Supporting information for

“Physicochemical Characterization of Hexacyanometallate-TiO$_2$ Composite Materials”

Mario Berrettoni,$^{a,b,*}$ Michela Ciabocco,$^a$ Marzia Fantauzzi,$^{a,e}$ Marco Giorgetti,$^{b,c}$ Antonella Rossi$^{d,e}$ and Eugenio Caponetti$^f$

$a$ Dipartimento di Chimica Industriale “Toso Montanari”, UOS, Campus di Rimini, Università di Bologna, Via dei Mille 39, 47921 Rimini – Italy. E-mail: mario.berrettoni@unibo.it

$b$ INSTM, UdR Bologna – Italy.

$c$ Dipartimento di Chimica Industriale “Toso Montanari”, Università di Bologna – Italy.

$d$ Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Campus di Monserrato S.S. 554 – Italy and INSTM, UdR Cagliari – Italy.

$e$ Centro Grandi Strumenti Università degli Studi di Cagliari – Campus di Monserrato S.S. 554 – Italy.

$f$ Dipartimento STEBICEF Università degli studi di Palermo – Italy.

**Cyclic Voltammetry**

Fig. S1 and S2 show the CV results for the compounds synthesized in 1:1 ratio.

Within the experimental error, our slopes of 56 mV and 52 mV, as shown in the inserts, are consistent with a single electron redox process involving K$^+$. 

![Fig. S1](image1.png)  
![Fig. S2](image2.png)

Fig. S1 CVs at 0.1 V/s of TiO$_2$-CoHCF 1:1 recorded in KCl solutions at different concentrations (1.0, 1.0 × 10$^{-1}$, 1.0 × 10$^{-2}$ M).

Fig. S2 CVs at 0.1 V/s of TiO$_2$-FeHCC 1:1 recorded in KCl solutions at different concentrations (1.0, 1.0 × 10$^{-1}$, 1.0 × 10$^{-2}$ M).

**TEM micrographs**

Fig. S3a,b show the typical spherical aggregate of TiO$_2$ particles covered with cubic aggregate of CoHCF (1:1 ratio) and with cubic aggregate of FeHCC (1:1 ratio).
Fig. S3a Typical spherical aggregate of TiO$_2$ particles covered with cubic aggregate of CoHCF (1:1 ratio).

Fig. S3b Typical spherical aggregate of TiO$_2$ particles covered with cubic aggregate of FeHCC (1:1 ratio).

XPS Spectra

Data were acquired under computer control (Avantage v 3.45). The spectra were processed using CASAXPS software. An iterated Shirley – Sherwood background subtraction routine was performed before curve fitting using the product of Gaussian and Lorentzian functions was used for curve fitting. Composition was calculated using the first-principle method assuming the homogeneity of the sample. Peak areas were corrected for the sensitivity factors calculated using Scofield’s photoionization cross-sections for the asymmetry parameter, the inelastic mean free paths (IMFP) and the intensity/energy analyzer response whose details are reported in literature. IMFP were calculated according to Seah et al. The accuracy of the calculated atomic concentrations is estimated to be ± 10%

Survey spectra of pure CoHCF and TiO$_2$-CoHCF samples are shown in Fig. S4, while in Fig. S5 are reported the survey spectra of pure FeHCC and TiO$_2$-FeHCC samples.

Fig. S4 XPS survey spectra of the samples TiO$_2$-CoHCF in 1:1, 10:1 and 100:1 ratios. X-ray source used: monochromatic Alkα.
XPS survey spectra of the samples TiO$_2$: FeHCC in 1:1, 10:1 and 100:1 ratios. X-ray source used: monochromatic Alkα.

**Fe$_2$p$_{3/2}$ and Co$_2$p$_{3/2}$**

High resolution XPS spectra of Fe$_2$p$_{3/2}$ and Co$_2$p$_{3/2}$ signals of pure CoHCF, pure FeHCC and TiO$_2$-MHCM samples are shown in Fig. S6 and S7 for CoHCF and FeHCC respectively.

**N$_{1s}$**

Detailed curve fitted N$_{1s}$ spectra of all the samples analyzed in this work are presented in Fig. S8 (CoHCF series) and in Fig. S9 (FeHCC series).

**Fig. S5** XPS survey spectra of the samples TiO$_2$: FeHCC in 1:1, 10:1 and 100:1 ratios. X-ray source used: monochromatic Alkα.

**Fig. S6** Fe$_2$p$_{3/2}$ and Co$_2$p$_{3/2}$ XPS high resolution spectra for CoHCF compounds.

**Fig. S7** Fe$_2$p$_{3/2}$ and Co$_2$p$_{3/2}$ XPS high-resolution spectra of FeHCC compounds.

**Fig. S8** N$_{1s}$ signal from CoHCF compounds.

**Fig. S9** N$_{1s}$ signal from FeHCC compounds.
Fig. S9 N1s signal from FeHCC compounds.

In TiO$_2$-FeHCC 100:1 (Fig. S8) a third component appears at ~ 400.8 eV, together with the main peak at about 398.3 ± 0.2 eV, ascribed to nitrogen of the cyano-groups coordinating a transition metal, and the less intense peak at 399.5 ± 0.2 eV, ascribed to the formation of M – CN – Ti surface complexes. By comparison with literature data the higher BE component in the TiO$_2$-FeHCC 100:1 sample could be ascribed to substituted amines or organic nitroso groups (http://srdata.nist.gov/xps/ last access 22 February 2014). According to experimental section all the samples were synthetized in the same way, so it is impossible for us to formulate a hypothesis of the appearance of the third peak on the basis of the synthetic procedure.

Fig. S10 Ti2p signal from TiO$_2$-CoHCF and TiO$_2$-FeHCC compounds at different TiO$_2$-MHCM ratios.
XAS

The data were recorded at Ti K-edge (4965 eV), Fe K-edge (7112 eV) and Co K-edge (7709 eV) in transmission mode using a ionization chamber filled with a mixture of Kr, Ar, N\textsubscript{2} and He in order to have 20%, 70% and 95% of absorption in the I\textsubscript{0}, I\textsubscript{1} and I\textsubscript{2} ion chambers, for all working energy range. The beam was monochromatized using a fixed exit monochromator equipped with a pair of Si(111) crystals. Harmonics were rejected by using the cut-off of the reflectivity of the platinum mirror placed at 3 mrad with respect to the beam upstream the monochromator and by detuning the second crystal of the monochromator by 30% of the maximum. The energy was defined by assigning to 4965 eV, 7112 eV, and 7709 eV the first inflection point of the spectrum of a titanium, iron or cobalt foil, respectively. The spectra of metallic Ti, Fe, or Co were collected simultaneously to those of the samples. This allowed a continuous monitoring of the energy during consecutive scans. No energy drifts of the monochromator were observed during the experiments. Spectra were collected with 2 s/point acquisition time. The pre-edge background was removed by subtraction of a linear function extrapolated from the pre-edge region, and the raw spectra were normalized to the unity by extrapolation of the atomic background evaluated using a polynomial function.

Fig. S11 XAS results of the Iron Hexacyanocobaltate (FeHCC) sample. The normalized X-Ray Absorption Near Edge (XANES) spectra are displayed in the panels (a) and (c) respectively for the Fe and Co K-edge. Panels (b) and (d) show the experimental Fourier Transforms (FTs) of the Extended X-Ray Absorption Fine Structure (EXAFS) spectra taken at the Fe and Co K-edge, respectively.