Electronic Supporting Information

Sequential Growth in Solution of NiFe Prussian Blue Coordination Network Nanolayers on Si(100) Surfaces

Simon Tricard,[a,*] Claire Costa-Coquelard,[a] Florence Volatron,[a] Benoît Fleury,[a] Vincent Huc,[a] Pierre-Antoine Albouy,[b] Christophe David,[c] Frédéric Miserque,[d] Pascale Jegou,[e] Serge Palacin[e] and Talal Mallah[a,*]

Figure S1 Infrared spectra of the CN groups of the precursor $K_4[Fe(CN)_6],3H_2O$ (2042 cm^{-1}) and the bulk material $Ni_2[Fe(CN)_6],12H_2O$ (2097 cm^{-1}). The absorption is reported to one atom of iron by dividing by the molar mass of each compound. The molar absorption coefficient is found 30% lower for the binding cyanides of the bulk material than for the non binding ones of the ferrocyanide.

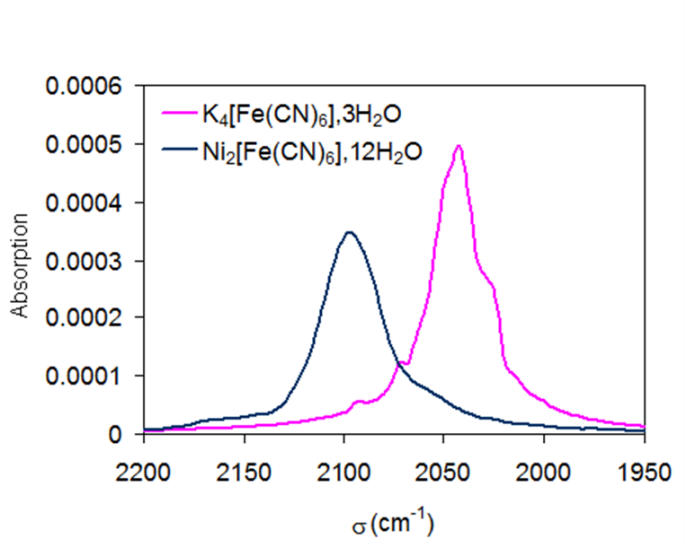


Figure S2 Infrared spectra for the acid, ligand, and *Ni0* formation of the synthesis of the anchoring monolayer. For the three reactions, we observed the C-H symmetrical and asymmetrical stretching bands of the aliphatic chains at 2883 and 2928 cm^{-1} and the band centred at 2100 cm^{-1} corresponding to unreacted Si-H. At the acid step, we observed the acid C=O stretching mode at 1719 cm^{-1} that disappeared at the next steps (ligand and *Ni0*) to give an amid C=O stretching mode at 1655 cm^{-1}. We did not observe any significant differences in IR between the ligand and the *Ni0* steps.

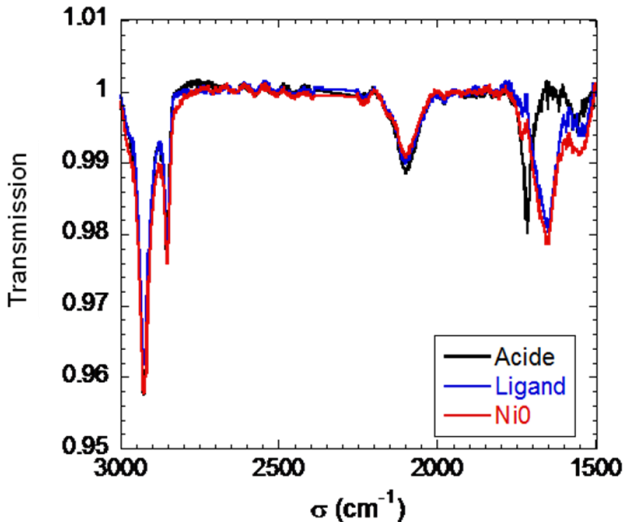
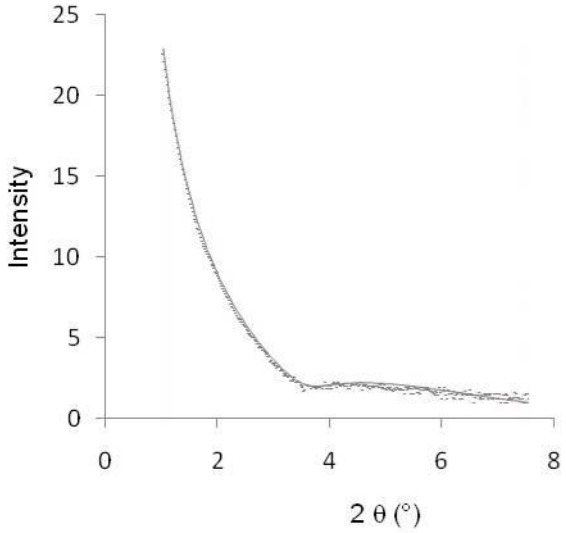


Figure S3 X-ray reflectograms (dots) and simulation (line) a) for the acid step – simulated by a 1.2 nm thick slab; and b) fot the *Ni0* step of the formation of the anchoring monolayer – simulated by a 1.8 nm thick slab.

a)



b)

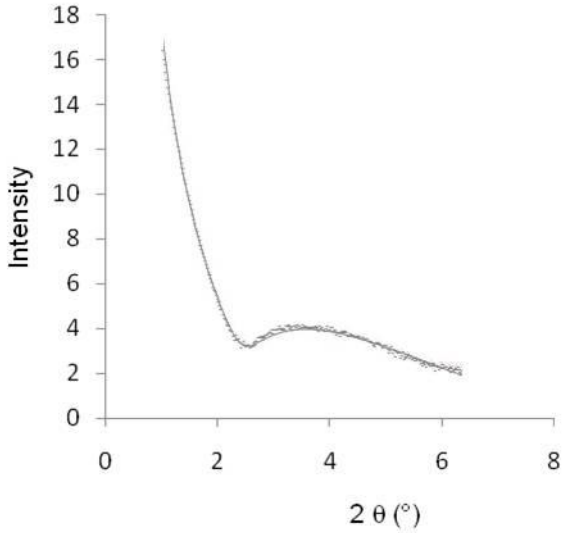
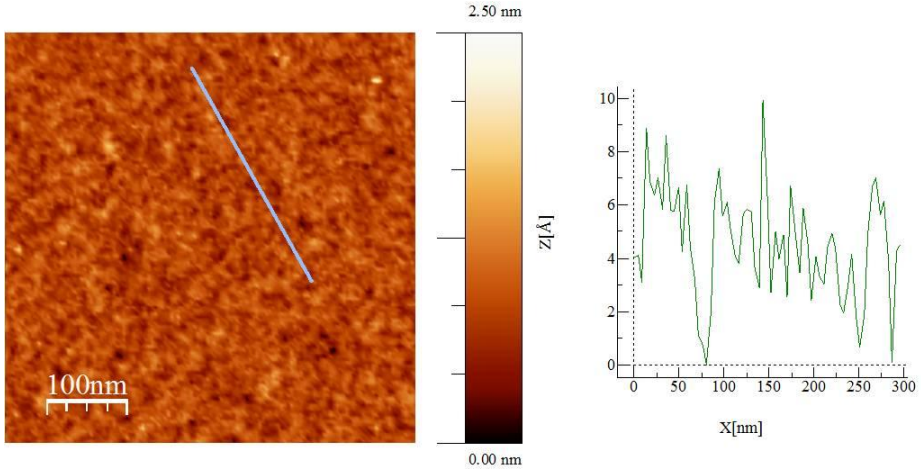
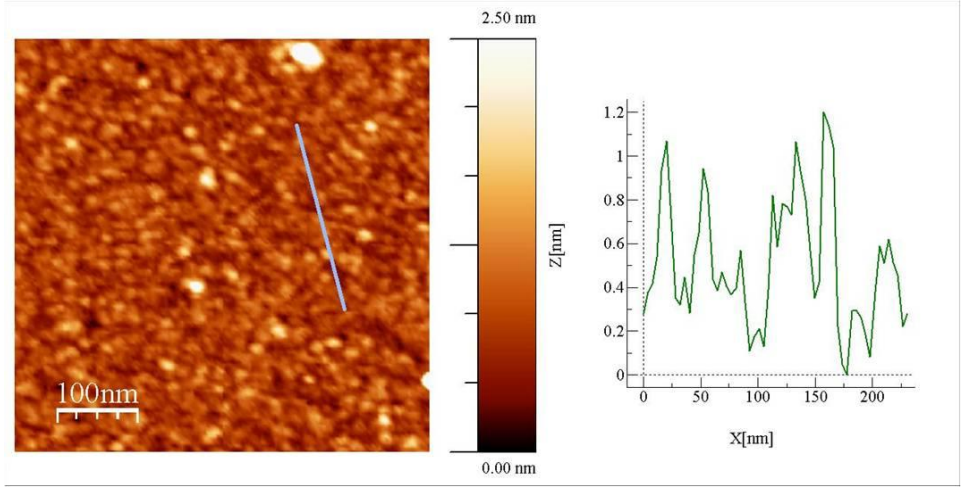


Figure S4 AFM images of the SiH, acid and *Ni0* steps of the formation of the anchoring monolayer: a) SiH step, roughness: 0.17 nm, b) acid step, roughness: 0.28 nm, b) *Ni0* step, roughness: 0.28 nm. The blue lines represent the cross section close to the image.

a)



b)



c)

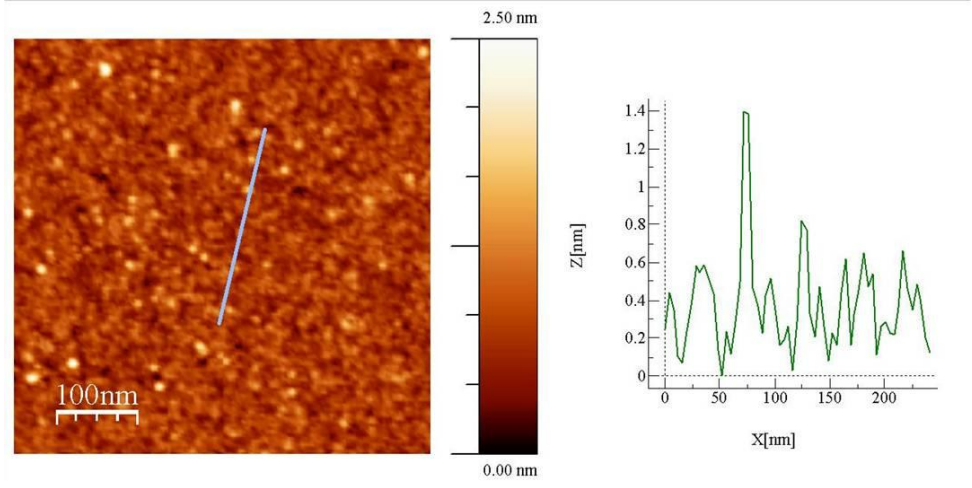


Figure S5 XPS spectra at the N1s and Ni2p edges at the step *Ni0*. The ratio N/Ni extracted with these spectra was equal to 4.

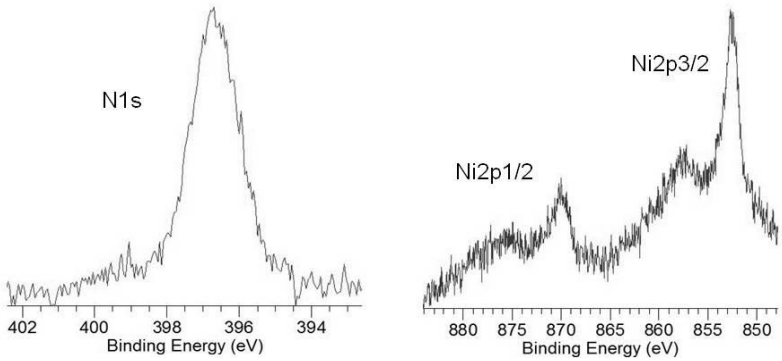


Figure S6 Infra-red spectra at 10^{-3} mol.L^{-1}: zoom of the IR signal of the first two steps showing a shift from 2060 to 2069 cm^{-1} (left); evolution of the IR signal at the *Nin* steps showing a shift from 2069 to 2096 cm^{-1} (right).

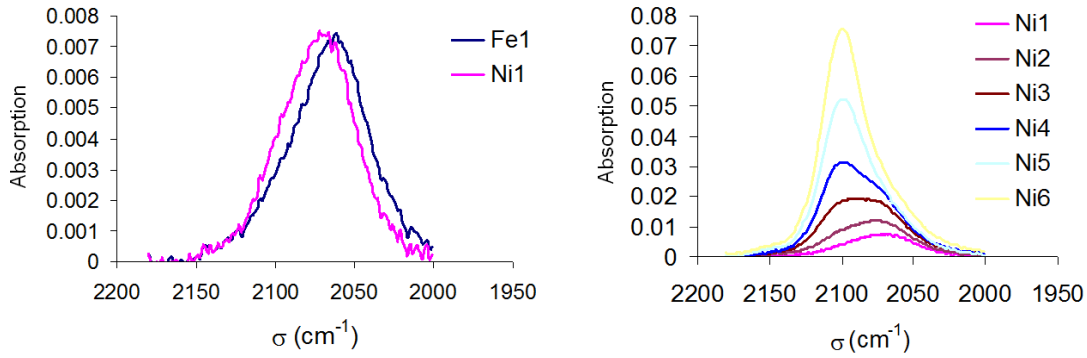


Figure S7 X-ray reflectograms (dots) and simulation (line) at the step *Ni6* of Ni-Fe growth for a concentration of the precursors in solution of 10^{-3} mol.L^{-1} (left – simulated by a 1.8 nm thick slab and a 6.7 nm thick slab) and 10^{-6} mol.L^{-1} (right – simulated by a 1.8 nm thick slab and a 0.4 nm thick slab) and.

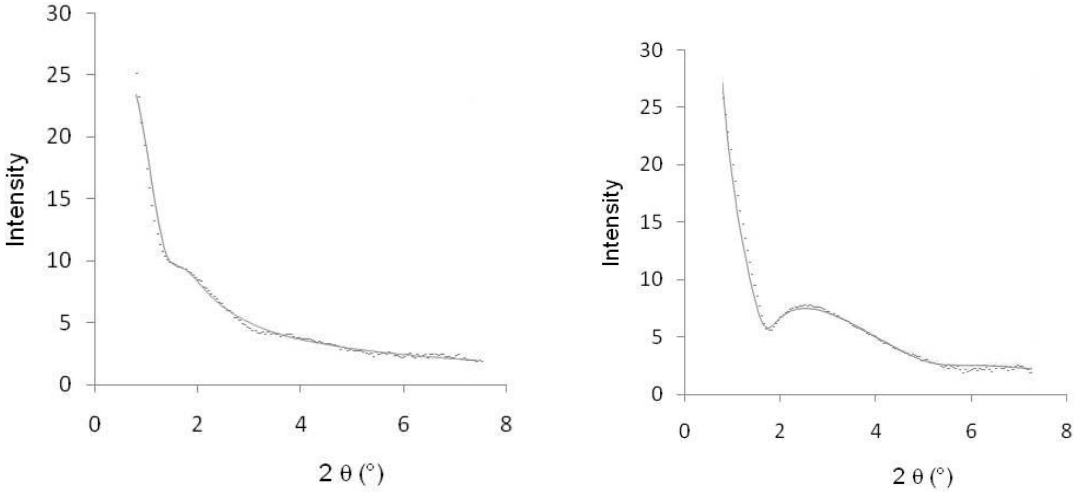
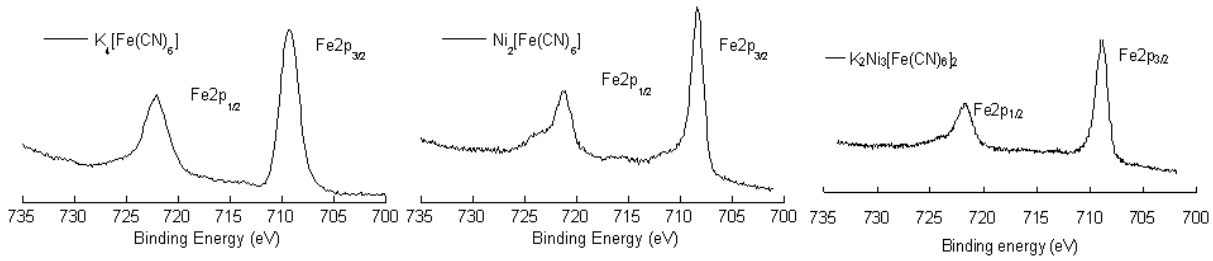
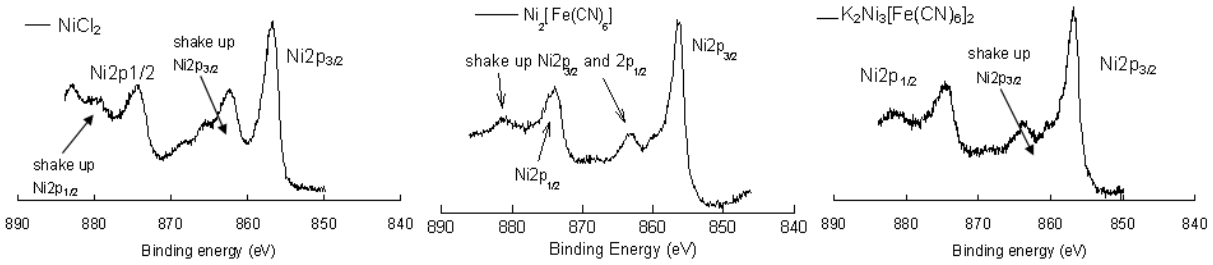


Figure S8 a) XPS spectra at the Fe2p threshold for the starting material $K_4Fe(CN)_6$ (left) and for the bulk compounds $Ni_2[Fe(CN)_6]$ (center) and $K_2Ni_3[Fe(CN)_6]_2$ (right). b) XPS spectra at the Ni2p threshold for the starting material $K_4Fe(CN)_6$ (left) and for the bulk compounds $Ni_2[Fe(CN)_6]$ (center) and $K_2Ni_3[Fe(CN)_6]_2$ (right). c) XPS spectra at the Fe2p and Ni2p edges at the step *Ni6* of NiFe growth for a concentration of the precursors in solution of: 10^{-6} mol.L^{-1} (left); 10^{-3} mol.L^{-1} (right).

a)



b)



c)

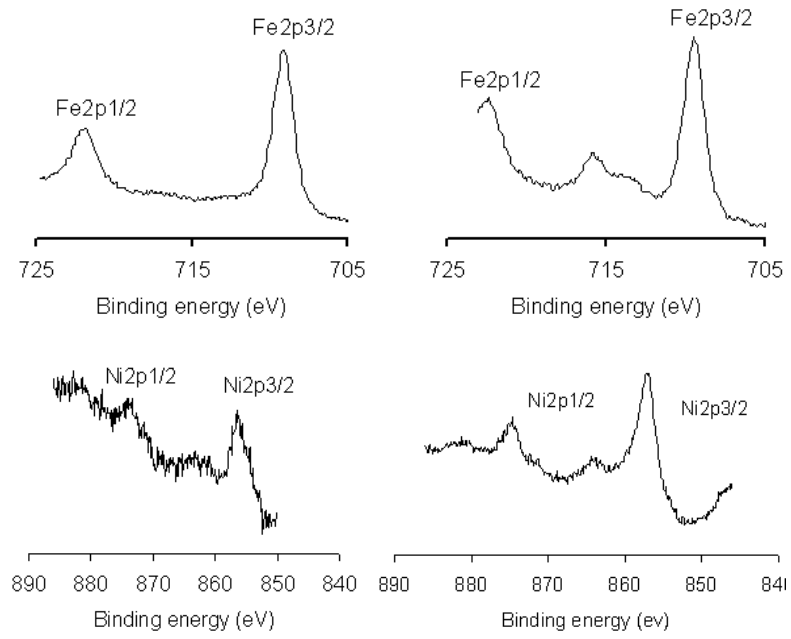
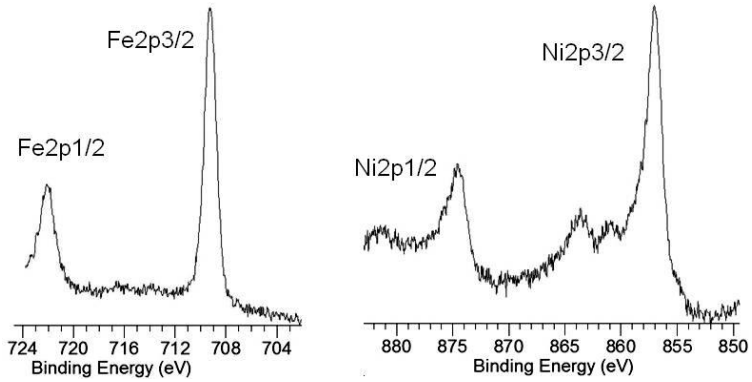


Figure S9 XPS spectra at the Fe2p and Ni2p edges at the step *Ni12* of NiFe growth for a concentration of the precursors in solution of 10^{-3} mol.L^{-1}.



	$Fe2p_{1/2}$	$Fe2p_{3/2}$	$Ni2p_{1/2}$	$Ni2p_{3/2}$	Ratio
Potassium Ferrocyanide	722,1 eV	709,2 eV	-	-	-
Nickel Chloride	-	-	874,2 eV	856,7 eV	-
Bulk Ni_2Fe	721,3 eV	708,3 eV	874,1 eV	856,5 eV	Fe/Ni = 0,5
Bulk $K_2Ni_3Fe_2$	721,6 eV	708,8 eV	874,3 eV	856,8 eV	Fe/Ni = 0,7
Ni12 10^{-3} mol.L^{-1}	721,6 eV	708,7 eV	874,0 eV	856,5 eV	Fe/Ni = 0,9

Comparison between concentrations in solution and on the surface.

Case where there is one molecule every n nanometers on the surface.

Surface taken by one molecule: n x n = n^2 nm^2

Surface concentration: $\boldsymbol{S}$ = 1 / (n^2 nm^2) = $(1/n^2).10^{18}$ m^{-2} = $(1/n^2).10^{14}$ cm^{-2}

= $(1/n^2).10^{-10}$ $mol.cm^{-2}$ = $\mathbf{100/n^2}$ **pmol.cm^{-2}**

Case where there is one molecule every n nanometers in solution.

Volume taken by one molecule: n x n x n = n^3 nm^3

Volume concentration: C =1 / (n^3 nm^3) = $(1/n^3).10^{27}$ m^{-3} = $(1/n^3).10^{24}$ dm^{-3}

= $(1/n^3).10^{24}$ L^{-1} = $\mathbf{1/n^3}$ **mol.L^{-1}**

Correspondence table:

Volume concentration C in mol.L^{-1}	10^{-6}	10^{-3}
Surface concentration S in pmol.cm^{-2}	10^{-2}	1
Intermolecular distance n in nm	100	10