

# Hematite nanostructuring using electrohydrodynamic lithography



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## ABSTRACT

Tailoring hematite thin film nanostructure is particularly interesting since this oxide's function is closely related to its structure, for example when implemented as a photoanode in water splitting solar cells. In this study, electrohydrodynamic destabilization was designed to grow hematite nanodroplets with morphologies controlled by a master electrode. A polymer/iron salt film was destabilized by electrohydrodynamic destabilization and the resulting structures were pyrolysed to achieve crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanodroplets of 30 nm height and 70 nm radius. NEXAFS spectroscopy proved that the structures contain ferrihydrite, which is converted into hematite during pyrolysis, while the polymer was decomposed. Homogeneous nanoparticle precipitation in the bulk of the polymer, due to encapsulation of the iron precursor in the polymer matrix, is accounted for the good preservation of the structures. This study represents the first step towards the use of electrohydrodynamic destabilization for nanostructuring of hematite thin films, with a control over the feature size.

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## 1. Introduction

Metal oxide thin films based on nanopillar array have been suggested as efficient photoanode systems for solar water splitting and hydrogen fuel generation in photo-electrochemical cells [1]. Iron oxides such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) are low-cost, environmentally benign and abundant semiconductors for use as such photoanodes. But hematite has the major disadvantage that its optical thickness is large (118 nm at  $\lambda = 550$  nm) [2] compared to its charge carrier recombination length (2–4 nm) [3]. To overcome this drawback, various approaches for micro- or nano-structuring of iron oxide into nanopillar, nanorod and nanotube arrays, for example by aqueous chemical growth [4] or anodization [5,6] have been investigated.

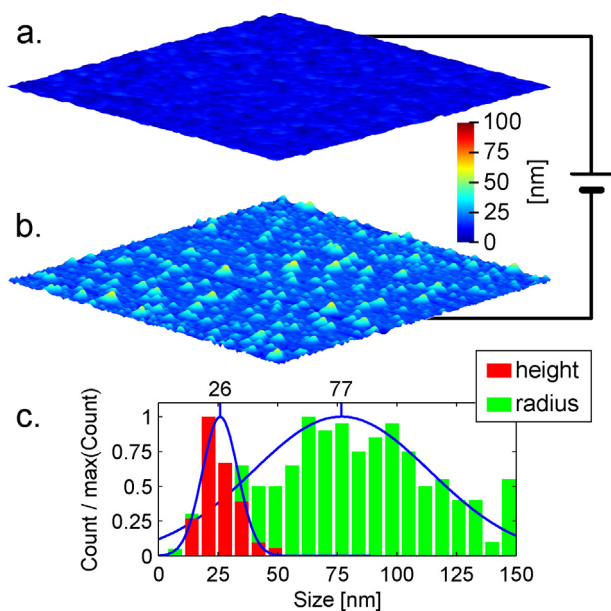
Here we present a novel and simple method of obtaining iron oxide structures, taking advantage of the self-organization occurring in molten polymers subjected to an external electric field. This phenomenon is known as electrohydrodynamic destabilization (EHD) and has been previously used to tailor micrometric droplets or pillar arrays [7,8]. The polymer structures obtained by Heier et al. [9], with spatially modulated electric fields, show

that the sizes and aspect ratios obtained can be controlled using parameters such as the electric field strength and the lateral field modulation. The control provided by such heterogeneous electric fields has been exploited by Schaffer et al. [10] to achieve features with lateral dimensions down to 140 nm using a structured electrode. Moreover this electrolithographic phenomenon is a determining factor in the upscaling of the destabilized region [11]. The use of this technique to oxide films has been initiated by Voicu et al. [12]. They destabilized titanium alkoxide-alcohol solutions and obtained micrometric TiO<sub>2</sub> patterns. To the best of our knowledge no other attempt has been made to use EHD to structure inorganic materials. Our study focuses on the development of electrohydrodynamic destabilization for the high-fidelity conversion of polymer/iron salt structures obtained by EHD destabilization into hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) structures. The strategy adopted is to encapsulate an iron salt in a polymer thin film and then tailor the polymer structure using EHD. After structuring, the film is pyrolysed at 500 °C in an air vented furnace to decompose the polymer matrix, whilst at the same time converting the iron to hematite.

## 2. Materials and methods

The thin film for destabilization was spin-coated from an aqueous solution on a silicon wafer. This solution was prepared by

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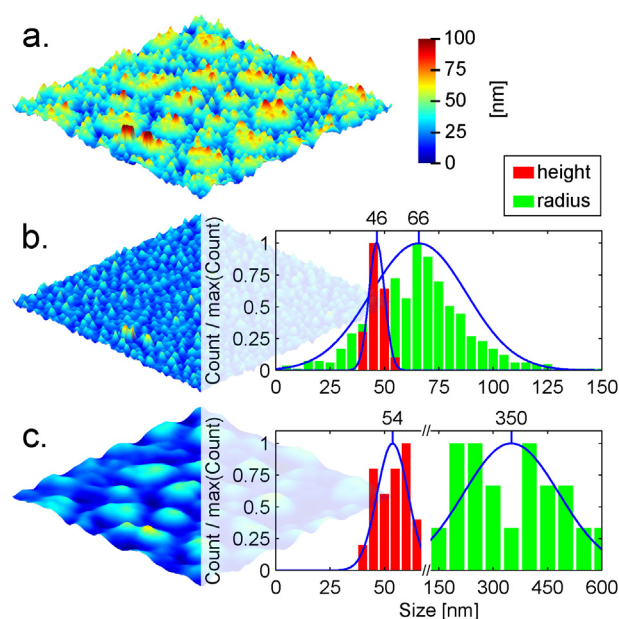


**Fig. 1.** The two adjacent electrodes used for thin film destabilization.  $5 \times 5 \mu\text{m}$  AFM scan of: (a) P4VP/FeCl<sub>3</sub> thin film surface before destabilization, (b) nanostructured aluminium thin film as obtained by evaporation (master electrode), and (c) size distribution of the master electrode features.

mixing 0.5 M in pyridyl groups of poly(4-vinylpyridine) (P4VP) ( $M_w \approx 60,000$ , Sigma–Aldrich) and 0.5 M of FeCl<sub>3</sub> (reagent grade, 97% anhydrous, Sigma–Aldrich) in double deionized water, leading to a 1:1 molar ratio between pyridyl groups and aqueous iron chloride. The resulting aqueous solution is acidic with a pH of 1.5. The spin coating was realized using a Primus STT15 spin-coater from ATMvision AG, with a holding time of 60 s at a spinning speed of 6000 rpm which was reached within 2 s. After spin-coating, the thin film was air-dried at room temperature for at least 2 days. The resulting film has a thickness of 180–200 nm (profilometer), and is flat with only nanometer scale roughness (Fig. 1a).

This film was then melted under an electric field, facing a nanostructured aluminium electrode (Fig. 1b and c). The nanostructured electrode acts as a master electrode and controls the size of the features developing at the surface of the polymer film. Since the present study is focused on controlling the size of the hematite structures, no attempts has been made to use a master electrode possessing an organized pattern as in the study of Voicu et al. [12]. The electrode nanostructure is obtained by evaporating aluminium in vacuum onto a silicon substrate. Aluminum evaporation pellets, 99.9996% pure, were thermally evaporated using a Univex 300 thermal evaporator from Oerlikon Leybold Vacuum. Arslan et al. [13] showed that vapor phase aluminium deposited on a silicon oxide surface followed with high fidelity the droplet deposition and coalescence model described by Family and Meakin [14] and obtained aluminium islands of nanometric dimensions after less than 2 min deposition. In the present study, the master electrode contains ten times larger droplets than the clusters obtained by Arslan. Since the droplet growth follows the Family and Meakin model, this difference is accounted for the longer deposition time (15–20 min), leading to more material coalescence and therefore larger features.

An air gap of less than 140–160 nm separated the polymer film surface and the master electrode. In order to maintain this submicrometric gap, SU8-2000 photoresist was spin coated, developed and etched on the master electrode surface to obtain a spacer. The wafers were then contacted and pressed together (see Supporting information – Details of the setup used for the



**Fig. 2.** (a)  $5 \times 5 \mu\text{m}$  AFM scan of the film surface after electrostatic destabilization (50 V), (b) high frequency features and their size distribution, and (c) low frequency features and their size distribution.

electrohydrodynamic destabilization). The entire assembly was placed in an oven for 3 h at 180 °C and 0.01 mbar vacuum with a bias of 50 V applied to the wafers. The heating temperature of 180 °C was chosen to melt the P4VP film, which has a glass transition temperature in the range 140–150 °C [15,16]. After heating, the assembly was cooled to room temperature while maintaining the 50 V bias. After destabilization the films were heated in an air vented furnace at 500 °C for 2 h, using a heating ramp of 5 °C min<sup>-1</sup>.

### 3. Results

The destabilization of the P4VP/FeCl<sub>3</sub> thin film results in the formation of two different kinds of features: oblate droplets with sub-micrometer size, and droplets with nanometer size (Fig. 2a). Using complementary Matlab and Fiji procedures (see Supporting Information/Matlab-Fiji code for image processing) the nanometric distribution has been mathematically separated from the submicrometric distribution by using a high pass filter (Figs. 2 and 3). The size distribution of the nanometric features (Fig. 2b) and of the master electrode (Fig. 1c) match quantitatively. Therefore, the nanometric droplets observed on the thin film surface most likely originate from heterogeneities in the electric field [9]. Where a feature of the master electrode is present the air gap is smaller, leading to a local enhancement of the electric field in the film. The electrostatically induced pressure is higher on the melted film surface in the regions facing a feature of the electrode, and the film surface replicates the electrode features. Since the mean height of the master electrode features is 26 nm and the air gap is in the 140–160 nm range, the increase in electrostatic pressure where a feature of the master electrode is present is in the range of 12–14%. In contrast, the sub-micrometric droplets originate from the average electric field. Indeed their order of magnitude matches the typical micrometer scale features obtained using homogeneous electric field for thin polymer film destabilization [7,8]. Although larger homogeneous electric field leads to smaller features, the minimum size that these features can reach is limited by viscous effects [17].

To convert this polymeric structure into an oxide, the film was pyrolysed at 500 °C in air. This thermal oxidative treatment allows precipitation and pyrolysis of iron oxide inside the film, whilst

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