

2-D Mesoparticulate Arrays of α -Cr₂O₃

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An inexpensive low-temperature aqueous thin film processing technique is presented for the fabrication of large two-dimensional (2-D) arrays of α -Cr₂O₃ without template, surfactant, or applied external field. The arrays consist of well-defined, monodispersed, and noninteracting crystalline spherical mesoparticles (250 nm) that are grown directly onto single crystalline silicon wafers (Si or SiO₂) or polycrystalline transparent conducting oxide (TCO) substrates by heteronucleation. Their UV–visible optical absorption properties are consistent with the electronic transitions of Cr³⁺ ions in *D*_{3d} symmetry but significantly blue-shifted compared to single crystal or polydispersed α -Cr₂O₃ samples. Such arrays could be of interest for theoretical and experimental studies of the unique nonreciprocal optical effects observed in α -Cr₂O₃.

Trivalent chromium oxides are widely studied for a variety of catalytic applications^{1–3} and are commonly used as a green pigment and as coatings to overcome industrial problems of microalloying of reactive elements because of its water repellent⁴ and refractory properties.⁵ Furthermore, its high hardness, low friction coefficient, and wear resistance⁶ properties make it an attractive candidate for tribological applications.⁷ More striking is the spontaneous nonreciprocal reflection of light that was predicted several decades ago⁸ but first observed⁹ in 1993 on α -Cr₂O₃ although numerous attempts were made to detect such time-parity violation effects in high-*T*_c superconductors. Consequently, a better fundamental understanding of its electronic structure and unique nonreciprocal optical properties^{10,11} is crucial to validate recent theories^{12,13} of optical effects in antiferromagnetic materials. In addition, such knowledge may contribute to develop better magnetoelectric and magneto-optic devices and to optimize the efficiency of solar thermal collectors¹⁴ and tunnel junction barriers.¹⁵ To achieve such goals, high quality particulate thin films and three-dimensional arrays consisting of stoichiometric, nonaggregated (antiferro) meso/microparticles with well-defined surface morphology and narrow size distribution rather than (superpara) nanoparticles are required.

The current synthetic processing techniques to generate thin films of the thermodynamically stable phase of Cr(III) oxide, i.e., the sesquioxide α -Cr₂O₃, include electrodeposition,¹⁶ magnetron sputtering,¹⁷ UHV thermal oxidation,¹⁸ MOCVD,¹⁹ and laser irradiation.²⁰ However, the generation of monolayer arrays consisting of monodispersed and nonaggregated spherical particles onto various substrates is not achievable with such techniques. Our strategy to control the shape and the orientation of crystallites involves an inexpensive chemical processing in which particulate thin films are directly grown onto the substrates from molecular to nano/microscales at low temperatures. The process involves the hydrolysis–condensation of aqueous metal salt precursors in solution and a monitoring of the thermodynamics and kinetics of heteronucleation and growth by controlling experimentally the interfacial tension. This novel approach has been pursued for the design of metal oxide thin film materials with controlled crystallite size, shape, and

orientation as well as overall thin film texture to probe, tune, and optimize their physical properties.^{21–25}

The achievement of a monolayer array of monodispersed spherical mesoparticles of α -Cr₂O₃ requires a very slow growth process from solutions of low supersaturation. Therefore, the synthesis consisted of the slow deprotonation (forced hydrolysis) of the *blue-violet* hexaaqua chromium(III) ions, [Cr(H₂O)₆]³⁺, the condensation of its neutral complexes, most probably [Cr(OH)₃(H₂O)₃]⁰ and [Cr₂(OH)₆(H₂O)₄]⁰, the growth of its *blue-grey* hydrated oxide by heteronucleation onto the substrates at mild temperatures, and finally the annealing to its thermodynamically stable *green* sesquioxide corundum phase, α -Cr₂O₃ (Figure 1). Typically, a regular screw-capped bottle containing substrates such as single crystalline Si or SiO₂ wafers and/or polycrystalline F–SnO₂ glass (e.g., Hartford Glass Inc.) and 1 mM aqueous solution (MilliQ, 18.2 M Ω cm) of KCr(SO₄)₂·12 H₂O was placed in a regular laboratory oven and heated at 75 °C for 36 h. The mesoparticulate thin films were thoroughly washed with (milliQ) water to remove any residual salts. Subsequently, the thin films were heat treated in air at 500 °C, based on thermal analysis data, for 1 h to obtain the stoichiometric and thermodynamically stable corundum phase of chromium sesquioxide, eskolaite (α -Cr₂O₃). Good adhesion of the mesoparticulate array was observed onto the substrates.

Figure 2 shows the scanning electron micrographs of the thin films grown onto Si wafers. A monolayer of well-defined, monodispersed and nonaggregated spherical particles of α -Cr₂O₃ of typically 250 nm in diameter is observed onto the substrates. The inset of Figure 2 clearly illustrates that the crystallites are not in contact with each other. The index of polydispersity, the ratio of the statistical variance over the average diameter of the particles, is 0.11, which indicates a very narrow particle size distribution and a good monodispersity. The particles are randomly and homogeneously distributed in very large arrays, ca. 20 cm². With larger substrate area, the technique could be used to obtain such arrays onto much larger areas. The film thickness is ~250 nm as determined by profilometry, which represents a single layer onto the substrate as observed by electron microscopy. Elemental analysis by energy dispersive spectroscopy performed at 30 kV under the SEM reveals the presence of only chromium and oxygen with atomic contents

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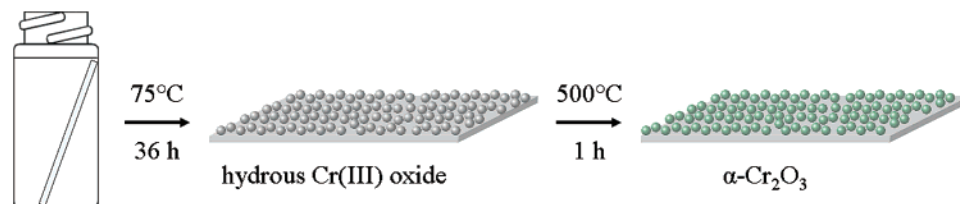


Figure 1. Scheme of the fabrication of large monolayer arrays of α -Cr₂O₃ onto various substrates by aqueous chemical growth.

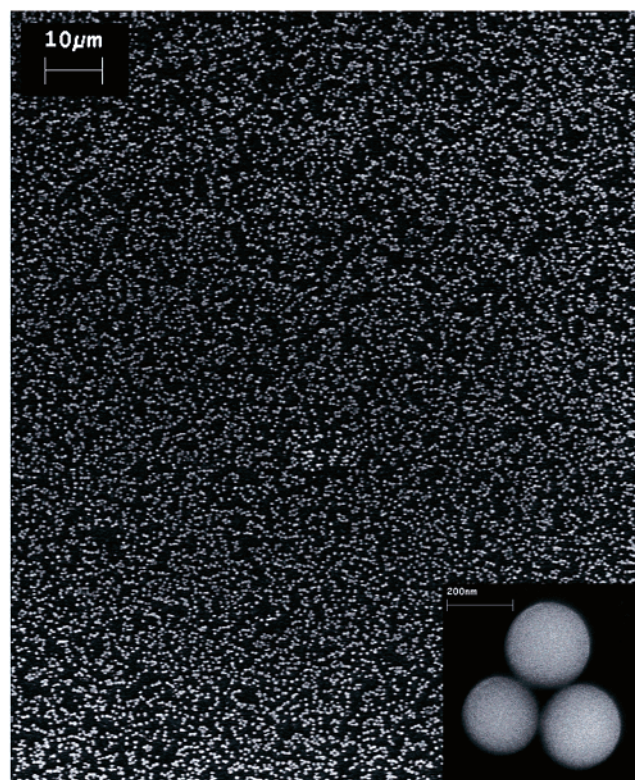


Figure 2. Scanning electron micrographs of a monolayer array of monodispersed α -Cr₂O₃ mesoparticles grown onto a Si wafer.

consistent with the Cr₂O₃ chemical formula, along with silicon from the substrate, confirming the good chemical purity of such arrays.

According to electron and X-ray diffractions, eskolaite (corundum, JCPDS 38-1479) was the only crystallographic phase detected and it showed high crystallinity (Figure 3). After statistical refinement²⁶ by minimization of the sum of squares of residuals in 2-theta of the 11 diffraction peaks, the unit cell parameters were calculated to be $a = 4.959 \pm 0.007$ and $c = 13.538 \pm 0.043$ Å, which are in excellent agreement with that reported for bulk α -Cr₂O₃. It crystallizes in the trigonal-hexagonal scalenohedral crystal system, space group R3c, and is isostructural with α -Al₂O₃ (corundum), α -Fe₂O₃ (hematite), and V₂O₃ (karelianite). It occurs in nature as the mineral eskolaite which was discovered in the late fifties²⁷ and named after the Finnish scientist P. Eskola. The lattice is built on a hexagonal close packed (HCP) array of oxygen in which four out of every six available octahedral sites are occupied by Cr. The octahedral and tetrahedral sites are located directly above one another in the HCP lattice and the tetrahedral sites are empty. The octahedra share faces along a 3-fold axis and are distorted to trigonal antiprisms because of the Cr–Cr repulsion across the shared face (inset Figure 3). This atomic arrangement gives the Cr³⁺ ions the centrosymmetric D_{3d} point group symmetry and leads to a highly dense structure offering high polarizability, high refractive index, and intense color. With their

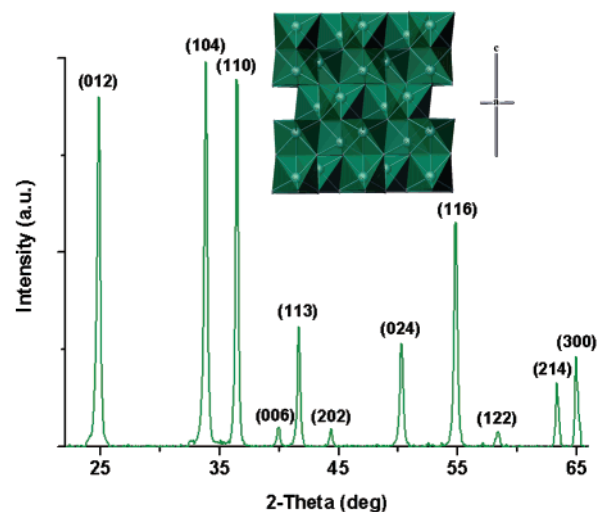


Figure 3. Indexed (background-subtracted) XRD pattern (CuK α) of α -Cr₂O₃ (JCPDS 38-1479) array grown onto a Si wafer. The inset shows the crystal structure of α -Cr₂O₃.

3d³ electronic configuration, the chromium ions experience a strong crystal field stabilization energy. The atomic structure and electronic configuration confer to this sesquioxide a unique combination of electronic, optical, and magnetic properties. Its electronic structure is of particular interest because of the simultaneous characteristics of a charge-transfer insulator (band gap 4.7–5 eV) and a Mott–Hubbard regime due to the location of Cr ions in the middle of the first-row transition series.²⁸ α -Cr₂O₃ shows antiferromagnetic ordering below $T_N \sim 307$ K with no net magnetic moment and consequently, magnetoelectric effect,²⁹ that is electrically polarized by magnetic fields and magnetized in electric fields. The optical properties of Cr³⁺ ions (3d³) in α -Cr₂O₃ originate from d–d electronic transitions between the splitted lower triply degenerated t_{2g} levels and the upper doubly degenerated e_g levels of the 5-fold degenerated 3d orbitals of the chromium ions in the centrosymmetric D_{3d} point group. The free ion LS terms in D_{3d} symmetry are ⁴F, ²G, and ⁴P. The ground state is ⁴F, which splits into ⁴A₂, ⁴T₂, and ⁴T₁. The excited state is ²G and splits into ²E, ²T₁, ²T₂, and ²A₁. The optical transitions originate from the *strong* spin-allowed but parity-forbidden ⁴A_{2g} → ⁴T_{2g} and ⁴A_{2g} → ⁴T_{1g} transitions as well as from the *weak* spin and parity-forbidden transitions ⁴A_{2g} → ²E_{2g}, and ⁴A_{2g} → ²T_{1g}.³⁰ The bandwidths of such transitions are usually large because of the strong electronic coupling to vibrations of the local environment as well as the stoichiometry, size, surface morphology, and monodispersity of the samples. The most striking feature of spin magnetoelectric α -Cr₂O₃ is the spontaneous nonreciprocal optical effects such as gyrotropic birefringence and respective dichroisms where both, time and parity symmetry, are broken; this was theoretically predicted decades ago but only discovered recently in α -Cr₂O₃. In addition, strong second harmonic generation signal³¹ originating from the ⁴A_{2g} → ⁴T_{2g} transition of Cr³⁺ ions in α -Cr₂O₃ due to the two-photon excitation of ⁴T_{2g} levels below

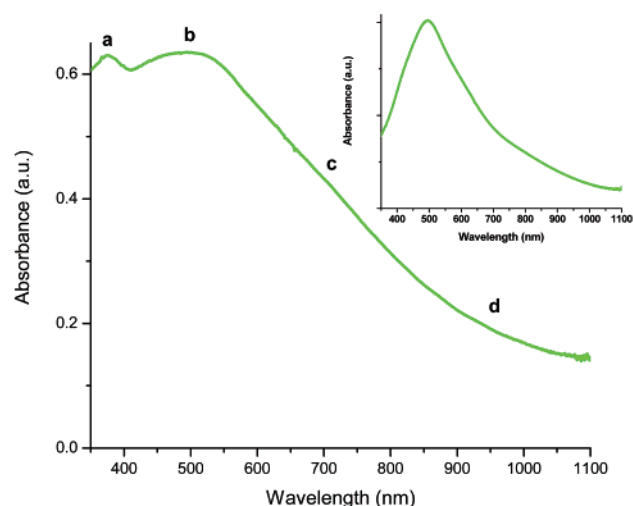


Figure 4. UV-visible absorption spectrum of a monolayer array of monodispersed α - Cr_2O_3 mesoparticles grown onto a transparent F-SnO₂ substrate. The contribution from the substrate has been subtracted. The inset shows the absorption spectrum of the as-prepared hydrous chromium(III) oxide monolayer (prior to annealing).

T_N ³² is observed and used to image the antiferromagnetic domains and determining magnetic symmetry.

The optical properties of a monolayer of noninteracting, spherical mesoparticles of narrow distribution of α - Cr_2O_3 grown onto transparent substrate (TCO) have been characterized by UV-visible spectroscopy in air on dry thin films on a HP 8453 spectrophotometer. Figure 4 shows the absorption spectrum of the α - Cr_2O_3 array after subtraction of the substrate contribution. Well-defined and well-resolved absorption peaks centered at 375 (a) and 495 nm (b) are observed, and they originate from the $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}$ and $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}$ electronic transitions, respectively. Such transitions appear significantly blue-shifted compared to the reported values in the literature.³³ Simple nonlinear statistical multipeak fitting leads to broad shoulders centered at 700 nm (c), attributed to the $^4\text{A}_{2g} \rightarrow ^2\text{T}_{1g}$, $^2\text{E}_{2g}$ electronic transitions, and at 950 nm (d), which extends into the near-IR region, that are characteristic of Cr^{3+} ions in distorted octahedral environment. The inset of Figure 4 shows the UV-visible spectrum of the as-prepared hydrous chromium(III) oxide monolayer array. A strong absorption feature is observed at 500 nm, most probably originating from the $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}$ transition of chromium ions in octahedral symmetry. The spectrum extends significantly in the visible and near-IR regions. Further studies of its structural and electronic properties are currently in progress.

Because of the synthesis process, narrow size distribution, and well-defined nonaggregated particles arranged as a monolayer, the main absorption features appear well-resolved and blue-shifted, offering a great opportunity for the in-depth study of the strong resonant second harmonic generation signal. Such designed materials may also have potential impact as model systems in the fundamental understanding and modeling of antiferromagnetic ordering by light³⁴ and in particular, for experimental studies of nonreciprocity in reflection and transmission of light in α - Cr_2O_3 ,³⁵ and large third-order optical nonlinearities of transition metal oxides.³⁶ In addition, such a very large monolayer array could be of great interest for

heterogeneous catalysis as well-defined catalysts, and support for catalysts as well as for probing and demonstrating the relationships between magnetic state, surface morphology, crystal structure, and catalytic activity.³⁷

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