Layer-by-layer assembly and intercalation reactions of iron(III) and iron(II) alkanebisphosphonates on gold surfaces

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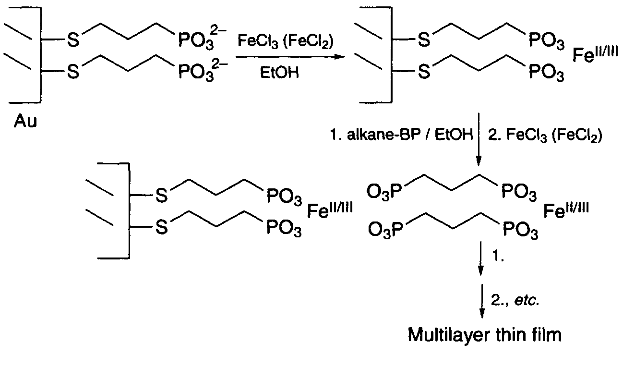
Multilayer films of Fe^{3+} and Fe^{2+} alkanebisphosphonates are assembled on gold surfaces, and the Fe^{3+} is found to oxidize pyrrole to produce mono/multilayer quantities of poly(pyrrole).

Transition-metal phosphates and phosphonates are lamellar solids with chemical and physical properties that make them potentially useful in such diverse applications as catalysis,[1] chemical sensing,[2] chiral separations,[3] ion exchange[4] and optics.[5] Recently, new lamellar Fe^{2+} and Fe^{3+} phosphonates, $Fe(RPO_3)\cdot H_2O$, $HFe(RPO_3)_2\cdot H_2O$ and $HFe(RPO_3H)_4$, were synthesized by reacting FeOCl with alkyl- and aryl-phosphonic acids.[5–7] The resulting bulk materials have displayed interesting optical[5a] and magnetic[6] properties.

In an effort to modify rationally the chemical properties of solid surfaces, we and others have previously developed techniques for growing mono- and multi-layer thin films of metal (Zr^{4+}, Hf^{4+}, Ln^{3+}, Al^{3+}, Cu^{2+}, Zn^{2+}, Mn^{2+}) organophosphonates on solid supports.[8–10] These methods involve sequential complexation reactions of a bisphosphonic acid and the metal cation from separate aqueous or non-aqueous solutions. The present communication describes an extension of this method to the synthesis of Fe^{3+} and Fe^{2+} alkanebisphosphonate thin films. To our knowledge, the Fe^{3+} films represent the first examples of phosphonate thin films that possess an electroactive metal ion within the layers. While the Fe^{3+} centres do not appear to be addressable electrochemically, we have found that they can initiate the oxidative polymerization of pyrrole to form a monolayer or even multilayer quantities of poly(pyrrole).

The preparation of Fe^{3+}–alkanebisphosphonate (Fe^{3+}-BP) thin films is shown in Scheme 1. A clean gold substrate† (EMF, Inc.) was placed in an EtOH solution containing 1 μg ml^{-1} of $H_2O_3PC_4H_8SSC_4H_8PO_3H_2$ for 24 h, in order to anchor the subsequently grown films to the surface. Multilayer Fe^{3+}-BP growth was accomplished by alternately immersing the substrate in a solution containing $FeCl_3$ (0.1 mol dm^{-3} in EtOH) followed by immersion in a solution of the desired alkanebisphosphonate (1 mmol dm^{-3} in EtOH) for 2 h each. Longer immersion times resulted in no further increase in film thickness. Identical procedures were used to grow Fe^{2+}-BP thin films using $FeCl_2$ in EtOH.



Scheme 1 Synthesis of $Fe^{II/III}$ alkanebisphosphonate multilayer films

Iron phosphonate film growth was monitored by thin-film ellipsometry.‡ Typical plots of film thickness *vs.* layer number for C_{10} and C_{16} Fe^{3+} alkanebisphosphonates are shown in Fig. 1. The plots are linear with slopes of 19.0, 16.8 and 15.4 Å per layer for the C_{16}, C_{14} and C_{10} bisphosphonates, respectively (the C_{14} data were excluded for clarity). Linear plots are also observed in the ellipsometry data of Fe^{2+} C_{10}-BP films [Fig. 1(*b*)].

Layer-by-layer assembly is further confirmed by monitoring the CH_2 stretches of the alkyl group (asymmetric stretch λ_{max} 2852 cm^{-1}, symmetric stretch λ_{max} 2926 cm^{-1}) with reflectance FTIR spectroscopy (Nicolet model 730). A linear increase in absorbance *vs.* layer number was observed for the Fe^{3+} C_{10}-BP. The presence of OH stretching vibrations of the POH group at 3040–3315 cm^{-1} is consistent with possible formulations of the film as $HFe(C_{10}\text{-BP})\cdot H_2O$ or $HFe(C_{10}\text{-BP})_2$.[6,7]

The composition of Fe^{3+}-C_{10} BP films was investigated with X-ray photoelectron spectroscopy (XPS). Although the iron oxidation state could not be determined unambiguously by

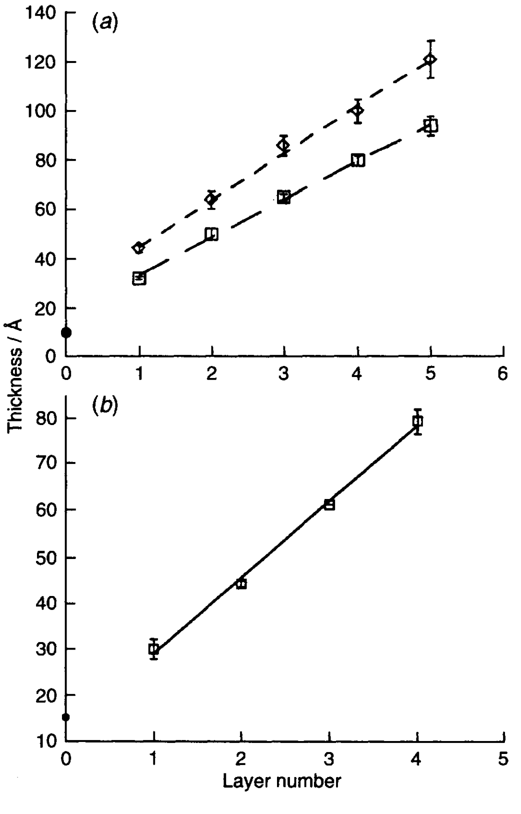


Fig. 1 (*a*) Ellipsometric film thickness *vs.* layer number for Fe^{3+} alkanebisphosphonate films; (●) sulfanylethylamine, (◇) Fe^{3+} + C_{16}-BP, (□) Fe^{3+} + C_{10}-BP. Each layer was terminated with Fe^{3+}. (*b*) Film thickness *vs.* layer number for Fe^{2+} C_{10}-BP. The error bars represent the deviations of five measurements taken in different locations on the surface.

XPS, the Fe : P peak area ratios for phosphate- and Fe^{3+}-terminated films were determined and compared with ratios calculated[9a] based on $HFe(C_{10}\text{-}BP)_2$ and $HFe(C_{10}\text{-}BP){\cdot}H_2O$ structural models. As shown in Table 1, the calculated values are consistent with the 4 : 1 Fe : P stoichiometry.

The Fe^{3+} in the Fe^{3+}-BP salts can be used to initiate the oxidative polymerization of adsorbed pyrrole vapour. This is accomplished by simply placing the film in a closed container above neat liquid pyrrole. In 24 h, the ellipsometric film thickness increased by *ca.* 5 Å per Fe^{3+} layer contained in the film, presumably due to the reaction of Fe^{3+} with pyrrole to yield poly(pyrrole) and Fe^{2+}. The presence of poly(pyrrole) polymerized onto a monolayer of Fe^{3+} C_{10}-BP was detected electrochemically (Fig. 2). For the film shown in Fig. 2, the anodic peak current was found to scale linearly with scan rate indicating a surface-bound redox interconversion.[12] No growth of polypyrrole was detected by ellipsometry in the case of the Fe^{2+}-BP films, consistent with the weaker oxidizing power of Fe^{2+}.

Table 1 Normalized Fe : P XPS peak area ratios for three-layer Fe^{3+} C_{10}-BP films

	Fe^{3+} terminated	C_{10}-BP terminated
Fe : P (obs.)	1.0	0.57
$HFe(C_{10}\text{-}BP)_2$ Fe : P calc.[a]	0.80	0.57
$HFe(C_{10}\text{-}BP){\cdot}H_2O$ Fe : P calc.[a]	1.6	0.12

[a] Normalized Fe : P peak area ratios were calculated using electron mean free paths of 68 and 44 Å, and atomic sensitivity factors of 0.412 and 2.87 for P and Fe, respectively (see ref. 9*a* for details).

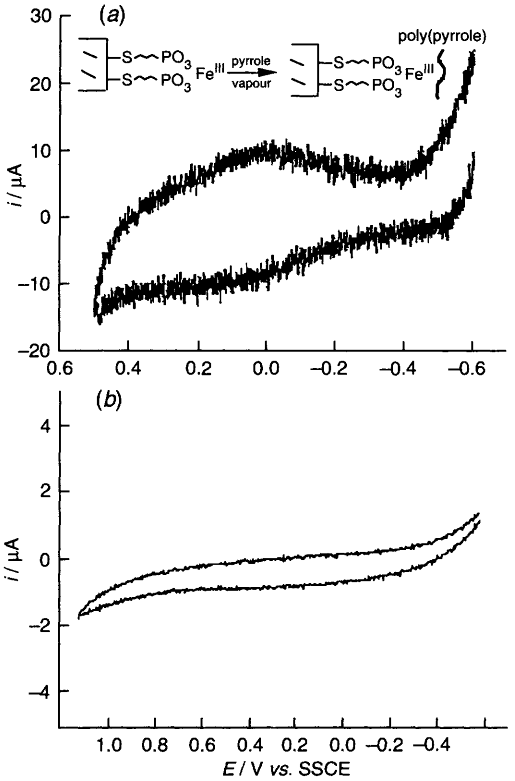


Fig. 2 (*a*) Cyclic voltammogram of one layer of Fe^{3+} phosphonate which had previously been exposed to pyrrole vapour and (*b*) of five layers of Fe^{3+} C_{10}-BP not exposed to pyrrole vapour; solvent MeCN–0.1 mol dm^{-3} NBu_4PF_6, the auxiliary electrode was a platinum wire and the reference was a saturated calomel electrode. Scan rate 100 mV s^{-1}.

We have described a method for multilayer film growth of Fe^{3+} and Fe^{2+} alkanebisphosphonates on solid surfaces based on sequential complexation reactions. This technique allows the rational design of surfaces with a material that is potentially useful for catalysis, electrocatalysis, magnetic applications and optical waveguides. Additionally, thin films of Fe^{3+} can be used to synthesize monolayers of conducting polymer films. This represents an alternate route to conducting polymer thin films to that described first by Simon *et al.* and more recently by Willicut and McCarley, in which monolayer-forming pyrrole derivatives were electropolymerized on silicon and gold surfaces.[13] We are currently examining the conductive properties of the polymer–iron bisphosphonate intercalation compounds.

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Footnotes

† Gold substrates were cleaned by dipping in H_2SO_4–H_2O_2 (3 : 1) for *ca.* 2 min followed by sonication in ethanol (95%) and deionized H_2O.

‡ Ellipsometric measurements were made with a Rudolf 437 ellipsometer as described previously.[11]

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