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Physicochemical Characterization of Hexacyanometallate-TiO$_2$ Composite Materials

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

The paper describes synthesis and characterization of novel TiO$_2$-Metal Hexacyanometallates (MHCMs) composite materials. The starting material, TiO$_2$, was modified by addition of cobalt-hexacyanoferrate (CoHCF) or iron-hexacyanocobaltate (FeHCC) at various concentrations. The resulting composites were characterized as follows: cyclic voltammetry (CV) followed the formation of TiO$_2$-MHCM clusters, TEM micrographs studied their morphology, XAS and XPS data indicated that MHCM bonds to TiO$_2$ through the nitrogen atom of its -CN group and modifies the environment of Ti compared to that of pure anatase. As expected, and confirmed by UV-Vis and XP-valence band data, the electronic properties of TiO$_2$ were substantially modified: the edge in the composite materials shifted by about $-2.0$ eV relative to TiO$_2$. 

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$^a$ Dipartimento di Chimica Industriale "Toso Montanari", UOS, Campus di Rimini, Università di Bologna, Via dei Mille 39, 47922 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. 594 – Italy and INSTM, UdR Cagliari – Italy.
$^e$ Centro Grandi Strumenti Università degli Studi di Cagliari – Campus di Monserrato S.S. 594 – Italy.
$^f$ Dipartimento STEBCEF Università degli studi di Palermo – Italy.
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Introduction

Composite materials consisting of semiconductors and inorganic compounds have often attractive photo-electrochemical properties. Among the semiconductor materials, TiO$_2$ is particularly promising due to its photo-electrochemical properties, high photo-activity, outstanding hydrophilicity, strong redox and catalytic activity; the range of its potential applications includes catalysis, photovoltaic cells, self-cleaning and antifogging surface treatments. In addition, TiO$_2$ is non-toxic, chemically very stable, and easily obtained as nanometer scale particles. The photo-catalytic properties of TiO$_2$ are strongly affected by its structure, interface, grain size and crystallographic orientation of the exposed faces in contact with solution. The photo-electrochemical characteristics are dependent upon porosity, morphology and the method of synthesis. Surface functionalization of TiO$_2$ has been achieved with many methods including doping with metal ions or nonmetallic elements, sensitization with organic dyes or semiconductors with a small band-gap.

The aim of this paper is the design, synthesis and characterization of new composite materials of TiO$_2$ and metal hexacyanometallates.

Metal-hexacyanometallates (MHCMs) are solid compounds of mixed valence with general formula: $A_xM_y[B(CN)_6]_nH_2O$ where M and B are transition metals, A an alkaline metal, x and y stoichiometric coefficients, n the hydration-intercalation molecules per unit formula (≤ 14). Metal hexacyanoferrates (MHCFs) are a class of mixed-valence compounds of major technological interest for their electrocatalytic, electrochromic, ion-sensing, ion-exchanging and photomagnetic properties and also for their possible applications in batteries and charge-storage devices. These salts present a face centered cubic (fcc) unit cell and depending upon the degree of peptization, can be described in the “soluble” and the “insoluble” form. Basically, the insoluble form lacks one-fourth of the B(CN)$_6$ units, which are replaced by coordinated and non-coordinated water molecules.

Among the hexacyanoferrates, cobalt hexacyanoferrate (CoHCF) has been extensively studied in literature due to its interesting chemical and electrochemical properties and its ease of synthesis by chemical and electrochemical deposition. Iron hexacyanocobaltate, FeHCC presents a cubic structure similar to that of CoHCF, but with metal centers differently coordinated to either carbon or nitrogen and with significantly different properties. The electrochemistry of FeHCC has not been as extensively investigated as that of CoHCF. However, in FeHCC only iron centers are electroactive while Co atoms in aqueous electrolytes display no activity.

Widmann et al. studied the solid mixtures KM[Co(CN)$_6$]$_x$, where M = Ni, Fe, Cu, and demonstrated the redox activity of high spin iron centre Fe$^{II}$/Fe$^{III}$. This activity is observed by cyclic voltammetry only in freshly synthesized FeHCC; after 2 days the features of low-spin iron appear, obviously due to a partial decomposition to Prussian green revealed by a change in color to light green. TiO$_2$ nanoparticles functionalized with Fe$^{II}$(CN)$_6$ have been investigated by electro-absorption spectroscopy. The iron complex is believed to bind at a surface Ti$^{IV}$-site via a monodentate cyanide ligand, (CN)$_2$Fe$^{II}$-CN-Ti$^{IV}$(particle), as suggested by IR and resonance Raman evidence. Other studies dealt with thin films prepared by mixing TiO$_2$ with metal-hexacyanometallates. To the best of our knowledge, no investigation of the CoHCF–TiO$_2$ composites has been reported while a detailed study of their FeHCC–TiO$_2$ counterparts has appeared.

An aim of this paper is to compare the photo-electrochromic and photo-electrochemical behavior of CoHCF–TiO$_2$ composites with that of their FeHCC–TiO$_2$ counterparts. Here, we will also detail the procedure of synthesis, and their influence upon optical properties, and the structural-electronic characterization performed with a wide range of experimental techniques.

Experimental

Chemicals and Solutions

All chemicals used in this work were reagent grade and were used as received from Sigma-Aldrich (FeCl$_3$, K$_3$[Co(CN)$_6$], K$_3$[Fe(CN)$_6$], CoCl$_2$, KCl, anatase TiO$_2$ 99%) and from Fluka (TiCl$_4$, >99.0%). Deionized water was used throughout this work. All experiments were carried out at room temperature and in air.

Electrochemical Measurement

Electrochemical measurements were carried out with a CH Instrument, model 660c, through a standard three-electrode electrochemical glass cell (10 cm$^2$) comprising a glassy carbon electrode (with a 3 mm diameter) as working electrode and a Pt auxiliary electrode; the reference was a silver–silver chloride electrode (Ag/AgCl) in a saturated solution of potassium chloride. All the potentials will be referred to the Ag/AgCl electrode.

An aqueous suspension of the sample was dropped on the glassy carbon electrode; after drying, an adherent deposit was
covering the electrode surface. Before deposition, the glassy carbon surface was polished with a 0.05 μm alumina slurry on a microcloth polishing pad and rinsed with deionized water.

**Chemical Synthesis**

Iron hexacyanocobaltate and cobalt hexacyanoferrate were synthesized by precipitation mixing 0.05 M water solution of FeCl₂ or CoCl₂ drop wise to an equivalent amount of K₃[Co(CN)₆] or K₃[Fe(CN)₆] and stirring at room temperature. All precipitates were allowed to stand for a night and air-dried at ambient conditions to improve the formation of the TiO₂-MHCM bond. Subsequently, they were carefully washed with deionized water to remove the unreacted salts and centrifuged to separate the solid product. Finally, the precipitate was dried at 80°C.

**Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDS)**

Each dispersion resulting by mixing the powder with isopropanol was deposited on a 300-mesh nickel grid, "holey carbon-coated". TEM experiments were performed on a high-resolution transmission electron microscope (HR-TEM) JEOL JEM-2100 operating at 200 kV. Elemental analysis was carried out using an energy dispersive X-ray detector (EDS), Oxford X-MAX 80Si computer operated at 20 kV and 10 μA. The spectra were deglitched, calibrated, and normalized using the Athena program.

**X-ray Diffraction (XRD)**

XRD measurements were performed on a Rigaku SmartLab X-ray source equipped with a Huber goniometer. Cell parameter, a, referred to the cubic structure, was calculated by the unit cell program.

**Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDS)**

Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDS) were used to investigate the microstructure and composition of the synthesized materials. TEM images were acquired using a Tecnai G2 F20 microscope operating at 200 kV. EDS spectra were acquired using a Link-ISIS energy-dispersive X-ray spectrometer attached to the TEM.

**X-ray photoelectron spectroscopy (XPS)**

X-ray photoelectron spectroscopy (XPS) analyses were performed with a Thetaprobe spectrometer (Thermo Fisher Scientific, Waltham MA, USA) at the University of Cagliari. The samples were mounted as pellets on a copper bi-adhesive tape. Spectra were collected using a 300 μm spot size Al Kα monochromatic beam operated at 4.7 mA and 15 kV. A flood gun was used for charge compensation. 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, O1s, Ti2p, N1s, Fe2p, K2p, Cl2p, and O1s 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 Ag3d₅/₂ signal for the high-resolution spectra was 0.83 eV. The linear response of the instrument was checked with periodic calibrations performed according to ISO 15472:2001. Binding energy values were corrected by referencing the aliphatic carbon to 285 eV. 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 applying a fitting procedure using a combination of Gaussian and Lorentzian shapes. Composition was calculated using the first-principle method and assuming a homogeneous sample.

**Fourier Transform Infrared Spectroscopy (FT/IR)**

Fourier Transform Infrared Spectroscopy (FT/IR) was used to study the vibrational characteristics of the synthesized materials. Spectra were recorded using a Nicolet 6700 FT-IR spectrometer in the range of 4000-400 cm⁻¹. The samples were prepared as KBr pellets, and the spectra were collected with 16 scans at a resolution of 4 cm⁻¹.
Results

Table 1 lists the TiO$_2$-FeHCC and TiO$_2$-CoHCF composite materials synthesized in different ratios and summarizes the techniques used for their characterization. The results of the thermogravimetric analyses and the XRD are also included. TGA allows the determination of the number of water molecules included in the structure of the hexacyanometallate. In Table 1 the XRD column reports the cell parameter, $a$, referred to the cubic structure, calculated by the unit cell program.

The diffractogram of the 100:1 TiO$_2$:FeHCC sample is not available being the concentration of FeHCC too low in this composite. The cell parameters, $a$, assume a value very close to 10 Å, typical of the hexacyanometallates.

Table 2 provides the stoichiometry of the compounds as measured by X-ray fluorescence (XRF) and X-ray photoelectron spectroscopy (XPS). K$^+$ is missing in the XRF data due to limitations of the experimental set up.

The low intensity of the cobalt signal, Co2p, did not allow calculation of the surface composition of the TiO$_2$:FeHCC sample in 100:1 ratio. The elemental ratios calculated with XPS and XRF are in reasonable agreement.

### Table 1 Summary of the compounds studied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CV</th>
<th>IR</th>
<th>UV-Vis</th>
<th>TGA ($\text{H}_2\text{O}$)*</th>
<th>XAS</th>
<th>XRD $a$ / Å*</th>
<th>XPS</th>
<th>TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$:CoHCF</td>
<td>1:1</td>
<td>X</td>
<td>x</td>
<td>x</td>
<td>3.0</td>
<td>10.07</td>
<td>x</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>10:1</td>
<td>X</td>
<td>x</td>
<td>x</td>
<td>6.5</td>
<td>10.30</td>
<td>x</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>100:1</td>
<td>X</td>
<td>x</td>
<td>7.8</td>
<td>10.26</td>
<td>x</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>TiO$_2$:FeHCC</td>
<td>1:1</td>
<td>X</td>
<td>x</td>
<td>x</td>
<td>5.2</td>
<td>10.30</td>
<td>x</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>10:1</td>
<td>X</td>
<td>x</td>
<td>x</td>
<td>6.3</td>
<td>10.13</td>
<td>x</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>100:1</td>
<td>X</td>
<td>x</td>
<td>7.4</td>
<td>-</td>
<td>x</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

*The last digit is only partially significant due to the statistical error.

### Table 2 Stoichiometry of the studied compounds, obtained by XPS and XRF techniques.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO$_2$:MHCM Ratio</th>
<th>XPS</th>
<th>XRF*</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ + CoHCF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1</td>
<td>K$_{1-x}$Co$_x$[Fe(CN)$_6$]</td>
<td>1.3</td>
<td>Co$_{0.1}$[Fe(CN)$_6$]</td>
</tr>
<tr>
<td>10:1</td>
<td>K$<em>{0.1}$Co$</em>{0.9}$[Fe(CN)$_6$]</td>
<td>1.5</td>
<td>Co$_{0.3}$[Fe(CN)$_6$]</td>
</tr>
<tr>
<td>100:1</td>
<td>K$<em>{0.1}$Co$</em>{0.9}$[Fe(CN)$_6$]</td>
<td>1.5</td>
<td>Co$_{0.3}$[Fe(CN)$_6$]</td>
</tr>
</tbody>
</table>

| TiO$_2$ + FeHCC|                     |     |      |
| 1:1            | K$_{0.1}$Fe$_{0.9}$[Co(CN)$_6$] | 0.7 | Fe$_{0.1}$[Co(CN)$_6$] |
| 10:1           | K$_{0.1}$Fe$_{0.9}$[Co(CN)$_6$] | 0.8 | Fe$_{0.1}$[Co(CN)$_6$] |
| 100:1          | -                     | -   | Fe$_{0.1}$[Co(CN)$_6$] |

*K$^+$ is not detected.

All the compounds prepared, TiO$_2$:FeHCC and TiO$_2$:CoHCF in different ratios, were fully characterized by CV, TEM, IR, UV-Vis, XAS and XPS in order to provide evidence of their formation, to determine the morphology of the aggregates, to verify the formation of the compounds and to shed a light on the effect of the FeHCC and CoHCF doping agents.
Cyclic voltammetry (CV)

TiO$_2$-FeHCC and TiO$_2$-CoHCF compounds were synthesized, deposited on glassy carbon and characterized by cyclic voltammetry. Fig. 1 shows the voltammograms for TiO$_2$-FeHCC (black line) and TiO$_2$-CoHCF (red line), both in a 1:1 TiO$_2$-MHCM ratio.

Fig. 1 CVs at 0.1 V/s of TiO$_2$-FeHCC 1:1 (black line) and TiO$_2$-CoHCF 1:1 (red line) in a 1.0 M KCl solution. Potentials are referred to the saturated Ag/AgCl electrode.

**Table 3**

<table>
<thead>
<tr>
<th>TiO$_2$-FeHCC</th>
<th>Ep$_c$</th>
<th>Ep$_a$</th>
<th>E$^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0.364</td>
<td>0.787</td>
<td>0.575</td>
</tr>
<tr>
<td>10:1</td>
<td>0.261</td>
<td>0.708</td>
<td>0.484</td>
</tr>
<tr>
<td>100:1</td>
<td>0.207</td>
<td>0.735</td>
<td>0.471</td>
</tr>
</tbody>
</table>

**Table 4**

<table>
<thead>
<tr>
<th>TiO$_2$-CoHCF</th>
<th>Ep$_c$</th>
<th>Ep$_a$</th>
<th>E$^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0.679</td>
<td>0.784</td>
<td>0.732</td>
</tr>
<tr>
<td>10:1</td>
<td>0.655</td>
<td>0.835</td>
<td>0.745</td>
</tr>
<tr>
<td>100:1</td>
<td>0.529</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

CVs were also performed in solution with different KCl concentrations (1.0, 1.0 × 10$^{-1}$, 1.0 × 10$^{-2}$ M) to verify the role of K$^+$. For both compounds, the peak potentials shifted in the negative direction with decreasing the electrolyte concentration, thus confirming that the redox process is associated with the intercalation of electrolyte K$^+$ cations (see Fig. S1 and S2 in the supporting information). Within the experimental error, the slopes of 56 mV and 52 mV are consistent with a single electron redox process assisted by K$^+$.
Similar results were obtained for TiO$_2$-FeHCC and TiO$_2$-CoHCF in 10:1 molar ratio (not shown).

**Transmission Electron Microscopy (TEM)**

All samples were characterized by transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) to provide evidence for the presence of the metal hexacyanometallate and to characterize the morphology of particles and aggregates. In particular EDS analyses performed upon various aggregates confirm the co-presence of Fe, Co, and Ti. The following observations apply to FeHCC and CoHCF compounds:

- Aggregates of TiO$_2$-CoHCF (1:1 ratio) and TiO$_2$-FeHCC (1:1 ratio) consist of typical spherical TiO$_2$ particles covered with grains of cubic CoHCF and FeHCC (see Fig. S3 a,b);
- In 1:1 samples, many isolated clusters of CoHCF or FeHCC with cubic structure and 100 – 200 nm in size are observed; however, FeHCC has less isolated clusters than CoHCF.
- In 10:1 samples, TiO$_2$ aggregates are larger, ranging from 100 to 600 nm, and consist of 5–20 TiO$_2$ spherical particles; Fig. 4 is a micrograph of TiO$_2$ and CoHCF in 10:1 ratio showing an aggregate of spherical TiO$_2$ particles covered with cubic nanocrystals of CoHCF.

**Fourier transform Infrared Spectroscopy (FT/IR)**

For sake of clarity and comparison, each Fourier transform infrared (FT/IR) spectrum presented below is overturned and individually normalized to its top transmittance value. Fig. 6 shows the spectra of FeHCC (red curve) and CoHCF (black curve) in the bulk form. The CN stretching bands are eventually decomposed by curve fitting in order to assign the main bands. The spectra of Fig. 6 agree with data from the literature $^{20,27}$.

In 100:1 samples, rare CoHCF or FeHCC grains and TiO$_2$-CoHCF or TiO$_2$-FeHCC aggregates are present, as shown in Fig. 5. These CoHCF or FeHCC grains are larger than in the 1:1 and 10:1 samples.
In the bulk CoHCF compound, we detected and assigned all the stretching bands due to the possible combinations Fe$^{II}$-CN:Co$^{III}$. In the bulk CoHCF, two stretching bands are observed at 2181 and 2167 cm$^{-1}$. The intensity of the band at 2181 cm$^{-1}$ is not influenced by the concentration, as shown in Table 6, so it can be referred to the FeHCC in bulk. In the case of FeHCC we observe a net shift between CN in the bulk form and CN in the TiO$_2$-linked form. Furthermore, the shift is inversely proportional to the FeHCC concentration. The spectra of the samples with CoHCF have more features than those with FeHCC, corresponding to a relatively minor complexity of the latter.

### X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were acquired with the full set of compounds. Survey spectra of TiO$_2$-CoHCF in 1:1, 10:1 and 100:1 ratios are shown in Fig. S4 of the supporting information. Signals from all the elements that belong to the compounds C, N, O, Fe, Co, Ti, K and a small amount of Cl have been detected. These elements are revealed on the surfaces of the samples with CoHCF aggregates at all dilutions (see Fig. S5 in the supporting information). The quantitative analyses are summarized in Table 2; we have a fairly good agreement with the energy dispersive spectroscopy data, compatible with the experimental uncertainties of the two techniques.

To obtain information about the chemical state of the elements, the spectra of iron, cobalt, nitrogen and titanium were curve fitted. Parameters such as the Gaussian-Lorentzian elements, the spectra of iron, cobalt, nitrogen and titanium were curve fitted. Parameters such as the Gaussian-Lorentzian ratio and the full width at half height (FWHH) of a component were obtained from the spectra of reference compounds taken under identical acquisition conditions. The quantitative analyses are summarized in Table 2; we have a fairly good agreement with the energy dispersive spectroscopy data, compatible with the experimental uncertainties of the two techniques.

Table 6 reports the same data for the observed CN stretching bands in FeHCC, without any assignment to a definite chemical structure, the bands are indicated only as $\tilde{\nu}$ 1, $\tilde{\nu}$ 2 and $\tilde{\nu}$ 3 because no reference data have been found in literature. Anyway, the whole IR band is in agreement with Berrettoni et al.$^{27}$ The difference in the relative intensity of the bands, especially relevant in the case of FeHCC, can be due to different particle size (i.e. the bulk surface features) and it will not be discussed here.

The intensity of the band at 2167 cm$^{-1}$, the dominant one in bulk FeHCC, decreases by dilution with TiO$_2$ while the intensity of the band at 2169 cm$^{-1}$, absent in bulk FeHCC, increases; the latter band is tentatively assigned to the FeHCC-TiO$_2$ bond. The intensity of the band at 2167 cm$^{-1}$ is not influenced by the concentration, as shown in Table 6, so it can be referred to the FeHCC in bulk. In the case of FeHCC we observe a net shift between CN in the bulk form and CN in the TiO$_2$-linked form. Furthermore, the shift is inversely proportional to the FeHCC concentration. The spectra of the samples with CoHCF have more features than those with FeHCC, corresponding to a relatively minor complexity of the latter.

### Table 6 CN stretching related to different chemical features of FeHCC

<table>
<thead>
<tr>
<th>Stretches</th>
<th>$\tilde{\nu}$ 1 / %</th>
<th>$\tilde{\nu}$ 2 / %</th>
<th>$\tilde{\nu}$ 3 / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>2167/21</td>
<td>2169/0</td>
<td>2181/79</td>
</tr>
<tr>
<td>1:1</td>
<td>2167/28</td>
<td>2169/38</td>
<td>2181/34</td>
</tr>
<tr>
<td>10:1</td>
<td>2167/74</td>
<td>2181/0</td>
<td></td>
</tr>
<tr>
<td>100:1</td>
<td>2167/44</td>
<td>2181/27</td>
<td></td>
</tr>
</tbody>
</table>

In the bulk compound, two stretching bands are observed at 2181 and 2167 cm$^{-1}$. The intensity of the band at 2181 cm$^{-1}$ is not influenced by the concentration, as shown in Table 6, so it can be referred to the FeHCC in bulk. In the case of FeHCC we observe a net shift between CN in the bulk form and CN in the TiO$_2$-linked form. Furthermore, the shift is inversely proportional to the FeHCC concentration. The spectra of the samples with CoHCF have more features than those with FeHCC, corresponding to a relatively minor complexity of the latter.

### Table 5 CN stretching frequencies in CoHCF and TiO$_2$-CoHCF from curve-fitting.

<table>
<thead>
<tr>
<th>Stretches</th>
<th>Fe$^{II}$-CN-Co$^{III}$</th>
<th>Fe$^{III}$-CN-Co$^{III}$</th>
<th>Fe$^{II}$-CN-Ti$^{IV}$</th>
<th>Fe$^{III}$-CN-Ti$^{IV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>2081/11</td>
<td>2102/36</td>
<td>2119/33</td>
<td>2133/0</td>
</tr>
<tr>
<td>1:1</td>
<td>2081/20</td>
<td>2102/16</td>
<td>2119/28</td>
<td>2133/35</td>
</tr>
<tr>
<td>10:1</td>
<td>2081/15</td>
<td>2102/17</td>
<td>2119/37</td>
<td>2133/31</td>
</tr>
<tr>
<td>100:1</td>
<td>2081/20</td>
<td>2102/8</td>
<td>2119/66</td>
<td>2133/0</td>
</tr>
</tbody>
</table>

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Please do not adjust margins

Fig. 7 TiO$_2$-CoHCF FT/IR spectra at different molar ratios in the region of CN stretching frequencies.

Fig. 8 TiO$_2$-FeHCC FT/IR spectra in different molar ratios in the in the region of CN stretching frequencies.

Table 6 CN stretching related to different chemical features of FeHCC. $\tilde{\nu}$ 1, $\tilde{\nu}$ 2 and $\tilde{\nu}$ 3 indicate the observed bands. Peak areas in percentage are also provided.

Table 5 CN stretching frequencies in CoHCF and TiO$_2$-CoHCF from curve-fitting.
literature\textsuperscript{38,39} (see Fig. S6 in the supporting information); this agrees with the IR spectra of CoHCF in the bulk form (Fig. 7 and Table 5). The absence of Fe$^{3+}$ in TiO$_2$-CoHCF samples with 1:1 (Fig. 9a) and 10:1 ratios (Supporting information Fig. S8) confirms the IR results. The presence of a component at 710 eV in the 100:1 sample (see Fig. S6 in the supporting information), associated with the presence of Fe$^{3+}$, is also in agreement with the IR findings.

The line shape of Fe2p$_{3/2}$ in the FeHCC compounds is very different from that in CoHCF (Figure 9a and Fig. S7 in the supporting information): the peaks are asymmetric, the full-width at half height (FWHH) is greater, and peak positions are shifted to higher binding energies. Curve fitting procedures performed according to literature\textsuperscript{40,41} lead to the conclusion that both Fe$^{3+}$ at 709.0 eV and Fe$^{3+}$ at 710.5 eV are present at the surface of FeHCC grains.

\textbf{Cobalt}

In Fig. 9b curve fitted Co2p$_{3/2}$ signals of 1:1 TiO$_2$-CoHCF and TiO$_2$-FeHCC samples are reported as examples. In the CoHCF compounds, the Co2p$_{3/2}$ feature has a main component at 782.0 ± 0.2 eV together with shake-up satellites peaks at higher binding energies. These satellites suggest the existence of Co(II)$^{42,43,44}$. No significant chemical shift is observed for Co$^{II}$ and Co$^{III}$-CN complexes\textsuperscript{45} but the co-presence of Co$^{III}$, which was revealed by IR spectroscopy, is supported by the difference in binding energy, $\Delta E = \text{Co2p}_{3/2} - \text{Co2p}_{1/2}$, which is about 15.6 eV, intermediate between the value reported for Co$^{II}$ (16 eV) and the one for Co$^{III}$ (15 eV). The absence of satellites in the Co2p$_{3/2}$ feature of the FeHCC compounds (Fig. 9b) and a binding energy separation Co2p$_{1/2}$ – Co2p$_{3/2}$ of 15 eV strongly implies that cobalt is present as Co$^{III}$ in these compounds.

\textbf{Nitrogen}

N1s signal for CoHCF and FeHCC samples without TiO$_2$ shows a single component at 398.3 ± 0.2 eV; in the presence of TiO$_2$, a second small component appears at higher binding energy (399.5 ± 0.2 eV) (Fig. 10a,b). The most intense signal could be ascribed to nitrogen of the cyano-groups coordinating a transition metal\textsuperscript{46}. The weaker signal might be assigned to the M–CN–Ti surface complexes, as described by Macyka et al\textsuperscript{47}. The intensity of the second component increases from TiO$_2$–MHCM 1:1 to TiO$_2$–MHCM 100:1 (Fig. 10c) and the increase of the intensity is more pronounced in the case of TiO$_2$-CoHCF than for TiO$_2$-FeHCC samples. The detailed N1s spectra of all the samples studied in this paper are provided in Fig. S8 and S9 of the supporting information.

\textbf{Titanium}

Ti2p peaks (Fig. S10 in the supporting information) were curve fitted, after Shirley-Sherwood background subtraction, with a doublet (Ti2p1/2 – Ti2p3/2) separated by 5.7 eV due to spin-orbit coupling. Each peak is symmetric; the binding energy of Ti2p3/2 peak is found at 458.8 eV in the 1:1 samples, as for TiO$_2$, and shifts to 459.2 eV in the 100:1 samples. The effective invariance of the above parameters could be due to the fact that the Ti2p signal is mainly due to the unbounded TiO$_2$ particles.

\textbf{XP-Valence Band}

XP-valence bands of TiO$_2$ and TiO$_2$–MHCM compounds have been recorded and results are shown hereafter (Fig. 11 and 12). Pure TiO$_2$ valence band edge shows the presence of two peaks, separated by ~2 eV that could be ascribed to $\pi$ (nonbonding) and $\sigma$ (bonding) O2p orbitals\textsuperscript{48}. Pure TiO$_2$ valence band edge shows the presence of two peaks, separated by ~2 eV that could be ascribed to $\pi$ (nonbonding) and $\sigma$ (bonding) O2p orbitals\textsuperscript{48}.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
TiO$_2$:MHCM & FeHCC & CoHCF \\
\hline
1:1 & 458.9 & 458.8 \\
10:1 & 458.8 & 458.8 \\
100:1 & 459.2 & 459.1 \\
\hline
\end{tabular}
\caption{Ti2p binding energy value for hexacyanometallate-TiO$_2$ composites.}
\end{table}

\textbf{CoHCF compounds}

Fig. 11 shows the valence bands of cobalt hexacyanoferrate without TiO$_2$ and in the mixtures 1:1 and 1:10 with TiO$_2$. The valence band of commercial TiO$_2$ (Sigma Aldrich) is provided for comparison. The band is due to the overlapping of the contributions due to Co-N $\sigma$ and $\pi$ bonding electrons, with Fe-C $\sigma$ and $\pi$ bonding and Co non – bonding electrons\textsuperscript{49}. Relative to pure TiO$_2$, the edge shifts to lower binding energies in bulk CoHCF and its mixtures with TiO$_2$ (Table 8).
Table 8 Comparison of the valence band edge binding energy of CoHCF and TiO₂-CoHCF compounds at different ratios.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Valence Band Edge binding energy (eV ± 0.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoHCF</td>
<td>2.0</td>
</tr>
<tr>
<td>TiO₂:CoHCF 1:1</td>
<td>1.2</td>
</tr>
<tr>
<td>TiO₂:CoHCF 10:1</td>
<td>1.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Fig. 11 XPS valence bands of CoHCF compounds and of commercial titania (0-15 eV region).

FeHCC compounds

Fig. 12 shows the valence bands of the iron hexacyanocobaltate compounds.

Table 9 Comparison of the valence band edge binding energy of FeHCC and TiO₂-FeHCC compounds at different ratios.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Valence Band Edge binding energy (eV ± 0.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeHCC</td>
<td>1.3</td>
</tr>
<tr>
<td>TiO₂:FeHCC 1:1</td>
<td>1.3</td>
</tr>
<tr>
<td>TiO₂:FeHCC 10:1</td>
<td>1.9</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.2</td>
</tr>
</tbody>
</table>

X-ray absorbance spectroscopy (XAS)

Relevant information on about the binding between TiO₂ and the hexacyanometallates can be gained by using an elemental analytical technique such as the X-ray Absorption Spectroscopy. In this case, all the three metal sites (Ti, Fe, Co) can be monitored and the results are shown in Fig. 13.
The normalized XANES spectra are given in the left column of Fig. 13, (a, c, e) whereas the right column provides the Fourier Transforms (FTs) of the Extended X-Ray Absorption Fine Structure (EXAFS) spectra. Of the composite samples, we report only the spectra of TiO$_2$–MHCM 1:1, taken as the most representative. The normalized curves at the Ti K-edge (panel (a)) give evidence that the presence of FeHCC or CoHCF modifies the local environment of titanium, in comparison with that of pure anatase phase. This is evident from the pre-edge structures (A peak), the main absorption edge (B) and the resonance (C) but the modification at the Ti site with either FeHCC or CoHCF dopant is essentially the same. The comparison of the Fourier Transform curves of the EXAFS signals relates to the K-edge of Ti confirms minor but significant modifications of the local structure of Ti. This is showed in the panel (b) where the FTs, which are related to the radial atomic distribution around the selected (photo-absorber) atom, display peaks intensity increasing following FeHCC or CoHCF doping. This might be due to a decreasing of the structural order in the three shells as indicated in Fig. 13b.

By tuning the x-ray beam to a precise metal edge, considerable information is available at the Fe and Co K-edges for both TiO$_2$–FeHCC 1:1 and TiO$_2$–CoHCF 1:1 samples. Panels (c), (d), (e), (f) display a selection of the XAS analysis concerning the CoHCF composites; comparison with bulk CoHCF is also provided. All panels indicate modification relative to the bulk sample of the XAS spectra, thus confirming the occurrence of a substantial interaction between TiO$_2$ and CoHCF.

A close inspection of the figures reveals the following details of the TiO$_2$–CoHCF binding. (1) the Fe local site is basically the same upon TiO$_2$ addition as seen from the XANES in the panel c but a shift towards lower energy of the curve is evidenced, indicating a partial reduction to Fe(II). (2) unlike the Fe, the Co local environment changes upon TiO$_2$ addition, as the overall shape of the XANES curve of panel (e) is strongly modified; furthermore, no changes in the pre-edge peak position has been detected and therefore the Co is in the Co(II) site.

The trend observed in the XANES data is confirmed by the corresponding FTs curves. The Fe display (panel (d)) similar peak positions and intensities, with the exception of the 3rd peak at ~5 Å, assigned to the Fe–Co distance, which decreases upon doping with TiO$_2$. On the contrary, all three peaks displayed in the panel (f) shift to lower distances, providing evidence for shorter bond lengths of the first, second and third shells around cobalt.

Similar comments apply to the comparison of the Fe and Co K-edges in FeHCC and TiO$_2$–FeHCC. The analysis, available in the supporting information, leads to the same conclusions if we swap the Co with Fe site. In this case the Fe site changes significantly upon TiO$_2$ doping while the Co one does not, as clearly visible from the XANES curve of Fig. S11, panels (c), (d).

This experimental finding is interesting and can be explained by considering the local probe characteristic of a XAS experiment. Regardless the long range structure, the XAS indicates that significant changes occur only at the metal site (either Co or Fe), which is linked to the N side of the CN moieties of the cyanide bridge.

### Discussion

#### Experimental evidence of the formation of composites

First of all, our findings prove how feasible and reliable is the synthesis of composite materials based on TiO$_2$ particles modified by CoHCF or FeHCC. In fact, electrochemical results and TEM micrographs give evidence of the formation of MHCM clusters on the TiO$_2$ surface. The optimum TiO$_2$–MHCM ratio is found between 1:1 and 10:1 since in these molar ratios the spherical grains of TiO$_2$ are covered by cubic nano-crystals of MHCM. Furthermore, the composite materials show a red shift of the threshold absorption edge in the UV region, due to a decrease of the titanium dioxide band gap.

The waves of cyclic voltammetry and their dependence upon the K$^+$ concentration demonstrate the successful synthesis of both CoHCF and FeHCC. In bulk CoHCF, two redox processes due to the Fe$^{2+}$/Fe$^{3+}$ and Co$^{3+}$/Co$^{2+}$ couples, respectively, can be observed; the second one becomes electroactive only when the compound is crystallized in the so-called “insoluble form” or in nano-sized form. In our bulk CoHCF, the peak potential and the E° values allow to assign the redox wave to Fe$^{2+}$/Fe$^{3+}$ couple. In the FeHCC compounds, the observed redox wave is still due the iron center, as confirmed by the E° values, while the cobalt center is non electroactive. Hence the observed redox waves in TiO$_2$–FeHCC and TiO$_2$–CoHCF are always due just to the Fe$^{2+}$/Fe$^{3+}$ couple.

From the CVs of TiO$_2$–FeHCC (Fig. 2 and Table 3) we obtain that, with increasing the TiO$_2$/FeHCC ratio, the kinetics of cation insertion becomes slower, since the cathodic peak shifts toward more negative potentials, while the kinetics of its release is faster, since the anodic peak shifts toward more negative potentials. Also the E° values show a negative shift in going from 1:1 to 10:1 composites, and no further changes in the 100:1 composite. The redox process is characterized by a relative high peak separation, in accordance with the published literature, while the peak shapes reflect the difference in the TiO$_2$–FeHCC synthesis. Actually, the modified electrode was realized by chemical synthesis (see experimental paragraph for details) while in the published literature, the TiO$_2$–FeHCC composite electrodes were electrochemically synthesized in situ on a TiO$_2$ thin film. In the case of TiO$_2$–CoHCF (Fig. 3 and Table 4), both cation insertion and release become more difficult at least for 1:1 and 10:1 compounds, while in 100:1 ratio the CV shape prevents the resolution of the voltammetric wave. In this case, as expected, the E° values remain constant.

#### Reaction Mechanism
The formation of MHCM cluster on the TiO$_2$ surface causes a clear modification of the IR spectra. The change in the intensity, that might be assigned to the different amounts of MHCM added and hence to the different degree of interaction with the TiO$_2$, is accompanied by a band shift towards lower wavenumbers and a shape morphology change (Fig. 7 and 8). IR results are in agreement with the XPS that allows to distinguish between Fe–CN (CoHCF) and Fe–NC (FeHCC) and confirm the absence of Fe$^{III}$ in TiO$_2$-CoHCF samples with 1:1 (Fig. 9a) and 10:1 ratios (Supporting information Fig. S6) and the presence of Fe$^{III}$ in the 100:1 sample (Supporting information Fig. S6). XPS and IR identification of cobalt species are also in agreement for both FeHCC and CoHCF samples. Furthermore XPS analyses provide the evidence of the interaction between nitrogen and titanium: cyanide groups may act as ligands for titanium ions at the surfaces, forming M–CN–Ti bonds, as also shown by the band shift towards lower wavenumbers and shape morphology change in IR spectra. The involved reaction might be thought as a nucleophilic substitution reaction with titanium ions playing the role of central ions and hexacyanoferate anions acting as ligands.

The combined XANES and EXAFS analysis at the Ti K-edge of Fig. 13a and 13b show that the presence of MHCM modifies the local environment of the titanium, relative to that in pure anatase. This suggests the same type of binding between the anatase and either FeHCC or CoHCF cubes. The analysis at the metal (Fe and Co) K-edges shows modification in the XAS spectra respect to the pure CoHCF sample (and the same holds true for the FeHCC case of Fig. S11), thus confirming the occurrence of a close interaction between TiO$_2$ and CoHCF (or FeHCC). Overall, these findings are explained by considering a close interaction between the anatase and the FeHCC or CoHCF cubes, most likely through the N side of the CN moieties, as previously evidenced by the IR and XPS analyses.

On the basis of these findings two mechanisms for the metal hexacyanoferrate (FeHCC or CoHCF) interaction to the anatase particles can be proposed. According to the first mechanism, the HCC or HCF salt reacts with either Fe(III) or Co(III) respectively to give the mixed hexacyanometallate (I step, Fig. 14a) and subsequently the insoluble species, consisting in a dendrimer-like structure, reacts with the N terminals (II step, Fig. 14a). It is worth noting that the role of the vacancies is important because they suppress the perfectly cubic structure and increase the surface adhesion. The presence of iron vacancies, and their concentration, in metal hexacyanoferrates certainly affects a range of properties$^{20}$. However, one may imagine another mechanism: the HCC or HCF salt reacts with anatase particles (I step, Fig. 14b) and, subsequently, the metal hexacyanometallate FeHCC or CoHCF synthesis occurs (II step, Fig. 14b). Presently, it is not possible to determine which of these two mechanisms is the predominant one.

**Modification of the TiO$_2$ optical properties**

Since XPS provides the information on the total density of states of the valence band, changes in the valence band may reflect a modification of the optical properties of the composites compared to pure TiO$_2$. By comparing valence band spectra in pure TiO$_2$ and in the composites, we note changes of line-shape (Fig. 11,12) and a shift of the edge towards lower binding energies (Tables 6,7). According to previous DOS studies of doped TiO$_2$,$^{53}$ the shift to lower energies determines the decrease in the band gap energy thus causing different optical properties for the composites compared to pure TiO$_2$.

In order to evaluate the effect of CoHCF or FeHCC doping upon TiO$_2$ absorption threshold, UV-Vis spectra were recorded in the 220–700 nm range in suspensions of TiO$_2$-CoHCF and TiO$_2$-FeHCC (Fig. 15,16). The progressive shift towards higher wavelengths of the TiO$_2$ absorption threshold is notable by adding K$_3$[Fe(CN)$_6$]$_3$ and CoCl$_2$ or K$_3$[Co(CN)$_6$]$_3$ and FeCl$_2$ with the formation of CoHCF or FeHCC, respectively, linked to the TiO$_2$. In both cases it is worth observing a shift of the threshold at lower energy that can be explained also on the basis of theoretical calculations$^{54}$. In addition, new absorption bands in the UV and Vis region related to MHCMs play a fundamental role in the promotion of *titania* electrons to the conduction band with the same mechanism of TiO$_2$ dye solar cells. These findings are much relevant in all the applications of TiO$_2$ depending upon its light absorption capability.
Evaluation of photocatalytic activity

TiO$_2$-CoHCF in 10:1 ratio compound has been directly used to evaluate its photocatalytic activity in photoelectrochemical degradation of methylene blue (MB) in aqueous solutions under UV irradiation. For comparison, native anatase TiO$_2$ was also tested.

MB has been chosen as a model to test the photocatalytic activity of surfaces in an aqueous medium according with the International Standard ISO 10678.

The tests were performed by following the methodology reported in the previous cited ISO standard. The degradation reaction kinetics are studied by monitoring the variation of the normalized dye absorption spectra in function of the irradiation time with UV light in the wavelengths range between 220 and 750 nm, as shown in Fig. 17. In the case of TiO$_2$-CoHCF in 10:1 ratio, the decrease of the absorbance vs. time is faster than native TiO$_2$; the value of dA/dt for TiO$_2$-CoHCF is about 20% higher than the native TiO$_2$. The results revealed that the CoHCF doped TiO$_2$ showed higher photocatalytic activity than that of native TiO$_2$.

Conclusions

New composite materials based on TiO$_2$-MCHM have been synthesized and characterized with a correlated use of many experimental techniques in order to assess the formation of MHCM compounds, to investigate its bonding to TiO$_2$ and, finally, to characterize the associated modifications of the optical properties of titania. In particular, the cyclic voltammetry and the morphological inspection by TEM, confirm the formation of CoHCF and FeHCC cubic crystals linked to TiO$_2$ particles in the composites. IR, XPS, and XAS suggest the formation of a well-defined bond between the nitrogen of the cyano-group and the titanium of the titania substrate. These findings suggest two possible mechanisms (Fig. 14) for the formation of MHCMs on titania surfaces. In the b mechanism in Fig. 14, the vacancy in the structures play a key role in the promotion of the N-Ti bond. This model is supported, in particular, by the evolution of the Co/Fe stoichiometric ratio going from the 1:1 to 100:1 in the TiO$_2$/CoHCF composites. Indeed, in the 1:1 compound, the Co/Fe ratio is 1, characteristic of the so called “soluble” form; with increasing the TiO$_2$ fraction, the Co/Fe region approaches the limit value of the so called “insoluble” form, rich in vacancies of the Fe(CN)$_6^{3-}$ group. A similar trend occurs in the case of FeHCC. These observations make the b path more likely.

UV-Vis spectra and the valence band measurement in the composites confirm a desirable reduction of the TiO$_2$ band gap. The versatility of the synthesis permits to obtain both bulk and thin films composite materials. Practical use of these materials can be envisaged in different areas, such as antibacterial treatments, protection of historical artifacts, self-cleaning surfaces, photovoltaic cells.

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finanziamento di Assegni di Ricerca”.
Electronic Supplementary Information (ESI) available free of
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