Colloids and Surfaces A: Physicochem. Eng. Aspects 444 (2014) 63–68

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Direct synthesis of different metal hexacyanoferrate nanoparticles in reverse microemulsions by using a ferrocyanide functionalized surfactant

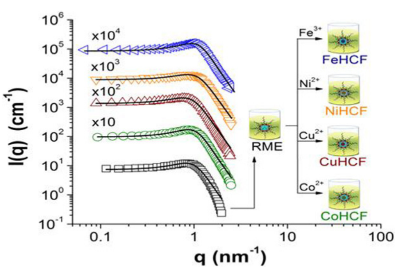
Alberto Gutiérrez-Becerra [a], Fernando Martínez-Martínez [a], Maximiliano Bárcena-Soto [a], Norberto Casillas [a], Israel Ceja [b], Sylvain Prévost [c], Michael Gradzielski [c], José I. Escalante [a,*]

[a] Chemistry Department, University of Guadalajara, Blvd. M. García Barragán 1451, Guadalajara 44430, Mexico
[b] Physics Department, University of Guadalajara, Blvd. M. García Barragán 1451, Guadalajara 44430, Mexico
[c] Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Straße des 17 Juni 124, Sekr. TC7, D-10623 Berlin, Germany

HIGHLIGHTS

- Different metal hexacyanoferrates were synthesized in reverse microemulsions.
- The synthesis process does not affect the structure of the reverse microemulsion.
- Nanoparticles are spherical whose size and shape coincides with the microemulsion droplet size.
- The lattice parameter values are similar as reported for the bulk.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 September 2013
Received in revised form
18 December 2013
Accepted 20 December 2013
Available online 31 December 2013

Keywords:
Reverse microemulsions
Nanoparticles
Metal hexacyanoferrates

ABSTRACT

Reverse microemulsions (RME) formed by the functionalized surfactant cetyltrimetyl ammonium ferrocyanide (CTAFeII) were used as reaction media to synthesize different metal hexacyanoferrates (MHCF). By just adding diluted solutions of $CoCl_2$, $NiCl_2$, $CuCl_2$ or $FeCl_3$ to the RME, spherical nanoparticles of CoHCF, NiHCF, CuHCF and FeHCF were obtained respectively. Bare RME and RME containing nanoparticles were measured by small angle X-ray scattering. The results obtained by the fits performed with the Teubner and Strey model show no significant difference in the periodicity (d_{TS}) and in the correlation length (ξ_{TS}), which suggests that the synthesis process does not affect the RME structure. Micrographs obtained by transmission electron microscopy confirm that the nanoparticles are consistently spherical with an average size of 4 nm for CoHCF and CuHCF, and 6 nm for NiHCF and FeHCF. The average value of the lattice parameter obtained by X-ray diffraction is completely agrees with the values reported in the literature for this type of coordination compounds. The surfactant CTAFeII opens the possibility to obtain nanoparticles of other coordination compounds by using a cationic surfactant in their functionalized form.

1. Introduction

Metal hexacyanoferrates (MHCF) with general formula $A_hM_k[Fe(CN)_6]_n{\cdot}mH_2O$ (where h, k, n, m represent stoichiometric numbers, A is the alkali metal cation and M is the transition metal ion) denote an important class of mixed-valence compounds, where Prussian blue is the classical prototype [1]. These compounds

* Corresponding author. Tel.: +52 3313785900.
E-mail addresses: escalant@hotmail.com, jose.i.escalante@gmail.com (J.I. Escalante).

0927-7757/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2013.12.038

are very attractive because of the peculiar physicochemical properties including electrochromism [2,3], photoelectrochromism [4], energy storage [5,6], electrolytic and sensing properties [1,7] by turning their constituents on transition metal ions M^{n+} in the structure. In recent years, MHCF nanoparticles have been used generally as biosensors due to their selective detections of H_2O_2, which is a side product of reactions catalyzed by many highly selective oxidases [8,9].

Early investigations about the synthesis of MHCF nanoparticles were made by Das et al. [10] and Mann et al. [11], in both cases were used reverse microemulsions (RME) systems formed by surfactant sodium bis-(2-ethylhexyl) sulfosuccinate (NaAOT) and its functionalized forms $Cu(AOT)_2$ and $Co(AOT)_2$ respectively. RME are homogeneous, transparent, thermodynamically stable dispersions of two immiscible liquids (typically water and oil) stabilized by a relatively large amount of surfactant [12]. Synthesis of nanoparticles by using RME is viable and attractive because it does not only produce nanoparticles that have a narrow size distribution, but also the particle size can be controlled by varying one or more of the RME parameters as droplet size, surfactant film flexibility, reactant concentration, *etc.* [13]. In a previous work [14] we proposed a RME system formed by a mixture of two cationic surfactants, the cetyltrimetyl ammonium bromide (CTAB) and its functionalized form cetyltrimetyl ammonium ferrocyanide (CTAFeII), and *n*-butanol as cosurfactant into *n*-hexane/water to synthesize NiHCF nanoparticles. The surfactant CTAFeII is obtained by exchanging the bromide ions (Br^-) of the surfactant CTAB by ferrocyanide ions ($[Fe(CN)_6]^{4-}$) following a metathesis reaction; the NiHCF nanoparticles were synthesized by adding a diluted $NiCl_2$ solution to the RME. The main advantage of this system over those formed by $M(AOT)_2$ surfactant, is the possibility to synthesize different MHCF by simply adding different salts to the RME. In this work, the synthesis of CoHCF, NiHCF, CuHCF and FeHCF nanoparticles in a RME formed by the surfactant CTAFeII is presented. The obtained nanoparticles were characterized *in situ* by small angle X-ray scattering (SAXS) and after separation from the RME, by transmission electron microscopy (TEM). X-ray diffraction (XRD) was used to calculate the lattice parameter of the MHCF. In all cases, the size and shape of the nanoparticles were similar to the size and shape of the RME droplets, which confirms the template effect of these types of systems. The use of the surfactant CTAFeII not only makes more convenient the synthesis of different MHCF nanoparticles, but also opens the possibility of using functionalized cationic surfactants to obtain nanoparticles of other coordination compounds.

2. Materials and methods

All the reactants used in this report were of analytical grade. CTAB was purchased from Sigma–Aldrich Inc. (99%); ferrocyanide salt ($K_4[Fe(CN)_6]\cdot 3H_2O$) from J.T. Baker (99%); *n*-hexane (C_6H_{14}) from Caledon Laboratories Ltd. (98%); *n*-butanol (C_4H_9OH) from Productos Químicos Monterrey (99%); $NiCl_2\cdot 6H_2O$ and $CoCl_2\cdot 6H_2O$ from Caledon Laboratories Ltd. (>99%); $CuCl_2\cdot 2H_2O$ (>99%) and $FeCl_3\cdot 6H_2O$ (97%) from Sigma–Aldrich Inc.

2.1. Preparation of the surfactant CTAFeII

Aqueous solutions of CTAB (0.040 M) and $K_4[Fe(CN)_6]$ (0.034 M) are mixed under stirring forming a yellowish precipitate that is CTAFeII. The resultant solution is kept at rest for 24 h to favor the complete metathesis reaction. The precipitate is separated by filtration, washing it several times with hot distilled water to remove the potassium (K^+) and Br^- ions and other non-reacted species. The surfactant CTAFeII is then dried in a vacuum oven to obtain a yellowish dust. Structural characterization of the surfactant can be found elsewhere [14].

2.2. Synthesis of MHCF nanoparticles in RME

RME were prepared as follows: CTAB, CTAFeII and *n*-butanol are mixed according to the weight ratios: CTAB:CTAFeII = 0.95:0.05 and *n*-butanol/(CTAB + CTAFeII) = 1. Under stirring, *n*-hexane is added to the mixture to reach a weight ratio of (CTAB + CTAFeII + *n*-butanol)/(CTAB + CTAFeII + *n*-butanol + *n*-hexane) = 0.4. Finally, also under stirring, water is added to reach global water weight fraction W_W = water/(CTAB + CTAFeII + *n*-butanol + *n*-hexane + water) = 0.06. The RME are transparent, yellowish colored with low viscosity. The RME are sealed to avoid solvent evaporation and kept at rest at 25 °C for 10 min prior to the synthesis. Solutions 0.010 M of MCl_n (where $n = 2$ when $M = Co^{2+}$, Cu^{2+} and Ni^{2+}; and $n = 3$ when $M = Fe^{3+}$) are then added (dropwise and vigorously stirred) to the RME to reach a value of $W_W = 0.12$. The total concentration of cations M^{n+} in the RME is therefore 0.005 M. When the solutions are added, the RME changes rapidly to the typical color of the respective MHCF, which indicates that the synthesis is carried out. RME containing nanoparticles remain stable by several days.

2.3. SAXS

SAXS measurements were performed on a SAXSess mc2 instrument from Anton Paar. The X-ray beam was emitted by a sealed-tube Cu-K_α microsource ($\lambda = 0.1542$ nm). The samples were measured in a capillary tube introduced into a temperature controlled sample stage. The scattering of the capillary and the *n*-hexane contribution were subtracted from each scattering spectrum. The measurements were carried out 5 min after the addition of the MCl_n solutions.

2.4. TEM and XRD

The method followed to separate the MHCF nanoparticles from the RME can be found elsewhere [14]. TEM images were obtained in a transmission electron microscope JOEL (JEM-1010) operating at 100 kV. A small quantity of the sample was dropped on a copper grid, and the solvent was evaporated at room temperature. XRD patterns were recorded with a STOE Theta/theta X-ray diffractometer using a Cu-K_α radiation ($\lambda = 0.15406$ nm) at room temperature in the 2θ range 10–40°.

3. Results and discussion

3.1. Synthesis of MHCF nanoparticles

The RME formed by the system CTAB + CTAFeII + *n*-butanol/*n*-hexane/water allows to incorporate $[Fe(CN)_6]^{4-}$ ions inside the droplets due to the dissociation of the surfactant CTAFeII according to the reaction:

$$CTA_4[Fe(CN)_6] \leftrightarrow 4CTA^+ + [Fe(CN)_6]^{4-}$$

where CTA^+ are the aliphatic tail and polar head of the surfactant $C_{16}H_{33}N^+(CH_3)_3$. Taking into account that the $N^+(CH_3)_3$ group is completely solvated with 5–6 water molecules [15], at $W_W = 0.12$ (approximately 14 water molecules per headgroup), the amount of water is sufficient to ensure the complete dissociation of $[Fe(CN)_6]^{4-}$ ions from CTAFeII. At these conditions, the calculated $[Fe(CN)_6]^{4-}$ ions concentration in the RME is 0.054 M. The reactant excess x ($x = [M^{n+}]/[[Fe(CN)_6]^{4-}]$) is therefore close to 1/10. In order to compare the distribution of $[Fe(CN)_6]^{4-}$ and M^{n+} ions in the RME,