In Situ Atomic-Scale Probing of the Reduction Dynamics of 2-Dimensional Fe₂O₃ Nanostructures

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Abstract

Atomic-scale structural dynamics and phase transformation pathways were probed, *in situ*, during the hydrogen-induced reduction of Fe₂O₃ nanostructure bi-crystals using an environmental transmission electron microscope. Reduction commenced with the α -Fe₂O₃ $\rightarrow \gamma$ -Fe₂O₃ phase transformation of one part of the bi-crystal, resulting in the formation of a two-phase structure of α -Fe₂O₃ and γ -Fe₂O₃. The progression of the phase transformation into the other half of the bi-crystalline Fe₂O₃ across the bi-crystalline boundary led to the formation of a single crystal phase of γ -Fe₂O₃ with concomitant oxygenvacancy ordering on every third {422} plane, followed by transformation into Fe₃O₄. Further reduction resulted in the coexistence of Fe₃O₄, FeO, and Fe *via* the transformation of a Swiss-cheese-like structure, induced by the significant volume shrinkage occurring upon reduction. These results elucidated the atomistic mechanism of the reduction of Fe oxides and demonstrated formation of hybrid structures of Fe oxides *via* tuning the phase transformation pathway.

Key words: α-Fe₂O₃, reduction, *in situ* TEM, phase transformation

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Metal oxides have many important functional properties, ranging from the catalytic activity of partially reduced cobalt oxide, to the magnetic data storage capacity of maghemite,¹ and the excellent energy capacity of lithium superoxide.² These functional properties can be tuned by adjusting stoichiometry, coordination, bonding, and phase of the oxide.³⁻⁵ However, there are significant challenges in controlling these compositional and structural features, particularly at the atomic scale. Controlled reduction of oxides could serve as a viable way to tune the morphology, phase, and atomic structure of oxides and to harness and optimize their functional properties. In order to realize this potential, a fundamental understanding of oxide reduction at the atomic scale is necessary. Unfortunately, this level of understanding is lacking for many oxides because of the difficulty in probing the fast local dynamics of the oxide reduction at the atomic scale using the traditional surface science and bulk materials science techniques. While iron oxides are common compounds that are widespread in nature and can be readily synthesized, understanding the atomistic mechanism of the reduction of iron oxides is even more challenging because of the complicated Fe-O phase diagram.⁶

Nanostructured α -Fe₂O₃ has been studied extensively due to its great potential for a wide range of applications including catalysis,⁷⁻⁹ water splitting,¹⁰⁻¹² gas sensing,^{13, 14} and drug delivery.^{15, 16} Various forms of nanostructured α -Fe₂O₃ have been synthesized,¹⁷⁻¹⁹ such as nanowires,²⁰⁻²³ nanobelts,²⁴ nanotubes,²⁵ nanorods²⁶ and nanoblades.²⁴ There are multiple ways to prepare nanostructured α -Fe₂O₃, such as thermal oxidation,^{20, 27, 28} chemical vapor deposition (CVD),^{29, 30} and laser ablation.³¹ Thermal oxidation of Fe is an efficient and cost-effective method of synthesizing high-quality α -Fe₂O₃ nanostructures at large-scale.^{23, 27, 32-35} Pretreatment of Fe foils by sandblasting can be used to form desired morphologies of nanowires or nanoblades.^{24, 35} In particular, the surface roughness of Fe substrates can be altered to favor the formation of α -Fe₂O₃ nanoblades with a bi-crystal structure.³⁶

Grain boundaries have been found to influence the mechanical and electronic properties of the crystals.³⁷ Several types of boundaries such as twin and coincidence-site-lattice boundaries (CSL boundaries or Σ boundaries) are an integral part of bi-crystals. Two crystalline grains with a specific

combination of misorientation axis and angle result in CSL boundaries. The degree of coincidence is represented by the reciprocal density of common lattice points, denoted as the \sum number.³⁸ Here we focus on the CSL boundaries with respect to their effect on the reduction behavior of the metal oxides. The α -Fe₂O₃ nanoblades formed from the thermal oxidation of Fe have their two-dimensional (2D) bi-crystal boundary parallel to the extended surface. The large grain boundary area associated with the nanoblade morphology makes it an ideal system to study the grain boundary effect on the reduction of metal oxides. As the large surface area is a key factor for catalysis, these α -Fe₂O₃ nanosheets may hold a great promise in heterogeneous catalysis either as a catalyst or a catalyst support. We have chosen to study the reduction of these nanosheets in order to probe both the surface stability and the phase transformations that occur in a reducing environment.³⁹ These conditions are typical of a number of catalytic gas-surface reactions such as methanol oxidation^{40, 41} and the water-gas-shift reaction⁴²⁻⁴⁴ for which H₂ is involved either as a reactant or a reaction product. By observing the microstructural evolution during reduction processes, especially at the atomic scale, we can establish an in-depth understanding of the material behavior in practical applications, and optimize the material properties.

Here, we present our observations of the *in situ* reduction process for the α -Fe₂O₃ nanoblades using an environmental transmission electron microscope (ETEM). Focusing on individual nanoblades, we examined the evolution of morphology and atomic structure of α -Fe₂O₃ nanoblades during reduction. We monitored the reduction process in time-resolved manner by heating α -Fe₂O₃ nanoblades in a H₂ gas flow, interpreted the *in situ* HRTEM videos frame by frame, and thereby elucidated the atomic processes underlying the morphology and phase evolution of these 2D bi-crystal nanostructures.

RESULTS AND DISCUSSION

Fig. 1 shows SEM images of the as-prepared α -Fe₂O₃ nanoblades and the samples after H₂induced reduction to different extents. The morphology of as-prepared nanoblades displays flower-like patterns, with smooth-edged nanoblades perpendicular to the substrate (Figs. 1(a, b)). Typical nanoblade widths range from 1 μ m to 5 μ m. The thickness of nanoblades varies from a few nanometers around the edge area to about 20 nm in the center. The as-prepared α -Fe₂O₃ were then reduced by H₂ and examined *ex situ* by SEM. Fig. 1(c) is an SEM image obtained from the sample reduced at 500 °C for 1 h, which shows that the edge area of the nanoblades developed a sawtooth morphology, as indicated in the area marked by a red rectangle in Fig. 1(c). Fig. 1(d) illustrates the morphology of the nanoblades after the hydrogen-induced reduction at 500 °C for 2 h, showing that the reduced nanoblades developed pits on the large surfaces. Through-holes are also visible around the edge areas of the reduced nanoblades. This is because the edge areas have a smaller thickness and the volume shrinkage induced by the oxide reduction leads to the formation of holes in these thin areas.

A typical low-magnification TEM image of as-prepared Fe₂O₃ nanoblades is shown in Fig. 2(a). Nanodiffraction (Fig. 2(b)) shows that the nanoblades have a bi-crystal structure with the CSL twist boundary (Σ boundary), which agrees with our previous work.³⁶ The size of area probed to generate the electron diffraction pattern is about 50 nm. The nanodiffraction pattern was taken on the area marked by the red square in Fig. 2(a). Based on the statistical measurements of multiple nanoblades, 60 % of the Fe₂O₃ nanoblades were found to have the CSL twist boundary with a rotation angle 21.8 ± 0.1° between two α -Fe₂O₃ single-crystal platelets in <0001> directions and $\Sigma = 7.^{36}$ Fig. 2(c) is the crystal model based on the diffraction pattern shown in Fig. 2(b), with two α -Fe₂O₃ unit cells stacked on top of each other and rotated by 21.79° such that the grain boundary is perpendicular to the direction of the incident electron beam. Usually the nanoblades are thicker in the center and thinner along the edge, Fig. 2(d) is a high-resolution TEM (HRTEM) image near the edge area. The inset in Fig. 2(d) is a simulated HRTEM image using the structure model shown in Fig. 2(c) and the simulation parameters of a specimen thickness of 4 nm (expected thickness at the edge) and a defocus value of -9 nm, which matches well with the experimental one.

Fig. 3 shows the low-magnification *in situ* ETEM observations of the morphology evolution of Fe_2O_3 nanoblades during the hydrogen-induced oxide reduction at 500 °C. To avoid possible long

electron beam exposure induced oxide reduction, the beam was on only when taking the TEM images. Fig. 3(a) illustrates the morphology of a typical as-prepared nanoblade before reduction. After 90 min, the formation of a Swiss-cheese-like structure, with tiny pits on it, started to develop (the regions showing brighter contrast in Fig. 3(b)). Upon continued reduction, the nanoblades shrank and pits expanded (Fig. 3(c)). After 240 min of reduction, some regions of the nanoblade decomposed into small particles (Fig. 3(d)).

The reduction process was further characterized at the atomic scale. Fig. 4(a) is an HRTEM image after 30 min of hydrogen-induced reduction at 500 °C. This image was taken from the same region marked by the red square in Fig. 2(a) and obtained by summing up 20 frames after drift-correction to enhance the image contrast. The lattice structure of the reduced sample (Fig. 4(a)) is significantly different from the as-prepared, pure α -Fe₂O₃ sample (Fig. 2(d)), indicating that the oxide underwent a phase transformation. Fig. 4(a) also shows that the lower part of the HRTEM image has a different lattice contrast feature from the upper part, which is caused by the slight deviation of the lower part from the zone axis. This local deviation from the crystallographic orientation is related to the bending effect during the oxide reduction induced phase transformation. Fig. 4(b) is a nanodiffraction pattern obtained from the same area on the nanoblade marked by the red square in Fig. 2(a). The area probed to generate the electron diffraction pattern was about 50 nm in diameter. The diffraction pattern was taken from the same region in Fig. 2(a), which consists of two sets of diffraction spots (marked by red and green circles, respectively). One set (marked by red) can be indexed as α -Fe₂O₃ oriented along the [0001] zone axis and the other (yellow) can be indexed as either γ -Fe₂O₃ or Fe₃O₄ along the <111> zone axis. The latter was confirmed as γ -Fe₂O₃ by measuring the white line ratio of the Fe L edge in EELS (Figs. 5(d-e)). The existence of α -Fe₂O₃ diffraction spots indicated that the nanoblade was partly transformed to γ -Fe₂O₃. The phase transformation, expected as the first step of reduction from single crystal reduction,³² started from the top layer of the bi-crystals because of its direct in contact with the H_2 gas, whereas the bottom part of the nanoblade was still not reduced because of its exposure to H₂ was limited by the SiN_x support

membrane of the TEM grid. From the composite diffraction pattern (Fig. 4(b)), an in-plane rotation angle of $30 \pm 0.1^{\circ}$ was measured between the γ -Fe₂O₃ <111> and α -Fe₂O₃ <0001> patterns. The orientation relationships are α -Fe₂O₃(0001)// γ -Fe₂O₃(111) and α -Fe₂O₃ <10 $\overline{10}$ >// γ -Fe₂O₃<110>. The {30 $\overline{3}0$ } planes in α -Fe₂O₃ are aligned with {440} in γ -Fe₂O₃ because the bright diffraction spots of α -Fe₂O₃ {30 $\overline{3}0$ } overlap with γ -Fe₂O₃ {440} ($g_{30\overline{3}0}$ = 6.8 nm⁻¹, g_{440} = 6.9 nm⁻¹). The preferred orientation relationship induced by the α -Fe₂O₃ (111) planes are close-packed planes with an in-plane six-fold symmetry at the interface, which is also in agreement with the previous report on the transformation γ -Fe₂O₃ $\rightarrow \alpha$ -Fe₂O₃.⁴⁵ The 30° rotation between the two platelets with the α -Fe₂O₃/ γ -Fe₂O₃ bi-layer structure is likely the most stable arrangement of the two structures that involves the minimum rearrangement of atoms in their closepacked planes from the transformation of one platelet of the parent bi-crystal α -Fe₂O₃ that has the original 21.79° rotation of the two platelets to the γ -Fe₂O₃.

As the reduction proceeded, the remaining α -Fe₂O₃ platelet (the bottom crystal) continued to transform to γ -Fe₂O₃. Fig. 5(a) is a HRTEM image captured during the *in situ* observation of the oxide reduction induced structure transformation in the area marked with the red square in Fig. 2(a), which shows two different lattice structures with moiré fringes in their boundary region. Figs. 5(b and c) are diffractograms obtained from the regions marked by red squares b and c in Fig. 5(a), respectively. By indexing the diffractograms, it can be concluded that both regions b and c have the cubic structure that can be either γ -Fe₂O₃ or Fe₃O₄. At this point, the CSL grain boundary disappears in the diffractograms. The absence of the grain boundary indicates that the other component (α -Fe₂O₃) of the bi-crystal nanoblades also transformed into γ -Fe₂O₃ component because the diffractograms of the HRTEM images yield only one set of diffraction spots (either Fig. 5(b) or (c)). The sequential transformation of the two crystals, stacked on top of each other, indicates that slow diffusion of the reactants (hydrogen and oxygen) or the

accumulation of oxygen vacancies at the bi-crystal boundary (*i.e.*, the boundary acts as a sink for vacancies) delayed the onset of reduction of the bottom crystal. As mentioned earlier, the space groups and lattice constants of γ -Fe₂O₃ and Fe₃O₄ are very similar (γ -Fe₂O₃: space group P4₁32, a = b = c = 0.8347 nm; Fe₃O₄: space group *Fd* $\overline{3}m$, a = b = c = 0.8394 nm) and cannot be distinguished on the basis of the diffractograms. In Fig. 5(b), there are two extra superlattice spots, indicating the d spacing of the newly ordered planes is 3 times of that of the original γ -Fe₂O₃ {422} crystal planes. This is most probably due to the ordering of oxygen vacancies parallel to {422} plane, with the d spacing three times of that of {422}, *i.e.*, with a vacancy present on every third {422} plane. The ordering of oxygen vacancies parallel to {422} plane smulation. The observed ordering is just one of the metastable vacancy ordered phases as other vacancy ordered phases such as with ordering of oxygen vacancies on every 4th (112)⁴⁶ or every 10th (3030)³² planes were also reported.

Figs. 5(d, e) are the respective EELS spectra of regions b and c marked by the red squares in Fig. 5(a) after background removal and deconvolution. Since γ -Fe₂O₃ and Fe₃O₄ are both cubic structures with very similar lattice constants, it is impossible to distinguish them by electron diffraction. However, the oxidation state of Fe is different in the two structures. Therefore, the L₃/L₂ ratio, which is proportional to the oxidation state, can be used to identify them. The L₃/L₂ ratios were calculated and compared with standard samples (commercial α -Fe₂O₃, γ -Fe₂O₃, Fe₃O₄, and FeO) to distinguish between the γ -Fe₂O₃ and Fe₃O₄ phases (details of the measurements and the analysis are given in the supporting information). Combined measurements from the diffractogram and EELS confirmed that region b in Fig. 5(a) has the γ -Fe₂O₃ structure with the ordering of oxygen vacancies and region c is Fe₃O₄. The γ -Fe₂O₃ with the oxygen vacancy ordering is an intermediate structure formed during the reduction process.⁴⁶ This is because of the oxide by reacting with adsorbed H to form H₂O molecules that desorbed from the oxide surface. Therefore, oxygen vacancies were continuously generated in the oxide and can dynamically self-order

into a sequence of superstructures⁴⁶ as the reduction proceeded. The superstructure observed from our experiments might be one of the relatively more stable oxygen-vacancy ordered superstructures.

With the continuous accumulation of oxygen vacancies, the intermediate phase of γ -Fe₂O₃ became increasingly unstable and transformed into the more stable Fe₃O₄. It can be noted from Fig. 5(a) that there are many tiny pits or internal voids (brighter dots) formed in region b. They are clusters formed by the coalescence of excess oxygen vacancies. It is also interesting to note from Fig. 5(a) that there are no pits in the Fe₃O₄ region (*i.e.*, the lower-right corner), suggesting that the Fe₃O₄ region is relatively free of oxygen vacancies and the reduction occurred mainly in the γ -Fe₂O₃ region at this stage. This is reasonable because the lower-right region already underwent the γ -Fe₂O₃ \rightarrow Fe₃O₄ transformation, in which oxygen vacancies were annihilated. As shown in Fig. 5(a), the Moiré fringe contrast occurred in the γ -Fe₂O₃/Fe₃O₄ interface region because the interface was inclined with respect to the incident electron beam. The occurrence of the Moiré fringe contrast only in γ -Fe₂O₃/Fe₃O₄ in the through-thickness direction of the nanoblade and the γ -Fe₂O₃ \rightarrow Fe₃O₄ transformation propagated laterally toward the γ -Fe₂O₃ region. This manner of the phase transformation is very different from the first stage of reduction of the parent α -Fe₂O₃ bi-crystals, for which only one of the two platelets of the bi-crystal was first transformed into the γ -Fe₂O₃, resulting in the γ -Fe₂O₃/ α -Fe₂O₃ bi-layer structure.

Fig. 6 illustrates a sequence of *in situ* TEM images (extracted from supplemental *in situ* HRTEM video 2) showing the next reduction step after the γ -Fe₂O₃ \rightarrow Fe₃O₄ transformation was completed. The diffractograms of the two regions marked by the red squares in Fig. 6(c) show that the newly transformed region (the slightly darker gray region) is FeO while the rest is Fe₃O₄. The propagation of the FeO region was accompanied with the concurrent retraction of the Fe₃O₄ region, which clearly demonstrated the transformation path Fe₃O₄ \rightarrow FeO. The *in situ* TEM images shown in Figs. 6(a-f) also confirm that the reduction reaction was a topotactic transformation with the crystallographic orientation relationship of Fe₃O₄<111>//FeO<111>. This orientation relationship is preferred because both Fe₃O₄ and FeO are cubic

(Fe₃O₄: space group $Fd \ \overline{3}m$, a = 0.8394 nm; FeO: space group: $Fm \ \overline{3}m$, a = 0.4354 nm) and the Fe₃O₄ \rightarrow FeO transformation along the Fe₃O₄(111)/FeO(111) interface would require minimal atomic rearrangement because the (111) planes are the closest-packed planes for both structures.

The reduction kinetics of the Fe_3O_4 component shown in Fig. 6 was also determined by measuring the shrinkage of the Fe_3O_4 from the *in situ* TEM video. To calculate the reaction rate, an automated image processing scheme (AIPS), which is a combination of algorithms developed at NIST and publically available, was used to obtain structural information from each frame extracted from videos. The video of atomic positions corresponding to the HRTEM video is available in the Supporting Information (SI movie 3). After identifying the atomic positions and measuring the spacing between every two nearest neighbors, the area occupied by Fe₃O₄ structure in each frame can be assigned and calculated. The Fe_3O_4 area (Fig. 6(g)) was measured as a function of time to determine the reaction rate. The reduction kinetics can be fitted linearly and the reaction rate (slope) was determined to be 0.48 ± 0.3 nm²·s⁻¹, where the uncertainty is a single standard deviation as determined by the fitting procedure. A linear fit assumed a zero-order reaction or a pseudo-zero-order reaction, which was reasonable in this case because only a small fraction of the Fe₃O₄ reacts, and this fraction was continuously replenished from the larger pool (the parent nanowire). Fitting the data in Figure 6(g) with an exponential decay function expected for a higher-order reaction gave $R^2 = 0.95$, which was an equivalent confidence level to the linear fit. The uncertainty shown in Fig. 6(g) was given by the standard deviation of multiple measurements. Because of the similarity of R² for the exponential vs. linear fits, it is not sufficient to determine the order of reaction for this transformation that would require the measurements on the reaction rate over many reactant concentrations.

The reduction of metal oxides has been traditionally described using an interface-controlled model, *i.e.*, the reduction rate depends on the interface area between the reduced phase and the parent oxide.⁴⁷⁻⁵⁰ As shown in Figs. 6(a-f), the Fe₃O₄/FeO interface area became larger during the course of the reduction, implying that the reaction rate should increase with time if the reduction were controlled by the

Fe₃O₄/FeO interface. The linear time dependence of the transformation from Fe₃O₄ to FeO observed in our experiment suggested that the reduction was a surface reaction limited process, which can be either due to the surface adsorption of H_2 molecules or the removal of H_2O molecules.

The reduced nanoblades show a porous morphology with sawtooth-like edges after 120 min of heating in the H_2 gas flow (Fig. 7(a)). The clustering of vacancies resulted in the formation of craters while the nanoblade body still remained as Fe_3O_4 (Figs. 7(a, b) and inset diffractograms). The diffractogram from the area marked in Fig. 7(c) indicates the existence of an amorphous structure, which is the SiN_x supporting membrane of the TEM grid, confirming the pit formation and the development of a through hole in the pit area. The morphology was in accordance with the SEM observation shown in Fig. 1(d) and the *in situ* TEM observation in Fig. 3(d). At this point, the structure of the nanoblade consists of two oxides of iron (Fe₃O₄ and FeO) and metallic Fe. Eventually, the entire α -Fe₂O₃ nanoblade was transformed into metallic Fe and fell apart into multiple Fe nanoparticles (Fig. 7(d)) and the inset diffraction pattern) due to the considerable specific volume shrinkage from α -Fe₂O₃ (cell volume = 0.5816 nm^{3}) to Fe (cell volume = 0.0439 nm^{3}). As shown in Fig. 7(d), the Fe nanoparticle has a core-shell structure with a thin layer of ultrafine nanocrystals grown on the surface. This is because metallic Fe nanoparticles are highly reactive⁵¹ and can easily re-oxidize immediately to form a thin surface oxide layer even in the low partial pressure of oxygen present in the TEM column. The in situ TEM observations demonstrated that the reduction by H_2 results in the formation of a porous structure in the parent Fe_2O_3 nanoblade, followed by its disintegration into Fe nanoparticles. Such dramatic morphology changes are induced by the significant volume shrinkage that occurs during the H₂-induced reductiondriven phase transformation from α -Fe₂O₃ to metallic Fe upon the loss of lattice oxygen from the oxide.

The reduction for bulk α -Fe₂O₃ by H₂ follows the reaction sequence of α -Fe₂O₃ \rightarrow Fe₃O₄ \rightarrow FeO \rightarrow Fe⁵² or α -Fe₂O₃ \rightarrow Fe₃O₄ \rightarrow Fe.⁵³ By contrast, we find the reduction of α -Fe₂O₃ nanoblades follows the transformation sequence of α -Fe₂O₃ $\rightarrow \gamma$ -Fe₂O₃ superlattice (Fig. 4) \rightarrow Fe₃O₄ (Fig. 5) \rightarrow FeO (Fig. 6) \rightarrow Fe (Fig. 7). The absence of the polymorph transition of α -Fe₂O₃ $\rightarrow \gamma$ -Fe₂O₃ in the reduction of the bulk oxide can be related to the kinetic constraints associated with the substantial distortion in the cell parameters of the α -Fe₂O₃ (hexagonal, a = b = 0.5036 nm, c = 1.3749 nm) to obtain γ -Fe₂O₃ (cubic, a = b = c = 0.8347 nm). However, such a kinetic hindrance to the γ -Fe₂O₃ formation may vanish for the reduction of α -Fe₂O₃ nanoblades because a large fraction of the atoms are located in a close proximity to the surface, which facilitate oxygen removal and self-ordering of oxygen vacancies as well as the cell distortion. Therefore, the reduction of the 2D nanosheets proceeds with more substeps compared with their bulk counterpart.

Fig. 8 schematically summarizes the reduction pathway of the bi-crystal α -Fe₂O₃ with the bicrystal boundary observed from our in-situ TEM experiments, where the reduction reaction starts from the surface that is directly exposed to H₂. The α -Fe₂O₃ nanoblades are first transformed into an α -Fe₂O₃/ γ -Fe₂O₃ bi-layer structure as one of the α -Fe₂O₃ platelets transforms into γ -Fe₂O₃. The α -Fe₂O₃/ γ -Fe₂O₃ bi-layer structure as one of the α -Fe₂O₃ platelets transforms into γ -Fe₂O₃. The α -Fe₂O₃/ γ -Fe₂O₃ with continued H₂ exposure, oxygen vacancies form in the γ -Fe₂O₃ nanoblade and self-order into a superstructure. However, if both surfaces are directly exposed to H₂, γ -Fe₂O₃ formation can occur on the two surfaces of the nanoblade with their respective crystallographic orientation with the parent α -Fe₂O₃ grain. As a result, a bi-crystal γ -Fe₂O₃ nanosheet may develop, instead of forming the α -Fe₂O₃/ γ -Fe₂O₃ bilayer structure and then a single-crystal γ -Fe₂O₃ sheet as shown schematically in Figs. 8(b and c). The continued accumulation of oxygen vacancies in γ -Fe₂O₃ results in the formation of clusters of oxygen vacancies with the concomitant γ -Fe₂O₃ \rightarrow Fe₃O₄ transformation. The subsequently formed Fe₃O₄ transforms into FeO and then to Fe upon further H₂ exposure at the elevated temperature. Due to the significant volume shrinkage along the transformation pathway of α -Fe₂O₃ $\rightarrow \gamma$ -Fe₂O₃ \rightarrow Fe₃O₄ \rightarrow FeO \rightarrow Fe, the parent α -Fe₂O₃ nanoblades disintegrate into Fe nanoparticles.

CONCLUSIONS

In summary, we have monitored the H₂-induced reduction process of α -Fe₂O₃ nanoblades and elucidated the reduction mechanism at the atomic scale. The parent α -Fe₂O₃ nanoblades have the CSL boundary formed by two platelets with a rotation angle of 21.79°. The reduction of the bi-crystal α -Fe₂O₃ nanoblades commences with the transformation of one of the platelets to γ -Fe₂O₃, resulting in a nanoblade of the α -Fe₂O₃/ γ -Fe₂O₃ hybrid structure formed by the alignment of the α -Fe₂O₃ and γ -Fe₂O₃ platelets with a rotation angle of 30°. The α -Fe₂O₃ platelet in the α -Fe₂O₃/ γ -Fe₂O₃ bilayer structure transformed into γ -Fe₂O₃, thereby forming a 2D single-crystal γ -Fe₂O₃. Upon further loss of lattice oxygen, the γ -Fe₂O₃ developed into a γ -Fe₂O₃ superstructure with the ordering of oxygen vacancies followed by the nucleation and growth of Fe₃O₄. Upon continued reduction, the ordered oxygen vacancies aggregated to form pits in the γ -Fe₂O₃ matrix. The transformed Fe₃O₄ was further reduced into FeO. Finally, the nanoblades were reduced to metallic iron and disintegrated into multiple Fe nanoparticles. These observations demonstrate that a high degree of control over the morphology, crystal structure, and oxidation state of the oxide nanostructures can be made by controlled oxide reduction.

METHODS

Materials Preparation. The α -Fe₂O₃ samples used for the *in situ* reduction experiments were prepared by the thermal oxidation of polycrystalline Fe foils (99.99 % pure). The high-purity Fe foils were first sandblasted using glass-bead abrasives with diameters ranging from 150 µm to 250 µm for 60 s at a pressure of 689.5 kPa (100 pounds per square inch) to modify the surface roughness. The sandblasted Fe foils were then thoroughly rinsed in deionized water followed by ultrasonication in acetone for 5 min. The cleaned iron foils were then placed on a substrate heater in a vacuum chamber and the sample temperature was monitored by a K-type thermocouple in contact with the substrate heater. The chamber was pumped to vacuum ($\approx 3 \times 10^{-4}$ Pa) and then filled with oxygen gas at a pressure of ≈ 270 Pa (99.999 % pure) and sealed. The Fe foil was then heated to 600 °C at a rate of ≈ 20 °C min⁻¹ in the oxygen gas and oxidized at 600 °C for 60 min. This yielded well-aligned, crystalline α -Fe₂O₃ nanoblades perpendicular to the Fe substrate. More details about the formation of nanostructured Fe₂O₃ by the thermal oxidation of Fe can be found in our previous work.^{20, 24, 45, 54} *Ex situ* reduction of the as-prepared α -Fe₂O₃ nanoblades was conducted in the same vacuum chamber by switching to the H₂ gas flow and at the reduction temperature ranging from 500 °C to 600 °C. The morphology changes before and after the reduction were examined by field-emission scanning electron microscopy (FEG-SEM).

In situ TEM Characterization. In situ experiments to monitor oxide reduction were performed in a dedicated ETEM equipped with an objective-lens aberration corrector and a gas manifold that enables control of the flow rate and partial pressure of various gases in the specimen area 55 . As-prepared α -Fe₂O₃ nanoblades were scratched off the Fe substrate and were dispersed in isopropanol by ultrasonication, followed by drop casting the suspension onto SiN_x membrane TEM grids. These were then loaded onto a heating holder and inserted in the ETEM. In our experiments, hydrogen (99.999 % pure) was first flowed through a liquid nitrogen trap to condense water molecules, and was then introduced into the specimen area in the ETEM column at a partial pressure of 0.5 Pa. The sample was then heated to 500 °C in the H₂ flow. In situ TEM observations, acquisition of high-resolution TEM (HRTEM) images and videos, nanobeam electron diffraction, and electron energy loss spectra (EELS) were performed under this reducing condition. In situ HRTEM imaging of the oxide reduction process was performed with 0.5 s per frame. Electron-energy loss spectroscopy (EELS) analysis was used to determine the oxidation state of the reduced oxide. Following background removal, the spectra were de-convoluted, and two arctangent functions were then applied 56 to remove the post-edge background to produce isolated Fe L₃ and L₂ edges for the calculation of the L_3/L_2 ratio (white line ratio),⁵⁶ which is proportional to the oxidation state of Fe. To minimize the effect of electron beam induced oxide reduction, the e-beam was blanked except for data acquisition. We also examined the possible effect of electron beam irradiation by comparing the oxide reduction with and without electron beam and different sample areas. Our results indicate the negligible effect of electron irradiation on the observed oxide reduction pathway.

ASSOCIATED CONTENT



S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Detailed procedure to distinguish between γ -Fe₂O₃ and Fe₃O₄ via EELS measurements of the oxidation state of Fe in the oxides.

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REFERENCES:

1. Kabelitz, A.; Guilherme, A.; Joester, M.; Reinholz, U.; Radtke, M.; Bienert, R.; Schulz, K.; Schmack, R.; Kraehnert, R.; Emmerling, F. Time-resolved *in situ* Studies on the Formation Mechanism of Iron Oxide Nanoparticles using Combined Fast-XANES and SAXS. *CrystEngComm* **2015**, *17*, 8463-8470.

2. Lu, J.; Jung Lee, Y.; Luo, X.; Chun Lau, K.; Asadi, M.; Wang, H.-H.; Brombosz, S.; Wen, J.; Zhai, D.; Chen, Z.; Miller, D. J.; Sub Jeong, Y.; Park, J.-B.; Zak Fang, Z.; Kumar, B.; Salehi-Khojin, A.; Sun, Y.-K.; Curtiss, L. A.; Amine, K. A Lithium–oxygen Battery Based on Lithium Superoxide. *Nature* **2016**, *529*, 377-382.

3. Giordano, L.; Cinquini, F.; Pacchioni, G. Tuning the Surface Metal Work Function by Deposition of Ultrathin Oxide Films: Density Functional Calculations. *Phys. Rev. B* **2006**, *73*, 045414.

4. Wang, Z. L. Functional Oxide Nanobelts: Materials, Properties and Potential Applications in Nanosystems and Biotechnology. *Annu. Rev. Phys. Chem.* **2004**, *55*, 159-196.

5. Chen, P.; Mitsui, T.; Farmer, D. B.; Golovchenko, J.; Gordon, R. G.; Branton, D. Atomic layer deposition to fine-tune the surface properties and diameters of fabricated nanopores. *Nano Lett.* **2004**, *4*, 1333-1337.

6. Sundman, B. An Sssessment of the Fe-O System. J. Phase Equilib. 1991, 12, 127-140.

7. Pham, A. L.-T.; Lee, C.; Doyle, F. M.; Sedlak, D. L. A Silica-Supported Iron Oxide Catalyst Capable of Activating Hydrogen Peroxide at Neutral PH Values. *Environ. Sci. Technol.* **2009**, *43*, 8930-8935.

8. Mema, R.; Yuan, L.; Du, Q.; Wang, Y.; Zhou, G. Effect of Surface Stresses on CuO Nanowire Growth in the Thermal Oxidation of Copper. *Chem. Phys. Lett.* **2011**, *512*, 87-91.

9. Feng, H.; Wang, Y.; Wang, C.; Diao, F.; Zhu, W.; Mu, P.; Yuan, L.; Zhou, G.; Rosei, F. Defectinduced Enhanced Photocatalytic Activities of Reduced α-Fe₂O₃ Nanoblades. *Nanotechnology* **2016**, *27*, 295703.

10. Charvin, P.; Abanades, S.; Flamant, G.; Lemort, F. Two-step water splitting thermochemical cycle based on iron oxide redox pair for solar hydrogen production. *Energy* **2007**, *32*, 1124-1133.

11. Tilley, S. D.; Cornuz, M.; Sivula, K.; Grätzel, M. Light-Induced Water Splitting with Hematite: Improved Nanostructure and Iridium Oxide Catalysis. *Angew. Chem. Int. Ed. Engl.* **2010**, *122*, 6549-6552.

12. Cesar, I.; Kay, A.; Gonzalez Martinez, J. A.; Grätzel, M. Translucent thin film Fe₂O₃ photoanodes for efficient water splitting by sunlight: nanostructure-directing effect of Si-doping. *J. Am. Chem. Soc.* **2006**, *128*, 4582-4583.

13. Arshak, K.; Gaidan, I. Development of a novel gas sensor based on oxide thick films. *Mater. Sci. Eng.*, *B* **2005**, *118*, 44-49.

14. Tandon, R.; Tripathy, M.; Arora, A.; Hotchandani, S. Gas and Humidity Response of Iron Oxide—Polypyrrole Nanocomposites. *Sens. Actuators, B* **2006**, *114*, 768-773.

15. Yang, X.; Hong, H.; Grailer, J. J.; Rowland, I. J.; Javadi, A.; Hurley, S. A.; Xiao, Y.; Yang, Y.; Zhang, Y.; Nickles, R. J. cRGD-functionalized, DOX-conjugated, and 64 Cu-labeled Superparamagnetic Iron Oxide Nanoparticles for Targeted Anticancer Drug Delivery and PET/MR Imaging. *Biomaterials* **2011**, *32*, 4151-4160.

16. Chertok, B.; Moffat, B. A.; David, A. E.; Yu, F.; Bergemann, C.; Ross, B. D.; Yang, V. C. Iron oxide nanoparticles as a drug delivery vehicle for MRI monitored magnetic targeting of brain tumors. *Biomaterials* **2008**, *29*, 487-496.

17. He, K.; Xu, C.-Y.; Zhen, L.; Shao, W.-Z. Hydrothermal Synthesis and Characterization of Singlecrystalline Fe₃O₄ Nanowires with High Aspect Ratio and Uniformity. *Mater. Lett.* **2007**, *61*, 3159-3162.

18. He, K.; Xu, C.-Y.; Zhen, L.; Shao, W.-Z. Fractal Growth of Single-crystal α-Fe₂O₃: from Dendritic Micro-pines to Hexagonal Micro-snowflakes. *Mater. Lett.* **2008**, *62*, 739-742.

19. He, K.; Zhang, S.; Li, J.; Yu, X.; Meng, Q.; Zhu, Y.; Hu, E.; Sun, K.; Yun, H.; Yang, X.-Q.; Zhu, Y.; Gan, H.; Mo, Y.; Stach, E. A.; Murray, C. B.; Su, D. Visualizing Non-equilibrium Lithiation of Spinel Oxide *via in situ* Transmission Electron Microscopy. *Nat Commun* **2016**, *7*.

20. Yuan, L.; Wang, Y.; Cai, R.; Jiang, Q.; Wang, J.; Li, B.; Sharma, A.; Zhou, G. The Origin of Hematite Nanowire Growth during the Thermal Oxidation of Iron. *Mater. Sci. Eng.*, *B* **2012**, *177*, 327-336.

21. Cao, X.; Wang, N. A novel non-enzymatic glucose sensor modified with Fe₂O₃ nanowire arrays. *Analyst* **2011**, *136*, 4241-4246.

22. Mohapatra, S. K.; John, S. E.; Banerjee, S.; Misra, M. Water Photooxidation by Smooth and Ultrathin α -Fe₂O₃ Nanotube Arrays. *Chem. Mater.* **2009**, *21*, 3048-3055.

23. Zhu, W.; Winterstein, J. P.; Sharma, R.; Zhou, G. Atomic-Scale Characterization of the Reduction of a-Fe₂O₃ Nanowires. *Microsc. Microanal.* **2015**, *21*, 995-996.

24. Yuan, L.; Cai, R.; Jang, J. I.; Zhu, W.; Wang, C.; Wang, Y.; Zhou, G. Morphological transformation of hematite nanostructures during oxidation of iron. *Nanoscale* **2013**, *5*, 7581-7588.

25. Yang, P.; Ding, Y.; Lin, Z.; Chen, Z.; Li, Y.; Qiang, P.; Ebrahimi, M.; Mai, W.; Wong, C. P.; Wang, Z. L. Low-cost High-performance Solid-state Asymmetric Supercapacitors Based on MnO₂ Nanowires and Fe₂O₃ Nanotubes. *Nano Lett.* **2014**, *14*, 731-736.

26. Hou, Y.; Zuo, F.; Dagg, A.; Feng, P. Visible Light-Driven α -Fe₂O₃ Nanorod/Graphene/BiV₁₋ _xMo_xO₄ Core/Shell Heterojunction Array for Efficient Photoelectrochemical Water Splitting. *Nano Lett.* **2012**, *12*, 6464-6473.

27. Yuan, L.; Wang, Y.; Mema, R.; Zhou, G. Driving Force and Growth Mechanism for Spontaneous Oxide Nanowire Formation during the Thermal Oxidation of Metals. *Acta Mater.* **2011**, *59*, 2491-2500.

28. Cai, R.; Li, T.; Wang, Y.; Wang, C.; Yuan, L.; Zhou, G. Formation of modulated structures in single-crystalline hexagonal α-Fe₂O₃ nanowires. *J. Nanopart. Res.* **2012**, *14*, 1-11.

29. Fu, Y.; Wang, R.; Xu, J.; Chen, J.; Yan, Y.; Narlikar, A.; Zhang, H. Synthesis of Large Arrays of Aligned α-Fe₂O₃ Nanowires. *Chem. Phys. Lett.* **2003**, *379*, 373-379.

30. Cvelbar, U.; Chen, Z.; Sunkara, M. K.; Mozetič, M. Spontaneous Growth of Superstructure α-Fe₂O₃ Nanowire and Nanobelt Arrays in Reactive Oxygen Plasma. *Small* **2008**, *4*, 1610-1614.

31. Morales, A. M.; Lieber, C. M. A Laser Ablation Method for the Synthesis of Crystalline Semiconductor Nanowires. *Science* **1998**, *279*, 208-211.

32. Zhu, W.; Winterstein, J.; Maimon, I.; Yin, Q.; Yuan, L.; Kolmogorov, A. N.; Sharma, R.; Zhou, G. Atomic Structural Evolution during the Reduction of α -Fe₂O₃ Nanowires. *J. Phys. Chem. C* **2016**, *120*, 14854-14862.

33. Zhu, W.; Winterstein, J. P.; Sharma, R.; Zhou, G. *In situ* Atomic-Scale Visualization of CuO Nanowire Growth. *Microsc. Microanal.* **2016**, *22*, 1588-1589.

34. Zhu, W.; Winterstein, J. P.; Sharma, R.; Zhou, G. The Growth of Catalyst-free NiO Nanowires. *Microsc. Microanal.* **2016**, *22*, 1620-1621.

35. Yuan, L.; Jiang, Q.; Wang, J.; Zhou, G. The Growth of Hematite Nanobelts and Nanowires — Tune the Shape *via* Oxygen Gas Pressure. *J. Mater. Res.* **2012**, *27*, 1014-1021.

36. Wang, Y.; Wang, C.; Yuan, L.; Cai, R.; Liu, X.; Li, C.; Zhou, G. Coincidence-Site-Lattice Twist Boundaries in Bicrystalline α-Fe₂O₃ Nanoblades. *J. Phys. Chem. C* **2014**, *118*, 5796-5801.

37. Glezer, A.; Stolyarov, V.; Tomchuk, A.; Shurygina, N. Grain Boundary Engineering and Superstrength of Nanocrystals. *Tech. Phys. Lett.* **2016**, *42*, 51-54.

38. Bollmann, W., *Crystal defects and crystalline interfaces*. Springer Science & Business Media: 2012.

39. Yuan, L.; Van Der Geest, A. G.; Zhu, W.; Yin, Q.; Li, L.; Kolmogorov, A. N.; Zhou, G. Reduction of CuO Nanowires Confined by a Nano Test Tube. *RSC Advances* **2014**, *4*, 30259-30266.

40. Yang, Y.; Luo, L.-M.; Guo, Y.-F.; Dai, Z.-X.; Zhang, R.-H.; Sun, C.; Zhou, X.-W. *In situ* Synthesis of PtPd Pimetallic Nanocatalysts Supported on Graphene Nanosheets for Methanol Oxidation Using Triblock Copolymer as Reducer and Stabilizer. *J. Electroanal. Chem.* **2016**.

41. Andersson, A.; Holmberg, J.; Häggblad, R. Process Improvements in Methanol Oxidation to Formaldehyde: Application and Catalyst Development. *Top. Catal.* **2016**, *59*, 1589-1599.

42. Watanabe, R.; Watanabe, S.; Hirata, N.; Fukuhara, C. Effect of Promoter Addition on Water Gas Shift Property over Structured-Type Iron Oxide Catalyst. *Catal. Lett.* **2016**, *146*, 2478-2484.

43. Dong, Z.; Wang, T.; Zhao, J.; Fu, T.; Wang, L.; Li, J.; Ding, W. Catalytic Performance of Iron Oxide Loaded on Electron-rich Surfaces of Carbon Nitride. *J. Energy Chem.* **2016**.

44. Lang, C.; Sécordel, X.; Kiennemann, A.; Courson, C. Water Gas Shift Catalysts for Hydrogen Production from Biomass Steam Gasification. *Fuel Process. Technol.* **2016**.

45. Kachi, S.; Momiyama, K.; Shimizu, S. An Electron Diffraction Study and a Theory of the Transformation from g-Fe₂O₃ to a-Fe₂O₃. *J. Phys. Soc. Jpn.* **1963**, *18*, 106-116.

46. Chen, Z.; Cvelbar, U.; Mozetič, M.; He, J.; Sunkara, M. K. Long-Range Ordering of Oxygen-Vacancy Planes in α -Fe₂O₃ Nanowires and Nanobelts. *Chem. Mater.* **2008**, *20*, 3224-3228.

47. Koga, Y.; Harrison, L. Comprehensive Chemical Kinetics. *Bamford, CH, Tipper, CFH, Compton, RG (Eds.)* **1984,** *21*, 120.

48. Rodriguez, J. A.; Hanson, J. C.; Frenkel, A. I.; Kim, J. Y.; Pérez, M. Experimental and Theoretical Studies on the Reaction of H_2 with NiO: Role of O Vacancies and Mechanism for Oxide Reduction. *J. Am. Chem. Soc.* **2002**, *124*, 346-354.

49. Kim, J. Y.; Rodriguez, J. A.; Hanson, J. C.; Frenkel, A. I.; Lee, P. L. Reduction of CuO and Cu₂O with H₂: H Embedding and Kinetic Effects in the Formation of Suboxides. *J. Am. Chem. Soc.* **2003**, *125*, 10684-10692.

50. Zhou, G.; Yang, J. C. Reduction of Cu₂O Islands Grown on a Cu(100) Surface through Vacuum Annealing. *Phys. Rev. Lett.* **2004**, *93*, 226101.

51. Wang, C. M.; Baer, D. R.; Thomas, L. E.; Amonette, J. E.; Antony, J.; Qiang, Y.; Duscher, G. Void Formation during Early Stages of Passivation: Initial Oxidation of Iron Nanoparticles at Room Temperature. *J. Appl. Phys.* **2005**, *98*, 094308.

52. Sharma, G.; Jeevanandam, P. Synthesis of Self-assembled Prismatic Iron Oxide Nanoparticles by a Novel Thermal Decomposition Route. *RSC Advances* **2013**, *3*, 189-200.

53. Jozwiak, W.; Kaczmarek, E.; Maniecki, T.; Ignaczak, W.; Maniukiewicz, W. Reduction Behavior of Iron Oxides in Hydrogen and Carbon Monoxide Atmospheres. *Appl. Catal.*, A **2007**, *326*, 17-27.

54. Yuan, L.; Jiang, Q.; Wang, J.; Zhou, G. The growth of hematite nanobelts and nanowires—tune the shape via oxygen gas pressure. *Journal of Materials Research* **2012**, *27*, 1014-1021.

55. Sharma, R. An Environmental Transmission Electron Microscope for *in situ* Synthesis and Characterization of Nanomaterials. *J. Mater. Res.* **2005**, *20*, 1695-1707.

56. Cave, L.; Al, T.; Loomer, D.; Cogswell, S.; Weaver, L. A STEM/EELS method for mapping iron valence ratios in oxide minerals. *Micron (Oxford, England : 1993)* **2006**, *37*, 301-309.

Figure captions:



Figure 1. (a) SEM images of α -Fe₂O₃ nanoblades formed by the oxidation of a sandblasted Fe substrate. (b) Cross-section SEM image of the nanoblades. (c) SEM image of nanoblades after 1 h of reduction at 500 °C in H₂, showing the "sawtooth" morphology along the edges (as marked by the red square). (d) SEM image showing the formation of holes after 2 h of reduction. The scale bar is 1 μ m.



Figure 2. (a) TEM image of a typical as-prepared α -Fe₂O₃ nanoblade (the ghosting effect seen in the image is due to the specimen charging under the electron beam). (b) Nanodiffraction pattern of the bicrystal α -Fe₂O₃ taken at the area marked by the red square shown in (a), which can be indexed as two overlaying α -Fe₂O₃ platelets oriented along the <0001> zone axis, with a CLS twist boundary of 21.79°; (c) an atomic structural model of two overlaying α -Fe₂O₃ unit cells rotated by 21.79° with respect to each other; (d) the HRTEM from the red square area in (a), inset is a simulated HRTEM (outlined by red rectangle) based on the structure model in (c), the image simulation parameters: sample thickness = 4 nm, defocus value = -9 nm.



Figure 3. The morphology evolution of α -Fe₂O₃ nanoblade during *in situ* heating at 500 °C with the flow of H₂ gas at the pressure of ≈ 0.5 Pa. (a) a nanoblade before reduction, (b) The reduction begins with the formation of pits, and (c) the nanoblade becomes thinner as the reduction continues, (d) the nanoblade breaks into small pieces. The observed ghosting effect in the images (a and b) is due to charging of the specimen by the electron beam.



Figure 4. HRTEM image (a) and nanobeam electron diffraction pattern (b) of the nanoblade, showing the parent bi-crystal α -Fe₂O₃ nanoblade is transformed into a bi-layer structure of α -Fe₂O₃ and γ -Fe₂O₃, with a rotation angle of 30°. The size of area probed to generate the electron diffraction pattern in Fig. 4(b) is about 50 nm, the diffraction pattern was taken from the same region on the nanoblade marked by the red square in fig. 2(a).



Figure 5. (a) *In situ* HRTEM visualization (supplemental *in situ* TEM video 1) of the transformation from γ -Fe₂O₃ to γ -Fe₂O₃-superstructure in the upper-left corner of the image. (b, c) the diffractograms from red boxed regions b and c, in (a), respectively. Note the presence of extra spots in (b), which are related to the ordering of oxygen vacancies in the γ -Fe₂O₃ region in the upper-left corner. (d, e) EELS spectra from the regions marked by red boxes b and c in (a), respectively. Both regions b and c marked in (a) are γ -Fe₂O₃, but the white line ratio in (e) is 5.05, slightly lower than 5.23 in (d), indicating the γ -Fe₂O₃ in upper-left corner region as marked by red box b in (a) has a slightly lower oxidation state induced by oxygen vacancies (Details of the measurements and the analysis are given in the supporting information).



Figure 6. Time sequence of high-resolution TEM images (extracted from supplemental *in situ* TEM videos 2 and 3) showing the phase transformation from Fe₃O₄ to FeO. (a) 0.5 s, (b) 25 s, (c) 50 s, (d) 60 s, (e) 75 s, (f, g) the diffractograms of the regions marked by "F" and "G" in (c), showing that the region before transformation (region "G") is Fe₃O₄<111> and then transform to FeO<111> (region "F") with the orientation relationship of the topotactic transformation of Fe₃O₄<111>//FeO<111>. (g) The reduction rate of the oxide measured from the *in situ* TEM video of the shrinkage of the Fe₃O₄ region. The error bars give single standard deviation uncertainties based on multiple measurements.



Figure 7. (a) HRTEM of the nanoblade edge region after heating in H₂ for 61 min, showing the sawtooth structure formed along the edge; the diffractogram of the marked square area is Fe₃O₄ <111>; (b) HRTEM image showing the formation of pits, the diffractogram of the pit area is consistent with FeO <111>; (c) HRTEM image with the formation of porous structure on the nanoblade, the diffractogram of the marked area indicates the presence of an amorphous material, which is the SiN_x membrane of the TEM grid, confirming the formation of a through hole; (d) HRTEM image obtained from a Fe nanoparticle formed during the final stage of the reduction, the inset is a nanobeam diffraction pattern along the Fe <001>.



Figure 8. Schematic illustration of the reduction pathway of α -Fe₂O₃: (a) bi-crystal α -Fe₂O₃, (b) α -Fe₂O₃/ γ -Fe₂O₃ bi-layer structure, (c) single-crystal γ -Fe₂O₃ superlattice, (d) γ -Fe₂O₃ \rightarrow Fe₃O₄, (e) Fe₃O₄, (f) a Swiss-cheese-like structure consisting of Fe₃O₄, FeO, and Fe nanoparticles. Red: α -Fe₂O₃; Green: γ -Fe₂O₃; Purple: Fe₃O₄; Blue: FeO; Yellow: Fe.

ToC graphic:

