Exploring (1 $\bar{1}2$)-related ordered structure in oxidation-synthesized α -Fe₂O₃ nanowhiskers

Ming-Wei Lai¹ and Hiroki Kurata^{1,*} ¹ Institute for Chemical Research, Kyoto University, Uji, Kyoto 6110011, Japan

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ABSTRACT

Hematite (α -Fe₂O₃) nanowhiskers (NWs) synthesized via oxidation of iron-based substrates are a promising photoanode material for photoelectrochemical water splitting. Such synthesized α -Fe₂O₃ NWs have been found to contain ordered axial structures. Herein, we reveal that the known (1 $\bar{1}2$)-related ordered structure actually exists in bicrystalline α -Fe₂O₃ NWs instead of single-crystalline α -Fe₂O₃ NWs and that it is associated with another known (3 $\bar{3}0$)-related ordered structure. Through a spherical aberration (C_s)-corrected high-resolution transmission electron microscopy (HR-TEM) investigation, the microstructural characteristic of the (1 $\bar{1}2$)-related ordered structure is verified to be periodic atomic column displacements serving as tensile strain accommodation. The HR-TEM observation are also supported by a monochromated O K-edge EELS analysis, which indicates that α -Fe₂O₃ NWs hosting the (1 $\bar{1}2$)-related ordered structure are indeed associated with lattice expansion. In sum, our microstructural study elucidates the root cause of the long-asserted relationship between the (1 $\bar{1}2$)-related ordered structure and oxygen vacancy ordering.

Introduction

Hematite (α -Fe₂O₃) has long been regarded as a promising photoanode material for photoelectrochemical (PEC) water splitting because of its superior chemical stability, prominent solar light absorption ability, favorable valence band edge position, abundance, and non-toxicity [1, 2]. Despite these attractive qualities, the intrinsically short hole diffusion length of α -Fe₂O₃ impedes the practical performance of α -

Fe₂O₃ photoanodes [3]. One feasible strategy to overcome this limitation is to construct α -Fe₂O₃ photoanodes from building blocks of aligned one-dimensional (1D) α -Fe₂O₃ nanostructures, which not only reduces the difficulty for the photogenerated holes to reach the semiconductor–electrolyte interface but also improves the majority carrier collection efficiency [1, 2].

Large-scale facile synthesis of aligned α -Fe₂O₃ nanowhiskers (NWs) can be achieved through

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Address correspondence to E-mail: kurata@eels.kuicr.kyoto-u.ac.jp

oxidation of an iron-based substrate under a suitable environmental condition [4–8]. α -Fe₂O₃ NWs synthesized via such a means normally exhibit tapered quasi-1D geometries with geometrically basal faces. The NW growth is suggested to be stress-driven, for which stress in the iron oxide scale that forms between the α -Fe₂O₃ NWs and iron-based substrate drives the outward diffusion of iron atoms to the NW growth fronts [9, 10]. Possibly connected with stress, ordered axial structures are observed in the α -Fe₂O₃ NWs. As the best-known case, a (3 $\bar{3}$ 0)-related ordered structure has been observed to exist in NWs with basal faces perpendicular to the [001] direction [5, 11–15]. Furthermore, a (1 $\bar{1}$ 2)-related ordered structure was reported to be present in NWs with basal faces perpendicular to the $[\bar{1}\bar{1}1]$ direction [6, 7, 12, 14].

For oxidation-synthesized α -Fe₂O₃ NWs, understanding the internal ordered structures is meaningful for evaluating their practical performance in PEC reactions. Through both microstructural and microchemical analyses, the (3 $\bar{3}$ 0)-related ordered structure has been verified to be linked to oxygen vacancy ordering [5, 11, 15]. Since the introduction of oxygen vacancies into an α -Fe₂O₃ photoanode can increase the photoanode's major carrier concentration [16–19], thereby suppressing reverse current flow in the photoanode during PEC reactions [20], the (3 $\bar{3}$ 0)-related ordered structure is expected to enhance the PEC performance of the host α -Fe₂O₃ NWs. Similarly, the (1 $\bar{1}$ 2)-related ordered structure is also considered to be associated with oxygen vacancy ordering [6, 7, 12, 14]. Although reasonable, this assertion is merely based on conventional HR-TEM observations, the limited resolving power of which is incapable of revealing the microstructural characteristic of this ordered structure. In other words, the origin of this ordered structure's relation with oxygen deficiency remains unclear. Following the development of spherical aberration (C_s)-corrected transmission electron microscopy (TEM), high-resolution (HR)-TEM observations are now available to have an information limit of 1 Å^{−1} or better [21, 22] and much reduced image delocalization. Moreover, the recently realized monochromated electron energy loss spectroscopy (EELS) [23, 24] enables the sensitive detection of crystal structure variations via a transmission/scanning transmission electron microscope (TEM/STEM)-based microchemical analysis.

These two microscopic advancements provide the opportunity for unequivocally ascertaining the (1 $\bar{1}$ 2)-related ordered structure. In this study, we investigated α -Fe₂O₃ NWs that were synthesized through a thermal oxidation process and exhibited the (1 $\bar{1}$ 2)-related ordered structure. We first revealed that the (1 $\bar{1}$ 2)-related ordered structure actually existed in bicrystalline α -Fe₂O₃ NWs and was associated with the (3 $\bar{3}$ 0)-related ordered structure. Using C_s -corrected HR-TEM and monochromated EELS, a link between the (1 $\bar{1}$ 2)-related ordered structure and tensile strain was verified, which explicates the connection between this ordered structure and oxygen vacancy ordering. Finally, through an EELS-based quantitative comparison, we further observed that the degree of oxygen deficiency of the (1 $\bar{1}$ 2)-related ordered structure is smaller than that of the (3 $\bar{3}$ 0)-related ordered structure.

Experimental details

An atmospheric thermal oxidation process with a reaction temperature and duration of 550 °C and 20 h, respectively, was adopted to synthesize α -Fe₂O₃ NWs on a 45 Permalloy substrate (The Nilaco Corp.). The morphology of the synthesized α -Fe₂O₃ NWs has been shown in our previous study [15] and is similar to those of α -Fe₂O₃ NWs synthesized via other thermal oxidation processes [5, 25–28]. A TEM sample of the α -Fe₂O₃ NWs was prepared by ultrasonically dispersing the NWs in ethanol and then transferring one small drop of the suspension to a holey carbon-coated copper grid. Analyses of the α -Fe₂O₃ NWs were performed utilizing a monochromator-equipped double- C_s -corrector TEM/STEM (JEM-ARM200F, JEOL Ltd.) operated at a 200-kV acceleration voltage. The C_s value for the HR-TEM observation of the (1 $\bar{1}$ 2)-related ordered structure was tuned to −14 μm. EELS spectra were acquired via the STEM-EELS method (with the convergence and collection semi-angles of 32.3 and 28.2 mrad, respectively) under the dual-EELS mode [29], for which the full-width-at-half-maximum (FWHM) values of the zero-loss peaks were 0.25 eV (monochromated O K-edge EELS) and 1.25 eV (wide-range EELS). Each acquired spectrum was based on summing all spectra within a spectrum image containing at least 9500 spectrum data. Simulated electron diffraction

patterns and HR-TEM images were calculated with the xHREM program (HREM Research Inc.); O K-edge near-edge EELS spectrum simulations were performed using the FEFF9 code [30].

Results and discussion

An HR-TEM image of an as-synthesized α -Fe₂O₃ NW is shown in Fig. 1a, in which superstructure modulation is clearly visible. The fast Fourier transform (FFT) pattern of the HR-TEM image (Fig. 1c) shows that the α -Fe₂O₃ NW grows along the [110] direction (as shown in Fig. S1, the [110] NW growth direction was also verified by using the shadow image method), which is the typical growth direction of α -Fe₂O₃ NWs synthesized via oxidation. More importantly, in addition to the prominent spots of Bragg diffraction along the $[\bar{1}11]$ zone axis, extra spots occur at one-fourth the reciprocal lattice vector of the $(1\bar{1}2)$ planes, indicating that an $(1\bar{1}2)$ -related ordered structure with a period of four times the interplanar

spacing of the $(1\bar{1}2)$ planes is present in the α -Fe₂O₃ NW. This finding agrees with the prior observed periodicity of the $(1\bar{1}2)$ -related ordered structure [6, 7, 12]. Further, the extra spots exhibit obvious intensity fluctuation, which we have also noticed in prior studies [6, 12]. This phenomenon is not common for superstructure-based TEM electron diffraction. After a careful spot identification, as shown in Fig. 2a, we determined that part of the brighter extra spots were associated with Bragg diffraction along the [001] zone axis (i.e., these spots are not only superstructure-based but also associated with Bragg diffraction along the [001] zone axis), meaning that the α -Fe₂O₃ NW possesses a $[\bar{1}11] \parallel [001]$ bicrystalline structure. Through this finding, the remaining brighter extra spots were then understood to be relevant to double diffraction [31] in the bicrystal (i.e., these spots are both superstructure- and rediffraction-related). It was found that multiple electron diffraction was incapable of reasonably explaining the emergence of the dim extra spots, thereby directly reflecting the existence of the $(1\bar{1}2)$ -related ordered structure. Based on our FFT pattern interpretation, a previously overlooked fact about the $(1\bar{1}2)$ -related ordered structure was revealed: instead of existing in single-crystalline α -Fe₂O₃ NWs, it actually exists in $[\bar{1}11]$ -oriented grains of $[\bar{1}11] \parallel [001]$ bicrystalline α -Fe₂O₃ NWs.

The emergence of $[\bar{1}11] \parallel [001]$ bicrystal has already been observed in the synthesis of α -Fe₂O₃ quasi-1D nanostructures via oxidation [4, 10, 26, 32], for which Wen et al. have pointed out that the corresponding bicrystal junction does not have a twin boundary [4]. Without considering lattice imperfections, we illustrate the lattice registration of the bicrystal junction for the $[\bar{1}11] \parallel [001]$ bicrystalline α -Fe₂O₃ NWs in Fig. 3a, where the $(3\bar{3}0)$ planes in the [001]-oriented grain can be seen coupling to the $(1\bar{1}2)$ planes in the $[\bar{1}11]$ -oriented grain. As indicated, the contraposition relation between these two plane sets is five times the interplanar spacing of the $(3\bar{3}0)$ planes (7.3 Å) against twice the interplanar spacing of the $(1\bar{1}2)$ planes (7.4 Å). The $\sim 1.4\%$ lattice mismatch implies that this bicrystal junction is accompanied by interfacial stress and is thus not thermodynamically preferred. Therefore, a supporting mechanism should be present that overcomes the anticipated energy barrier of the formation of the $[\bar{1}11] \parallel [001]$ bicrystalline α -Fe₂O₃

Figure 1 **a** HR-TEM image of an as-synthesized α -Fe₂O₃ NW. **b** Low-magnification TEM image of this α -Fe₂O₃ NW. The red box marks the HR-TEM observation area. **c** FFT pattern of (a). To definitely reflect the variation in spot intensity, the original complex-numbered FFT result is converted to a real-numbered format by taking the modulus of each complex number. The repetition of the extra spots, indicated by the red arrows, corresponds to 1/4 the reciprocal lattice vector of the $(1\bar{1}2)$ planes.

Figure 2 **a** Interpretation of the FFT pattern in Fig. 1c. The yellow dotted circles and red circles respectively indicate the Bragg diffraction spots according to the $[111]$ and $[001]$ zone axes. The green circles indicate the extra spots associated with double diffraction; as examples, the green arrows show that the $g(224)$

diffracted beam is re-diffracted by the $(\bar{1}20)$ and (210) planes in the $[001]$ -oriented grain. **b** and **c** Simulated electron diffraction patterns (involving dynamical electron scattering) of $\alpha\text{-Fe}_2\text{O}_3$ along the $[111]$ and $[001]$ zone axes, respectively.

NWs. According to Shen et al. [33], who synthesized bicrystalline Zn_3P_2 and Cd_3P_2 nanobelts, formation of bicrystalline structures in vapor–solid quasi-1D nanomaterial growth is possible to stem from strain relaxation. Since the growth of the studied bicrystalline $\alpha\text{-Fe}_2\text{O}_3$ NWs is stress-driven [9, 10, 15], an analogous reason is considered to explain their formation.

For the synthesis of $\alpha\text{-Fe}_2\text{O}_3$ NWs via oxidation of iron-based substrates, the layered iron oxide scale forming beneath the synthesized $\alpha\text{-Fe}_2\text{O}_3$ NWs has been investigated by Yuan et al., who indicated that the constitution of the iron oxide scale was $\alpha\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4/\text{FeO}$ when the process temperature was above 570°C (i.e., the threshold temperature of forming the FeO phase), and $\alpha\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ when below [10]. On the basis of this conclusion, the thermal oxidation condition used in this study would result in the iron oxide scale comprising upper $\alpha\text{-Fe}_2\text{O}_3$ and lower Fe_3O_4 layers (Fig. 3b). The topotaxial relation between these two layers, i.e., $\alpha\text{-Fe}_2\text{O}_3 [001] \parallel \text{Fe}_3\text{O}_4 [111]$ [34], implies that the $\alpha\text{-Fe}_2\text{O}_3$ layer suffers from interfacial tensile stress exerted by the Fe_3O_4 layer [35]. As elaborated in our previous study [15], this leads to the grown $\alpha\text{-Fe}_2\text{O}_3$ NWs being tensile-strained, for which the $(3\bar{3}0)$ -related ordered structure, identified to be periodic $(3\bar{3}0)$ -related interplanar gap expansions induced by oxygen vacancy accumulations, is a thermodynamically preferred route for strain accommodation. Thus, assuming that

the formation of the $[111] \parallel [001]$ bicrystalline $\alpha\text{-Fe}_2\text{O}_3$ NWs is based on $[001]$ -oriented matrix grains containing the $(3\bar{3}0)$ -related ordered structure (Fig. 3b), their emergence is reasonable. Associated with lattice expansion, the $(3\bar{3}0)$ -related ordered structure eliminates the anticipated energy barrier of developing an $[111]$ -oriented epitaxial grain on an $[001]$ -oriented matrix grain. From another perspective, the wider matching spacing of the $(1\bar{1}2)$ plane set in the $(1\bar{1}2)$ – $(3\bar{3}0)$ coupling (Fig. 3a) signifies that the $[111]$ -oriented epitaxial grain only inherits a reduced strain degree from the $[001]$ -oriented matrix grain. Therefore, the formation of the $[111] \parallel [001]$ bicrystalline $\alpha\text{-Fe}_2\text{O}_3$ NWs can be considered to be originating from strain relaxation. In light of our deduction, as illustrated in Fig. 3c, the $(3\bar{3}0)$ -related ordered structure in $[001]$ -oriented grains of the $[111] \parallel [001]$ bicrystalline $\alpha\text{-Fe}_2\text{O}_3$ NWs must result in periodic $(1\bar{1}2)$ -related lattice expansions in $[111]$ -oriented grains of the NWs, which we believe is the microstructural characteristic of the $(1\bar{1}2)$ -related ordered structure. Referring to prior studies, we have noticed that the periodicity of the $(1\bar{1}2)$ -related ordered structure ($14.7\text{ \AA}$) is substantively the same as the most observed periodicity of the $(3\bar{3}0)$ -related ordered structure ($14.5\text{ \AA}$). This coincidence provides a vital demonstration of the correlation between these two ordered structures.

Figure 4 **a** TEM image of an α -Fe₂O₃ NW segment in which the bottom simultaneously contains regions dominated by the $[\bar{1}11] \parallel [001]$ bicrystal and $[001]$ -oriented grain. **b–e** HR-TEM images and

the corresponding FFT patterns (real-numbered format) of areas 1–4 in (a). **f** $(\bar{1}23)/(\bar{1}20)$ intensity ratios for the FFT patterns in (c–e).

information for the adopted supercell), calculated with a thickness value of 50.5 nm and an underfocus of 11 nm, is displayed in Fig. 5b. It can be seen that the experimental image and simulated image closely resemble one another, indicating that the projected potential of the $[\bar{1}11]$ -oriented grain dominated in the HR-TEM observation of the bicrystalline α -Fe₂O₃ NW. Therefore, an approximated insight into the microstructural characteristic of the $(1\bar{1}2)$ -related ordered structure should be obtained by analyzing the superstructure modulation evident in Fig. 5a.

The simulated HR-TEM image in Fig. 5b includes three types of image spots, designated as types A, B, and C; their corresponding crystallographic positions are illustrated by the superimposed lattice model. Comparing the experimental HR-TEM image with the simulated image, we noticed that half of the type-B spots at the superstructure modulation were distorted into a streak-like shape and that the type-A spots next to the distorted type-B spots are slightly shifted along the $[110]$ direction (Fig. 5c). This represents the presence of atomic column displacements around the superstructure modulation. In addition, measuring a series of interval values between

adjacent type-A and type-C spots (Fig. 5d), each of which corresponds to the interplanar spacing of the $(1\bar{1}2)$ planes, we found that spots flanking the superstructure modulation had wider interval values, signifying that the atomic column displacements are due to tensile strain. Overall, the HR-TEM observation suggests that the $(1\bar{1}2)$ -related ordered structure is periodic atomic column displacements that serve as tensile strain accommodation.

Based on the HR-TEM image spot variations, we deduce that the atomic column displacement scenario of the $(1\bar{1}2)$ -related ordered structure is the splitting of neighboring atomic columns to accommodate tensile strain. A specific illustration of this is shown in Fig. 5e, where a row of atomic column splits is introduced into the supercell to simulate the HR-TEM image shown in Fig. 5b. With the same calculation parameters, a simulated HR-TEM image based on this locally distorted supercell is shown in Fig. 5f, wherein the experimentally observed type-B spot distortion and type-A spot shift are reproduced at positions corresponding to the atomic column splits. Although the simulation does not perfectly reproduce the experimental image details of the $(1\bar{1}2)$ -

Figure 5 **a** Enlarged image of the area within the red box in Fig. 1(a). The red arrows indicate the superstructure modulation. The orange double-headed arrows and green arrows highlight the type-B spot distortion and type-A spot shift, respectively. **b** Simulated HR-TEM image based on pristine α -Fe₂O₃. The inset shows the lattice model along the $\bar{1}11$ axis. **c** and **d** Intensity profiles corresponding to the white dashed and yellow dashed

profile lines in (a), respectively. The blue and green dotted lines represent the center positions of type-A spots and type-C spots, respectively. **e** α -Fe₂O₃ supercell in which a row of atomic column displacements is introduced. The upward displacements are 0.4 Å (O column) and 0.2 Å (Fe column); the downward displacements are 0.05 Å (O column) and 0.1 Å (Fe column). **f** Simulated HR-TEM image calculated on the basis of the supercell shown in (e).

related ordered structure, understood to be mainly attributed to a local expansion that is not really introduced into the supercell and the use of a single-crystal approximation, it verifies the plausibility of the deduced atomic column displacement scenario.

Being exempt from the multiplet effects [36], O K-edge core excitation spectra of α -Fe₂O₃ effectively reflect its structural characteristic. Therefore, by comparing the O K-edge EELS spectrum fine structure of the $\bar{1}11 \parallel [001]$ bicrystalline α -Fe₂O₃ NWs with that of pristine α -Fe₂O₃, microchemistry-based evidence that supports the existence of tensile strain in the NWs should be obtained. Figure 6a shows monochromated O K-edge near-edge EELS spectra of the bicrystalline α -Fe₂O₃ NW displayed in Fig. 1 and a stoichiometric α -Fe₂O₃ reference sample (α -Fe₂O₃ powder from Sigma-Aldrich Inc., which was further atmospherically annealed at 500 °C for 20 h). The spectra have been normalized to the maximum of peak A1, and their onsets were determined using the intensity of the first inflection in the reference sample spectrum. Peaks A1 and A2 are known to be pre-peaks [37], which correspond to the electronic transitions from O 1s orbitals to the portion of O 2p orbitals hybridizing with Fe 3d orbitals. We noticed that the pre-peak interval in the NW spectrum

is ~ 0.05 eV smaller than that in the reference sample spectrum. This ligand field splitting reduction may imply that the NW has a lower Fe 3d–O 2p hybridization degree than the reference sample [37], i.e., the NW possesses a longer average Fe–O interatomic distance. Peak B can be regarded as the near-edge main peak; its formation, in the light of the real-space multiple scattering theory, is substantially attributed to the first-oxygen-shell scattering resonance of the excited 1s core electrons [38]. That is, for each of the acquired EELS spectra, the energy interval between the spectrum onset and peak B (ΔE) is connected with the average radius of the first oxygen shell surrounding an excited oxygen anion (R) via the relation in Eq. 1 [38]:

$$\Delta E \times R^2 = \text{constant}. \quad (1)$$

R is essentially equivalent to the average interatomic distance between two adjacent oxygen anions (R_{O-O}). The ΔE values in the spectra of the NW and reference sample were found to be 11.9 and 12.0 eV, respectively, meaning that R_{O-O} in the α -Fe₂O₃ NW is 0.4% longer than that in pristine α -Fe₂O₃. Since the lattice framework of α -Fe₂O₃ is constructed by close-packed oxygen anions, this reconfirms the HR-TEM

Figure 6 **a** Measured O K-edge near-edge EELS spectra of the α -Fe₂O₃ NW shown in Fig. 1 and the α -Fe₂O₃ reference sample. The determined spectrum onsets are indicated by the black dotted lines in the inset, which enlarges the region within the dashed box. **b** Simulated O K-edge near-edge EELS spectra of α -Fe₂O₃ with and without 0.4% lattice expansion.

observation result that the α -Fe₂O₃ NW has tensile strain.

The slightly expanded lattice of the α -Fe₂O₃ NW is also reflected by the onset shift in the EELS spectra. Through fitting an experimentally acquired monochromated Fe L₃-edge EELS spectrum of the reference sample with the charge transfer multiplet calculation [39, 40], we evaluated the average Fe–O bonding covalency in α -Fe₂O₃ to be only approximately 21.9% (see supplementary information for details), indicating a high ionicity of this material. Therefore, for α -Fe₂O₃, the binding energy of O 1s core electrons is considerably affected by the Madelung potential at oxygen anions. To this extent, when the lattice of α -Fe₂O₃ is tensile-strained, the increased average Fe–O interatomic distance will reduce the binding energy of the O 1s core electrons [41] and will thus result in a lower O K-edge onset energy.

This argument tells that the relative left shift of the NW spectrum's onset in Fig. 6a is a sign of an expanded average Fe–O interatomic distance in the α -Fe₂O₃ NW. Displayed in Fig. 6b, O K-edge near-edge EELS spectra of α -Fe₂O₃ with and without 0.4% lattice parameter expansion were calculated (see supplementary information for details); the onset shift in the simulated spectra affords definite theoretical support to the connection between lattice expansion and O K-edge downward shift for α -Fe₂O₃.

For transition metal oxides, oxygen vacancy formation can be facilitated by introducing tensile strain [42–44]. Since the microstructural characteristic of the (1 $\bar{1}$ 2)-related ordered structure has been verified to be periodic local lattice expansions, this ordered structure must be oxygen deficient. Although definite lattice positions of the oxygen vacancies still require further investigations, our study results elucidate the

Figure 7 **a** and **b** Wide-range EELS spectra (green curves) of two $[\bar{1}11] \parallel [001]$ bicrystalline $\alpha\text{-Fe}_2\text{O}_3$ NWs having differing crystal constitutions. Revealed by the difference in the $(\bar{1}2\bar{3})/(\bar{1}20)$ intensity ratio between the inset FFT patterns (real-numbered format), transformed from HR-TEM images of the NWs, the spectrum in **(a)** corresponds to the NW with the higher $[\bar{1}11]$ -

oriented grain proportion. The red curves are the O K-edge and Fe L-edge near-edge signals extracted by the power-law-based background subtraction method. **c** EELS-based quantitative comparison of the $\alpha\text{-Fe}_2\text{O}_3$ NWs using the extracted near-edge signals.

root cause of the long-asserted connection between the $(1\bar{1}2)$ -related ordered structure and oxygen vacancy ordering. Per the explanation given above, the difference in strain degree between the $(1\bar{1}2)$ - and $(3\bar{3}0)$ -related ordered structures should cause the former to have lighter oxygen deficiency than the latter. To verify this, wide-range EELS spectra of two $[\bar{1}11] \parallel [001]$ bicrystalline $\alpha\text{-Fe}_2\text{O}_3$ NWs with differing crystal constitutions were acquired (Fig. 7a and b). By extracting the O K-edge and Fe L-edge near-edge signals from the spectra (the adopted signal window was 24 eV, determined on the basis of the $L_{2,3}$ -edge energy width) and normalizing them on the O K-edge signal area, we conducted an EELS-based quantitative comparison between the two $\alpha\text{-Fe}_2\text{O}_3$ NWs. The result is shown in Fig. 7c, wherein the explicit difference in the Fe L₃-edge signal intensity reflects that the $\alpha\text{-Fe}_2\text{O}_3$ NW with the higher $[\bar{1}11]$ -

oriented grain proportion has a lower Fe/O atomic ratio, i.e., it is less oxygen deficient. Therefore, in comparison with the $(3\bar{3}0)$ -related ordered structure, the $(1\bar{1}2)$ -related ordered structure indeed contributes less oxygen deficiency to the $[\bar{1}11] \parallel [001]$ bicrystalline $\alpha\text{-Fe}_2\text{O}_3$ NWs. This further reinforces the fact that the presence of oxygen vacancy ordering in $\alpha\text{-Fe}_2\text{O}_3$ NWs synthesized via oxidation of iron-based substrates is attributed to tensile strain.

Conclusions

In summary, for oxidation-synthesized $\alpha\text{-Fe}_2\text{O}_3$ NWs, the known $(1\bar{1}2)$ -related ordered structure was observed to actually occur in $[\bar{1}11]$ -oriented grains of $[\bar{1}11] \parallel [001]$ bicrystalline $\alpha\text{-Fe}_2\text{O}_3$ NWs and originate in the $(3\bar{3}0)$ -related ordered structure of $[001]$ -

oriented grains of the NWs. Interpreting the C_S -corrected HR-TEM observation results, we further revealed that the microstructural characteristic of the (1 $\bar{1}2$)-related ordered structure was periodic atomic column displacements serving for accommodating tensile strain. This HR-TEM finding is supported by the monochromated O K-edge EELS analysis, which indicates that, in comparison with pristine α -Fe₂O₃, α -Fe₂O₃ NWs hosting the (1 $\bar{1}2$)-related ordered structure have larger average O–O and Fe–O interatomic distances. The association of the (1 $\bar{1}2$)-related ordered structure with local lattice expansion explicates its long-asserted relevance to oxygen vacancy ordering. The difference in oxygen deficiency degree between the (1 $\bar{1}2$)- and (3 $\bar{3}0$)-related ordered structures, verified by the EELS-based quantitative comparison, also suggests that the oxygen vacancy ordering in oxidation-synthesized α -Fe₂O₃ NWs is strain-induced.

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Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest.

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