Supporting information for

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

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Cyclic Voltammetry

Fig. S1 and S2 show the CV results for the compounds synthetized 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$^+$.

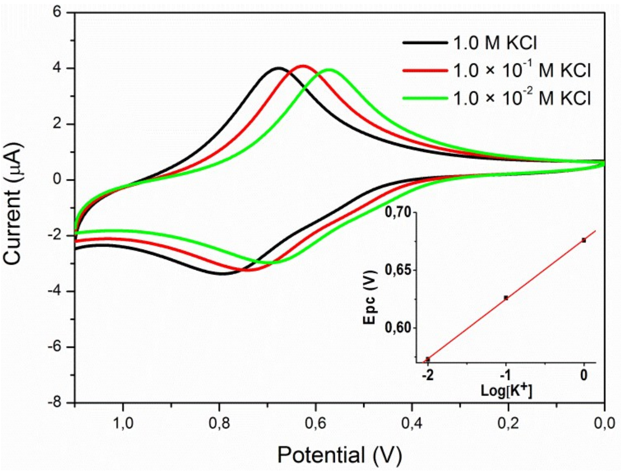

Fig. S1 CVs at 0.1 V/s of TiO$_2$-CoHCF 1:1 recorded in KCl solutions at different concentrations (1.0, 1.0 × 10^{-1}, 1.0 × 10^{-2} M).

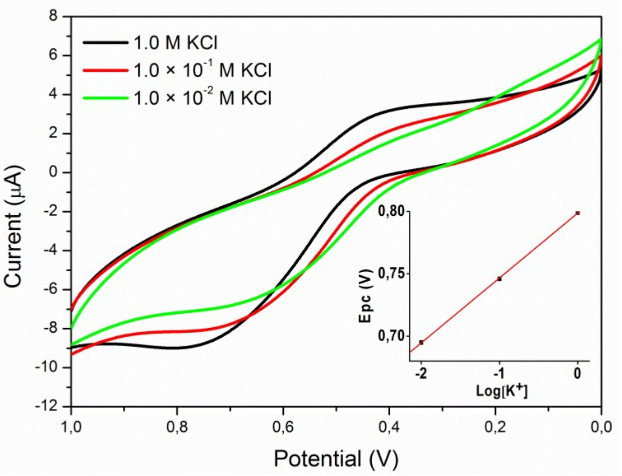

Fig. S2 CVs at 0.1 V/s of TiO$_2$-FeHCC 1:1 recorded in KCl solutions at different concentrations (1.0, 1.0 × 10^{-1}, 1.0 × 10^{-2} M).

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).

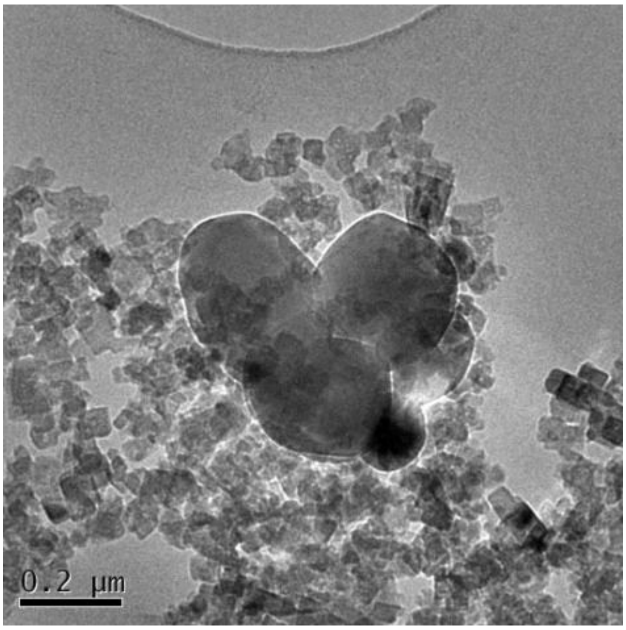

Fig. S3a Typical spherical aggregate of TiO_2 particles covered with cubic aggregate of CoHCF (1:1 ratio).

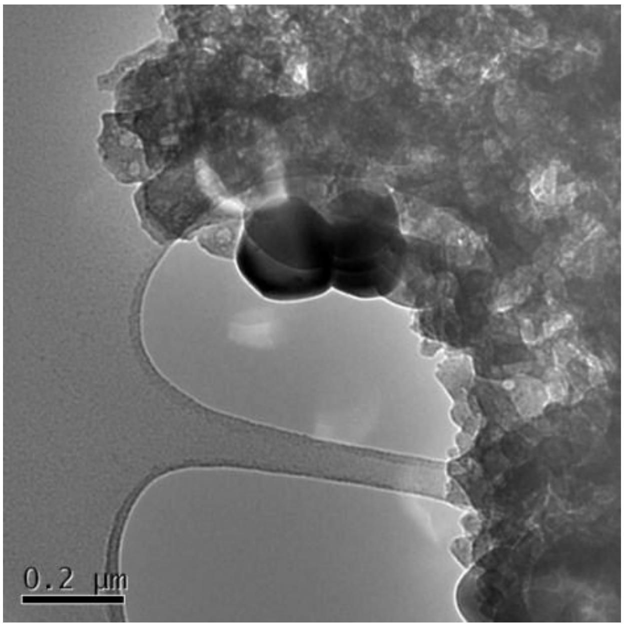

Fig. S3b Typical spherical of aggregate of TiO_2 particles covered with cubic aggregate of FeHCC (1:1 ratio).

XPS Spectra

Survey spectra were acquired in fixed analyzer transmission mode (FAT) using a pass energy (PE) of 200 eV, while the high-resolution spectra of C1s, Cl2p, Co2p, Fe2p, K2p, N1s, O1s, Ti2p were collected with a PE of 100 eV selecting the standard lens mode; the full-width at half-maximum of the peak height, FWHM, of the silver Ag3d$_{5/2}$ signal for the high-resolution spectra was 0.83 eV. To verify the linear response of the instrument, periodic calibrations were performed according to ISO 15472:2001.[1]

Data were acquired under computer control (Avantage v 3.45). The spectra were processed using CASAXPS software.[2] An iterated Shirley – Sherwood[3] 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[4] assuming the homogeneity of the sample. Peak areas were corrected for the sensitivity factors calculated using Scofield's photoionization cross-sections σ,[5] for the asymmetry parameter,[6] the inelastic mean free paths (IMFP) and the intensity/energy analyzer response whose details are reported in literature.[7]

IMFP were calculated according to Seah et al.[8] 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.

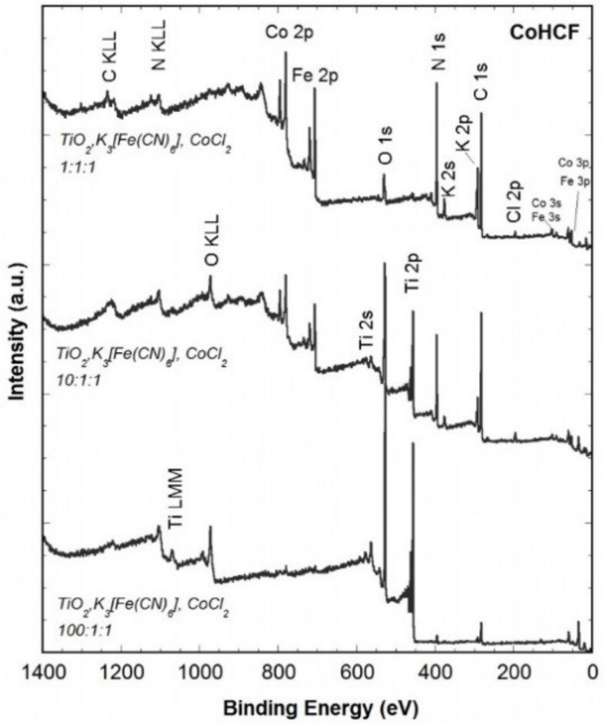

Fig. S4 XPS survey spectra of the samples TiO_2-CoHCF in 1:1, 10:1 and 100:1 ratios. X-ray source used: monochromatic Alkα.

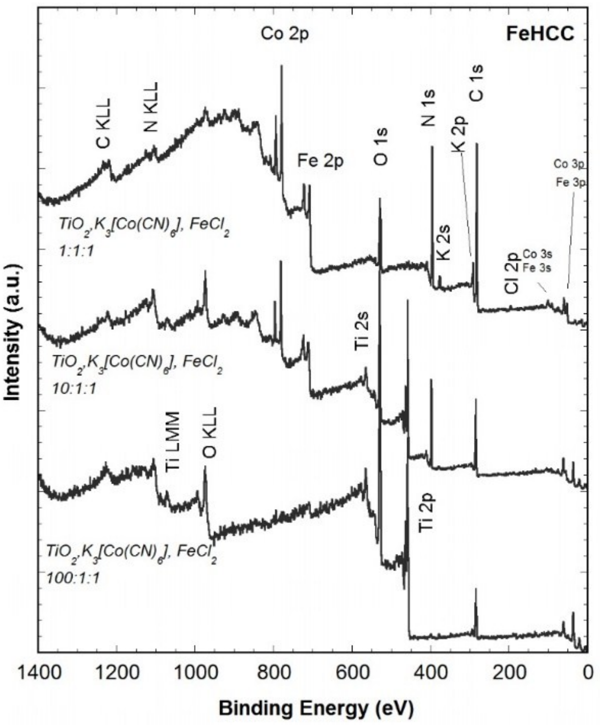

Fig. S5 XPS survey spectra of the samples TiO_2: FeHCC in 1:1, 10:1 and 100:1 ratios. X-ray source used: monochromatic Alkα.

$Fe2p_{3/2}$ and $Co2p_{3/2}$

High resolution XPS spectra of Fe2p3/2 and Co2p3/2 signals of pure CoHCF, pure FeHCC and TiO_2-MHCM samples are shown in Fig. S6 and S7 for CoHCF and FeHCC respectively.

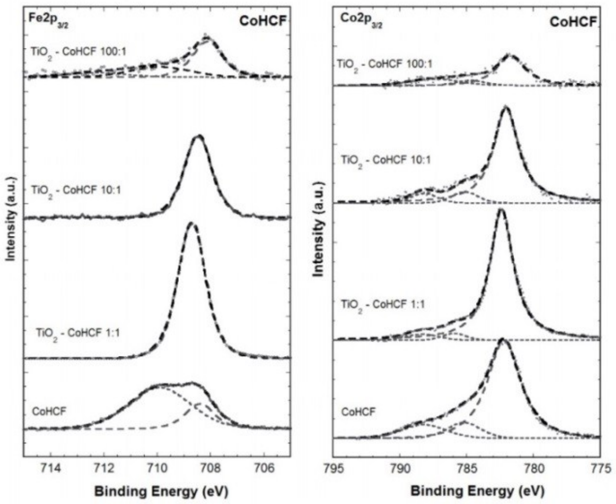

Fig. S6 $Fe2p_{3/2}$ and $Co2p_{3/2}$ XPS high resolution spectra for CoHCF compounds.

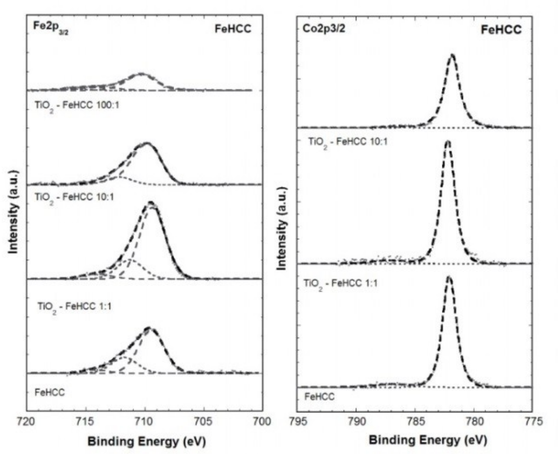

Fig. S7 $Fe2p_{3/2}$ and $Co2p_{3/2}$ XPS high-resolution spectra of FeHCC compounds.

N1s

Detailed curve fitted N1s spectra of all the samples analyzed in this work are presented in Fig. S8 (CoHCF series) and in Fig. S9 (FeHCC series).

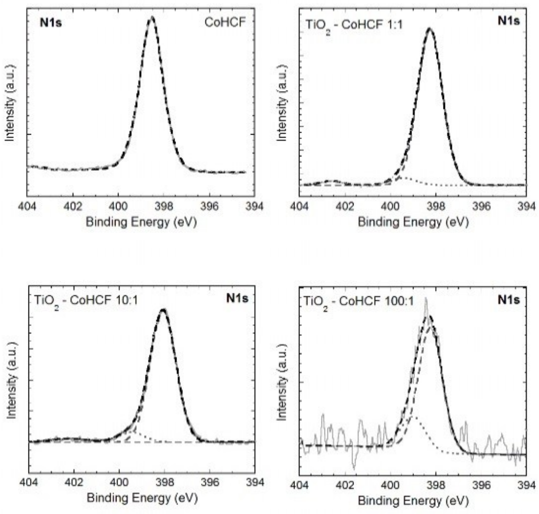

Fig. S8 N1s signal from CoHCF compounds.

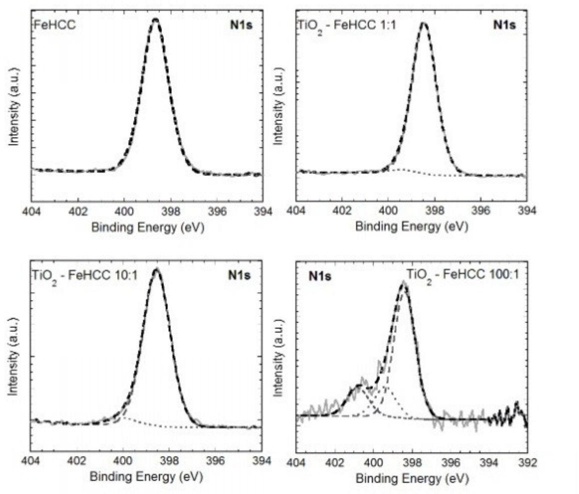

Fig. S9 N1s signal from FeHCC compounds.

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.

Ti2p

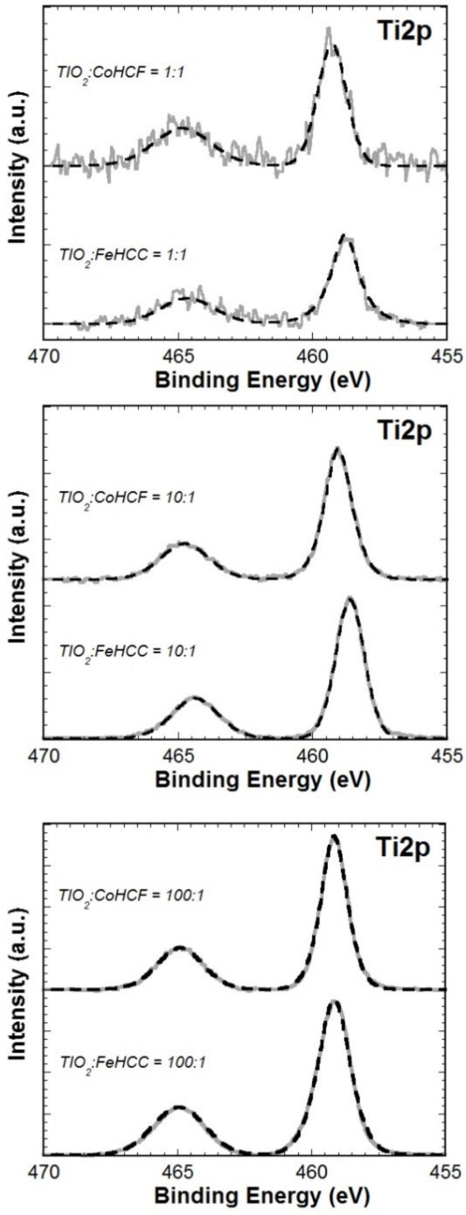

Fig. S10 Ti2p signal from TiO_2-CoHCF and TiO_2-FeHCC compounds at different TiO_2-MHCM ratios.

XAS

The data were recorded at Ti K-edge (4965 eV), Fe K-edge (7112 eV) and Co K-edge (77709 eV) in transmission mode using a ionization chamber filled with a mixture of Kr, Ar, N_2 and He in order to have 20%, 70% and 95% of absorption in the I0, I1 and I2 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.

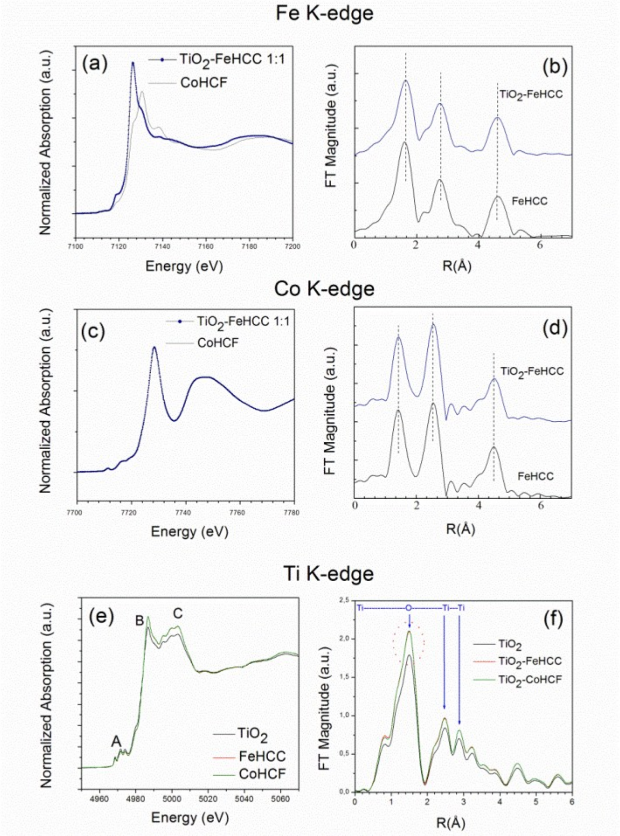

Fig. S11 XAS results of the Iron Hexacyanocobaltate (FeHCC) sample. The normalized X-Ray Absorption Near Edge (XANES) spectra are displayed in the panels (a) and (c) respectively for the Fe and Co K-edge. Panels (b) and (d) show the experimental Fourier Transforms (FTs) of the Extended X-Ray Absorption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

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