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Communications

Formation of Oriented Iron Oxide Particles in Cast Multibilayer Films

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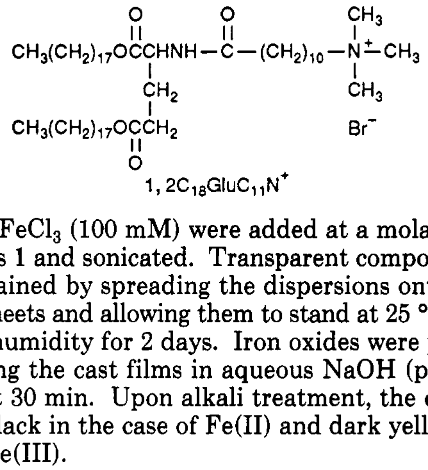
The formation of ordered iron oxide particles in the biological cell constitutes a most remarkable example of biomineralization.[1] Biomimetic regulation of the structure and size of iron oxides was recently reported by using lipid bilayer membranes. Mann and Hannington[2] obtained nanometer-size iron oxide by precipitation in the inner core of aqueous phospholipid vesicles. Zhao et al.[3] observed formation of magnetic Fe_3O_4 particles on the surface of planar bilayer membranes (BLM) of glyceryl monooleate.

It would be interesting scientifically as well as practically if we could produce these iron oxide particles in the macroscopic dimension. It has been shown that regular multilayered films are readily obtainable by casting of aqueous dispersions of synthetic bilayer membranes.[4] The polar interbilayer space is highly anisotropic and provides sites suitable for anisotropic incorporation of guest molecules.[5] This space can be used for anisotropic production of other materials such as cross-linked organic polymers[6] and silicone polymers.[7] We describe in this paper the in situ production of iron oxide particles that retain magnetic anisotropy in a cast multibilayer film.

N-(ω-(Trimethylammonio)undecanoyl)dioctadecyl-L-glutamate bromide (1) was prepared in these laboratories and identified by IR and NMR spectra and by elemental analyses. Powdery 1 was dispersed in deionized water by sonication to give colloidal 20 mM dispersions. Aqueous $FeCl_2$ or $FeCl_3$ (100 mM) were added at a molar ratio of 0.8 versus 1 and sonicated. Transparent composite films were obtained by spreading the dispersions onto fluorocarbon sheets and allowing them to stand at 25 °C in 60% relative humidity for 2 days. Iron oxides were produced by dipping the cast films in aqueous NaOH (pH ca. 12) for about 30 min. Upon alkali treatment, the cast films turned black in the case of Fe(II) and dark yellow in the case of Fe(III).



$$\begin{array}{l} CH_3(CH_2)_{17}O\overset{O}{\overset{\|}{C}}CHNH-\overset{O}{\overset{\|}{C}}-(CH_2)_{10}-\overset{CH_3}{\overset{|}{N}}{}^{+}\underset{\overset{|}{CH_3}}{}-CH_3 \quad Br^- \\ \qquad\qquad\qquad\;\; |\;CH_2 \\ CH_3(CH_2)_{17}O\underset{\underset{O}{\|}}{C}CH_2 \end{array}$$

1, 2C$_{18}$GluC$_{11}$N$^+$

The X-ray diffraction pattern (Rigaku Denki, RAD-R-32, CuKα radiation) of the cast film showed a long spacing of 67 Å up to the fifth order. This long spacing is the same as that observed without introducing iron oxides. The lamellar structure of the cast film was also confirmed by scanning electron microscopy. Figure 1 shows a SEM picture of the cross section of the cast film. These data indicate that the iron compounds are placed between bilayers and that the composite cast films maintain the multibilayer structure.

Subsequently, the iron oxide was extracted from the composite cast films by dissolving the bilayer component in chloroform. Transmission electron micrography shows that the iron oxides are mainly rectangular plates with a maximum size of about 100 nm. Figure 2 shows an electron diffraction pattern of the iron oxide. The electron diffraction pattern coincided with that of a single crystal of the spinel structure.[8] The measured *d* spacings correspond to those of magnetite (Fe_3O_4, Table I). Apparently, oxidation of Fe(II) is moderately retarded in cast films, and the formation of magnetite is favored, in contrast with

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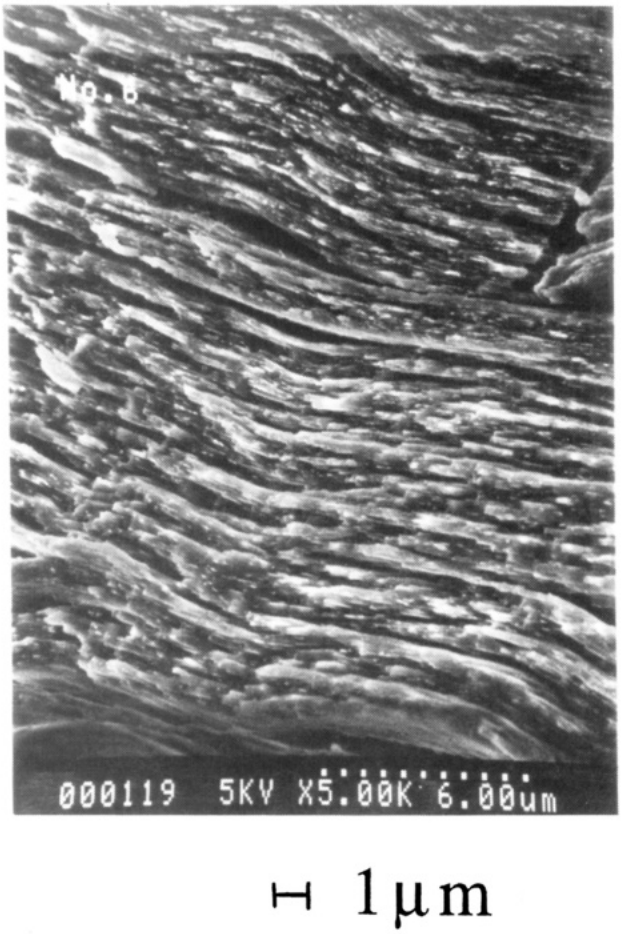

Figure 1. Scanning electron micrograph of the cross section of a composite cast film.

Table I. Electron Diffraction Data for Iron Oxides in an Fe(II) Cast Film

spacings/Å		
Fe(II) cast film	Fe_3O_4[a]	Miller indices for Fe_3O_4[a]
2.95	2.97	(220)
	2.53	(311)
	2.42	(222)
2.09	2.10	(400)
	1.71	(422)
	1.62	(511)
1.47	1.49	(440)
	1.42	(531)
1.32	1.33	(620)

[a] Powder X-ray diffraction (XRD) file data from National Bureau of Standards, Monograph 25, Sec. For iron oxides, spacing values of ED well coincide with those of XRD.[2]

the formation of hydrous Fe(III) oxides such as goethite and lepidocrocite, which usually occur in bulk solution due to rapid oxidation.[2]

The iron compounds obtained from Fe(III) composite films were finely divided particles. Their electron diffraction patterns were diffuse, and the *d* spacings corresponded to those of poorly ordered goethite (α-FeOOH).

The magnetite particle is placed anisotropically in the composite cast film. The magnetization curve of composite cast films was measured by a vibrating sample magnetometer (Riken Denshi, Model BHV-35) at room temperature as shown by Figure 3. The composite cast film derived from $FeCl_2$ behaves as ferromagnet. Its coercivety is 20 Oe. The saturation isothermal magnetization is 0.71 emu/g, and the isothermal remnant magnetization is 0.11 emu/g. This composite cast film was magnetized more readily by applying a magnetic field parallel to the film plane rather than vertical to it. In contrast, the composite cast film derived from $FeCl_3$ was paramagnetic and did not display any magnetic anisotropy.

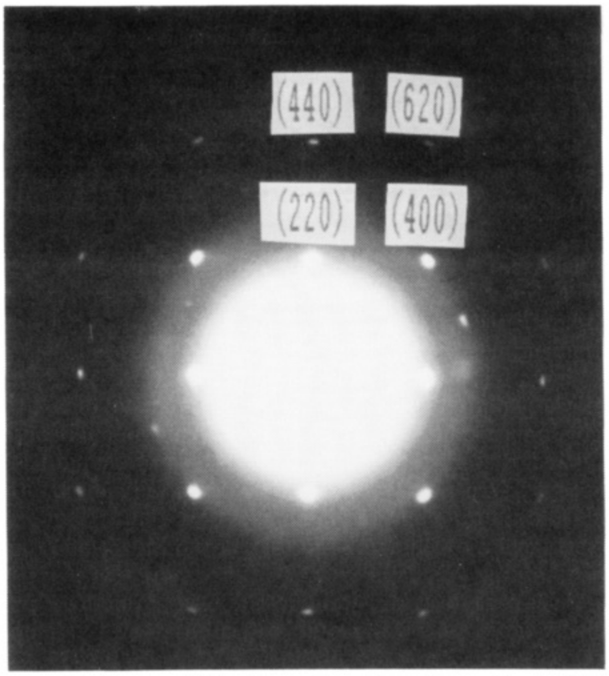

Figure 2. Electron diffraction pattern from iron oxides in Fe(II) cast film. The iron oxide was extracted from the composite film by dissolving the matrix film in chloroform, and one drop of it was placed on a carbon-coated copper electron-microscope grid. The single crystal pattern corresponds to the [001] zone. Camera length = 80 cm, acceleration voltage = 75 kV.

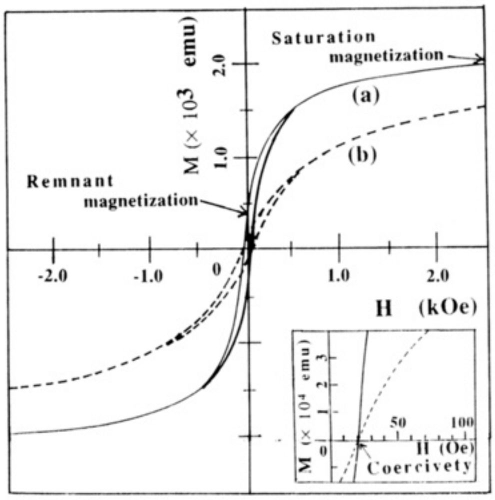

Figure 3. VSM measurement of a Fe(II) cast film. The sample size is 3 mm × 9 mm × 0.1 mm. (a) Magnetic field is parallel to the film plane. (b) Magnetic field is perpendicular to the film plane.

The magnetic anisotropy was further investigated by electron spin resonance (JEOL RE-2, X-band). The composite cast films of $FeCl_2$ were placed either parallel or perpendicular to the magnetic field. Figure 4 shows the variation of the resonance magnetic field with changing angle, θ, between the film plane and the applied magnetic field. The resonance magnetic field, H_r, varied from 2.9 to 4.2 kOe by changing θ from 0° (the film plane parallel to the magnetic field) to 90° (the film plane perpendicular to the magnetic field). This difference in H_r is consistent with the magnetic anisotropy observed with VSM. The ESR spectrum did not change by in-plane rotation of the composite cast film which is placed parallel to the magnetic field.

Subsequently, the effect of temperature on the magnetic properties was studied to determine the origin of the

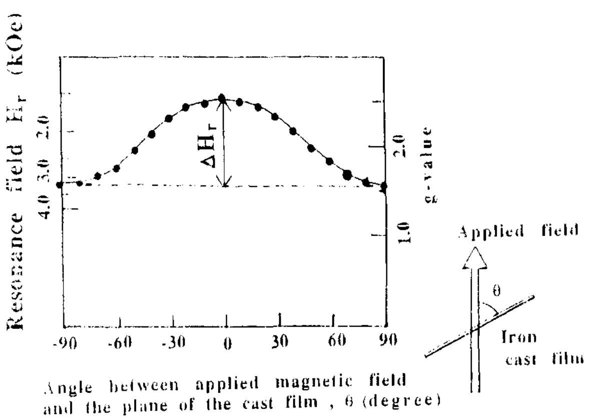

Figure 4. Angular dependence of the resonance magnetic field of a composite cast film of $FeCl_2$.

magnetic anisotropy. The composite cast films were maintained at given temperatures (20–80 °C) for an hour and their ESR spectra were measured at room temperature. The ΔH_r remained unchanged up to 60 °C but drastically decreased from 1.3 to 0.3 kOe at the temperature region between 60 and 80 °C. The gel-to-liquid crystal phase transition of the matrix bilayer was shown to occur at 68 °C by differential scanning calorimetry.[9] X-ray diffraction of this composite film gave peaks only up to the second order after heat treatment at 80 °C for an hour, indicating that the multilayered structure of the cast film became disordered by heat treatment at temperatures above the phase transition. Therefore, the observed magnetic anisotropy is produced by anisotropic crystal growth during the hydrolysis of $FeCl_2$. The magnetite particles formed remain anisotropic due to the regular, multilayer structure of the matrix film. However, once the multilayer structure is disordered by its phase transition to the liquid-crystalline state, the original orientation of magnetite particles is lost.

In this paper, the in situ formation of iron compounds in cast multibilayer films and their magnetic properties are described. Magnetite was produced as confirmed by electron diffraction. The magnetic anisotropy of iron oxide composite film is achieved by ordered orientation of magnetite particles in a ordered multibilayer film.

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Registry No. Fe_3O_4, 1317-61-9.

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Hydrothermal Synthesis and Single-Crystal Structural Characterization of the Layered Vanadium(IV) Phosphate $VOC_6H_5PO_3 \bullet H_2O$

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Metal organophosphonates form a group of layered solid compounds with alternating organic and inorganic layers. Such compounds exhibit interesting sorption and catalytic properties and serve as models for organic/inorganic interfaces.[1,2] Vanadyl organophosphonates have been shown to intercalate alcohols by coordination of the intercalating molecule to the vanadium atom in the inorganic vanadium phosphate layer.[3] Previous interpretation of the mechanisms of these intercalation reactions has relied on assessment of the variation in unit cell dimensions determined by powder X-ray diffraction data as both the size of the organic group attached to phosphorus and the intercalating alcohol molecule were varied. Detailed structural information has been unavailable due to the lack of suitable single crystals for X-ray analysis, despite numerous and varied attempts at crystal growth. We have now found that crystals of vanadium organophosphonates and the corresponding arsenates can be grown under hydrothermal conditions. In this report, we describe the hydrothermal synthesis and single-crystal structure of $VO(C_6H_5PO_3)\cdot H_2O$ and compare its structure and properties with a phase of similar composition previously described.[3a]

An excess (0.952 g) of $C_6H_5PO(OH)_2$ was added to 0.30 g of V_2O_3 (both reagents obtained from Alfa, V:P = $^2/_3$), and the mixture[4] was placed in a 23-mL Teflon-lined autoclave (Parr Instruments). The reaction vessel was filled to 80% capacity with distilled water, sealed, and maintained at 200 °C and autogenous pressure for 4 days. At the end of this period the resulting platy, light green solid (0.660 g, 68.5% yield based on V) was removed, washed several times with distilled water (a blue filtrate indicated the presence of unreacted VO^{2+}), and dried in air at ambient temperature.

Powder X-ray diffraction analysis indicated a single-phase, layered material had been produced with multiple orders of a 14.2-Å layer spacing readily apparent. Chemical analysis[5] suggested the formula $VOC_6H_5PO_3\cdot H_2O$. Thermogravimetric analysis (2 °C/min) in air showed a multistep weight loss starting at 200 °C corresponding to loss of a water molecule followed by loss and/or reaction of the organic component. The total weight loss observed (31.8%) corresponded to complete conversion of the material to $VOPO_4$. A crystal of $VOC_6H_5PO_3\cdot H_2O$ of reasonable quality was selected for structural characterization[6] by X-ray crystallography after survey of a large number of inferior crystals that were twinned along the layer stacking axis. Despite the modest quality of the data obtained, a consistent structural solution was found.

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[4] Similar experiments substituting V_2O_4 and $VOSO_4$ as vanadium sources resulted in polycrystalline materials (87.1% and 41.5% yields, respectively); V_2O_5 as starting reagent produced low yields (24.9%) of single-crystal material. Powder X-ray diffractograms were identical in all cases with those obtained from V_2O_3 generated samples.

[5] Bulk elemental analysis: 20.38% V, 12.74% P, 29.87% C, 2.90% H. Calcd for $VPO_5C_6H_7$: 21.13% V, 12.85% P, 29.90% C, 2.92% H.

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