Electron transfer in cobalt hexacyanoferrate nanoparticles promoted by reverse microemulsions prepared with Cetyltrimethylammonium surfactants

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GRAPHICAL ABSTRACT
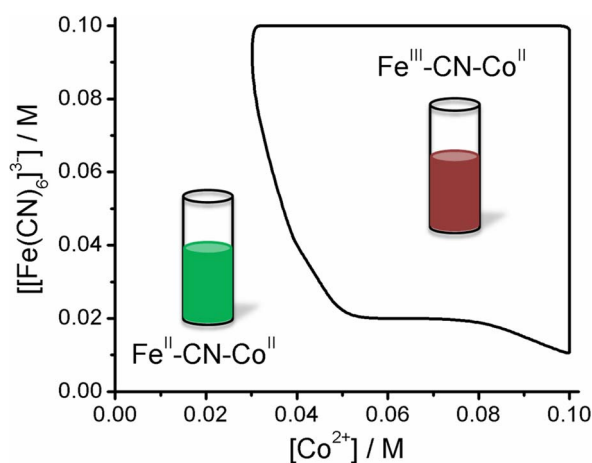
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ABSTRACT

Reverse microemulsions (RME) formed with the systems CTAX + pentanol/hexane/water (where X = Br$^-$, Cl$^-$ or p-toluensulfonate) were used as synthesis media of cobalt hexacyanofarrate nanoparticles (CoHCF-NP). In this work, the effect that these RME have on the final structure of the CoHCF-NP is presented. Starting with a reaction between the reactant ions (RI) Co^{2+} and [Fe(CN)$_6$]$^{3-}$, CoHCF-NP with the expected structure based on the chain Fe^{III}-CN-Co^{II} can be obtained. By changing variables that defines the RME, it is possible to promote an electron transfer inside the CoHCF-NP to change the structure from Fe^{III}-CN-Co^{II} to Fe^{II}-CN-Co^{II}. Variables as water concentration, distribution of the RI in the RME droplets, the surfactant counterion, and the concentration ratio of the RI showed a remarkable effect on the CoHCF-NP. CoHCF-NP in which the chain Fe^{III}-CN-Co^{II} predominates in the structure can be synthesized using RME formed with: i) CTAB at high RI and water concentration; ii)

CTAT, when the concentration of RI is higher than 0.02 M. On the other hand, CoHCF-NP with predominance of Fe^{II}-CN-Co^{II} can be synthesized using RME formed with: i) CTAB at low RI and water concentration; ii) CTAC, regardless the RI and water concentrations. This information is summarized in a concentration diagram where it is possible to predict the structure of the CoHCF-NP. To the best of our knowledge, this type of diagrams has not been constructed before for any of the Prussian blue analogues synthesized in RME.

1. Introduction

Cobalt hexacianoferrate (CoHCF), with the general composition $M_xCo_b^i$ $[Fe^j(CN)_6]_y \cdot zH_2O$ (where x, b, y and z are stoichiometric coefficient; i and j are the oxidation state of cobalt and iron ions respectively; H_2O and M are water molecules and the alkali ions necessary to the electroneutrality) is a Prussian blue analogue compound that has reached high attention due to its peculiar physicochemical properties as electrochromism, thermochromism, photochemical magnetism, electrocatalisist and sensing [1,2]. These properties are based on the electron transfer between the Fe^{3+} and Co^{2+} ions in the crystalline structure, according to Fe^{III}-CN-Co^{II} (HS) $\leftrightarrow$ Fe^{II}-CN-Co^{III}(LS), where HS and LS stand for high spin and low spin respectively [3], induced by an external perturbation (for instance, temperature changes for thermochromism, or electric potential changes for electrochromism). The electron transfer process also occurs spontaneously, but in a lesser extent, when different concentration ratios of the reactive ions (RI) Co^{2+} and $[Fe(CN)_6]^{3-}$ are used. It has been observed that the final structure of the CoHCF is a mixture of three different chain sequences, Fe^{III}-CN-Co^{II}, Fe^{II}-CN-Co^{III} and Fe^{II}-CN-Co^{II}, regardless that the initial oxidation states of the RI are Fe^{3+} and Co^{2+} [3,4]. Taking into account that the properties above mentioned depend strongly on the oxidation state of the metallic ions in the CoHCF, it is important to control the synthesis method in order to control the final structure. When CoHCF is synthesized in the nanometric scale, the spontaneous electron transfer has been also observed [5–7]. When reverse microemulsions (RME) formed by the surfactant cetyltrimethylammonium bromide (CTAB) are used as synthesis media to obtain CoHCF nanoparticles (CoHCF-NP), the electron transfer causes that the initial red-brown color, typical for CoHCF with the predominant chain Fe^{III}-CN-Co^{II} in the crystal structure, changes to emerald green, typical for CoHCF with predominance of Fe^{II}-CN-Co^{II} [7]. This change takes 6 h to be completed, after that, no further changes were observed. The authors concluded that this time-dependent electron transfer is caused by the substitution of the coordinate water molecules around the Co^{2+} ions by the surfactant counterion Br-, resulting in the dehydration of the CoHCF-NP. RME are dispersions of water droplets, in a no-polar solvent stabilized by surfactant molecules, and have been used successfully as a reaction medium to synthesize nanoparticles of controlled size and shape [8]. The substitution of water molecules by Br^- ions is possible in this type of systems because of the high concentration of Br^- and CoHCF-NP inside the RME droplets; therefore, the electron transfer can be controlled by controlling the amount of Br^- from CTAB and CoHCF-NP in the droplets. In this work, we studied this interaction by preparing CoHCF-NP at different RME conditions such as water concentration, distribution of the RI in the RME droplets, the surfactant counterion, and the concentration ratio of the RI. The results were summarized in a concentration diagram where it is possible to predict which chain predominates in the structure of the synthesized CoHCF-NP. To the best of our knowledge, this type of diagrams has not been constructed before for any of the Prussian blue analogues synthesized in RME.

2. Experimentation

All the reactants used in this report were of analytical grade. CTAB, CTAC and CTAT were purchased from Sigma–Aldrich Inc. Potassium ferricyanide ($K_3[Fe(CN)_6]$) from J.T. Baker; hexane (C_6H_{14}) from Caledon Laboratories Ltd. Cobalt nitrate ($Co(NO_3)_2$) and pentanol ($C_5H_{11}OH$) from Golden Bell.

2.1. Characterization of the RME

Three different systems were studied, CTAX + pentanol/ hexane/ water (where X = Br^-, Cl^- or *p*-toluensulfonate, and water refers to the amount of RI solutions). The molar ratio of the components CTAX: pentanol: hexane was established as 1:4.1:12.7 respectively. Three different water ratios (W = $[H_2O]/[CTAX]$) were established, W = 4, 10 and 16. The dilution method was performed to characterize the RME. The procedure can be found elsewhere [9,10]. Briefly, in a known volume of RME placed in a thermostated water bath at 25 °C, a known volume of hexane is added to destabilize the RME, resulting in a cloudy solution. Small volume of pentanol is then added to form a clear RME again. The procedure was repeated several times noting the volumes of hexane and pentanol necessary at each step for obtaining a clear and stable RME. With this information it is possible to calculate the amount of pentanol at the droplet interface and the droplet size.

2.2. Synthesis of CoHCF-NP

To synthesize the CoHCF-NP, two RME at the same molar ratio are mixed, one containing a solution of $Co(NO_3)_2$ (RME1) and the other containing a solution of $K_3[Fe(CN)_6]$ (RME2), both at the same W. The final RME is placed at rest for 20 s (RME3), to allow the droplets to collide, forming the CoHCF-NP.

2.3. Characterization of CoHCF-NP

RME3 was divided in two samples. One sample was used in the UV–vis spectroscopy measurements, performed on a HACH DR3900 spectrometer. The second sample was centrifuged at 3500 rpm for 5 min. The supernatant was decanted to obtain a solid precipitate. This precipitate was used in the measurements of infrared spectroscopy (FTIR) and transmittance electron microscopy (TEM). In order to obtain more reliable FTIR measurements, the addition of solvents to remove the surfactant from the CoHCF-NP was avoided. The precipitate was measured directly on an ATR device adapted to a Bruker Alpha FTIR instrument. Taking into account the time spent in the preparation of the samples, all the FTIR and UV–vis measurements were then carried out 6 min after the mixture of RME1 and RME2. For TEM (JEOL, JEM1010), the precipitate was re-dispersed in hexane and placed in an ultrasonic bath for 10 min in order to reduce the agglomerates caused by the centrifugation. A drop of the dispersion was placed directly on a carbon-coated copper grid.

3. Results and discussion

3.1. Synthesis of CoHCF-NP

The mixture of RM1 and RM2 allows forming CoHCF-NP. Fig. 1 shows a representative micrograph of CoHCF-NP synthesized in the system CTAB + pentanol/ hexane/ water at W = 10 and a concentration of RI (Co^{2+}:$[Fe(CN)_6]^{3-}$) = 0.05 M:0.05 M. Spherical nanoparticles with an average diameter of ca. 5.7 nm (± 2.1 nm) are observed. As it is expected due to the sample preparation process, particle agglomeration is evident. This behavior has been also observed in similar systems where nanoparticles of different hexacyanoferrate