

Growth of cubic crystals of cobalt-hexacyanoferrate under the octadecyl amine monolayer

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Abstract

Highly oriented cubic crystals of Cobalt (II)-hexacyanoferrate (III) (Co-hcf) are formed at the air–water interface under the compressed Langmuir monolayer of octadecyl amine (ODA) when we react $K_3Fe(CN)_6$ solution with cobalt (II) chloride solution in the sub-phase, while no crystals are formed at the air–water interface without the ODA monolayer. X-ray diffraction and electron diffraction studies indicate that these Co-hcf crystals are oriented with their $\{100\}$ plane parallel to the monolayer. Transmission electron microscopy and atomic force microscopy reveal that cubic crystals with sides of 50–300 nm are initially formed, which grow further with time and coalesce to form a thin film. Cyclic voltammetry on those Co-hcf films, transferred on gold coated glass, indicates the presence of a surface couple corresponding to $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system. Present study gives an insight into the in situ growth behaviour of crystals and has implications in the design and development of advanced materials for devices.

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1. Introduction

Prussian blue (PB), $Fe_4^{III}[Fe^{II}(CN)_6]_3 \cdot nH_2O$ ($n = 14–16$) is one of the oldest co-ordination compounds, interest in which has been rekindled due to interesting magnetic and photomagnetic

properties exhibited by it and its analogues [1–5]. Although several investigators have focussed on the relationship between magnetic properties and the structural aspects of these materials, studies on the growth process of the crystals of these magnetic materials are rather few. This is because crystals of Prussian blue analogues (PBAs) are difficult to grow by conventional means due to the inherent structural disorder arising from a certain degree of exchange within different cationic sites [6]. An understanding of the growth behaviour is

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crucial for the design of new molecule-based hexacyanate magnets and photomagnetic devices based on them [7]. There have been reports on crystal growth of inorganic compounds [8–16] as promoted by an organic template, such as, a Langmuir monolayer at the air–water interface, which has a simple two-dimensional organised structure. The functional groups of amphiphilic molecules constituting the Langmuir monolayer essentially serve as nucleation sites or/and growth sites for crystallisation, and determine the morphology and orientation of the crystal under growth. Recently, we have demonstrated the use of a Langmuir monolayer as a templating agent for growth of crystalline films of nickel-hexacyanoferrate [17], a PBA. Synthesis of Prussian blue nano-particles in microemulsion medium [18] and deposition of ferromagnetic Langmuir–Blodgett films of Prussian blue [19] and its analogues [20,21] have also been reported by Mingotaud and co-workers.

Cobalt-hexacyanoferrate is a member of the Prussian blue family and is of particular interest because of its interesting electrochromic properties which depend on the oxidation states of the Co/Fe ions as well as the nature of alkali metal ion incorporated in it during electrodeposition [22,23]. It also exhibits reversible photoinduced magnetisation [24,25] and substantial catalytic activity [26,27] when used as an electrode. However, like other PBAs it is difficult to grow crystals of Co-hcf due to structural disorder. In the present study, we describe growth behaviour of the oriented cubic crystals of Co-hcf at the air–water interface using octadecyl amine (ODA) monolayer as a template. These crystallites grow with time and coalesce into a continuous film. This is an important development because well-organised film of Co-hcf are a pre-requisite to facilitate its application in future photomagnetic devices.

2. Experimental section

2.1. Materials

ODA was purchased from Fluka, and cobalt chloride (CoCl_2) and potassium ferricyanide

$[\text{K}_3\text{Fe}(\text{CN})_6]$ from S.D. Fine Chemicals. All these chemicals were used as received. Chloroform (CHCl_3), which was used as a spreading solvent in this study, was HPLC grade. Water used throughout this study was from a Millipore Milli-Q filter system and had a resistivity of $18 \text{ M}\Omega \text{ cm}$.

2.2. Instrumentation

Crystals of Co-hcf were grown at the air–water interface using KSV 5000 Langmuir–Blodgett (LB) trough. X-ray diffraction (XRD) was recorded with Phillips PW1710 diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation at room temperature. Transmission electron microscopy (TEM) was carried out with a JEOL-2000FX microscope operating at 160 kV. AFM images of the deposited film were taken using a Scanning Probe Microscope (NT-MDT model-SPM Solver P47) in contact mode using Silicon Nitride tips. Cyclic voltammetric measurements were performed with an EcoChemie (The Netherlands) Autolab PGStat20 potentiostat/galvanostat, controlled by GPES software, using Ag/AgCl as reference electrode.

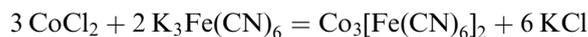
2.3. Crystallisation experiments

Crystallisation of the Co-hcf was carried out at room temperature under the Langmuir monolayer at the air–water interface in the LB trough. A few drops of concentrated $\text{K}_3\text{Fe}(\text{CN})_6$ solution were added to a $1.5 \times 10^{-4} \text{ M}$ solution of CoCl_2 in this trough to make a final concentration of the solution to be $\sim 1.0 \times 10^{-4} \text{ M}$. Quickly after this, ODA (1 mg/ml in CHCl_3) was immediately spread onto the surface of an aqueous sub-phase containing CoCl_2 and $\text{K}_3\text{Fe}(\text{CN})_6$ solution, using a Hamilton microsyringe, so as to form the Langmuir monolayer where the area of ODA was $20 \text{ \AA}^2/\text{molecule}$. It may be mentioned that the crystallisation of PBAs is not dependent on the surface pressure as reported by us recently [17]. The concentrated $\text{K}_3\text{Fe}(\text{CN})_6$ solution mixed gradually with CoCl_2 solution, allowing $\text{Fe}[\text{CN}]_6^{3-}$ anions to react with Co^{2+} cations to yield the Co-hcf film below the surface of the ODA Langmuir

monolayer. The appearances of sections of a brown film floating under the ODA monolayer indicate the onset of the Co-hcf crystal formation. A brown precipitate was also formed gradually at the bottom of the trough. It is to be noted that just a precipitate of $\text{Co}_3[\text{Fe}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ powder was obtained in the trough if Langmuir monolayer was not employed. It took three to six days for Co-hcf crystalline film to get deposited under ODA monolayer. It was collected by transferring it onto a suitable substrate by inserting the latter through the surface film and lifting the substrate horizontally. The substrate used were glass, Cu grid, mica or gold-coated glass, and examined by XRD, TEM, AFM and cyclic voltammetry (CV).

3. Results and discussion

In the absence of ODA monolayer, a brown precipitate of cobalt-hexacyanoferrate was formed in the sub-phase, according to the following reaction:



The reaction mixture was kept for a day to facilitate the settling of the precipitate at the bottom of the trough. It is known that PBAs have face-centered cubic (fcc) structure with $\text{Fe}(\text{CN})_6$ vacancies in some of its lattice sites, so that six cyano groups get replaced by six water molecules [28]. The powder XRD pattern of the $\text{Co}_3[\text{Fe}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ precipitate formed in absence of the monolayer shown in Fig. 1(a), is consistent with the reported fcc structure. The unit cell lattice parameter, a , was calculated to be $\sim 10.3 \text{ \AA}$.

On the other hand, in the presence of the ODA monolayer, a thin reddish brown film of Co-hcf is formed under the monolayer. Additionally, a brown precipitate is also formed at the bottom of the trough in the aqueous sub-phase. Fig. 1(b) is the XRD pattern of the Co-hcf precipitate thus formed at the bottom of the trough. This pattern is identical to that shown in Fig. 1(a), and therefore, corresponds to bulk Co-hcf. Fig. 1(c), presents the XRD pattern recorded on the Co-hcf film which got deposited right under the ODA monolayer

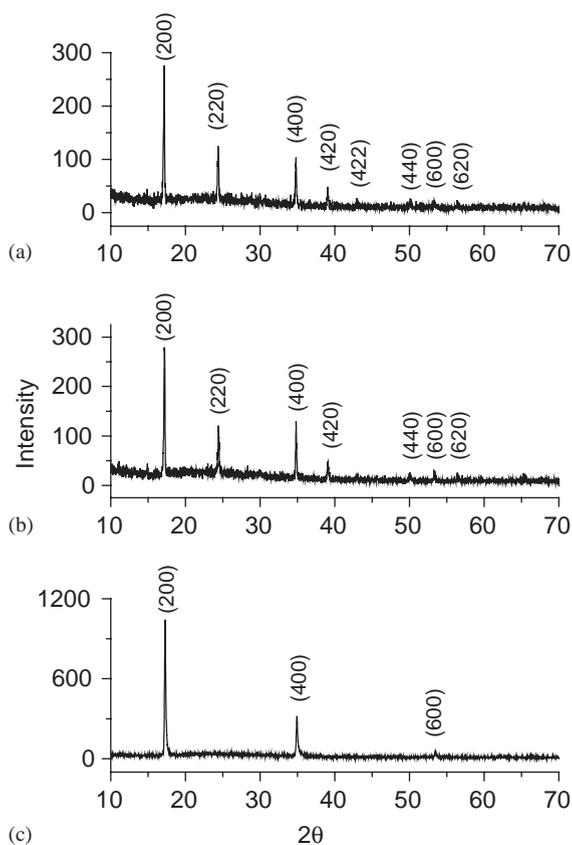


Fig. 1. XRD patterns of: (a) $\text{Co}_3[\text{Fe}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ precipitate formed without ODA monolayer; (b) Co-hcf precipitate formed at the bottom of the trough in presence of ODA monolayer; and (c) Co-hcf film formed at the air–water interface and transferred on glass.

over a period of six days, and subsequently transferred on glass. In this case, we observe sharp intense peaks only at 2θ values 17.24° , 34.9° and 53.37° corresponding to the $\{200\}$, $\{400\}$ and $\{600\}$ reflections expected for an fcc lattice with $a \sim 10.3 \text{ \AA}$. It implies a preferential orientation of Co-hcf fcc crystals during growth under the ODA monolayer template.

The Co-hcf film grown over a period of six days under the ODA monolayer, at air–water interface, was transferred on a holey carbon coated copper grid and analysed by TEM. The TEM photograph shows, in Fig. 2(a), isolated cube-shaped crystals (size 50–300 nm) of Co-hcf, the growth process of more and more of them during the six-day

period ultimately resulting in the formation of a continuous thin film. Electron diffraction (ED) pattern of selected area taken from the overlapping region is shown in Fig. 2(b). It corresponds to the $[001]$ zone for a fcc structure with lattice constant of $a = \sim 10.3 \text{ \AA}$, typical of PBA [17] and indicates the parallel alignment of $\{100\}$ crystal face of Co-hcf along the ODA monolayer surface. The spot pattern of ED gradually changes to continuous rings upon prolonged exposure of the film to the electron beam. Further studies are required to understand this phenomenon well. TEM image also showed quite a few numbers of thick particles, which are not transparent to the electron beam. These particles could be formed due to epitaxial growth of $\{100\}$ oriented cubic crystals. Our main observation is that the ODA monolayer directs the growth of $\{100\}$ oriented cubic Co-hcf crystals which gradually coalesce to form a crystalline thin film.

The Co-hcf film was also examined with atomic force microscopy (AFM) to investigate the growth process of Co-hcf crystals under the ODA monolayer template. A two-dimensional $5 \mu\text{m} \times 5 \mu\text{m}$ image of a Co-hcf film grown at the air–water interface under the ODA monolayer for three days and transferred on mica substrate is shown in Fig. 3(a). The shape of the crystals are cubic and their size is in the range of 50–300 nm. It is clear from the image that the cubic crystals are in the process of overlapping with each other to grow into a thin film. The thickness of the crystals is estimated to be between 100 and 300 nm. A typical three-dimensional AFM photograph of a few cubic Co-hcf crystals is shown in Fig. 3(b). The surface covered by the overlapping of the crystals increases as one allows more and more time for their growth at the air–water interface. The AFM image of the Co-hcf grown over a period of six days shown in Fig. 3(c) depicts a much larger

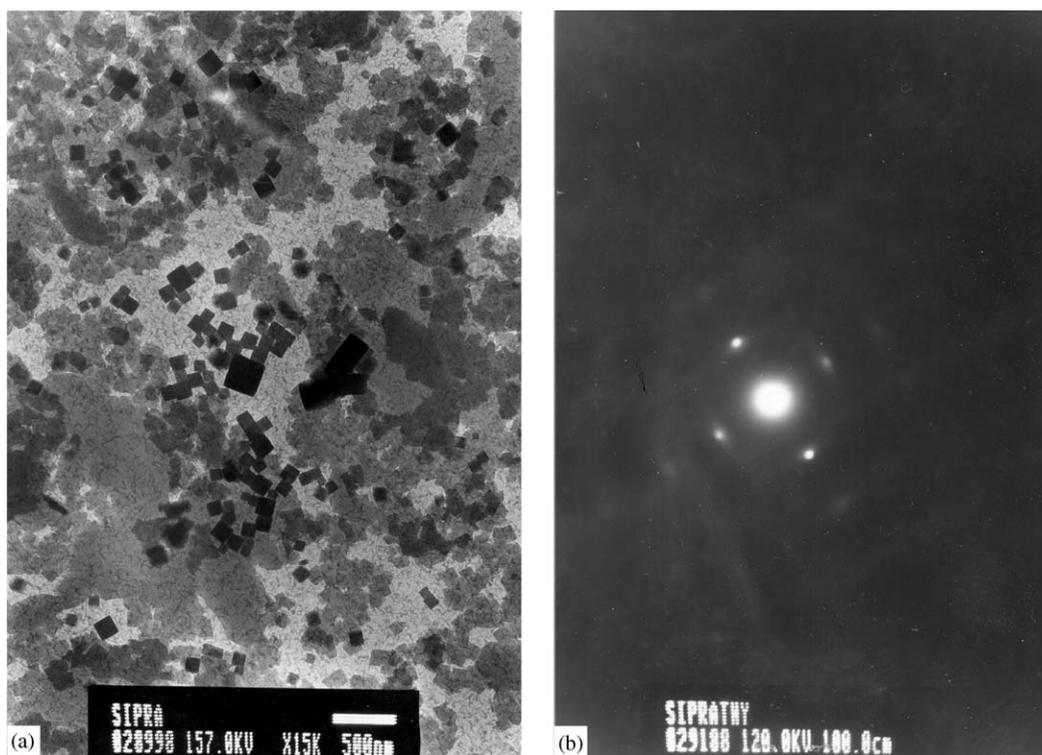


Fig. 2. Transmission electron micrograph (a), and the ED pattern (b) of Co-hcf film grown under ODA monolayer for 6 days and transferred on carbon coated copper grid.

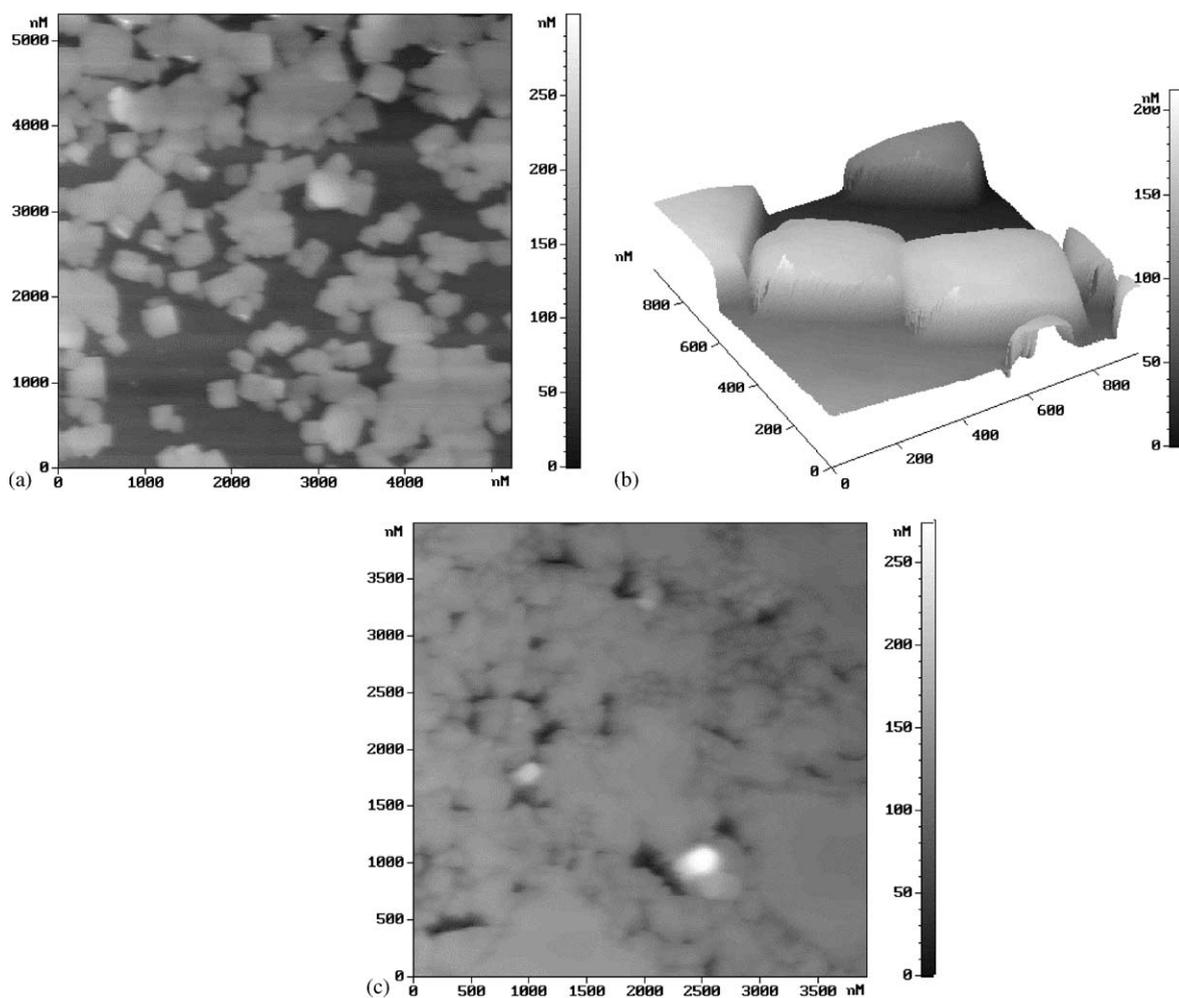


Fig. 3. AFM images of selected areas of Co-hcf film grown at air–water interface under the ODA monolayer and transferred on mica substrate. (a) two-dimensional image of area $5000 \times 5000 \text{ nm}^2$; (b) three-dimensional image of area $900 \times 900 \text{ nm}^2$; and (c) two-dimensional image of area $4000 \times 4000 \text{ nm}^2$. (a) and (b) pertain to a film grown over a period of three days whereas (c) depicts the film grown for six days.

coverage of the area by the crystals, supporting our conjecture.

The formation of Co-hcf was also established through electrochemical analysis. CV measurements on Co-hcf film was performed by transferring it on gold-coated glass electrode in 0.1 M KCl solution as supporting electrolyte. The reference electrode was saturated Ag/AgCl electrode with a salt bridge containing 3 M KCl aqueous solution. A platinum wire was used as a counter electrode. The voltammogram is shown in Fig. 4. A scan rate of 50 mV/s was employed in the lower potential

range 0–0.7 V because amine group from ODA monolayer is not oxidisable in this range [29]. This potential range falls below the potential needed to reduce the Co(II) ion in the film. The redox peak in Fig. 4 with the mid-point potential ($E_{1/2}$) of 0.51 V vs. Ag/AgCl electrode corresponds to the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ state in the hexacyanoferrate couple [30]. The peak current increases linearly with the potential scan rate upto 300 mV/s indicating an electrode process involving surface attached redox species.

Our results demonstrate the role of a Langmuir monolayer as a template for the growth of oriented

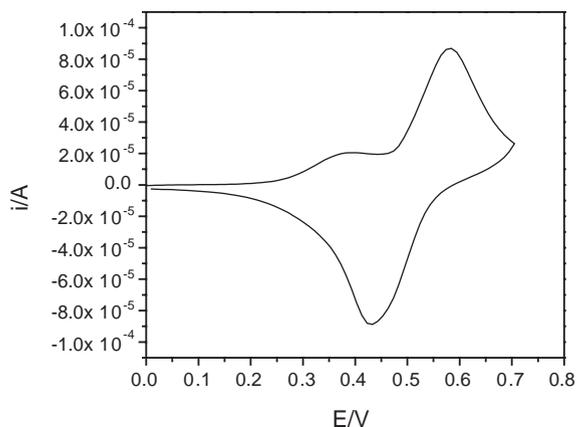


Fig. 4. Cyclic voltammogram of Co-hcf film (transferred gold-coated glass electrode) in 0.1M KCl solution. (Scan rate = 50 mV/s Reference Electrode is Ag/AgCl.)

crystals, of Co-hcf, a molecular material. The various possible factors responsible for the controlled growth under the Langmuir monolayer could be the crystallographic matching of a closed packed monolayer with a particular face of the nucleating crystal, stereochemistry and electrostatic interaction. In our earlier study [17], we underlined that the crystallographic matching between ODA monolayer (assuming it to be hexagonally closed-packed) and the nucleating face of PBAs may not be the main driving factor for crystallisation. Instead, the strong electrostatic interaction between the protonated amine head group of ODA monolayer at the experimental condition of pH = 5.8, and the $[\text{Fe}(\text{CN})_6]^{3-}$ ion in the solution is the principle factor behind such oriented crystallisation. This is supported by the fact that no crystals are formed under negatively charged or under a neutral monolayer. Oriented cubic crystals of size 50–300 nm were formed and overlap of these cubic crystals leads to the formation of a thin film of Co-hcf as indicated by TEM and AFM images.

4. Conclusions

Cubic crystals of Co-hcf are grown at the air–water interface with their $\{100\}$ planes aligned

parallel to the ODA surface. An insight into the growth process of the Co-hcf crystallisation is obtained from the TEM and AFM images. Although small cubic crystallites of the size of 50–300 nm are formed initially, a smooth film is finally formed from their fusing together.

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