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ARTICLE

Oxyhydroxide of metallic nanowires in a molecular H₂O and H₂O₂ environment and their effects on mechanical properties[†]Gurcan Aral,^{*a} Md Mahbulul Islam,^b Yun-Jiang Wang,^c Shigenobu Ogata,^{d,e} and Adri C. T. van Duin^f

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To avoid unexpected environmental mechanical failure, there is a strong need of fully understanding the details of the oxidation process and intrinsic mechanical properties of reactive metallic iron (Fe) nanowire (NW) under various aqueous reactive environmental conditions. Herein, we employed ReaxFF reactive molecular dynamics (MD) simulations to elucidate the oxidation of Fe NWs exposed to molecular water (H₂O) and hydrogen peroxide (H₂O₂) environment, and the influence of oxide shell layer on the tensile mechanical deformation properties of Fe NWs. Our structural analysis shows that naturally oxidation of Fe NWs and the formation of different iron oxide and hydroxide phases in the aqueous molecular H₂O and H₂O₂ oxidizing environments. We observe that the resulting microstructure due to the pre-oxide shell layer formation reduces the mechanical stress via increasing the initial defect sites in the vicinity of oxide region to facilitate the onset of plastic deformation during the tensile loading. Specifically, oxide layer of Fe NW formed in the H₂O₂ molecules has a relatively significant effect on the degradation of mechanical properties of Fe NW. The weakening of the yield stress and Young modulus of H₂O₂ oxidized Fe NW indicates the important role of local oxide microstructures on mechanical deformation properties of individual Fe NWs. Notably, deformation twinning is found as the primary mechanical plastic deformation mechanisms of all Fe NWs, but it is initially occurred at the low strain and stress level for the oxidized Fe NWs.

1. Introduction

Unfortunately, readily formation of thin oxide layers on the exposed surface of Fe materials is naturally inevitable during their production, storage, and working conditions.¹⁻⁴ There is no effective way of preventing progressive oxidation of reactive metallic materials, specifically when they are exposed to reactive ambient conditions.²⁻⁴ However, the surface oxidation can be circumvented only under extremely high vacuum conditions and with specific surface coatings.^{1,4,5,7-9} Generally, in aqueous working condition, metallic Fe materials commonly produces in various crystalline phases of Fe oxide and oxyhydroxide such as green rust (Fe(OH)₂), goethite (α-FeOOH), etc.^{3,6,10-13}

Overall, progressive oxidation of metallic Fe materials is usually associated with corrosion, and their detrimental effects are prevalent in many practical applications of the materials.^{1-3,6,10} The

environmental conditions dictate the strength, lifetime, and failure of reactive metallic materials.^{3,14,15} In particular, the resulting oxide shell layer drastically alters the physical and chemical properties of the exposed surface layer, and as a result, eventually, the strength of Fe NWs may be weakened in an uncontrolled way compared to corresponding un-oxidized counterparts.^{2,3,10,16,17} However, the presence of undesirable and desirable (oxide-coating) of oxide shell layer on the free Fe NW surfaces is associated with surface/interface finite-size effects which help distinctly to achieve potentially additional interesting and unique chemical,³ physical,⁸ optical,¹⁸ mechanical,¹⁷ and magnetic properties^{5,8,11} as compared to un-oxidized counterparts.^{4,10,12,19-21} All of these unique features make oxide-coated Fe-based nanomaterials very promising in many different research areas.^{1,4,5,7-9} The Fe nanomaterials and their oxide-coated derivatives have been successfully used in many nanoscale applications such as in biomedical science,^{5,7,13} magnetic data storage, etc.^{4,5,20} Nowadays, of special interest, oxide-coated Fe NWs

are either used as a typical core–oxide shell layer (Fe–Fe_xO_y) or a fully oxidized iron such as hematite, magnetite, and wüstite structure.^{1,5,7,11,13,18–23} The diversity (nature) of surface oxide shell layers serve as the composition of the tunable gain medium, which provides a variety of opportunities and challenges to improve Fe NWs properties.^{1,7,8,13,19,23} In particular, relevant surface modifications including a subtle deviation of surface oxide chemistry, unique size, shape, oxide shell layer thickness, oxide layer density, constituents, overall morphology, porosity, and crystals phase are strongly coupled with intrinsic functional properties as well as correlation with the performance of core–shell structure of Fe NWs.^{1,7,8,12,20–25} Generally, the presence of oxide layer on the metallic materials not only alters and but also have a pivotal role on the naturally various physical and chemical processes such as adsorption/desorption,^{7,11,12} corrosion, catalysis,^{4,7,11} corrosion,^{2,3} and wetting processes.^{4,5,9,12,19,21}

Undoubtedly, detailed fundamental understanding of oxidation mechanism, microstructures of resulting oxide layers of nanoscale Fe materials associated with the type of oxidizer in the various reactive atmosphere is essential in the coating technology as well as the corrosion processes of Fe metal and steel.^{1–4,7,24–26,27} Especially, reactive H₂O and H₂O₂ environment may provide effective options to control the surface properties of Fe NW in order to improve the functionality such as corrosion resistance and catalytic performance.^{2–4,10,13} The overall oxide growth of Fe associated with H₂O and H₂O₂ molecules is usually incorporated consecutively with the adsorption, dissociation, segregation, diffusion and eventually reconstruction on the free surface of Fe nanomaterials via physical and/or chemical reactions.^{1–4,10,27} In general, oxidation process causes the creation of various defects on the developed oxide region and the interface between the metallic core of Fe NW and the oxide shell layer, which influences the mechanical properties of the NW.¹⁷ Therefore, it is essential to understand quantitatively how the H₂O and H₂O₂ molecular species oxidize the metallic Fe NW free surfaces and how the oxidize shell layers affect the mechanical elastic properties and intrinsic strength.

Recently, Landau et al. performed experimental to investigate the effect of helium on the mechanical properties, and deformation mechanism of as-fabricated and helium implanted single crystalline iron nanopillars under both tensile and compression loading.¹⁶ They reported that, the tensile deformation, both as-fabricated and helium implanted samples display three distinct regimes: elastic loading, substantial strain hardening, and a “steady state” region. For example, yield and ultimate strength as well as flow stress significantly increase for helium-implanted samples compared to as-fabricated ones. Furthermore, numerous MD studies have been performed to investigate the strengthening of the pure Fe NWs using fix charged interatomic potentials under tensile and compressive loading.^{14,15,28–32} In these studies, Fe NWs were considered simply in vacuum, and thereby, the effects of the surface oxide layer on the mechanical behaviors were ignored. Many of these studies have focused on exploring the influence of geometry, size, loading, grain size, surface geometry, and temperature on the mechanical deformation mechanisms and related properties of the metallic Fe NWs. These studies demonstrated that the mechanical deformation mechanisms and associated properties of metallic Fe NWs are strongly contingent on these parameters. For example, using EAM potential, Sainath et al. have studied the size effect on mechanical deformation mechanism of metallic <100>/[100] and <110>/[111]-oriented single crystal BCC Fe NWs under tensile and compressive loading.^{29,30} They observed the crystal orientation dependent behavior of tensile deformation of single-crystal bcc Fe NW such at

various initially orientated <100>, <112>, <102>, <110> and <111> Fe NWs.²⁸

However, only a few recent studies have been conducted to quantify and confirm the importance of surface oxidation on the mechanical properties of metallic NW by using reactive variable charge potential models. Meanwhile, it has been realized that the deformation and related mechanical properties of oxidized metallic nano materials drastically differ from their un-oxidized counterparts.^{17,32–35} It was shown that the mechanical properties at the nano scale are directly related to surface oxide shell features, such as oxide thickness, type of oxide microstructure, and morphology.²³ For example, in our previous study, MD simulation with ReaxFF potential was used to study oxidation of Fe NWs with O₂ molecules and the effect of oxidizing layers on the mechanical deformation mechanism and related properties as a function of oxide shell thickness.¹⁷ We found that the thicknesses of oxide shell layer on the free surface of Fe NWs play an important role in the tensile mechanical properties. Sen et al. studied oxide shell layer dependent deformation mechanism of metallic aluminum (Al) NWs by using the ReaxFF method.^{32,33} They reported that the oxide shell layer on the Al NW free surface helps to change the elastic mechanical response from brittle to ductile transition behavior. Our previous studies indicated that the influence of surface oxide shell layer on the mechanical properties of Ni NWs is most significant in smaller diameters than larger diameters.³⁴

The effects of each resulting pre-hydroxylated shell layer—occurred due to the reactions with H₂O and H₂O₂ molecules—on the mechanical tensile deformation response of Fe NWs have not been explored yet. For this reason, we have carried out MD simulations using the ReaxFF potential, which was developed by Aryanpour et al.⁶

2. Computational approach and methods

2.1 Reactive Force Field (ReaxFF) potential

The complexity of oxidation of Fe NWs and its effects on the mechanical behaviour is not easily accessible to quantify independently by using existing experimental methods. Particularly, there are difficulties with the high specific surface areas of reactive Fe NW, involved small spatio-temporal scale related to the experimental characterization.^{16,26} In this respect, MD simulations with fix charge potential models are limited in describing complex chemical reactions as well as interfacial properties of oxide coated Fe NWs. The fixed charge potential models disregards the surface oxidation effects, leading to incorrect predictions of mechanical properties of oxidized Fe NWs.^{15,16,26} For these reasons, recently, several variable charge methods have been developed.^{6,36,37}

In order to account the dynamical description of charges as well as the formation and breaking of chemical bonds to describe complicated reaction processes, we used ReaxFF reactive force field method.^{6,36,37} ReaxFF is a bond order based variable charges method, enabled us to quantify directly the nature of the formation of oxide shell layer on free surface of Fe NWs and predict their effects on the mechanical responses.¹⁷ The ReaxFF Fe/O/H force field, developed by Aryanpour et al., used in this study to describe accurately the entire range of intermediate interactions among Fe/O/H atoms including both covalent and ionic bonds, capture the bond formation and breaking.⁶ The Fe/O/H has already demonstrated its capability in predicting the mechanical properties of Fe NWs as a function of oxide shell layer thicknesses.¹⁷ Using the force field MD simulations

are performed to make quantitative predictions as well as elucidate the influence of oxidized shell layer on mechanical properties and provide atomistic insight into the mechanical deformation process of [001]-oriented Fe NWs. The details of the ReaxFF method can be found in recent reviews.^{6,38,39}

2.2 Setup of Simulation System and computational methods

We performed the MD simulations with the ReaxFF potential as implemented within the LAMMPS code.⁴⁰ We carried out simulations mainly in two parts: oxidation process and mechanical tensile loading. The simulated system is similar to that we previously used to study the mechanical deformation mechanism of oxidized-Fe NWs as a function of surface oxide shell layer thickness under tensile loading.¹⁷ The Fe lattice has a BCC crystalline structure, with a lattice constant a = 2.86 Å. To perform the simulation, an initial size of orthogonal periodic MD simulation box has been chosen (50 × 50 × 50) × a, using this lattice constant a = 2.86 Å, that results in having with a size of 14.315 nm in the all directions in the Cartesian coordinate system. The initial configuration of an infinitely long cylindrical shape of the metallic Fe NW with a diameter of ~5.0 nm and a length of ~14.3 nm are schematically shown in Fig. 1, where red color represents Fe atoms. The diameter-to-length aspect ratios of the pure Fe NW is ~1:3, containing a total of 24,050 iron atoms. The metallic Fe NW is placed in the middle of an MD box in [001] oriented direction. First, a comparative investigation of oxidation process in between the H₂O and H₂O₂ molecular environments is conducted under same conditions. H₂O and H₂O₂ molecules are separately used as the two different oxidizing environments to oxidize the metallic Fe NWs. Before starting oxidation simulations, 1334 H₂O molecules are placed in random orientations into the vacuum space at about 6 Å far from the Fe NW surface, as shown in Fig. 1. Then, we allowed oxidation to occur to form a pre-oxide shell layer. All oxidation process simulations were carried out at a temperature of 300 K using a canonical ensemble (NVT) with Nose-Hoover thermostat.⁴¹ The simulation of the oxidation of the metallic pure Fe NW was performed with periodic boundary conditions in all directions. Consequently, thin oxide shell layers are formed on the free surfaces of pure Fe NWs during the oxidation simulations. The H₂O molecules, which did not contribute to the formation of oxide shell layer, were removed from the simulation box. The same set of oxidation simulations with the same conditions were then repeated in the H₂O₂ molecular environment, initially containing 1000 H₂O₂ molecules in the vacuum region. The oxidation simulations were run until oxidizing shell layer associated with H₂O and H₂O₂ oxidizer molecules are 3764 (2509 H and 1255 O atoms) and 3736 (1866 H and 1870 O atoms) that were consumed in the simulation of ~0.4 and ~1.1 ns duration, respectively. The resulting oxide shell layer with different phases (Fe_xO_yH_z) is formed on the free surfaces, depending on the oxidizer types. The snapshots of Fe NW before (Fig. 1) and after oxidation (Fig. 2) are presented to illustrate the atomic configuration of the oxidation process as well as resulting oxide shell layers on the free surface of NWs in the atomic resolution.

Once the pure and pre-oxidized Fe NWs were prepared with H₂O and H₂O₂ molecules (two different surface oxide phases), the tensile mechanical deformation simulations were performed in two steps similar to our previous work.¹⁷ Prior to perform the tensile test, starting from the initial configuration, first, energy minimization is performed for all NWs using conjugate gradient method to obtain the minimum energy configurations. Next, we carried out equilibration simulations with a Nose-Hoover isobaric-isothermal (NPT) at T = 300 K and zero pressure in the z-direction to allow structural relaxation in order to remove surface tension due to the internal residual stresses.⁴²

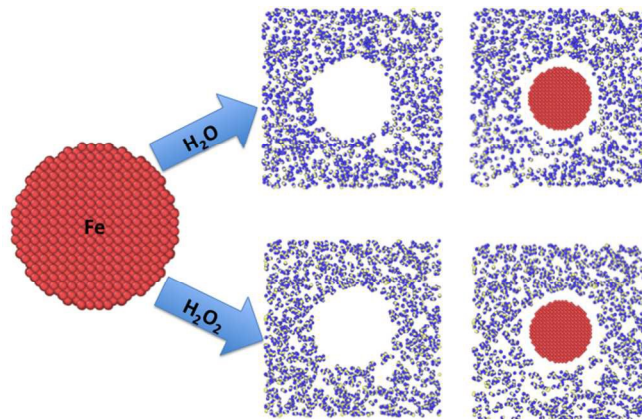


Fig. 1 Schematic diagram illustrating of the initial pristine Fe NWs in contact with molecular H₂O and H₂O₂ environments. In all the figures, the red, blue and yellow atoms are the Fe, H, and O atoms.

After equilibration process, all Fe NWs were subjected to uniaxial tension loading along the [001] direction by applying a constant uniform strain rate of 0.01% ps⁻¹ (10⁸s⁻¹). A periodic boundary condition is only applied in the loading direction in order to remove surface effects, thus resembles an infinitely long NW. In deformation simulations, all atoms are uniformly displaced in a stepwise manner until 15% of the initial box length. These simulations are performed with the NVT ensemble at a constant temperature of T = 300 K using Nose-Hoover thermostat.⁴¹ An explicit time-reversible Velocity-verlet integrator with a time step of 0.25 fs is used to numerically integrate the equation of motions.⁴³ Total duration of the mechanical deformation simulations are 1.5 ns. Atomic charges are determined at every MD time step to minimize the electrostatic potential energy.^{39,44}

3. Results and Discussion

3.1 Resulting oxide growth processes and hydroxyl formation with respect to H₂O and H₂O₂ molecules

In this work, we focus on the comparatively understanding of the oxidation process of the metallic Fe NW with the two different oxidizing agents - molecular H₂O and H₂O₂ by carefully controlling the temperature in the NVT ensemble. The oxidation processes of Fe NWs with a diameter of 5.0 nm are discussed for similarities and differences in terms of two different oxidizers environment (H₂O and H₂O₂ atmosphere) in the gas phase. The high reactivity of H₂O and H₂O₂ molecules causes rapid oxidation of Fe NW with correspondingly distinct chemical reaction paths and also to create the core Fe-Fe oxide shell nanostructures. Therefore, the growth of oxide shell layers changes the morphology and forms a core-shell structure, is clearly visible in Fig. 2. The Fe NWs oxidize faster in the H₂O atmosphere than in the H₂O₂ atmosphere. Mainly, the metallic Fe NW with an excess of clean surface areas readily interacts with H₂O and H₂O₂ molecules, which can be attributed to the dissociative chemisorption of H₂O and H₂O₂ molecules at the free surface sites. Namely, the complicated surface geometric nature of cylindrical NW provides inhomogeneous distribution of adsorption sites and structure, such as different crystal orientation, vacancy defects, etc., which may influence the reactivity of adsorption and dissociation process of

molecules, promote the specific interaction, and surface reactions. The reaction mechanisms of oxidation process and chemical reactivity of H₂O molecules towards Fe NW in gas phase differs significantly from H₂O₂ molecules. We find that H₂O and H₂O₂ molecules react with the metallic Fe NW at specific free surface sites to readily form bonds with Fe atoms via both molecularly as well as dissociatively on the free surface of NW at room temperature.

The progressive oxidation process in the molecular H₂O atmosphere shows that the O atom of the H₂O molecule is attracted to the free surface Fe atom of metallic NW that forms a weak Fe–O bond facilitated by the difference in electron affinity between the O for Fe atoms. Therefore, most of the H₂O molecules remain in the outermost layer of NW—without breaking O–H bonds—via physisorption onto the surface. Thus forms an ordered H₂O molecular plane over the free surface of Fe NW with weak O–Fe bonding. During the continuous oxidation process, the total number of 1195 H₂O molecules are physisorbed to the free surface of Fe NWs in the form of interfacial H₂O–Fe bonds, exhibiting preferentially radially up orientation of H atoms of these H₂O molecules, leading to the polarization of H₂O molecules. This observation can be attributed to the existence of attractive electrostatic interactions between Fe and O atoms. The vertical orientation of the H₂O molecules at the outer most surface of the NW, with O–H bonds directed towards the surface, as seen in Fig 2. However, we also observed dissociation of a small number of H₂O molecules during the oxidation process. Approximately, a total number of 60 H₂O molecules are segregated via the breaking of O–H bonds into more reactive hydroxyl ions (OH[•]) and H ion. The result indicates that approximately only 6.5% of the H₂O molecules are dissociated. The low percentage of hydroxyls relative to that of H₂O molecules also contributes to the formation of the oxide shell layer. Since the large difference in charges between dissociated hydroxyl ions and Fe surface resulted in the stronger Coulombic interaction that helps the ions to diffuse into the core of metallic NW as well as recombination with surface Fe atoms. Thus, the hydroxyls ions can oxidize Fe surface more easily as well as faster than H₂O molecules, and as a result they facilitate the growth of a thicker oxide shell layer. However, the small number dissociated ions from the H₂O molecules have a relatively less influence on the composition of Fe oxides and the mechanical deformation mechanism. The resulting oxide shell layer primarily contains physisorbed/chemisorbed H₂O molecules and minor components of OH and H ions. This result suggests that oxidation of the metallic Fe NW in a H₂O environment resulted in predominantly adsorbed H₂O molecules. As a result, there is no significant structural change in the top layer of Fe NW. We note that the total number 1108, 60, 27 of H₂O molecules are bonded primarily with one, two and three Fe atoms on the outer surface of metallic NW in the form of interfacial H₂O–nFe bonds, respectively.

Our result including the mostly physisorption of H₂O and dissociation of H₂O molecules on the Fe–NW surface are consistent with previous studies of oxidation of Fe materials with H₂O molecules. For example, Baro et al. investigated the absorption of H₂O at 130 K on the Fe(110) using electron energy loss spectroscopy.⁴⁵ Their observation indicated that H₂O was dissociatively absorbed at low water exposures on the surface yielding hydroxyl species. Eder et al. studied the interaction details of H₂O molecules with Fe (100) and (110)-oriented surfaces using DFT calculations.⁴⁶ These studies provided us a fundamental understanding of the initial stages of Fe oxidation and the dissociation process of H₂O on both surfaces. For example, the closed packed Fe (110) is chemically less reactive than the more open Fe (100) surface and moreover, dissociation of H₂O molecules

is a weakly activated process on both surfaces. They showed that at low coverage, H₂O dissociates spontaneously into H atoms and OH groups. Dwyer et al. experimentally observed that the interaction of H₂O molecules with the clean Fe(110) surface lead to the decomposition into a mixed ad layer of H atoms and surface OH groups at 225 K.⁴⁷ Pan et al. studied oxidation of iron in molecular H₂O environment at temperature (298 K) and under atmospheric pressure (1 ATM) by using the reactive force field.^{2,3} They observed that the O–H bond dissociation in some of the H₂O molecules immediately results into the generation of new chemicals species (the generation of H⁺ and OH[•] ions) and recombination of them with the Fe atoms as time progresses. They showed that Fe atoms were bonded with a collection of primarily H₂O molecules and hydroxyls. For example, some H₂O molecules of top iron layers are bonded with one, two or three Fe atoms to form a crystalline-like structure of Fe oxides in near vicinity. This behaviour is mostly consistent with our observations. Moreover, the OH ionic termination also reported to form three types of structures with Fe atoms, which are bonded with O atoms such as HO–Fe, HO–2Fe, and HO–3Fe.^{2,3}

During the oxidation process, the interaction of the total number of ~934 H₂O₂ (out of the initial total number of 1250 H₂O₂) molecules on the free surface of Fe NW that consequently dissociate into hydroxyl (OH), water (H₂O), O, ·OO· and H ions. After the oxidation process, we observe the overall total number of 1 ·OO·, 42 H₂O, 43 H, 51 H₂O₂, 88 O, and 1680 OH ions and molecules as a result of reactions of H₂O₂ molecules with Fe on the vicinity of oxide region. The final dissociated products are consistent with previous MD simulations with respect to the existence of oxidation products with H₂O₂ molecules. For example, Chen et al. observed similar spontaneous decomposition of unstable structure of H₂O₂ molecules and the formation a large variety of reactive species such as H[•], ·OH, ·O·, ·OO· and ·OOH during the reaction of C atoms with the reactive H₂O₂ molecules.⁴⁸ Our result indicates that the dissociation of the O–O bond of a H₂O₂ is mainly accompanied by the formation of reactive OH ions. Primarily, three distinct coexistence of hydroxyl types in between H and O atoms (OH, H₂O and H₂O₂) are observed on the free surface of Fe NW upon the oxidation process. Especially, hydroxyl (OH) and O ions are highly reactive toward Fe and penetrate deep into the core region and react with subsurface and bulk Fe atoms, leading to oxidized Fe NWs.^{4,17,22} Therefore, the oxidation of Fe NWs in the H₂O₂ environment exhibits a significant morphology and structural change in the vicinity of its surface oxide region. The simultaneous growth of the oxide shell layer with reactive ions triggers the formation of an un-ordered phase in the vicinity of the oxide region. Thereby, these reactive hydroxyl OH[•] and O anions play a central role in aqueous corrosion of Fe as well as influence the degradation of overall mechanical properties of Fe NW.^{4,22}

Our result reveals that H₂O₂ molecules interact with the metallic Fe NW more strongly to form the oxide shell layer as compared to the molecular H₂O. Specifically, the surface modification is strongly correlated with the number of dissociated molecules into any reactive ions. The number of reactive ions dictates the degree of surface reconstruction and defectiveness in the oxide region. The dissolved molecules into reactive ions such as OH and O ions diffused quickly into the subsurface of NW, reacted with Fe atoms at different adsorption sites via charge transfer and resulted in a significant surface reconstruction.⁴ It is noted that the majority of the oxidation products in both aqueous oxidation environments are OH ions. As a result, the presence of the OH ions has the major impact on the mechanical properties of Fe NWs. In this concern, the oxide-coated Fe NW in the H₂O environment has a relatively smaller effect on the mechanical properties of the NW. Our results reveal that the

oxide shell layer properties of the metallic Fe NW surface depend on the type and reactivity of oxidizing species.

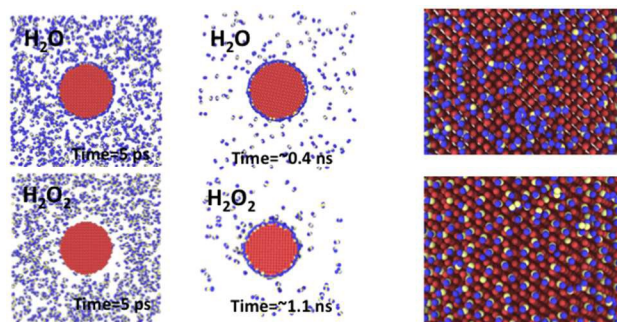


Fig. 2 The two different molecular environments are used to form the core-shell ($\text{Fe}-\text{Fe}_x\text{O}_y\text{H}_z$) structure of NWs. Evolution of the formation surface oxide shell layer depends on the existence of molecular environments. Additionally, zoomed in snapshots of the oxide surface are also shown. The red, blue and yellow atoms are the Fe, H, and O atoms.

3.2 Surface reconstruction: segregation and diffusion over the free surface of metallic Fe NW

In order to determine the total average thickness of the oxide shell layer, expansion of the Fe core, the density of the oxidation, the depth of penetration of the ionic species inside the core of NW (inward diffusion) and change of diameter of all Fe NWs (outward diffusion) are analysed using the atomic radial number density distribution profiles of Fe, O, and H atoms. This analysis elucidates the dynamics of oxidation process as well as the modification of NW structure upon oxidation process. The core of NWs consists of only Fe atoms, while as a result of outward (Fe) and inward (O and H) diffusions, the Fe, O and H atoms are present in the vicinity of developed oxide region at the free surface of Fe NW, as seen in Fig. 3 (a)-(c). Hence, our result reveals that the consequence of the outward and inward diffused species in the resulting oxidized shell layer through charge transfer process and modification of intrinsic surface properties of the Fe NWs. The modified surfaces primarily correlate the formation of the total growth of the oxide layer and radial volume extension of metallic Fe NW. Comparing Fig. 3 (a) the density of O and H atoms of oxide-coated NW formed in the H_2O molecular environment, H_2O -Fe reactions form a sharper interface than the H_2O_2 molecular environment case, due to the limited mobility of the ionic reactive species on the surface. At the same time, the reduced average radial number density of O and H atoms is observed in a range between the inner radial distance (r_{inner}) of ~ 23.4 Å to the outer radial distance (r_{outer}) of ~ 27.6 Å for H_2O_2 case, while the range is in between r_{inner} of ~ 24.2 Å and the r_{outer} of ~ 25.1 Å for H_2O case in the oxide free surface region. Outer and inner difference indicates that the total thickness of the oxide layer are ~ 4.2 Å and ~ 0.9 Å for H_2O_2 and H_2O molecular case, respectively. It is noted that the final average diameters of oxidized Fe NW with H_2O molecules has approximately average diameter of ~ 2.5 nm, which is very close to the initial diameter of the pristine Fe NW. The oxidation of the Fe NW with H_2O environment indicates that absence of a large number of ions and their diffusion does not resulted into an obvious change in the radial diameter of the metallic Fe NW within our MD simulation timescales. In particular, the resulting radial number density curve of H and O atoms in the H_2O case has relatively sharp pronounced peaks and variation in its height

around the top most free surface of NW, which also suggest that significant amount of H_2O molecules remain radially oriented and ordered at the free interface to form an oxide shell layer that consists solely of Fe-O bonds. Therefore, oxidized Fe NWs with H_2O molecules likely consisted of a core crystalline structure of Fe NW surrounded by H_2O molecules without a significant radial extension. On the contrary, the curve shape of overall continuous radial density distributions of Fe, O and H atoms reveals that H_2O_2 molecules exhibit stronger interactions with the metallic Fe NW. Large amount of decomposed ionic species from H_2O_2 molecules penetrate deeper into the core of metallic Fe NW, which causes to push the Fe atoms into the radially outward direction of the NW. As a result to accommodate this large amount of decomposed ionic species inside of the NWs, Fe atoms diffuses from the core layer to the outer surface of the NWs. It is evident that diffusion of ionic species leads to expansion of metallic Fe NW, increase of the volume including the surface to volume ratios, large mechanical strains, and distortion of the NW in the vicinity of the oxide shell layer. Diffusion of ionic species perturbs Fe atom positions, which may facilitate the initiation of initial dislocation.^{17,34} Therefore, the average diameter increases from 2.5 nm to 2.8 nm, corresponds to an expansion of $\sim 11\%$. The diffusion is associated with an increase in the molar volume, thus, the surface diffusion, and the resulting thickness of the oxide shell layer formed by H_2O molecules exposure are smaller than the ones for H_2O_2 molecules, in qualitative agreement with the density profiles, as clearly seen from Fig. 2. Moreover, the influence of the H_2O activity on the free surface of Fe NWs and penetration into core region is negligible compared to the H_2O_2 molecular case.

The growth of the oxide shell layer is a synergistic process of the migration of reactive ionic species into the core of metallic Fe NW and the Fe ions toward the free surface. Thus, it is suggested that both inner and outer diffusion of ionic species in and/or out are associated with the surface chemical reactions, thus effects the size, volume, local structural, lattice distortion, density, morphologies, oxide shell layer thickness, and nanostructured roughness. As a result, each of oxide Fe NWs has its own diameter and unique crystalline Fe oxide structure. Thereby, the surface properties of oxide coated metallic NWs can be controlled by the atomic diffusion, which is driven by a strong affinity of Fe atoms to hydroxyl ions. Diffusion of ionic species associated with oxidation reactions of Fe NWs may also result in increasing of initial dislocation sites by the creation of higher defects around the vicinity of oxide shell layer.^{8,17,28} In addition to a different bonding nature of oxide atoms including phase transformation, surface stresses may play an important role in the mechanical properties of oxide-coated Fe NWs.⁸ Due to the high surface-to-volume ratio of NWs, owing to the diffusion into the core region may be a reason why surface oxide has more pronounced influences on the overall mechanical strength of the oxide-coated Fe NW, resulting in a reduction of the related mechanical properties.

The resulting unique oxide shell layer on the free surface of Fe NWs are composed of a total number 1255 of O and 2509 of H atoms (a ratio of $\sim 1:2$) for the molecular H_2O case, and 1870 of O and 1866 of H atoms (ratio of $\sim 1:1$) for the molecular H_2O_2 case, respectively. The chemical composition of the oxide-coated Fe NW is consisted of $\sim 86.5\%$ Fe, $\sim 9.0\%$ H and $\sim 4.5\%$ O atoms for H_2O case in the oxide region (24.2-25.1 Å). In molecular H_2O_2 oxidizer case, 86.6% Fe, $\sim 6.7\%$ H and $\sim 6.7\%$ O atoms contribute to the overall chemical composition in the oxide region (23.4-27.6 Å). The overall total number of 22,291 and 21,168 of Fe atoms are not associated with the bonding with O and/or H atoms in the oxide surface region upon the H_2O and H_2O_2 oxidizer environments, respectively. The surface oxide dependence of mechanical

deformation properties is coupled with the metallic Fe core and the Fe oxide shell layers are explained naturally based on the overall number of oxidized/un-oxidized Fe atoms. The associated numbers (11.9 % and 7.3 % for H_2O_2 and H_2O , respectively) are especially significant at the nano scale. Associated Fe atoms with oxide layer may play an interactive role between the pristine core and the oxide shell layer to explain the mechanical degradation achieved in the core-shell layer of NWs. Apparently, increasing numbers are beneficial to the enhancing disordered surface structures. Actually, we already proved the existence of a correlation and cooperation between the metallic core size and the oxide shell for the oxide-coated Ni NWs.³⁴ In smaller diameter, the metallic Ni core experiences a greater effect from the Ni oxide shell layer, because of the higher Ni oxide-to-Ni ratio. Due to the incorporation of ionic species into the metallic Fe core, the total number of Fe-Fe bonding decreases, while the number of Fe-O/H bonding increases, which causes a reduction in the remaining metallic core. Hence, the surface oxide structural disorder and the volume-to-surface ratio increase with the increasing diffusion depth of ionic species. We conclude that the overall number ratio of oxidized/un-oxidized Fe atoms is relatively high in H_2O_2 oxidizer environment, which results in a significant degradation of mechanical properties of the NW.

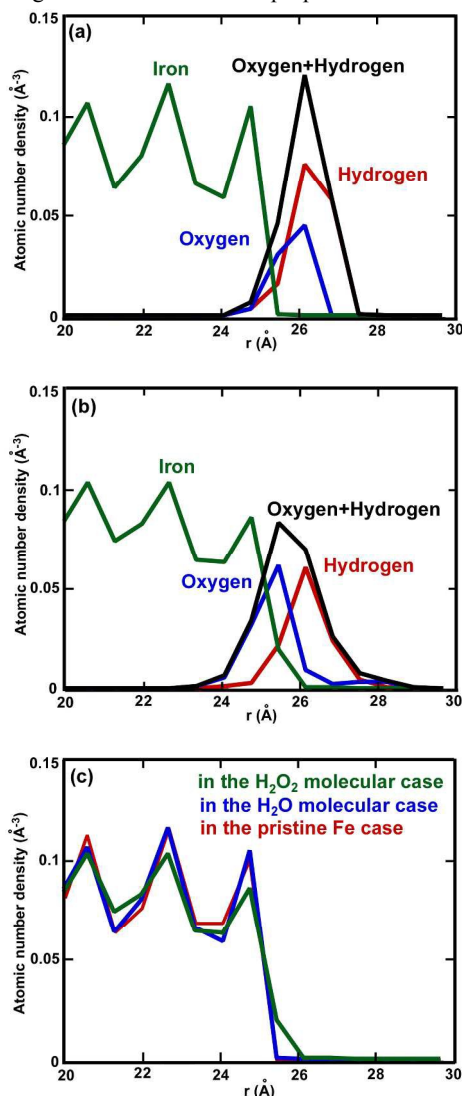


Fig. 3 The radial density profiles of Fe (solid green line), O (blue), H (red), and, H and O (black) in the oxide Fe NW for (a) H_2O and (b) H_2O_2 molecules at the end of the oxidation simulation, respectively, where the radial radius r is the distance from the centre of NWs, with respect to each radial shell width of 0.7 Å. Further, to compare what happens on the metallic core of NW's upon the oxidation processes, (c) we show the radial density profiles of metallic core for pure (red), oxide-coated Fe NW with H_2O (blue) and H_2O_2 (green) molecules, respectively. From these snapshots, one also sees that ionic species penetrates deeper upon oxidation process with H_2O_2 molecules.

3.3 Surface phases and local structural properties of the hydroxylation shell layer associated with the H_2O_2 and H_2O molecules

Herein, for a better understanding of oxide surface properties, the nature of local short-range crystalline microstructure properties and correlations of the resulting oxide shell layer on the NWs are investigated carefully by using radial pair distribution functions (RDF), coordination numbers, radial density profiles, phase composition, and morphology on free surface of NW.

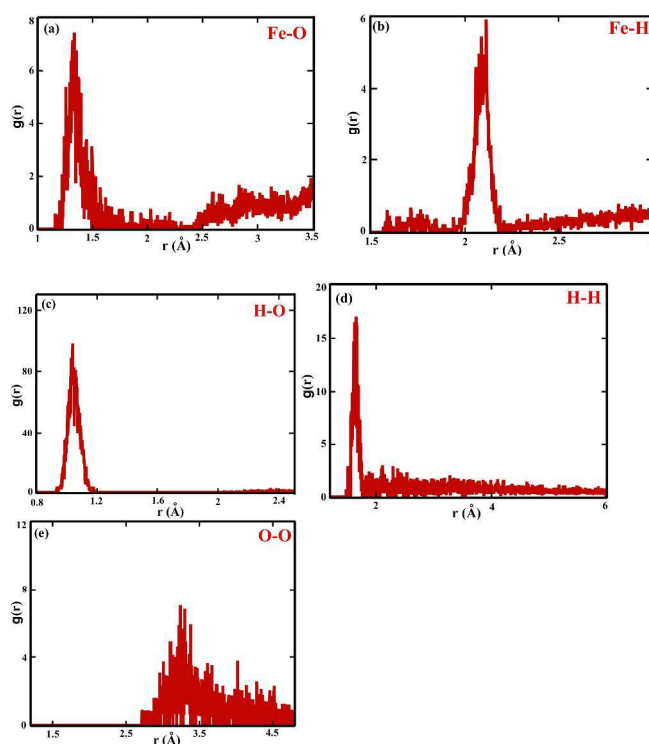


Fig. 4 RDF between (a) Fe-O, (b) Fe-H, (c) O-H, (d) H-H, and (e) O-O atoms shown for the oxide shell layer associated with H_2O molecules (21–25 Å).

To gain more quantitative insight into the oxide shell formation, RDF between Fe, O, and H atoms are calculated to quantify the bond lengths within the oxide regions, as shown Fig. 4 and 5. Oxidation with H_2O molecules resulted in terminating the Fe NW surface by H_2O , H, and OH. Based on the RDFs, we found the average O-H bond length including the distance between the O and H atoms in OH and H_2O molecules is in the range of 0.95–1.15 Å. The peak is located at 1.05 Å—slightly larger than the average OH-bond of H_2O

molecules and OH ions—which indicate that the influence of hydrogen bonds with the surface. In addition to that, the O-H bonding suggests a slightly more ordered structuring of H₂O and OH within the oxide region. Relatively, a small number of the OH ions are segregated out from the H₂O molecules. Gutsev et al. calculated the OH bond length of 0.98 Å, which is slightly longer than the experimental value of 0.96 Å.⁴⁹ The H-H partial RDF has sharp maximal peak lying with the large amplitude at 1.65 Å. It should be noted that the Fe-H bond length exhibits two peaks – a very weak peak at 1.7 Å, and a stronger peak appears at 2.1 Å. The first peak is in agreement with the computational study of Liu et al.⁵⁰ For the dissociation of H atoms from H₂O molecules, they computed the forming of H-Fe distance that is in the range of 1.63–1.68 Å, which is very close to our first peak of Fe-H. In the case of Fe-O, the intense peak occurs at 1.35 Å, which correspond to the presence and diffusion of OH ions. However, the distance between the surface Fe and the O atom vary from 1.2 to 2.5 Å, which suggests the process of the hydroxylation on the free surface of Fe NW. Due to the presence of very weak chemical interactions between the H₂O molecule and the metallic surface, a varying bond length in the range of ~1.8–2.5 Å is observed due to the vertically-oriented H₂O molecules above the surface of NW at different facets of the cylindrical NW, indicating variations in the height of the H₂O layer above the free surface of Fe NW as well as available adsorption sites. This result is consistent with previous MD and experimental studies.⁴⁸ The experimental and simulation reported Fe-O bond length of hydrated ferric ions are in the range of 1.94–2.08 Å and ~1.92–2.30 Å, respectively. For example, Zhang et al. indicated that an average Fe-O bond lengths are 2.26 Å and 1.86 Å based on the interaction of Fe³⁺ ions with H₂O and OH⁻, respectively.⁵¹ Using density functional theory calculations and ab initio atomistic thermodynamics, Liu et al. showed that the most stable adsorption configuration of a H₂O molecule on the Fe(110) surface is at the top sites, where H₂O molecules are parallel to the Fe surface and the Fe-O distance is 2.18 Å.⁵² Ossowski et al. reported that the H₂O molecule binds to the clean and perfectly flat metallic Fe surfaces through the O atom. Our results are in agreement with their prediction of the O-Fe and O-H bond lengths that are in the range of 2.26–2.30 Å and 0.97 Å, respectively.⁵³ Radial distribution function in Fig. 4(e) shows that O-O bonds are not recognizable.

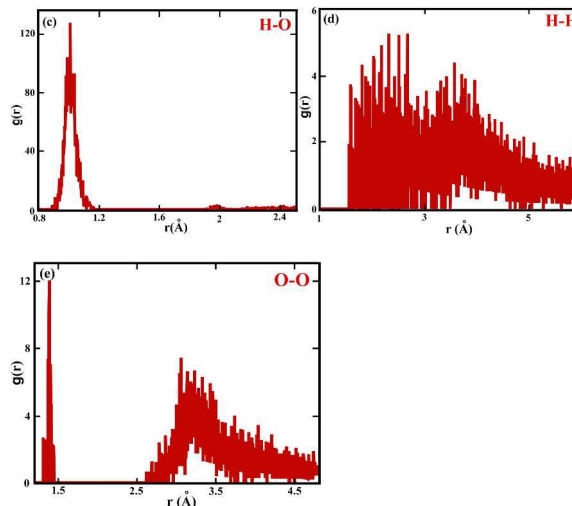
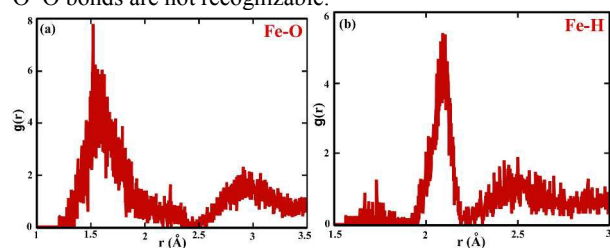


Fig. 5 RDF between (a) Fe-O, (b) Fe-H, (c) O-H, (d) H-H, and (e) O-O atoms shown for the oxide shell layer associated with H₂O₂ molecules (21–25 Å).

For the molecular H₂O₂ case, dissociation resulted in OH and H ions, the OH species adsorbs on the Fe NW surface to form bonds such as Fe-OH, Fe-H. The average Fe-O bond length varies in the range of 1.2–2.4 Å, but it has a distinct peak at 1.6 Å, which is slightly longer than the molecular H₂O case. In O₂ molecular case, the Fe-O bond length was shorter as observed in a previous study on oxidation of Fe NWs with O₂ molecules.¹⁷ For the average O-H bond length, there is a strong peak at 1.0 Å, which is closer to an average OH-bond distance equivalent to the bond length in OH ions and H₂O₂ molecules. Additionally, Fe-H bond length shows a distinct transition at 1.7 Å, which corresponds to that of the dissociated H atoms (total number of 43 H atoms) combined with Fe atoms to form the Fe-H bond, while a main average dominant peak is located at 2.1 Å. In addition to that, the average O-O bond length exhibits a sharp peak at around 1.4 Å and the second broad peak is at around 3.25 Å. The sharp peak at 1.4 Å presumably corresponds to the distances between the oxygen atoms in the existing H₂O₂ molecules at the oxide region. The distribution H-H bonds length are not recognizable by the appearance of the peaks.

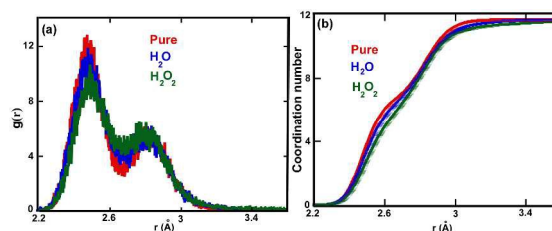


Fig. 6 Solid red, blue and green lines indicate that (a) RDF between Fe-Fe atoms and (b) the coordination number of Fe-Fe atoms for pure, oxide-coated Fe NW with H₂O and H₂O₂ molecules, respectively.

In order to evaluate the structural changes on the metallic bonding of Fe-Fe atoms at the

vicinity of the surface (21–26 Å) upon the oxidation processes, we calculate and further compare the difference between Fe–Fe overall coordination numbers and RDF before and after the oxidation process. The peak in Fe–Fe pair correlation split into two peaks, the primary peak with bigger amplitude is located at ~2.50 Å, but slight transition with relatively lower amplitude is at ~2.82 Å. The main promotional role of the formation of native oxide surface layer leads to rearrangement of the initial crystal structure via the breaking and reforming of Fe–Fe bonds, which explains why the strength decrease for the oxide-coated Fe NWs. It is apparently visible that the area under the $g(r)$ of Fe–Fe pair and the number of coordinated Fe–Fe atoms decrease for the oxide-coated Fe NWs upon the oxidation process, as shown in Fig. 6. Surface adsorption and dissociation of H_2O_2 and H_2O molecules are the key mechanisms in perturbation of metallic Fe atoms in the vicinity of oxide region and then eventually reduce the coordination numbers. The positions of some atoms are considerably altered by the diffusion of ionic species and even inducing the outward diffusions of some of these Fe atoms upon oxidation process with H_2O_2 molecules. On the contrary, most of the H_2O molecules, which remain mainly at the free surface of metallic Fe NW does not seem to be highly disturbed in the molecular H_2O environment. Thus, breaking and distortion of bonding between Fe–Fe at the vicinity of oxide region may also have a relatively insignificant role on the strength of the oxide-coated NW elastically compared to the un-oxide counterpart. The associated number ratio of 11.9 % and 7.3 % for H_2O_2 and H_2O with Fe atoms, respectively, due to the large surface-to-volume ratio. The substantial difference of the associated number ratio between H_2O_2 and H_2O molecules may probably provide a reasonable explanation why the oxide-coated Fe NW with H_2O_2 is easier for the initiation of partial dislocations on the free surface than the oxidized Fe NWs with H_2O molecules. This larger number indicates a significant increase in the contribution of the surface reconstruction to the overall mechanical properties of the NWs. Thus, it may play an essential role in determining their mechanical properties of oxide Fe NW deformation, especially by reducing the NW core dimensions.

Here, we also present the coordination number of Fe– H_2O and Fe–OH bonding on the resulting oxide shell layer. The integrated RDF of the Fe–O pairs up to 1.8 Å shows that the coordination of Fe atoms around O atoms of H_2O molecules is predominantly a mixture of 1-fold (total number of $OFe_1=1108$), 2-fold (total number of $OFe_2=60$), and 3-fold (total number of $OFe_3=27$) coordinated structures, reflecting the coexistence of various phases. As a result of the continued oxidation process, the absence of diffusion suggests that most of the H_2O molecules are directly absorbed on top of the free surface of Fe NWs in the form of H_2O –Fe bonds during the hydration stage. Thereby, coordination of 1-fold FeO is the dominant structure in the oxide shell layer, which confirms that the coexistence of ordered H_2O molecules is placed on the one-fold site of the outermost top site of the free surface of NW. Namely, most of H_2O molecules are directly bonded to the Fe atoms of the outermost layer. These results indicate that the chemical interactions between the H_2O molecules and the surface of Fe NW are relatively weak

binding that is reflected on the higher coordination number of 1-fold. Furthermore, the coordinated of O atoms from OH ions with Fe atoms in 2-fold (total number of $OFe_2=50$), and 3-fold (total number of $OFe_3=10$) coordinated structures are observed. After the dissociation of H_2O molecules, the OH ions that are bonded to Fe atoms in the surface layer diffuse to the inner core of the NW. Thus, the reaction between the OH ions and surface Fe ions results in the formation of the oxide layer with the different coordination number. Thus, the O atoms in OH ions bond with more Fe atoms, resulting in more complicated species of Fe oxides.

The composition of oxidation products in the molecular H_2O_2 case, integrated RDF of the O–Fe pairs up to 2.4 Å indicates the coordination of O atoms around Fe atoms is predominantly a mixture of 0-fold (total number of $OFe_0=237$), 1-fold (total number of $OFe_1=669$) 2-fold (total number of $OFe_2=752$), 3-fold (total number of $OFe_3=198$), 4-fold (total number of $OFe_4=8$), and 5-fold (total number of $OFe_5=6$) coordinated structures, reflecting the loss of crystalline order, coexistence of various bonds, and formation of the amorphous layer. One-fold is the dominant crystalline phase, while 5-fold is present only at a minor quantity. Moreover, integration of the RDF of the H–Fe pairs up to 2.2 Å depicts the coordination of H atoms around Fe atoms is predominantly a mixture of 0-fold (total number of $HFe_0=329$), 1-fold (total number of $HFe_1=1491$) 2-fold (total number of $HFe_2=19$), 3-fold (total number of $HFe_3=23$), 4-fold (total number of $HFe_4=1$), and 5-fold (total number of $HFe_5=3$) coordinated structures. Due to the coordination between Fe and O and H, oxide surface is comprised of many mixed oxide phases. This coordination number ratio changes the physical properties of the NW and makes the nanostructure more complex. Structural coordination number comparisons indicate that the formation of oxide shell layer on the metallic Fe–NWs has unique structural features such as the overall local oxide microstructure, types of chemical bonding, and stoichiometry, which are strongly dependent on the oxidizer environment. In comparison, the resulting oxide shell layer with the H_2O molecules do not cause a significant structural change since the most of H_2O molecules did not dissociate upon oxidation process as compared to the H_2O_2 molecular case. In addition to that, the oxide shell layer with H_2O_2 molecules is found to retain a large number of OH groups. Comparison of the oxidation process in between the molecular H_2O and H_2O_2 cases depicts that the aqueous H_2O_2 molecule has a high oxidizing ability toward the metallic Fe NW, leading to the more modification of the free surface structure of pristine Fe NW. Thus, the type of oxidizing environment influences the phase composition and microstructure of the formed surface layers. However, we find that the oxidizer species of O and H atoms are randomly distributed along the oxide region of the NWs. Since, the cylindrical free surface of Fe NW has a surface anisotropy, which may be responsible for these random distributions. In particular, the coexistence of surface anisotropy incorporates with the oxidation process results in the random distributions, which reflects the stochastic nature of the oxidation process.

3.4 Tensile mechanical properties of Fe NWs subjected to pre-oxhydroxide treatment

We have investigated the surface oxide microstructure-dependent intrinsic mechanical tensile properties of oxide-coated Fe NW with H_2O and H_2O_2 molecules. The pristine Fe NW is also considered as a reference to compare degradation of mechanical properties in the presence of the oxide shell ($Fe_xO_yH_z$) layer. We have already shown that the resulting growth of surface oxide layer on the free surface of Fe NW is structurally different, depending on H_2O and H_2O_2

oxidizer environment. Therefore, the local structural changes on the free surface of oxide-coated Fe NWs is likely to be correlated with the tensile mechanical properties.

The average engineering Virial stresses components are used to obtain the stress-strain relations for all Fe NWs, as is seen in Fig. 7.⁴³ Tensile mechanical deformation mechanism of all the simulated Fe NWs reveals a similar trend of the constitutive relationship in their stress-strain curves in [001] direction. The stress-strain curve can be classified into three distinct stages: a linear elastic regime, a nonlinear elastic regime, and a plasticity deformation regime under the uniaxial tension loading. Noticeably, we observe a significant amount of structural transformation from a BCC crystal to a FCC crystal structure, which is mainly responsible for accumulation of the non-linear elastic deformation.^{54,55} Once the twin is formed and consequently, the significant number of 'FCC' atoms suddenly drops to zero. Our results for Fe NWs with and without oxide are consistent with Landau's recent uniaxial nano deformation experimental study on pure Fe nano-pillars using high-resolution transmission electron microscopy.¹⁶ Landau et al. reported qualitatively similar three stages in the tensile stress-strain curves for Fe NWs, considered as the stages: I, II, and III, respectively.¹⁶ Sainath et al. studied the influence of temperature, ranging from 10 to 1000 K, on the tensile deformation and fracture behavior of <111> BCC Fe NWs using MD simulation under constant strain rate of $1 \times 10^8 \text{ s}^{-1}$.¹⁴ Similarly, they also observed that the subsequential deformation of all the NWs exhibits non-linear deformation behaviour after initial linear elastic regime until the onset of the plastic deformation regime at relatively high strains $> \sim 0.04$, which is in a close agreement with our linear yield strain values. Notably, non-linear deformation highly depends on the temperature of the system. The microstructure of surface oxide coating influences the stress-strain curves resulted in the different level of strain and stress, as shown clearly in Fig. 7. The oxide coating significantly reduces the strength of NWs evident from the reduction of the linear and maximum critical yield stress and strain. The extracted mechanical properties of all Fe NWs are shown in Table I. Importantly, the similarity of stress responses for all NWs implies that tensile mechanical deformations in all cases have the same tendency, involving the similar deformation mechanism.

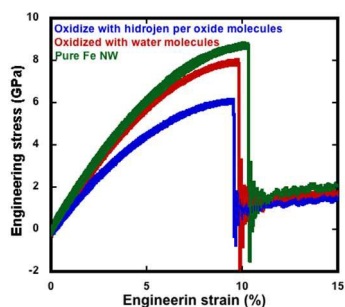


Fig. 7 Engineering stress-strain curve for pure (solid green lines), oxide of Fe NWs with H_2O (solid red lines) and H_2O_2 (solid blue lines) molecules, respectively. It can be seen that the pre-hydroxylated shell layers exhibit different effects on the mechanical degradation of core-shell structures.

In the linear elastic region for all NWs, the stress increases linearly with the increase of strain until it reaches the linear yield state. In regime II, in between the linear yield strain and maximum critical strain level, which is corresponding to the nonlinear elastic region where the stress varies slowly in a nonlinearly manner with the increasing strain. As soon as the strain reaches the maximum

critical yield strain level, twin seed (defects) start to nucleate from the free surface and/or interface region, resulting in the onset of plastic deformation. Near the maximum critical yield state; further increases in the strain cause a sharp drop of stress to a relatively lower value. Beyond the maximum critical yield state; the NWs deform plastically to continue in a ductile manner in regime III with the increasing strain. In addition to that, the variation of flow stress level remains relatively constant at low-stress level and fluctuates around the average value due to twinning deformation. The flow stress value of the pure Fe NWs is consistent with Li et al. and Landau et al. results.^{16,55}

Table 1 presents the tensile mechanical properties of all the Fe NWs. The corresponding linear yield strains and stress values are 6.0, 4.9, and 4.8% and 6.8, 5.6, and 4.3 GPa for the pristine, oxide-coated Fe NW with H_2O molecules, and H_2O_2 molecules, respectively. The pristine Fe NW exhibits significantly higher linear yield strain and yield stress relative to their oxide counterparts. The drop of linear yield stresses is shifted to lower strain value as compared to the pristine Fe NW. Especially, oxide NW with H_2O_2 molecules requires less work to overcome the linear yield stress barriers in comparison to H_2O case. This observation could be due to the relatively increased potential defects on the free surface of Fe NW, as compared to that of the pure and H_2O coated Fe NWs. Moreover, the corresponding maximum critical strains are about 10.4, 9.8, and 9.6% and maximum critical stresses are 8.7, 8.0, and 6.0 GPa for the pristine, oxide-coated Fe NW with H_2O and H_2O_2 , respectively. In the absence of any surface oxide layer, the Fe NW is mechanically hard. The onset of plastic deformation for oxide-coated NW with H_2O_2 molecules is slightly shifted to lower maximum critical strain levels. The required maximum critical stress to commence plastic deformation decreases from 8.7 GPa to 6.0 GPa ($\sim 31\%$) for the oxide shell layer formed by H_2O_2 as compared to its pristine counterpart. But, this change is less significant ($\sim 8\%$) for H_2O molecules case. The results indicate that the oxide local microstructure types on the free surface of crystalline metallic cylindrical Fe NWs are strongly correlated with the initiation of initial dislocation. The initiation of dislocations results in a reduction on the onset of the plastic deformation as well as the tensile intrinsic mechanical properties of Fe NWs including the linear yield strain and the stress, and the maximum critical yield strain and stress. Thus, the oxide-coated NW with H_2O_2 molecules shows significantly lower maximum critical stress at the final inelastic deformation stage. Oxide-coated with H_2O_2 molecules thereby make the NW easier to deform in the elastic regime, and consequently leading to a lower elastic modulus. Once plastic deformation is begun for all NWs, the nucleation and growth of twinning occurs at a relatively smaller stress value, but it fluctuates almost at a constant value of the flow stress, as seen from the stress-strain curves.^{14,17,55} The work of hardening rate of all the Fe NWs is obtained by integration of the area under the tensile stress strain curves.³³ The oxide shell layer including local structure have an effect on the work of hardening rate as it is noticed from the tensile stress-strain curves. Our result is consistent with the previous MD simulation studies of plasticity for Fe NWs, for example, a large maximum stress is required to onset the plastic deformation, e.g. create the twins initially, but subsequently follows the tensile twinning process with comparatively lower stress as strain increases.^{17,55}

The Young's modulus values are found to be 114.8 GPa, 117.0 GPa, and 91.9 GPa for the pristine, oxide-coated with H_2O and H_2O_2 molecules, respectively. The comparison of the Young's modulus indicates that the onset of softening depends on the surface microstructure. For example, the absorption of H_2O molecules on the free surface of metallic Fe NW is relatively weak. Therefore, it is

covered by mostly H₂O molecules, which affect slightly the Young's modulus. Most importantly, the Young modulus of oxide-coated Fe NW with H₂O₂ molecules is considerably smaller than its pristine counterpart, namely $\sim 20\%$. Plastic deformation of the oxide-coated Fe NW with H₂O₂ molecules starts at a lower stress value as compared to the pure Fe NW and oxide-coated with H₂O molecules. This implies significant structural changes in the vicinity of the free surface of Fe NW during oxidation process with H₂O₂ molecules. Thus, the softening effects and mechanical strength in Fe NWs are correlated with the resulting oxidation shell layer microstructure. On the other hand, there is a relatively small distinguishable difference in the Young's modulus between the pure and oxide with H₂O molecules case of Fe NWs.

In addition, chemical reactions during oxidation process causes the crystalline symmetry to be broken on the free surface, the exchange of bonds of surface atoms, the reduction of coordination number, the changes of chemical variations, stoichiometry and local structure of oxide shell. Diffusion of atoms into oxide region may account for at least some of correlated defects at the interface and/or oxide region, which acts as a productive source to initiate initial dislocation sites as well as act as a corrosion initiation site, thus promoting the initial activities of partial dislocations.^{17,23,34} Namely, the diffusion of ionic species breaks the symmetry and opens up a number of possible dissociation sites within the vicinity of oxide shell layer that could act as an activator for the initiation of initial dislocations to onset of the plastic deformations. Thus, the aforementioned issues lead notably in the different mechanical deformation properties distinct from those in pristine counterparts. Thereby, mechanical strength and properties of the metallic Fe NWs can be controlled effectively by simply controlling the oxide surface layer local microstructure associated with oxidizer environment.

There are several studies that indicate the existence of H₂O and H₂O₂ molecules degrades the mechanical properties of nanomaterials.^{20,56,57} For example, Khoei et al. studied the mechanical properties of the pristine graphene and graphene oxides at various percentages of O, OH and O/OH under tensile and shear loadings using MD simulations.⁵⁶ They indicated that the increase of the oxide agents facilitates the reduction of the Young modulus and the ultimate tensile stress in the graphene sheet, and the failure behavior of the graphene sheet changes from brittle to ductile. Verners et al. studied stress corrosion properties and the dislocation behavior of Ni metal nano plates structures in H₂O environments using ReaxFF potential.⁵⁷ In similarity, they indicated that the reactions of H₂O molecules with metallic Ni result in the reduction of dislocation nucleation barriers, e.g. the tensile stress barriers, as well as reduction of overall material strength and ductility, as compared to the counterpart of pristine Ni plates in a vacuum.

TABLE I. Mechanical properties of the pure and oxide-coated Fe NWs with H₂O and H₂O₂ molecules at constant strain rate. The values of linear yield strain (ϵ_z^{lin}), linear yield stress (σ_z^{lin}), maximum critical yield strain (ϵ_z^{max}), maximum critical yield stress (σ_z^{max}), and Young's modules (E) are shown. Two different oxidizing environments are used to the formation of the oxide shell layers.

System	ϵ_z^{lin} (%)	σ_z^{lin} (GPa)	ϵ_z^{max} (%)	σ_z^{max} (GPa)	E(GPa)
Pure	6.0	6.8	10.4	8.7	114.8
H ₂ O molec	4.9	5.6	9.8	8.0	117.0

H ₂ O ₂ molec	4.8	4.3	9.6	6.0	91.9
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3.4 The role of pre-oxhydroxide on tensile deformation behaviours of metallic Fe NWs

To obtain a comprehensive insight into the existence and movement of dislocation activities occurring inside the deforming NWs, the evolution of defect structure of the NW is closely monitored. In order to identify accurately the possible intrinsic plastic deformation mechanisms and further to make comparison, we performed the common neighbor analysis (CNA) using OVITO.⁵⁸ All the atoms are colored according to their CNA such as blue, green, orange colors stand for perfect BCC, FCC, and unknown atoms, respectively. Defects associated with the local crystalline disordered atoms are in the same color at oxide region, interior defects such as dislocation core and twin boundaries. The oxidation of Fe NWs associated with H₂O and H₂O₂ molecules leads to a relatively drastic modification of the existing surface local microstructure, the homogeneity, the symmetry, and the nature of the unique chemical bonding at the oxide of free surface and/or interface in between the oxide and core region. Furthermore, the free surface of Fe NWs is covered by heterogeneous crystalline oxide structures, which depends on the types of oxidizer environment. In this regard, the resulting oxidation processes cause to increase the number of initial dislocation emission sites on the oxide shell layer as well as interface between the core and shell. The aid of more active dislocation emission sites reduces effectively the activation barriers for the initial emission of partial dislocations to trigger the plastic deformation process. Overall, these active sites are potentially more sensitive to activate the initial dislocation sources at stress below the critical maximum stress to initiate the plastic deformation mechanism. Therefore, the presence of oxide layer acts initially as sources and sinks to facilitate as well as accelerate the onset of plastic deformation mechanisms by assisting initiation of initial dislocation activity, i.e., the reduction of critical maximum stress. Specifically, activation of initial dislocations strongly depends on the stress state of the free surface and interface, which is modified upon the oxidation process using different reactive oxidizers. Thus, the largest stress concentrations mainly shift to these oxide imperfection sites, and thereby, initiation of defects will preferentially start at the energetically favorable edge on the free surface, oxide region, and/or interface regions of the NW where the local maximum stresses exist. Especially, the presence of oxide layer decreases corresponding yielding stress in complex ways to begin the initial dislocation activities based on mechano-chemical reactions, thereby, softening the oxide Fe NWs.^{17,33,34} Comparison of our results, in particular, the resulting oxidation of Fe NW with H₂O₂ molecules provides relatively very little mechanical resistance to the onset of plastic deformation, which occurs at low-stress level due to the significant surface modifications. It indicates that the number of initial dislocation sites is relatively higher in case of the oxidation with H₂O₂ molecules than that of the H₂O molecules to nucleate initial dislocations.

The onset of plasticity for the [001] oriented pure and oxide Fe NWs promotes by specifically nucleation through partial dislocation on the {112} crystallographic glide planes.^{14,17,31,55,59} However, the

yielding to the onset of plastic deformation for the oxidized Fe NWs occurs at relatively lower strain and stress values than that of the pure NW, i.e., the mechanical resistance to plastic deformation decreases. Initial dislocations emission considered as nucleation of twin seed commences from the free surface, oxide shell layer and/or interface to onset plastic deformation. Then, the nucleation and the growth of parallel partial dislocations occurs on $\langle 111 \rangle \{112\}$ -glide plane bounded by dislocation loops. Once a dislocation is initiated, increasing the applied tensile strain, consecutive and continuous motion of closed partial dislocations loop commences to propagate laterally from one surface toward the opposite ends of free surface of NW along the restricted glide plane. Finally, they encounter at the opposite surface of the NWs to form a pair of stacking faults to realize a twin. Subsequently, with further increasing the strain results in the formation of a pair of parallel high symmetry stacking faults considered as twin boundaries (coherent twin interfaces), as is seen in Fig. 8 and 9. It is worth to note that the nucleation of closed dislocation loops and formation of the twin on the coherent twin boundary are observed for all Fe NWs. Surprisingly, the abrupt crystallographic lattice reorientation in between closed dislocation loop begins immediately with the formation of the initial closed dislocation loop. Namely, the nucleation of a dislocation loop and subsequently formation of twinning converts the elastic to plastic deformation process. At the same time, the ductile and softening of plastic deformation of all Fe NWs are achieved vertically and laterally through the repeated nucleation, formation, growth, propagation and thickening of twinning, which are restricted in between its existing internal twin boundaries. The imposed constant strain rate is entirely maintained by only one pair of twinning boundary including the gliding partial dislocation defects on the twin boundaries during tensile mechanical loading. The similarity of subsequently propensity for dislocations glides on the primary slip system $\{112\}$ atomic planes was commonly observed. Particularly, only a pair of twin boundaries is activated within the wires the (112) , $(11\bar{2})$ and $(\bar{1}12)$ slip plane for oxide-Fe NWs with H_2O and H_2O_2 molecules and pristine NW, respectively.

We also observe some minor dislocation activities. The strain evolution of the plastic deformation mechanisms in the oxide-NW with H_2O_2 molecules is presented in the Fig. 8 and 9, which gives a detailed picture of the inhomogeneous nucleation of dislocations as the initiation of twin seed from the oxide region, formation of stacking faults, and thickening processes of the twin slab. In the case of H_2O_2 oxidized NWs, nucleation of two twin seeds are created initially from the oxide shell layer of the NW to onset the plastic deformation, as is seen in the snapshot of Fig. 8. As the deformation continues, one of the twin seeds was lived for a short period and then disappeared in the NW. It is worth to note that another twin seed is rapidly able to complete the formation of a twin in the NWs (Fig. 8 (c)-(d)). Finally, the twin boundaries with a width of two atomic layers are formed along the longitudinal axis for all NWs, which are divided in all the NWs into two domains by forming a (112) twin plane one in between twin boundaries with the new lattice orientations, as shown in Fig. 8 and 9.

Relatively large maximum critical stress associated with the assistance of external forces is required for the formation of a twin.^{14,55} Subsequently, the majority of further evolution of plastic deformation continues via twinning progression, which is occurred readily by relatively small constant twin-propagation stress value, implying that the high propensity of the propagation of twin boundaries is consistent with the previous observations.^{14,31,55,59} On the other hand, onset of plastic deformation process associated with the distortion of the stress-strain curve (sharp decline in the stress-strain curve) results in relieving NW's high stress, which coincides

with the generation and the subsequent propagation of partial dislocations. Additionally, the lattice reorientations within the existing twin boundaries (the twinned domains) occur progressively into a new orientation of $[011]$ axis with respect to the initial orientation of $[001]$ axis in each NW. The actual lattice orientation and re-orientation in between twin boundaries are seen in Fig. 8 with the increase of tensile strain during the twin propagation. Lattice reorientation through twinning on the twinned domain planes proceeds during the plastic deformation process. However, local configuration still remains in BCC structure inside the NW and no structural phase transition occurs for all Fe NWs during the entire plastic deformation process except the twin boundaries and oxide region. Thus, an atomic reorientation in between the existing closed dislocation loop and consequently the existing twin boundaries associated with flow stress moves collectively in the same direction to accommodate the plastic strains during the rest of the tensile loading. Consequently, simultaneous occurrence of twin migration and the changes of twinned grain reorientation are responsible for the ductile and softening plasticity of all Fe NWs, implying that twinning process is the dominant mechanism to facilitate the plastic deformation process. The increasing and/or decreasing length of twin boundary spacing including lattice re-orientations in consequence, which are also associated with crystallographic reorientations of the free surfaces of NWs that results in giving the relatively small continuous zigzag-shaped structures behavior around a mean stress value.⁵⁵ Likewise, NW can adjust the overall twinning stress relatively easily by changing its free surface orientation and increasing the surface areas as well as re-orientation of twin domain, which is collaborated by the propagation of dislocation. Only one twin is created, which is responsible for the overall plastic deformation.⁵⁵

The large differences in the linear yield and maximum critical stresses values indicate that the maximum yield stresses are correlated with surface local oxide microstructures, which are significantly different from each other. Namely, surface oxide layer promotes initiation of deformation twinning but not the overall subsequent plastic deformation behavior. On the other hand, the plastic deformation mechanism of all NWs is dominated by deformation twin progression, which is not changed significantly by the existence of the oxide layer. Thereby, the plastic deformation behaviors and evolution trends are qualitatively quite similar to absorb external stress regardless of with and without the surface oxide during the plastic deformation process. Moreover, with the onset of plastic deformation, maximum stress associated with a high resolved shear stress acted as the driving force to provide high mobility as well as glide quickly the partial dislocation and the twin boundaries. Therefore, beyond initial dislocation emission, the oxide local microstructure has the ability to control the initial cross-slip partial dislocations propagation speeds to form the twinning. Thus, twinning activities facilitate as well as control the overall plastic deformation and the mechanical ductability of all the Fe NWs.

To the best of our knowledge, there are no experimental and simulation results published on the effects of the pre-oxide Fe NW with H_2O and H_2O_2 molecules on the tensile deformation mechanical mechanism and related properties. Therefore, we make some qualitative comparisons, which very well confirm the overall trend in mechanical deformation process for only pristine $[001]$ oriented Fe NWs. We remark that our results for the overall plastic deformation mechanism and behaviour also exhibit quantitative similarities as well as agreements with the previous simulations and experimental studies.^{14,17,31,55,59} These studies suggested that the mechanical deformation mechanism and related properties in BCC Fe NWs and nanopillars are quite sensitive to orientation, applied

strain, temperature, and pre-existing defects. These observations indicate that the ductility and softening of plastic deformation process are associated with complex twinning-dominated mechanochemical reactions, which undergo stochastic collective behaviours including the initiation and motion of partial dislocation, followed by formation of pair of twin boundaries.¹⁷ It is also noteworthy that surface defects contribute to activate initial dislocations more easily. Generally, previous simulations revealed that single crystal BCC Fe NWs experience primarily the similar deformation processes, which also indicated that the twinning on the slip system $\{112\}$ atomic planes is the dominating plastic deformation mechanism at high strain rates and low temperatures during tensile loading.^{17,55} Following yielding, twin thickening at the coherent boundaries requires other mechanisms such as the decreasing/increasing twin boundary pair spacing assisted by atomic specific re-orientations, changing geometrical and crystallographic reorientation of NW surface, and increase of the free surface area of NW in the plastically deformed region.

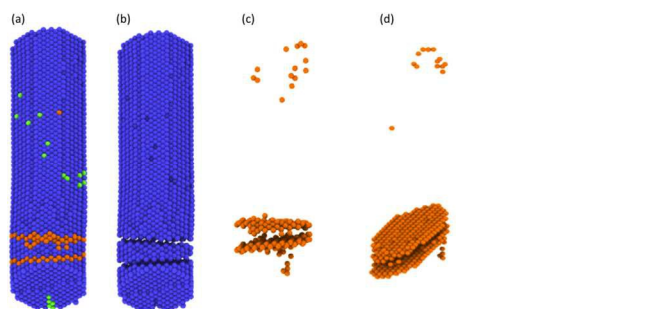


Fig. 8 The successive nucleation, growth, propagation and thickening of twinning in the oxide NW with H_2O_2 molecules based on CNA under the mechanical tensile loading. The green, blue and orange colours represent FCC, BCC and the unknown (amorphous) structure atoms, respectively. (a) The surface unknown structure atoms are removed from the full NW to show the interior perfect BCC atoms and the defects. The perspective view shows the initiation and evolution of the deformation at the interface; and (b) only BCC atoms are shown. For clarity, (c)-(d) only the interior defective atoms (unknown atoms) in the NW are shown from the different perspective.

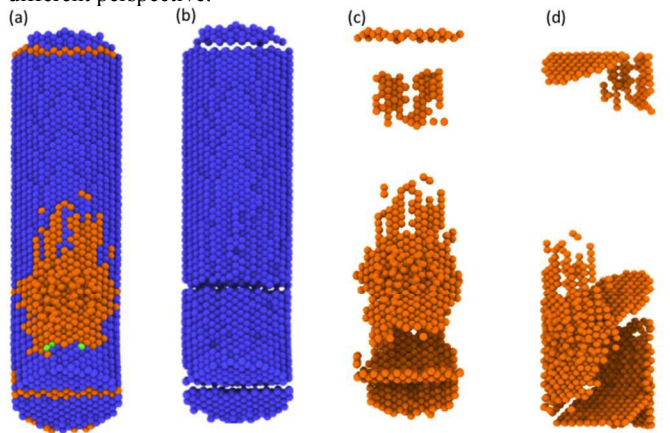


Fig. 9 The successive growth, propagation and thickening of twinning, as the strain increases further.

4. Summary and concluding remarks

Here, employing MD simulations with ReaxFF potential, we demonstrate comparatively importance of the resulting surface oxide

shell layer on the mechanical properties of metallic Fe NW. First, we investigate the oxidation process of the metallic Fe NW in the presence of two oxidizer environments (H_2O and H_2O_2 molecules). Our results show that the local unique microstructure and morphology of pre-oxide shell layer highly contingent on the types of oxidizing species in question, obtaining the different oxide phases. Especially, the dissociation and chemisorption of H_2O_2 on Fe NW modifies the NW surface, thus, exhibits significantly different mechanical properties compared to the pristine Fe NW. The mostly physisorption of H_2O on the Fe-NW surfaces—consistent with previous studies—has a relatively lesser effect on the mechanical characteristics compared to H_2O_2 cases.^{2,3} Our study reveals an interesting correlative dependence between the surface oxide local microstructure and mechanical deformation properties under uniaxial tensile loading. It is worth to note that the surface oxide layer spawn increased amount of initial dislocation nucleation and emission sources to dictate the plastic deformation of NW in comparison with the pristine Fe NW. Particularly, the amount of yield stress is reduced significantly to initiate the plastic mechanical deformation process, which fundamentally correlates with the degradation of mechanical strength and related properties of the cylindrical Fe NWs. Thus, oxide-coated Fe NWs exhibit interesting and distinctly different mechanical properties from their un-oxide counterpart. Our results indicate particularly that the surface oxide shell layer microstructure controls fundamentally the initiation of initial dislocations to onset plastic deformation, which in turn largely governs and manipulates the strength of metallic Fe NW with respect to proper selection of the type of oxidizer environment such as H_2O_2 and H_2O molecules in the direct oxidation process. Our study provides an understanding of oxidation and its effects on the mechanical properties as well as evolution of the resulting mechanical response of Fe NWs on the atomic scale. Understanding of such atomistic knowledge may have significant practical implications associated with the corrosion and oxidation processes, mechanical reliability, predictable and tolerance of Fe/Fe-oxide-related devices in inhospitable aqueous environments, and nano applications.

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- 1 Z. Ai, Z. Gao, L. Zhang, W. He and J. J. Yin, *Environ. Sci. Technol.*, 2013, **47**, 5344–5352.
- 2 T. Pan and A.C.T. van Duin, *Mater. Lett.*, 2011, **65**, 3223–3226.
- 3 T. Pan, *Chem. Phys. Lett.*, 2011, **511**, 315–321.
- 4 W. Xiang, B. Zhang, T. Zhou, X. Wu and J. Mao, *Sci. Rep.*, 2016, **6**, 24094.
- 5 Y. P. Ivanov, A. Alfadhel, M. Alnassar, J. E. Perez, M. Vazquez, A. Chuvilin and J. Kosel, *Sci. Rep.*, 2016, **6**, 24189.
- 6 M. Aryanpour, A. C. T. van Duin and J. D. Kubicki, *J. Phys. Chem. A*, 2010, **114** (21), 6298–6307.
- 7 A. Ali, H. Zafar, M. Zia, I. U. Haq, A. R. Phull, J. S. Ali and A. Hussain, *Nanotechnology, Science and Applications*, 2016, **9**, 49–67.
- 8 M. Kaur, J. S. McCloy, W. Jiang, Q. Yao and Y. Qiang, *J. Phys. Chem. C*, 2012, **116**, 12875–12885.
- 9 W. Wu, Q. He and C. Jiang, *Nanoscale Res. Lett.*, 2008, **3**, 397–415.
- 10 K. H. Chew, R. Kuwaharac and K. Ohno, *Phys. Chem. Chem. Phys.*, 2018, **20**, 1653.
- 11 K. Gandha, J. Mohapatra, M. K. Hossain, K. Elkins, N. Poudyal, K. Rajeshwar and J. P. Liu, *RSC Adv.*, 2016, **6**, 90537–90546.
- 12 J. Yue, X. Jiang and A. Yu, *J. Phys. Chem. C*, 2012, **116**, 8145–8153.
- 13 Y. Jia, T. Luo, X. Y. Yu, B. Sun, J. H. Liua and X. J. Huang, *RSC Adv.*, 2013, **3**, 15805–15811.
- 14 G. Sainath and B. K. Choudhary, *J. Appl. Phys.*, 2017, **122**, 095101.
- 15 P. Chowdhury and H. Sehitoglu, *J. Eng. Mater. Technol.*, 2017, **140**(2), 020801.
- 16 P. Landau, Q. Guo, P. Hosemann, Y. Wang and J. R. Greer, *Mater. Sci. Eng. A*, 2014, **612**, 316–325.
- 17 G. Aral, Y. J. Wang, S. Ogata and A. C. T. van Duin, *J. App. Phys.*, 2016, **120**, 135104.
- 18 K. Rout, M. Mohapatra, S. Layek, A. Dash, H. C. Verma and S. Anand, *New J. Chem.*, 2014, **38**, 3492–3506.
- 19 W. Zhu, J. Winterstein, I. Maimon, Q. Yin, L. Yuan, A. N. Kolmogorov, R. Sharma, and G. Zhou, *J. Phys. Chem. C*, 2016, **120**, 14854–14862.
- 20 G. Zhang, Y. Liao and I. Baker, *Mater. Sci. Eng. C Mater. Biol. Appl.*, 2010, **30**(1), 92–97.
- 21 C. A. F. Vaz, A. Balan, F. Nolting and A. Kleibert, *Phys. Chem. Chem. Phys.*, 2014, **16**, 26624.
- 22 Z. Ai, L. Lu, J. Li, L. Zhang, J. Qiu and M. Wu, *J. Phys. Chem. C*, 2007, **111**, 4087–4093.
- 23 M. Krajewski, K. Brzozka, W. S. Lin, H. M. Lin, M. Tokarczyk, J. Borysiuk, G. Kowalski and D. Wasik, *Phys. Chem. Chem. Phys.*, 2016, **18**, 3900–3909.
- 24 R. Subbaraman, S. A. Deshmukh and S. K. R. S. Sankaranarayanan, *J. Phys. Chem. C*, 2013, **117**, 5195–5207.
- 25 B. Jeon, Q. V. Overmeere, A. C. T. van Duin and S. Ramanathan, *Phys. Chem. Chem. Phys.*, 2013, **15**, 1821–1830.
- 26 B. R. S. Rogne and C. Thaulow, *Philos. Mag.*, 2014, **95**, 1814.
- 27 H. Wu, J. J. Yin, W. G. Wamer, M. Zeng and Y. M. Lo, *J. Food Drug Anal.*, 2014, **22**, 86–94.
- 28 G. Sainath and B.K. Choudhary, *Comput. Mater. Sci.*, 2016, **111**, 406–415.
- 29 G. Sainath, B.K. Choudhary, T. Jayakumar, *Comput. Mater. Sci.*, 2015, **104**, 76–83.
- 30 G. Sainath and B.K. Choudhary, *Mater. Sci. Eng. A*, 2015, **640**, 98–105.
- 31 C. J. Healy and G. J. Ackland, *Acta Mater.*, 2014, **70**, 105.
- 32 F. G. Sen, Y. Qi, A. C. T. van Duin and A. T. Alpas, *Appl. Phys. Lett.*, 2013, **102**, 051912.
- 33 F. G. Sen, A. T. Alpas, A. C. T. van Duin and Y. Qi, *Nat. Commun.*, 2014, **5**, 3959.
- 34 G. Aral, Md M. Islam and A. C. T. van Duin, *Phys. Chem. Chem. Phys.*, 2018, **20**, 284.
- 35 X. Li, S. Schönecker, E. Simon, L. Bergqvist, H. Zhang, L. Szunyogh, J. Zhao, B. Johansson and L. Vitos, *Sci. Rep.*, 2015, **5**, 16654.
- 36 T. J. Campbell, G. Aral, S. Ogata, R. K. Kalia, A. Nakano and P. Vashishta, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **71**, 205413.
- 37 A. Hasnaoui, O. Politano, J. M. Salazar and G. Aral, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **73**, 035427.
- 38 T. P. Senftle, S. Hong, Md. M. Islam, S. B. Kylasa, Y. Zheng, Y. K. Shin, C. Junkermeier, R. E. Herbert, M. J. Janik, H. M. Aktulga, T. Verstraelen, A. Grama and A. C. T. van Duin, *npj Comput. Mater.*, 2016, **2**, 15011.
- 39 K. I. Nomuro, R. K. Kalia, A. Nakano and P. Vashishta, *Comput. Phys. Commun.*, 2008, **178**, 73–87.
- 40 S. Plimpton, *J. Comput. Phys.*, 1995, **1**, 117.
- 41 G. J. Martyna, D. J. Tobias and M. L. Klein, *J. Chem. Phys.*, 1994, **101**, 4177.
- 42 G. J. Martyna, M. L. Klein and M. Tuckerman, *J. Chem. Phys.*, 1992, **97**, 2635.
- 43 M. P. Allen and L. J. Tildesley, *Computer Simulation of Liquids*, Oxford University Press, New York, 1987.
- 44 W. J. Mortier, S. K. Ghosh and S. Shankar, *J. Am. Chem. Soc.*, 1986, **108**, 4315.
- 45 A. M. Baro and W. Erley, *J. of Vac. Sci. and Technol.*, 1982, **20**(3), 580–583.
- 46 M. Eder, K. Terakura, and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **64**, 115426.
- 47 D. J. Dwyer, S. R. Kelemen and A. Kaldor, *J. Chem. Phys.*, 1982, **76**(4), 1832–1837.
- 48 W. Chen, H. T. Duan, M. Hua, K. L. Gu, H. F. Shang and J. Li, *J. Phys. Chem. B*, 2014, **118**, 10311–10318.
- 49 G.L. Gutsev, M.D. Mochena and C.W. Bauschlicher, *Chem. Phys.*, 2005, **314**, 291–298.
- 50 S. Liu, X. Tian, T. Wang, X. Wen, Y. W. Li, J. Wang and H. Jiao, *J. Phys. Chem. C*, 2015, **119**, 11714–11724.
- 51 H. Zhang, G. A. Waychunas, and J. F. Banfield, *J. Phys. Chem. B*, 2015, **119**, 10630–10642.
- 52 S. Liu, X. Tian, T. Wang, X. Wen, Y. W. Li, J. Wang and H. Jiao, *Phys. Chem. Chem. Phys.*, 2015, **17**, 8811.
- 53 T. Ossowski, J. L. F. Da Silva and A. Kiejna, *Surf. Sci.*, 2018, **668**, 144–149.
- 54 X. Ou, J. Sietsma and M. J. Santofimia, *Modelling Simul. Mater. Sci. Eng.*, 2016, **24**, 055019.
- 55 S. Li, X. Ding, J. Deng, T. Lookman, J. Li, X. Ren, J. Sun and A. Saxena, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **82**, 205435.
- 56 A. R. Khoei and M. S. Khorrami, *Fullerenes, Nanotubes and Carbon Nanostruct.*, 2016, **24**(9), 594–603.
- 57 O. Varners and A.C.T. van Duin, *Surf. Sci.*, 2015, **633**, 94–101.
- 58 A. Stukowski, *Modell. Simul. Mater. Sci. Eng.*, 2010, **18**, 015012.
- 59 T. U. Xu, Z. Q. Zhu, S. F., Geng and H. Y. Song, *Phys. Lett. A*, 2017, **381**, 3222–3227.