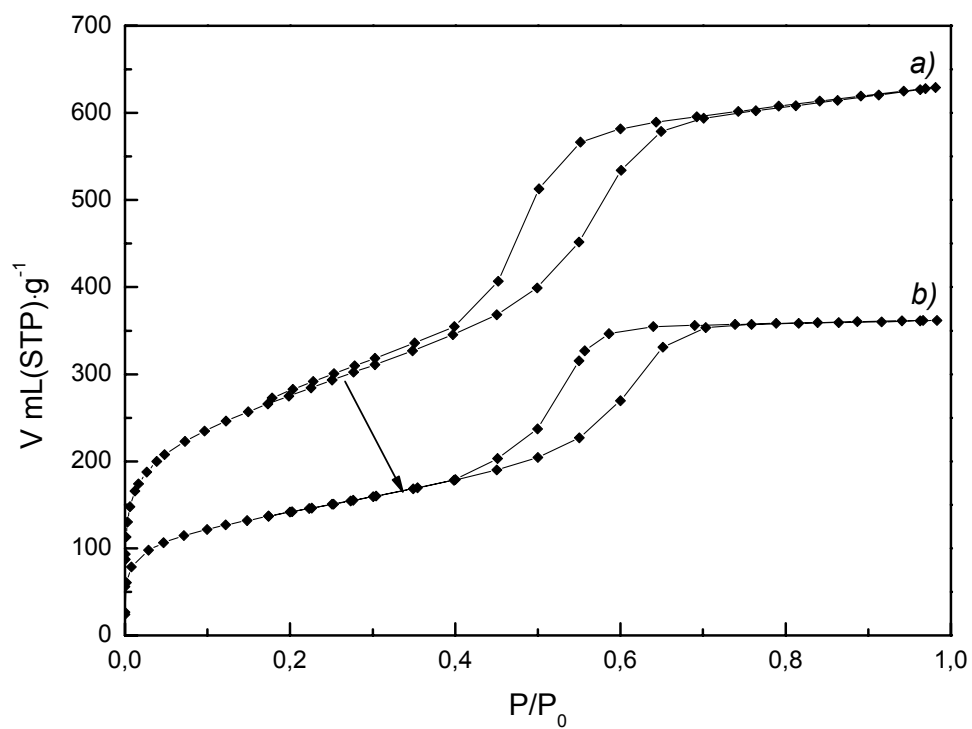


Figure S3. N₂ adsorption/desorption isotherms of **a)** calcined Co²⁺-containing monolith; **b)** calcined Co²⁺-containing monolith after impregnation with K₃[Fe(CN)₆] solution.

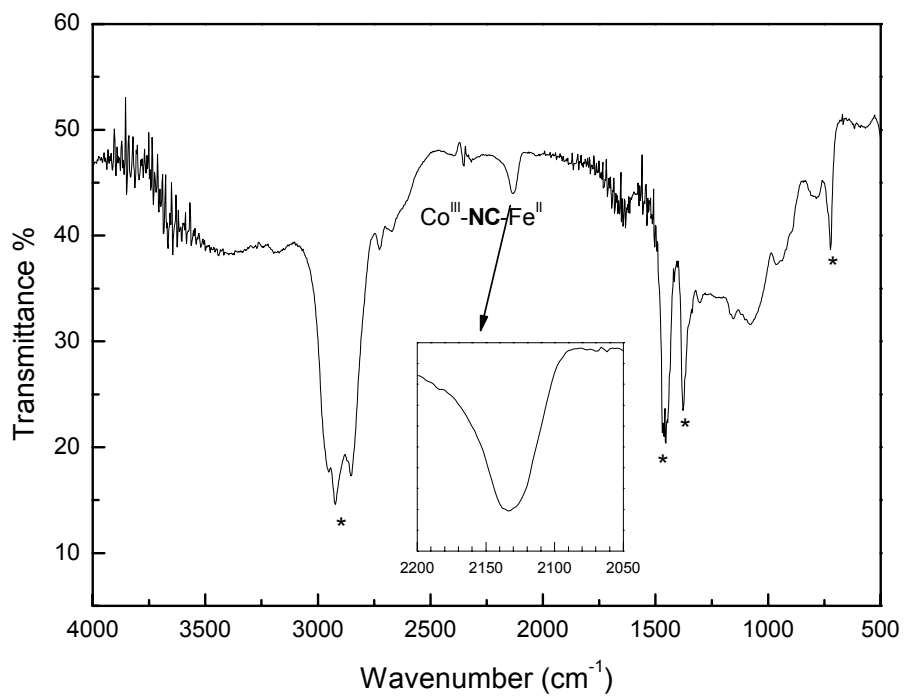


Figure S4. FTIR spectrum of the CoFe PBA – silica nanocomposite. The band around 2130 cm⁻¹ is attributed to the cyanide stretching vibration in Co^{III}-NC-Fe^{II} linkages. Features marked with asterisks correspond to nujol oil.

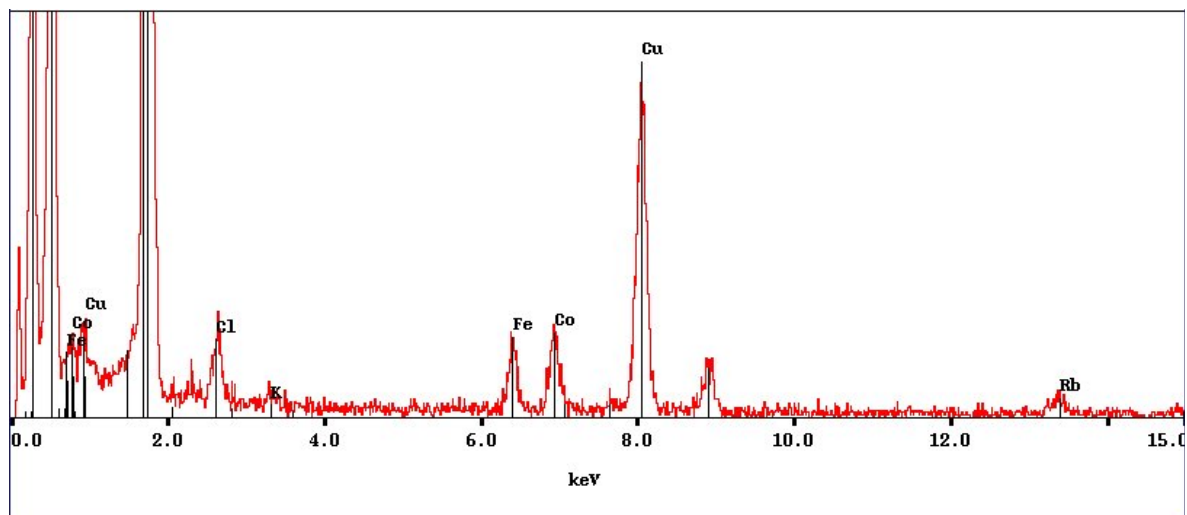


Figure S5. EDX analysis of the CoFe PBA – silica nanocomposite.

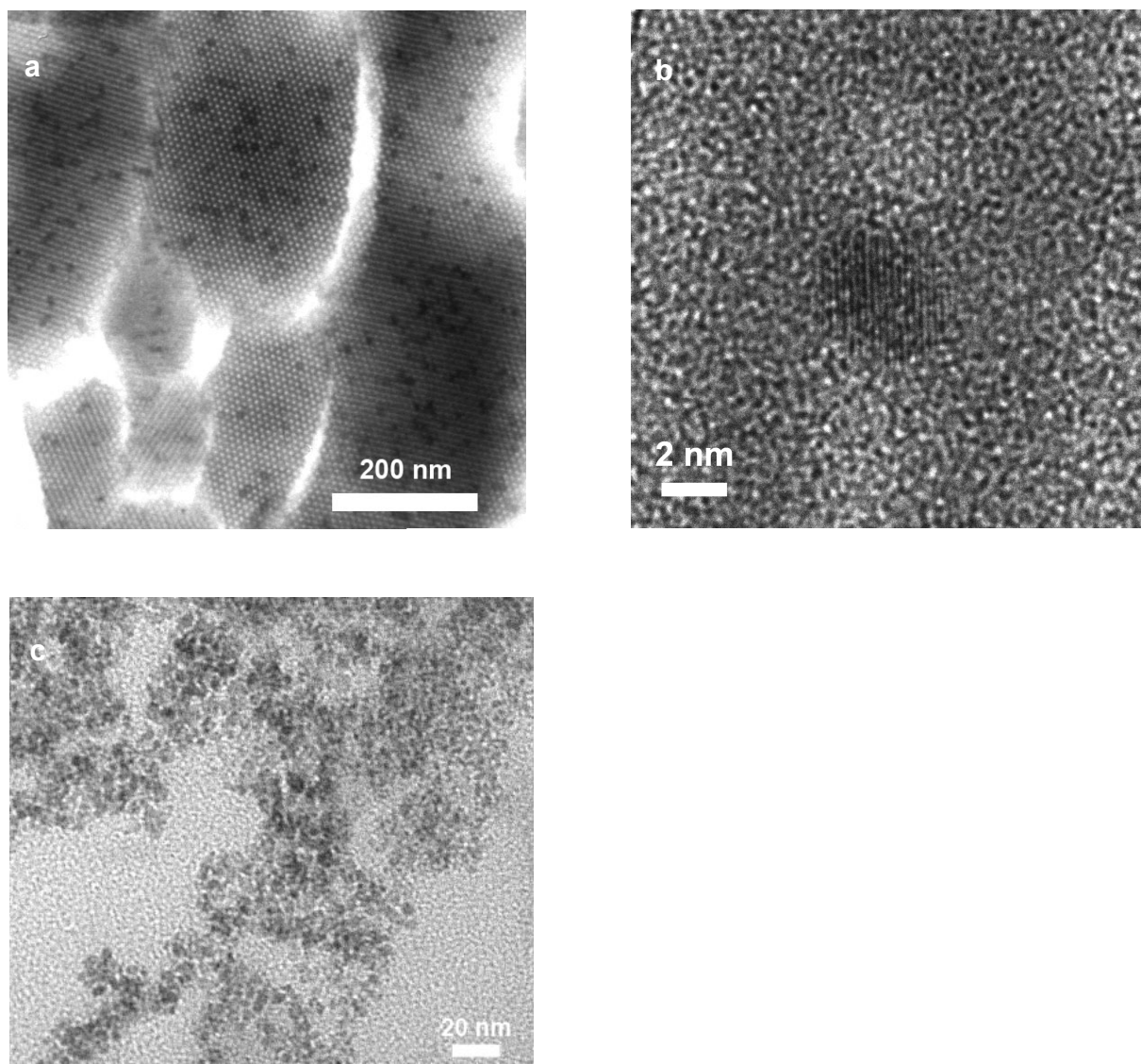


Figure S6. **a)** TEM micrograph of CoFe oxide / silica nanocomposite (microtomed sample) with 2D hexagonal mesostructure obtained after thermal treatment at 800°C CoFe PBA / silica nanocomposite; **b)** HRTEM micrograph of the CoFe oxide / silica nanocomposite (microtomed samples) and **c)** TEM micrograph of the oxide particles recovered after HF treatment on CoFe oxide / silica nanocomposite.

Because PBA particles aggregate making very difficult their visualization, the nanocomposite was first calcined at 800 °C in air to transform PBA particles into robust oxide ones. The size of the particles within the calcined monolith (Fig. S6 a and b) and the size of the particles recovered after HF treatment doesn't exceed 5 nm (Fig. S6 c), which confirms the confining role of the hard template for all of them.

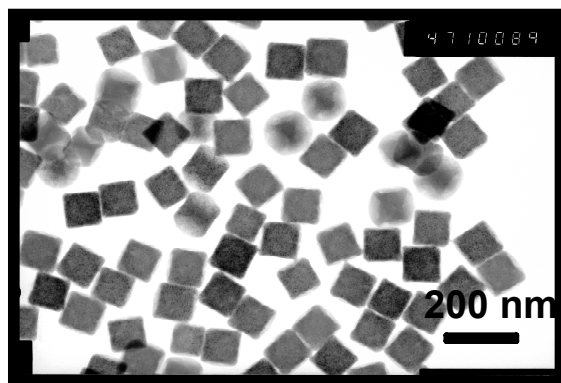


Figure S7. Typical TEM micrograph of powdered CoFe Prussian blue analogues synthesized in aqueous solution, diluted conditions and excess of rubidium metal ions.

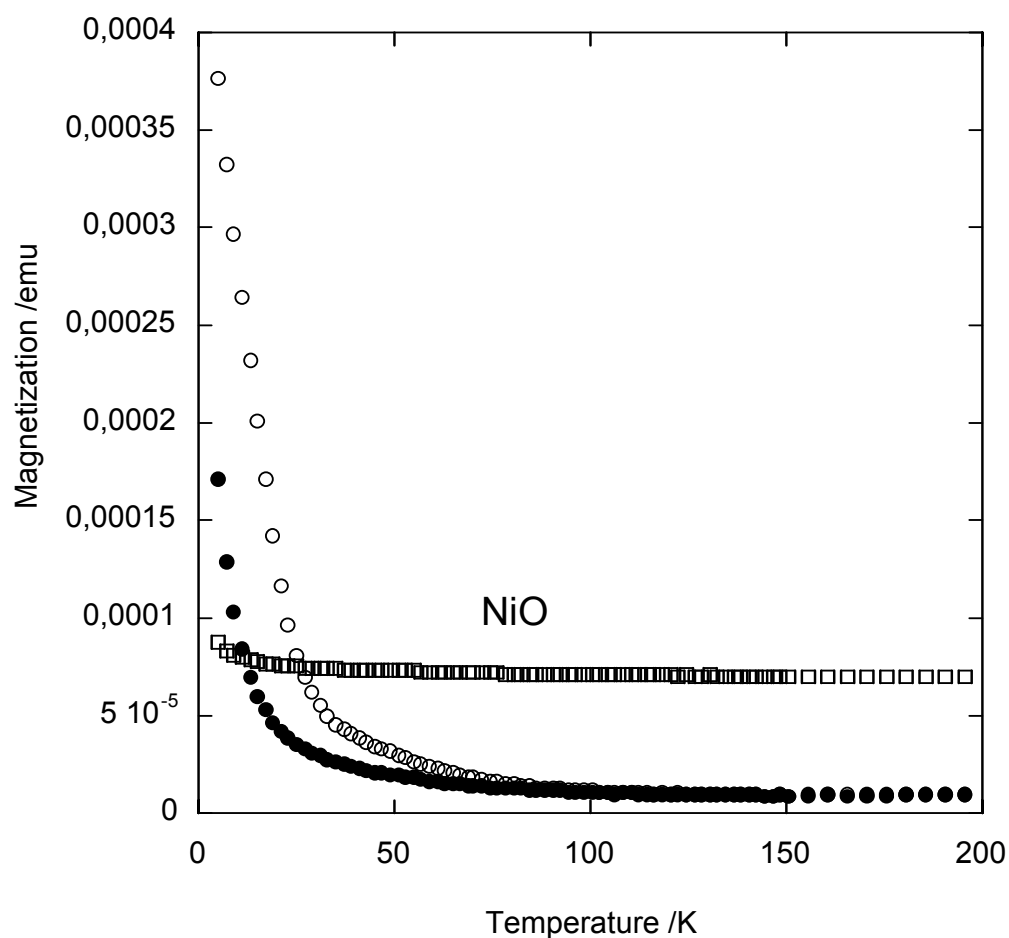


Figure S8. Temperature dependence of the magnetization of the NiO pellet (white square) and temperature dependence of the difference between the magnetization of the PBA-silica nanocomposite and the magnetization of the NiO pellet before (●) and after (○) irradiation ($H=5000$ Oe, irradiation condition : $\lambda=642$ nm, $T=10$ K, $P=15$ mW.cm⁻²). Because the magnetization of the nanocomposite is too weak to be directly measured, an NiO antiferromagnetic thin pellet was placed under the sample in order to optimize the signal to noise ratio. The profile of temperature dependence of the magnetization of the nanocomposite is not affected by the magnetization of the NiO pellet.