GIXD and XAFS Analysis of a Two-Dimensional Metal Cyanide Grid Network in a Langmuir-Blodgett Film

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Introduction

Supermolecular systems are currently being pursued for their potential host-guest, catalytic, optical, electronic, and magnetic properties.[1] This synthetic strategy may eventually prove to be a new route to future nanoscale electronic and magnetic devices. In order to extend the potential applications of this class of materials, new synthetic methods for forming these structures at an interface need to be developed. Reaction of an amphiphilic pentacyano-ferrate(III) complex with aqueous Ni^{2+} ions at an air-water interface has resulted in the formation of a two-dimensional Fe-CN-Ni grid network. Multilayer films comprising these networks have been transferred to solid supports by the Langmuir-Blodgett technique. Structural characterizations on these films by x-ray absorption fine structure (XAFS) and grazing incidence x-ray diffraction (GIXD) verify the presence of an extended covalent network in these films. This synthetic approach demonstrates the potential for forming coordinated covalent networks at surfaces.

Materials and Methods

A monolayer of pentacyano(4-octadecylamino-pyridine)ferrate(III) was reacted with aqueous Ni^{2+} ions at the air-water interface. The 39 bilayer film was transferred to a glass slide made hydrophobic with a monolayer of octadecyltrichlorosilane for GIXD experiments and to Mylar for XAFS measurements (100 bilayers). For the GIXD experiments, the x-ray wave-length was 1.254 Å and made incident on the glass surface at an angle below the critical angle for total external reflection. XAFS scans were taken for the iron and nickel K edges in the fluorescence mode using a Lytle detector. Energy calibration was accomplished by simultaneously recording an XAFS spectrum of a Ni or Fe reference foil.

Results and Discussion

Three-dimensional analogues of the polymeric cyanide-bridged octahedral hexacyanides of the transition metals form face-centered cubic isomorphs of the well-known Prussian blue structure. The M_A-CN-M_B-NC-M_A motif consists of a linear cyanide bridge with a typical M_A-M_A separation of ~10 Å. The octahedral geometries of M_A and M_B introduce 90° (NC)-M_A-(CN) and (CN)-M_B-(NC) bond angles into the structure. Thus, one layer of the Prussian blue structure comprises an extended two-dimensional square grid network. Evidence for this same square grid network in the LB film prepared from the nickel-bridged amphiphilic pentacyanoferrate complex can be inferred from the GIXD pattern for the film shown in Fig. 1.

The peaks have d spacings of 5.10 Å, 3.62 Å, and 2.55 Å. This pattern conforms to the one expected for a face-centered square lattice and can be assigned to the (2,0), (2,2) and (4,0) Bragg planes, respectively, yielding a unit cell with a = 10.2 Å. Interpretation of the diffraction peak width yields an average coherence length of ~60 Å. The cell edge corresponds to the iron-iron separation and is in the range expected for a Fe-CN-Ni-NC-Fe bridge.

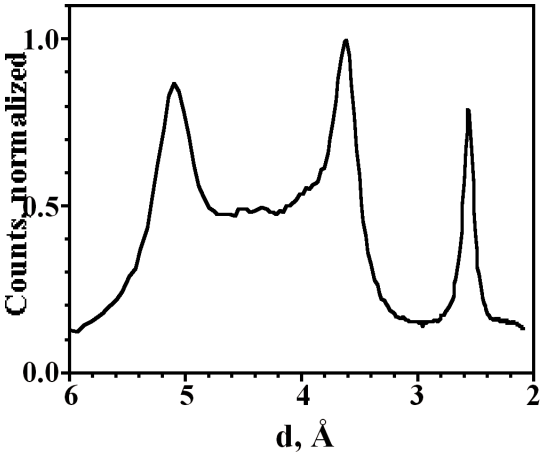

FIG. 1. GIXD pattern for a 39 bilayer LB film containing an iron-nickel-cyanide network.

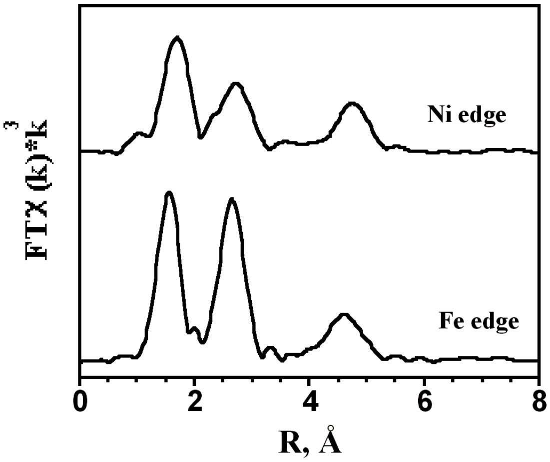

FIG. 2. Fourier transforms of the k^3 weighted XAFS data for an LB film containing an extended iron-nickel cyanide square grid network.

Further evidence for the existence of a linear Fe-CN-Ni structural unit is seen in the Fourier transform of the k^3 weighted XAFS data for the grid network, shown in Fig. 2. Transforms of both the Fe and Ni XAFS show the expected three coordination shells. For the Fe edge, the shells correspond to the C, N, and Ni atoms, and for Ni, the N, C, and Fe atoms. The comparatively high intensity of the third-shell peaks centered around ~5 Å is consistent with a focusing effect of the linear cyanide bridge as found for other cyanide systems.[2] A fit to the first two coordination shells of the Ni data using FEFF7 theoretical XAFS parameters yields Ni-N, Ni-C, distances of 2.10 Å and 3.22 Å. From crystallographic data on a similar pentacyanoferrate(III) complex, the Fe-C bond length is known to be 1.90 Å. Therefore, the Fe-Ni separation as determined from the XAFS data is 5.12 Å, in close agreement with the results of the GIXD experiment. From these results, we can conclude that the reaction of the amphiphilic pentacyanoferrate(III) complex with aqueous nickel ions at the air-water interface indeed results in a square grid supramolecular network coherent over 3600 Å^2.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract No. W-31-109-Eng-38. Support by the National Science Foundation DMR9900855 is also acknowledged.

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