# Tracking Morphology and Phase Transformations of Ordered Iron Oxide Nanostructures via X-ray Spectroscopy and Microscopy

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**Summary**
X-ray spectroscopic and microscopic techniques have been employed to investigate the morphology and phase transformations of highly ordered iron oxide nanotubes (NTs) synthesized by the anodization of an iron foil in a fluorine-containing electrolyte followed by thermal annealing. Scanning electron microcopy (SEM) results (Figure 1) show that the as-grown NTs annealed under 300 ℃ maintain the nanotubular structure, whereas instant morphology transformations to ordered nanoplates (NPs) and nanoflakes (NFs) are observed after annealing at 400 ℃ and 500 ℃, respectively, and a compact film with rough surface is obtained after annealing at 600 ℃. X-ray diffraction (XRD) analysis (Figure 2) suggests that NTs annealed under 300 ℃ sustain their amorphous structure, whereas a mixed phase of polycrystalline magnetite ($Fe_3O_4$) and single crystal-like hematite ($Fe_2O_3$) with preferential alignment along the [110] axis, is present within the NTs annealed at 400 ℃ and 500 ℃, and NTs annealed at 600 ℃ develop into a polycrystalline mixed-phase of magnetite and hematite. On the other hand, X-ray absorption near-edge structure (XANES) at the Fe $L_{3,2}$-edge, the O K-edge and the F K-edge (Figure 3), coupled with synchrotron-based X-ray photoemission spectroscopy (XPS, Figure 4), show that only crystalline hematite phase is present for the NTs annealed at 400 ℃, 500 ℃ and 600 ℃.

We have found that the inconsistency between XRD and XANES as well as XPS results is mainly due to the probing depth of the techniques. To confirm that, scanning transmission X-ray microscopy (STXM) analysis (Figure 5) at the Fe $L_{3,2}$-edge and the O K-edge has been used to take a closer look at an individual specimen of NPs and NFs. The results show that they are pure hematite, suggesting that NTs annealed at 400 ℃ and 500 ℃ are layered heterostructures, whereas NPs and NFs, with their single crystal-like hematite nanostructure are vertically aligned on the top surface region with the formation of polycrystalline magnetite thin film located between the top nanostructure and bottom iron foil. Furthermore, consistent evidence is found in SEM examination on cross-sections.
It is interesting to note that NTs annealed under 300 ℃ contain a significant amount of $F^-$ ions which are self-doped into the iron oxide lattice from anodization and occupy the substitutional O sites revealed by XANES (Figure 3d and Figure 4c). We have found that the inclusion of $F^-$ ions can interfere with the crystallization of iron oxide, resulting in the morphology transformation. A coupling interaction mechanism between self-doped fluorine and thermal crystallization is proposed. Hence, the fluorine incorporation can be used as a morphology tailoring tool for engineering efficient iron oxide nanostructures (with anisotropic conductivity) as promising energy materials, as in the case of $TiO_2$. This study establishes a benchmark in tracking the local effect of wide band gap metal oxide semiconductors induced by incorporated dopant via soft X-ray spectroscopy and microscopy.

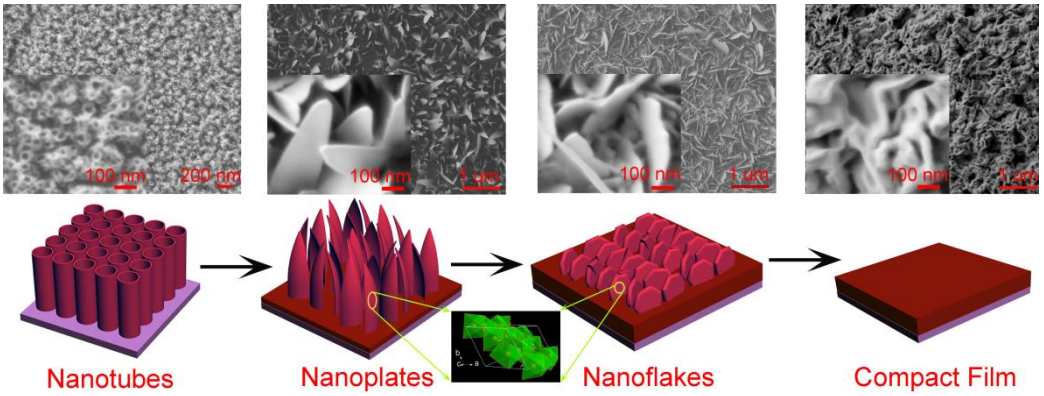


Figure 1: SEM images of various iron oxide nanostructures with their corresponding schematic views.

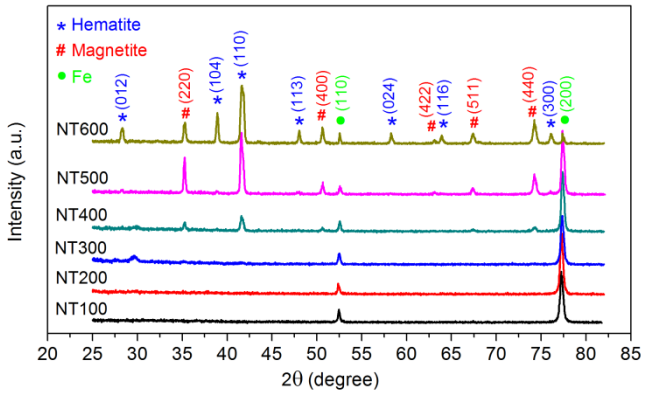


Figure 2: XRD patterns of anodic iron oxide NTs annealed from 100 ℃ to 600 ℃.

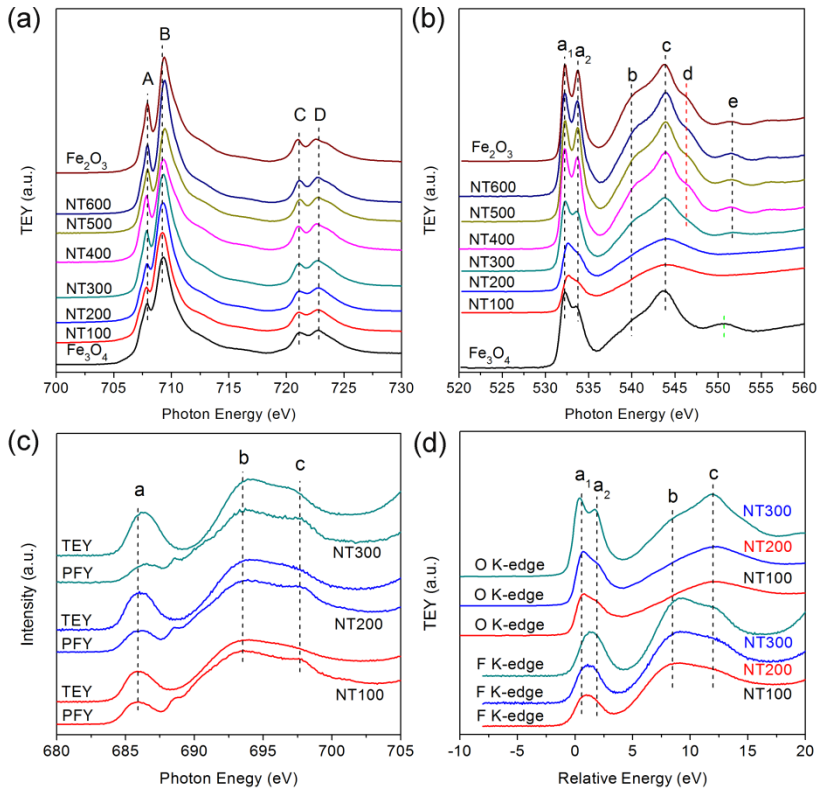

Figure 3: XANES at (a) Fe $L_{3,2}$-edge, (b) O K-edge, and (c) F K-edge of anodic iron oxide NTs annealed from 100 ℃ to 600 ℃. (d) Alignment of O K-edge and F K-edge relative to their absorption edge threshold (reflection point). Hematite ($Fe_2O_3$) and Magentite ($Fe_3O_4$) standards are included for comparison.

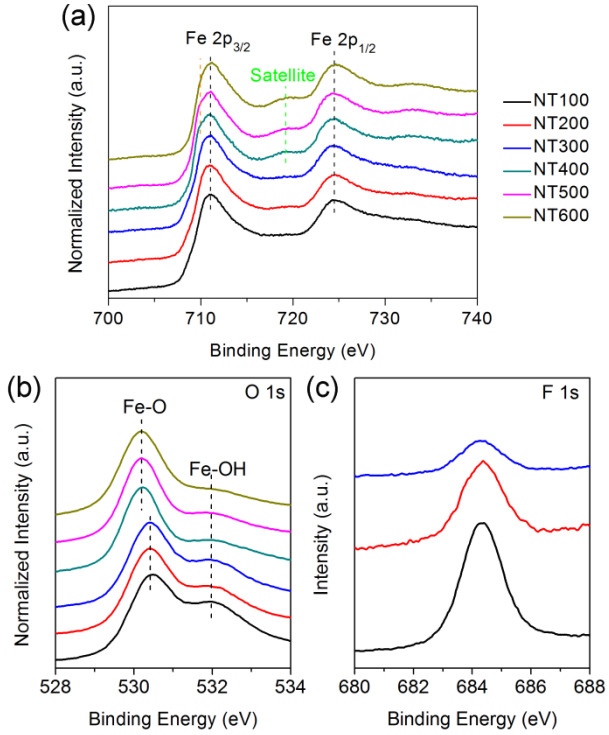


Figure 4: Synchrotron XPS results at (a) Fe 2p, (b) O 1s, and (c) F 1s of anodic iron oxide NTs annealed from 100 ℃ to 600 ℃. The absence of F 1s XPS in NT400, NT500 and NT600 is due to the total release of F. The excitation energy used for XPS measurements is 1200 eV.

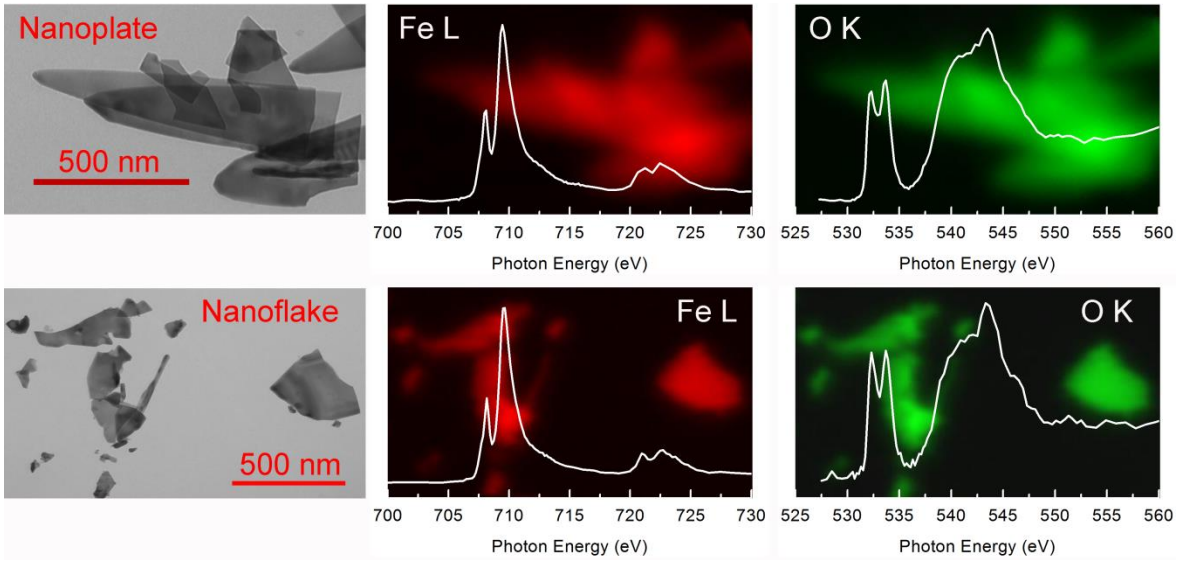


Figure 5: TEM views and the STXM mappings (Fe L-edge and O K-edge) together with the extracted XANES data from STXM analysis (insets of STXM images) at the same sample regions of interest of NPs (top panel) and NFs (bottom panel) obtained by annealing the as-grown NTs at 400 ℃ and 500 ℃, respectively.

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