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Communications

Controlled Aqueous Chemical Growth of Oriented Three-Dimensional Crystalline Nanorod Arrays: Application to Iron(III) Oxides

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The creation of ordered and aligned anisotropic nanoparticles in large arrays as well as the large-scale production of low-cost and clean nanomaterials are essential challenges scientists have to take up to unfold the full potential and great promises of nanotechnology. The outcome should contribute to the development of a new era of smart functional designed materials: the materials of the 21st century. So far, the production of anisotropic nanoparticles has been mostly achieved using chemical growth inhibitors (i.e., surfactant),¹ or confined volume (i.e., microemulsion),² and the ability to generate aligned and ordered nanocrystallites onto a substrate is typically reached by using masking/patterning techniques such as templating³ or lithography.⁴ We are reporting here on the inexpensive fabrication of large arrays of iron oxide (hematite, α -Fe₂O₃) and oxyhydroxide (akaganeite, β -FeOOH) with a uniquely designed architecture (i.e., monodisperse perpendicular

ly oriented single-crystalline nanorods) grown directly onto a polycrystalline (or single-crystalline) substrate, from an aqueous solution of ferric salts, without any template, neither membrane nor surfactant.

In its various allotropic forms, iron oxides represent an important basic material⁵ due to their large occurrence on Earth and Mars.⁶ They are extensively studied for catalysis^{7,8} and magnetic storage devices and are under scrutiny for the crucial industrial and environmental standpoint of corrosion.⁹ Because of their non-toxicity, low cost, and hue, they are also widely used as polishing materials and roof tiles and for colorants in the pigment and paint industry.¹⁰ Their thermodynamically stable crystallographic phase is hematite (α -Fe₂O₃), which represents the most important ore of iron considering its high iron content and its natural abundance. Therefore, designing novel iron oxides materials is of great significant fundamental importance in basic physical, earth, and life sciences and of relevance for various fields of industrial applications.

Our strategy is the experimental outcome of a novel general theoretical concept¹¹ called "purpose-built materials", well-sustained by a thermodynamic model of monitoring of the nucleation, growth, and aging processes.¹² The goal of such a concept is to design novel

(5) Cornell, R. M.; Schwertmann, U. *The Iron Oxides*; VCH: New York, 1996.

(6) Morris, R. V.; Golden, D. C.; Shelter, T. D.; Lauer, H. V., Jr. *Meteorit. Planet. Sci.* **1998**, *33* (4), 743–751.

(7) Pestman, R.; Koster, R. M.; Boellaard, E.; Van der Kraan, A. M.; Ponc, V. J. *Catal.* **1998**, *174*, 142–152.

(8) Lin, S.-S.; Gurol, M. D. *Environ. Sci. Technol.* **1998**, *32*, 1417–1423.

(9) Oh, S. E.; Cook, D. C.; Townsend, H. E. *Corrosion Sci.* **1999**, *41*, 1687–1702.

(10) Morse, P. G. *Chem. Eng. News* **1998**, *76* (41), 42–62.

(11) Vayssieres, L.; Hagfeldt, A.; Lindquist, S.-E. *Pure Appl. Chem.* **2000**, *72* (1–2), 47–52.

(12) Vayssieres, L. Ph.D. Thesis, Université Pierre et Marie Curie Paris, 1995.

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(1) Peng, X. et al. *Nature* **2000**, *404*, 59–61.

(2) Zarur, A. J.; Ying, J. Y. *Nature* **2000**, *403*, 65–67.

(3) Martin, C. R. *Chem. Mater.* **1996**, *8*, 1739–1746.

(4) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823–1848.

metal oxide nanomaterials from molecular precursors with the proper morphology, texture, and orientation to probe, tune, and optimize their physical properties. The main idea is to monitor the thermodynamics and kinetics of nucleation and growth of the system by controlling experimentally the interfacial tension (surface free energy). Such control allows one to obtain, for instance, the ability to separate the nucleation and the growth stage, which yields to the generation of monodisperse nanoparticles with narrow size distribution and has been well-illustrated¹³ on the nanoparticle size control of magnetite (Fe_3O_4) by performing the aqueous precipitation far from the typical point of zero charge (PZC) of the metal oxide. According to the acid–base surface properties of metal oxides, decreasing (or increasing) the pH of precipitation from the PZC increases the surface charge density by adsorption (or desorption) of protons and consequently reduces the interfacial tension of the system. In addition, a high ionic strength will increase the surface charge density by screening the electrostatic repulsion at the interface, allowing more surface sites to charge up, which contributes to further lowering of the interfacial tension of the system. Thermodynamic colloidal stability^{12,13} may thus be reached, resulting in a considerable lowering of the ripening processes, henceforth avoiding ripening and the phase (and eventual morphological) transformation. For instance, the phase transition of akaganeite to hematite is accompanied by a morphological change from rodlike particles to spheroid ones.¹⁴ Crystallographic phase transformation in solution usually operates through a dissolution–recrystallization process to minimize the surface energy of the system. Indeed, when a solid offers several allotropic phases, it is generally the one with the lowest stability and the highest solubility (i.e., the crystallographic metastable phase), which precipitates first and is understood by considering the nucleation kinetics of the solid.¹⁵ At a given supersaturation ratio, the germ size is as small and the nucleation speed as fast as the interfacial tension of the system is low. Thus, because the solubility is inversely proportional to the interfacial tension, the precipitation of the most soluble phases and consequently the less stable thermodynamically is therefore kinetically promoted (Ostwald step rule). Indeed, because of its solubility and metastability, this particular phase is more sensitive to ripening, which leads to more stable crystallographic phases, essentially by heteronucleation. Usually, the growth and aging processes are delicate to control and the phase transformation appears within a few hours to a few days in solution, resulting in an undesired mixing of the various allotropic phases. However, lowering the interfacial tension will result in significantly stabilizing the metastable (akaganeite) phase, avoiding therefore the phase and morphological transformation. Accordingly, by lowering the pH of precipitation to a minimum value (i.e., where the hydrolysis–condensation is barely occurring), in a medium with high ionic strength, highly

charged anisotropic nanoparticles of akaganeite will be obtained.

The ability to grow and align anisotropic nanoparticles into large arrays on a substrate requires one to take into account the homogeneous and heterogeneous nucleation phenomena for developing a novel thin film processing technique using more conventional means such as solution chemistry. In most cases, homogeneous nucleation of solid phases (metal oxide in particular) requires a higher activation energy barrier and therefore heteronucleation will be promoted and energetically more favorable. Indeed, the interfacial energy between the crystal and the substrate is smaller than the interfacial energy between the crystal and the solution, and therefore nucleation may take place at a lower saturation ratio onto a substrate than in solution. Nuclei will appear on the entire substrate and if their rate is controlled and maintained limited by the precipitation conditions, epitaxial crystal growth will take place from these nuclei, along the easy direction of crystallization, and if the concentration of precursors is high, a condensed phase of single-crystalline nanorods perpendicular to the substrate will be generated. Growing thin films directly from a substrate does considerably improve the adherence and the mechanical stability of the thin film compared to standard solution and colloidal deposition techniques such as spin coating, dip coating, screen printing, or doctor blading.

Accordingly, to grow large arrays of monodisperse-oriented ferric oxide nanorods on a substrate, all one needs is a high concentration of precursors, a low pH, and a high ionic strength (of noncomplexing ions). Therefore, the experiment was performed with reagent-grade chemicals in an aqueous solution (MilliQ, 18.2 M Ω) containing 0.15 M of ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and 1 M of sodium nitrate (NaNO_3) at pH 1.5 (set by HCl) in a regular stopped flask containing, so far, a polycrystalline tin oxide glass substrate (e.g., Libbey Owens Ford) or a single-crystalline Al_2O_3 substrate (sapphire) and heated in a regular oven at 100 °C for up to 24 h. Subsequently, the durable and scratch-resistant thin films are thoroughly washed with water to remove any residual salts. According to XRD, the pure akaganeite phase is obtained first, and an additional heat treatment in air at $T \geq 390$ °C (according to DSC analysis) for an hour is required to obtain the pure thermodynamically stable crystallographic phase of ferric oxide (i.e., hematite) skillfully designed with the required nanorod morphology. Well-aligned single-crystalline nanorods of typically 5 nm in diameter (Figure 1), self-assembled as a bundle of about 50 nm in diameter, are grown in fairly perpendicular fashion onto the substrate and arranged in very large uniform arrays (Figure 2).

Indeed, several tens of cm^2 arrays (and potentially much larger with larger substrates and containers) are easily produced. The length of the nanorods, which essentially represents the thickness of a homogeneous monolayer of the thin film, may be experimentally tailored to any required dimension of up to about 1 μm by varying the time or temperature of aging in solution (i.e., nanorods of 100 nm in length are produced after 1 h at 100 °C). The aspect ratio is 1:20 for the nanorod bundle and 10:200 for the individual nanorods, respec-

(13) Vayssieres, L.; Chaneac, C.; Tronc, E.; Jolivet, J.-P. *J. Colloid Interface Sci.* **1998**, *205* (2), 205–212.

(14) Morales, M. P.; Gonzales-Carreno, T.; Serna, C. J. *J. Mater. Res.* **1992**, *7* (9), 2538–2545.

(15) Nielsen, A. E. *Kinetics of Precipitation*; Pergamon Press: Oxford, 1964.



Figure 1. TEM micrograph of hematite nanorods, self-assembled as a bundle.

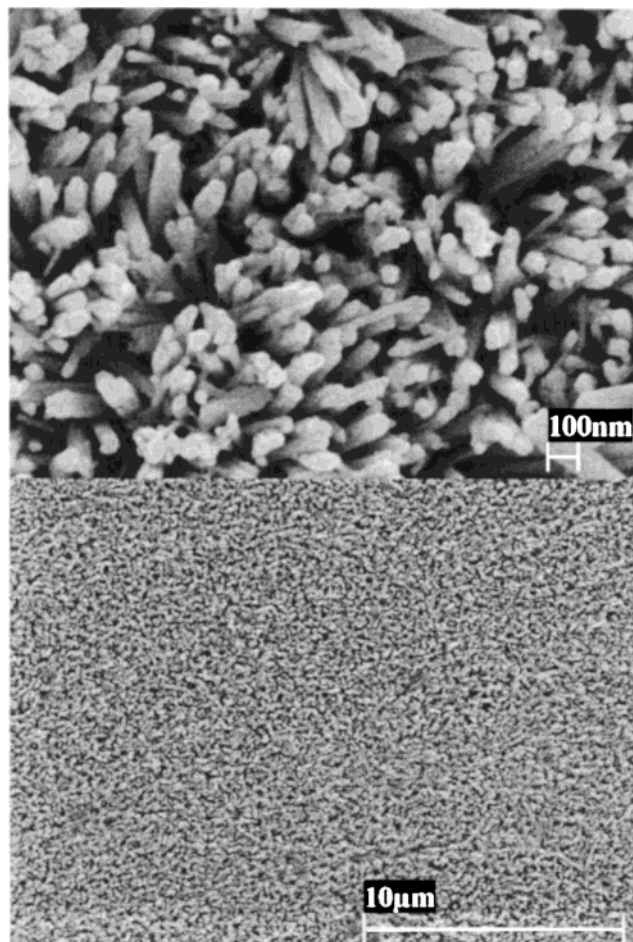


Figure 2. FEG-SEM micrographs of oriented self-assembled bundles of hematite nanorods grown onto a tin oxide glass substrate.

tively. Chemical and surface analysis (ESCA, EDX) indicates that the material is clean and that no sodium,

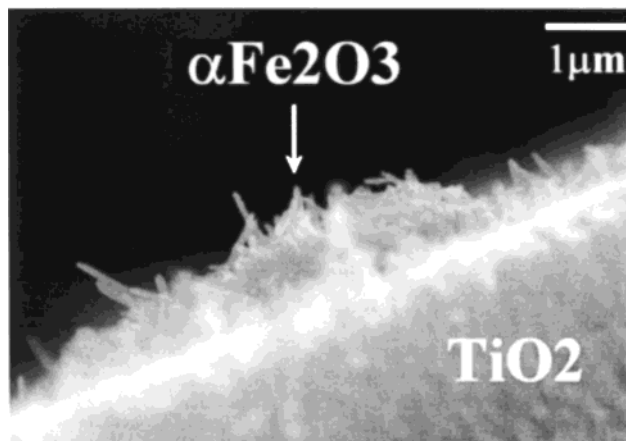


Figure 3. SEM cross-section micrograph of a thin film of oriented self-assembled bundles of hematite nanorods chemically grown onto TiO_2 mesoporous thin film (deposited on a glass substrate).

neither nitrate, nor chloride contamination is detected, which represents a great improvement compared to surfactant- or membrane-based synthesis.

This method combines the high degree of control and flexibility of solution chemistry and the simplicity, low toxicity, and low cost of aqueous precursors to the thin solid film processing technology. Upscaling is potentially easily feasible, and this simple synthetic method is theoretically applicable to all water-soluble metal ions likely to precipitate in solution. Another advantage is to allow the fabrication of multilayer thin films for instance of various thicknesses, morphologies, and/or various chemical compositions (e.g., multi-band gap (Figure 3) or doped thin films). The complete thin film architecture may thus be designed and monitored on various types of substrates to match the function of its application, which should improve, in most cases, the physical and chemical properties of the materials as well as create novel and/or improved devices. In addition, the use of metal salts precursors and aqueous solution are great advantages. Besides the obvious environment-friendly aspect, the purity of the material is substantially improved because no organic compounds or solvents are used.

The optical, electronic, and magnetic properties of the oriented hematite nanorod arrays and related devices are currently under investigation. This simple, and potentially universal, concept and synthetic thin film processing method are currently pursued for the creation of a new generation of smart thin film materials on various substrates. It offers great technological, economical, and environmental advantages and is a significant achievement for the development of novel materials.

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