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Textured films of chromium phosphate synthesized by low-temperature vapor diffusion catalysis

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Abstract

The application of kinetically controlled vapor diffusion catalysis to the synthesis of films of chromium phosphate produces a novel, nanostructured film morphology. The resulting material consists of a thin, flat backplane (3 μm thick) with needles of $CrPO_4 \cdot 6H_2O$ projecting from one surface of the film. The reaction process occurs at low temperature (25 °C) and mild pH.

Keywords: Chromium phosphate; Ammonia; Vapor diffusion; Thin film; Nanostructure

1. Introduction

We have developed a kinetically controlled, low-temperature vapor diffusion method for the catalytic formation of sub-micron textured films of oxides and hydroxides [1–3] and perovskite nanoparticles [4]. The effect of surface tension during the formation of these films results in the material having one smooth surface, formed at the air/liquid boundary and one textured surface formed at the film/liquid interface. The material formed at the underside of the film grows from the hydrolysis and polycondensation of a molecular precursor in a reaction environment structured by a gradient of the catalyst of hydrolysis, resulting in the growth of a nanoscale textured surface. We report here the formation of chromium phosphate textured films using our vapor diffusion method.

Chromium phosphate has been reported as a catalyst for oxidative dehydrogenation of isopropanol [5] and acid catalyzed isomerism of cyclohexane [6]. The material also has been shown to exhibit potentially useful ion-sorption properties [7]. The nanostructured films described here may be advantageous for these and related uses.

2. Experimental

All starting materials used in this study were obtained from Aldrich Chemical Company and used without further purification. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS) were performed on washed and dried films using a Tescan Vega 5130 SEM. Powder X-ray diffraction (XRD) was performed on powdered samples using a Bruker D8 diffractometer with monochromatic Cu Kα radiation (1.540 Å) and platinum heating stage. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed using a TJA High Resolution IRIS ICP Atomic Emission Spectrometer.

Preparation of textured Chromium phosphate, $CrPO_4 \cdot 6H_2O$: 50 cm^3 of aqueous 0.1 M $Cr(NO_3)_3$ solution was mixed with 50 cm^3 of 0.1 M $(NH_4)_2HPO_4$ in a 12 cm diameter dish and the dish was placed in a sealed chamber containing 100 cm^3 of 0.75% aqueous ammonia solution in a second dish. After 24 h, the resulting purple film was collected from the surface of the liquid by inserting a glass microscope slide underneath

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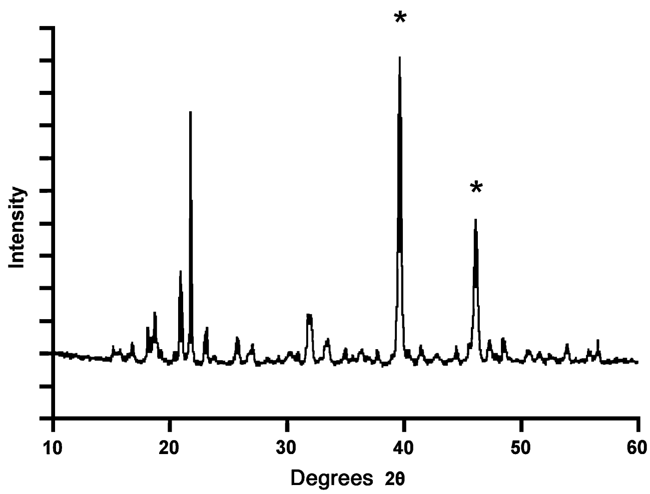

Fig. 1. Powder X-ray diffraction pattern of $CrPO_4 \cdot 6H_2O$. The two peaks labeled * are from the diffractometer's platinum stage.

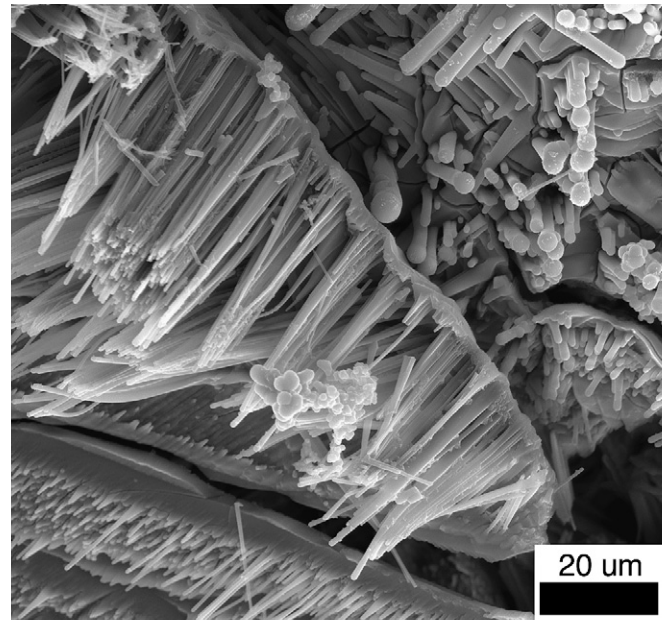

Fig. 2. SEM image of $CrPO_4 \cdot 6H_2O$ showing needles growing from a ~3 μm thick film.

the film and slowly lifting the film from the solution surface. The material was washed twice with deionized water and ethanol, and then dried in vacuo. Found: Cr, 19.6%, P, 5.9%, calc.: Cr, 20.4%, P, 6.1%.

3. Results and discussion

The kinetically controlled, vapor diffusion method introduces a gaseous catalyst into a static solution (preferably isolated from vibration) of one or more molecular precursors of the desired material; the resulting hydrolysis and polycondensation form an insoluble product, typically at the air/solution interface. This interface is used as a template to produce a flat film, suspended by surface tension. This method employs mild conditions of low temperature, mild pH changes and aqueous solutions with no organic additives. Under the conditions described above, the chromium phosphate material grows as a violet film on the surface of a mixture of chromium (III) nitrate and dibasic ammonium phosphate solutions when ammonia vapor is allowed to diffuse into the solution at the appropriate rate. The ammonia gradient establishes a reaction zone close to the surface, promoting the growth of films covering large areas (>90 cm^2). Once collected from the solution, washed and dried, powder X-ray diffraction of the purple material shows sharp peaks corresponding to the database pattern [8] for $CrPO_4 \cdot 6H_2O$ (Fig. 1). Nitrogen gas porosimetry measurements of chromium phosphate film using the Brunauer–Emmett–Teller (BET) method reveal a surface area of 7.1 m^2/g, consistent with a highly textured surface.

Scanning Electron Microscopy (SEM) of the films reveals that the chromium phosphate films exhibit a smooth upper surface and a nanoscale textured lower surface (Fig. 2). The

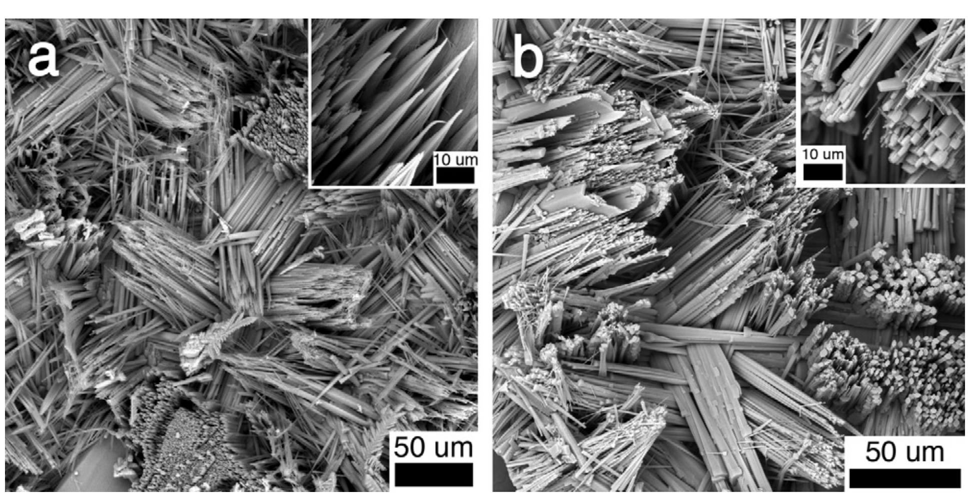

Fig. 3. (a) SEM image of an area of $CrPO_4 \cdot 6H_2O$ needles predominantly tipped with a faceted crystal. Patches of needles tend to orient in a similar direction. Patches are irregularly shaped and approximately 30–100 μm in diameter. (Inset: detail of crystal tips.) (b) SEM image of an area of $CrPO_4 \cdot 6H_2O$ needles predominantly tapered at the tip. (Inset: detail of tapered tips).

chromium phosphate film exhibits spikes or needles projecting from the lower surface of the flat film. Surface tension of the solution templates the smooth upper surface, with the needle-like formations of $CrPO_4 \cdot 6H_2O$ growing down into the reaction solution (Fig. 2).

Approximately half of the needles exhibit a distinct, faceted crystal (1–2 μm in diameter) at the distal end, resembling a match head (Fig. 3a, inset), while the other half of the needles taper to a point (Fig. 3b, inset). The needles are approximately 30–50 μm long and 0.5–2 μm wide. The needles grow out from a continuous, thin (approx 3 μm thick) film of the same material at a variety of angles. Irregularly shaped clusters, roughly 30–100 μm in diameter, consist of needles exhibiting the same angle of growth with the same tip type. This indicates that the needles grow in an orientation influenced by their contact with the underside of the crystalline backplane.

4. Conclusion

The results reported here demonstrate that the vapor diffusion catalysis method can be used to grow thin films of chromium phosphate with nanoscale textured morphology in the absence of organic templating agents. Applications for high-surface area catalysis are envisioned.

Acknowledgments

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