

## Synthesis of organized inorganic crystal assemblies

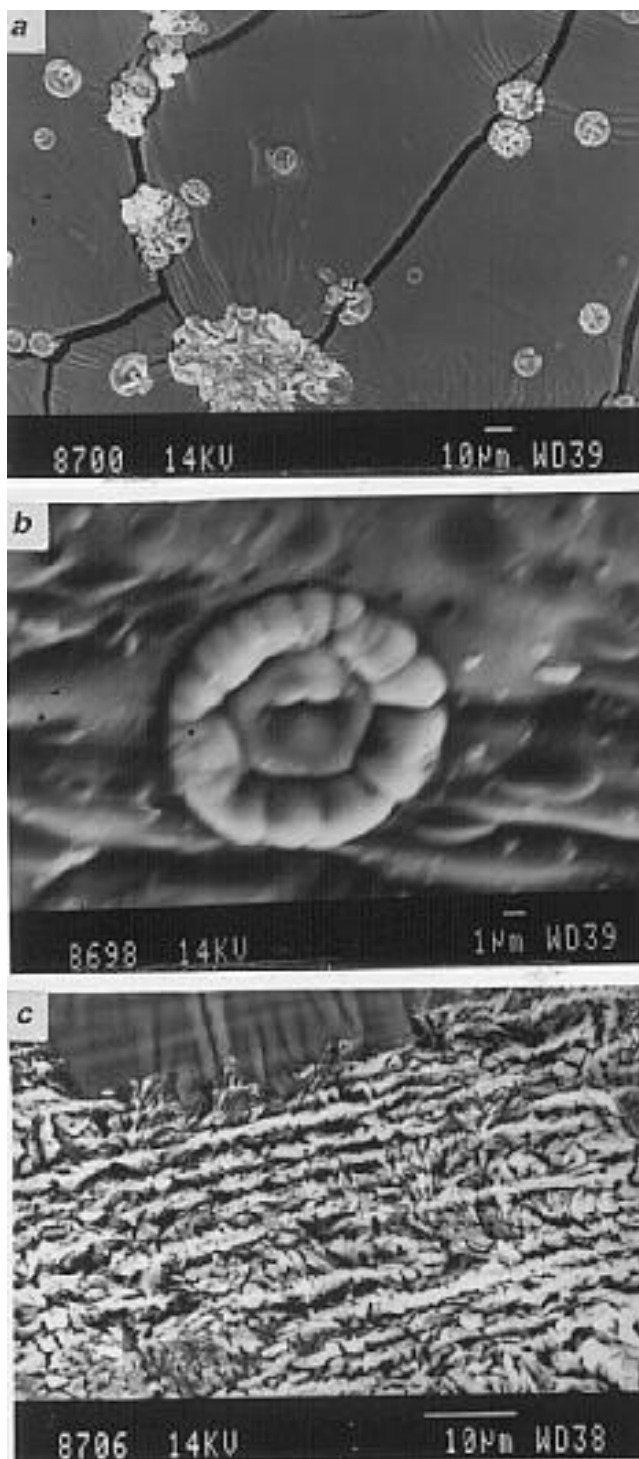
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**Organized crystalline assemblies of cobalt salt and *g*-iron oxide have been produced by *in situ* matrix-mediated biomimetic route. The process makes use of an organized supramolecular matrix and produces cobalt chloride crystals with characteristic morphology of *coccolith of alga* and nacreous structure of *Pinctada martensii*. Crystals of *g*-iron oxide have been produced with typical morphology of aragonite spherulites in regenerated shell of *Pomacea paludosa*.**

NATURE has synthesized many inorganic crystals in living organisms with the help of biopolymers. The natural route consists of pre-organization of a supramolecular matrix, mineralization of it through interfacial molecular recognition leading to the nucleation, growth and organization of the inorganic phase. A signature of the natural synthesis is the production of the same inorganic phase with several distinctly different morphologies. For example, calcium carbonate crystals can grow in the form of plates, rods or complex tubules<sup>1</sup>. Recent efforts in the laboratory, to duplicate this natural method of natural synthesis, have come to be known as *biomimetic methods for synthesis*<sup>2</sup>. An understanding of the mechanism involved in such matrix-mediated synthesis has been recognized to be of great potential in the production of engineering materials. Thus, catalyst particles of controlled size and morphology, magnetic materials with appropriate anisotropy, highly porous materials, composites and well-organized crystallite assemblies can be produced through biomimetic synthesis. A variety of technically important inorganic materials such as CaCO<sub>3</sub>, CdS, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, nano-sized copper and silver have been produced by the biomimetic route<sup>3-8</sup>. While these materials exhibited much of the sophistication expected in terms of shape, size and orientation, however, complex and unusual morphologies found in living organisms could not be produced. The present communication reports the synthesis of cobalt chloride and iron oxide particles with morphologies that are characteristic of the *coccolith of alga*, nacreous structure of *P. martensii* and aragonite spherulites in the regenerated shell of *P. paludosa*<sup>9</sup>. In this respect, these results open up the exciting possibility of imitating nature more closely through the control of experimental conditions and producing several morphologies of the inorganic material in the same system.

In the present investigation polyvinyl alcohol (PVA) has been used as the supramolecular matrix. Being a water-soluble polymer with a monoclinic crystal structure, PVA having rigid carbon backbone and inter-chain hydrogen



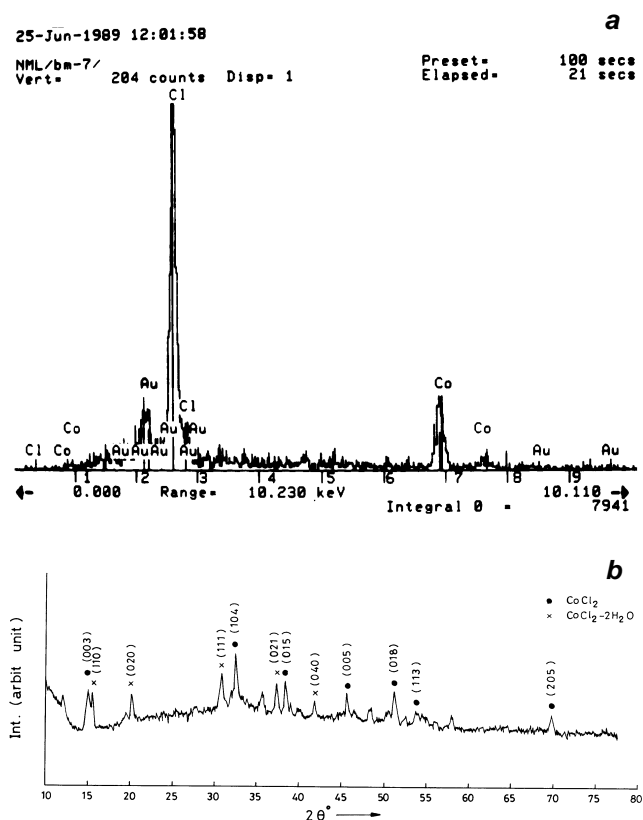
**Figure 1.** *a*, Random distribution of cylindrical-shaped cobalt salt particles in a supernatant PVA film; *b*, Growth of cobalt salt precipitate with morphology typical of *coccolith of algae*; *c*, Cobalt salt precipitate with morphology similar to nacreous structure of *P. martensii*.

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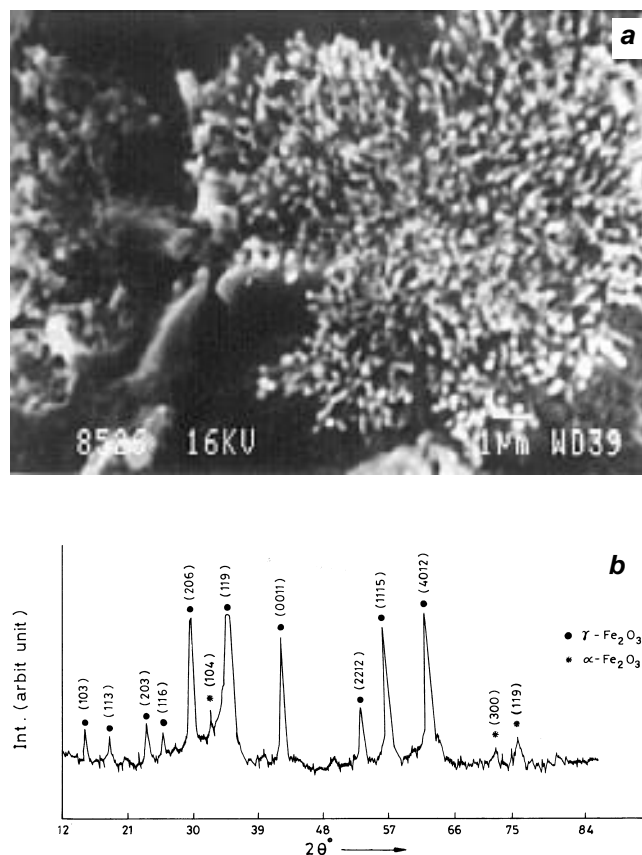
bonds, has the ability to solvate. It can also undergo cross-linking and a series of gelation reactions. The gel can be crystalline and the degree of crystallinity is a function of time. The presence of inorganic salts is also known to enhance gelation. Aqueous solutions containing different concentrations of PVA were produced by dissolving the polymer in deionized water at 90°C. The concentrations varied between 2.5 wt% and 10 wt% of PVA. Two different inorganic salts, viz.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were employed in the present study. The salts were dissolved in deionized water at room temperature to prepare 0.5 to 1.0 molar solutions and were filtered. Salt solutions were mixed with the aqueous solution of PVA in various proportions, stirred and allowed to react for a time period extending from 15 min to 15 days. Samples were drawn at regular intervals either by dipping a clean glass slide or by lifting the supernatant layer after the lapse of about a week or more. In the case of iron sulphate solutions, the polymer films with iron salt were reacted with a cold solution of sodium borohydride and dried under controlled oxygen atmosphere. The borohydride reduces the iron salt to the metallic state through a combined process of hydrolysis and reduction<sup>10</sup>. The nano-sized metal particles were then re-oxidized at room temperature to yield *g*- $\text{Fe}_2\text{O}_3$  in a single step. The films so obtained were examined under scanning electron microscope (SEM). The

The composition and structure of the film constituent were confirmed by X-ray diffraction (XRD).

The pink-coloured supernatant films as well as the films coated on glass slides containing cobalt salt developed localized regions of blue colour under the polymer surface, when preserved in dry atmosphere at room temperature for several days. The SEM study of the films containing cobalt salt showed randomly distributed particles with a hollow cylindrical morphology (Figure 1 a). Examination of the film at a higher magnification showed that these particles are the aggregates of crystals arranged in a circle around a rim of PVA (Figure 1 b). This morphology is identical to the *coccolith of the alga, coccolithus huxleyi*, made of radial growth of calcite in a biopolymer<sup>9</sup>. On the other hand, the films obtained on glass slide dipped into the PVA–cobalt chloride solution immediately after mixing, showed a distinctly different microstructure (Figure 1 c). In this case, a nacreous structure of cobalt salt aligned in rows perpendicular to polymer crystals was obtained. This also resembled the nacreous growth of *P. martensii* lamellae composed of aragonite crystals<sup>9</sup>. Both the above morphologies have been synthesized through the biomimetic route for the first time substituting  $\text{CaCO}_3$  by cobalt salt.



**Figure 2.** a, EDAX analysis of the cobalt salt precipitate; b, XRD of the sample with ring-shaped aggregates of cobalt salt in polymer.



**Figure 3.** a, *g*-iron oxide particles having growth arrangement similar to aragonite spherulites in regenerated shell of *P. paludosa*; b, XRD of the produced *g*-iron oxide particles.

In a recent publication, crystallization of a hexamer duplex [d (TGCGCG) and d (CGCGCA)] in similar ring-shaped crystals of hexadeoxyribonucleotide has been reported in the presence of cobalt hexamine<sup>11</sup>. However, the EDAX analysis has indicated that the ring-shaped samples as well as rod-shaped samples produced by the present investigators are rich in cobalt and chlorine (Figure 2 a). XRD of the ring-shaped aggregates encapsulated in polymer confirmed the presence of CoCl<sub>2</sub> and CoCl<sub>2</sub>·2H<sub>2</sub>O phases embedded in PVA matrix (Figure 2 b). However, the XRD of the film coated on the glass slide showed a diffused broad peak characteristic of the glassy substrate. In the case of the films of the PVA–FeSO<sub>4</sub> system, *g*-Fe<sub>2</sub>O<sub>3</sub> formed with a range of morphologies extending from diffusion-limited aggregates to spherulite structures. Of these, the spherulite-like morphology of *g*-Fe<sub>2</sub>O<sub>3</sub> in PVA resembled aragonite spherulites in the regenerated shell of *P. paludosa*<sup>9</sup> (Figure 3 a). Formation of the phase was confirmed by XRD which showed the presence of *g*-Fe<sub>2</sub>O<sub>3</sub> as a major phase along with *α*-Fe<sub>2</sub>O<sub>3</sub> (Figure 3 b).

There are several reports available in the literature on the synthesis of agglomeration-free fine-sized transition metal powders using PVA and other hydrophilic polymers<sup>12,13</sup>. However, the present study highlights the possibility of producing inorganic materials with morphologies similar to those observed in living organism through biomimetic synthesis. This can be exploited to develop materials for magnetic and humidity sensors with high sensitivity.

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