Enhanced oxidation resistance of active nanostructures via dynamic size effect

Yun Liu\textsuperscript{1,2,*}, Fan Yang\textsuperscript{1,*}, Yi Zhang\textsuperscript{1,2}, Jianping Xiao\textsuperscript{1}, Liang Yu\textsuperscript{1}, Qingfei Liu\textsuperscript{1,2}, Yanxiao Ning\textsuperscript{1}, Zhiwen Zhou\textsuperscript{1,2}, Hao Chen\textsuperscript{1,2}, Wugen Huang\textsuperscript{1,2}, Ping Liu\textsuperscript{3} & Xinhe Bao\textsuperscript{1}

A major challenge limiting the practical applications of nanomaterials is that the activities of nanostructures (NSs) increase with reduced size, often sacrificing their stability in the chemical environment. Under oxidative conditions, NSs with smaller sizes and higher defect densities are commonly expected to oxidize more easily, since high-concentration defects can facilitate oxidation by enhancing the reactivity with O\textsubscript{2} and providing a fast channel for oxygen incorporation. Here, using FeO NSs as an example, we show to the contrary, that reducing the size of active NSs can drastically increase their oxidation resistance. A maximum oxidation resistance is found for FeO NSs with dimensions below 3.2 nm. Rather than being determined by the structure or electronic properties of active sites, the enhanced oxidation resistance originates from the size-dependent structural dynamics of FeO NSs in O\textsubscript{2}. We find this dynamic size effect to govern the chemical properties of active NSs.
nanostructures (NSs) of a few nanometres in size often exhibit prominent size-dependent properties. With reducing size, surface defects become more prominent, and the electronic structure of NSs can fluctuate due to electron confinement. The origin of size effects in chemical reactions has usually been attributed to the size-dependent geometric structures or electronic properties, which have been measured statically and in the absence of reactant molecules. Much less is known regarding the dynamic interaction between NSs and reactant molecules, despite its essential role in the reaction. Among the large volume of studies on the oxidation of NSs, detailed studies on the oxidation mechanism, especially on the oxidation of Fe NSs, have been very limited. The oxidation of NSs has often been described by the Cabrera–Mott model, which suggests that the growth rate or the thickness of oxide shell is inversely dependent on the size of NS. A recent atomic study on the oxidation of Fe NSs has shown, however, that the Cabrera–Mott theory might not be accurate to explain the oxidation of NSs and the formation of oxide shells could facilitate metal oxidation via the strain-mediated ionic transport, surpassing the prediction by the Cabrera–Mott model.

Indeed, the studies of size effects on oxidation kinetics have been particularly difficult because of the structural variations among NSs introduced when producing different-sized NSs. Several nanocrystalline materials were reported previously to exhibit improved oxidation resistance with respect to bulk materials and have been applied as anti-corrosion coatings on steels. When pristine Fe is exposed to O₂, FeO forms spontaneously and is the desired phase for applications in catalysis and in electronic devices. FeO NSs supported on Pt have also been shown as a remarkable catalyst for the preferential oxidation of CO at low temperatures. Supported FeO NSs on Pt have also been shown as a remarkable catalyst for the preferential oxidation of CO at low temperatures.

In this work, combining in situ scanning tunnelling microscopy (STM) and density functional theory (DFT) methods, we report a detailed study on the size-dependent oxidation of FeO NSs. By resolving the interaction between different-sized NSs and O₂ at the atomic scale, we demonstrate a dynamic size effect, which is dominant for NSs with dimensions below 3 nm and could occur on NSs with the same atomic structure or electronic properties.

Results
Size-dependent oxidation of supported FeO NSs. FeO NSs were prepared on Pt(111) and display typically the shapes of triangles or hexagons. The structure of FeO islands on Pt(111) has been well characterized as a polar FeO(111) bilayer, with the Fe layer in contact with Pt and the O layer exposed at the topmost plane. Due to lattice mismatch, Fe atoms occupy successively the fcc, hcp and top positions on Pt(111), forming moiré domains on FeO (ref. 31). When exposed to O₂ at elevated temperatures, FeO NSs could be oxidized by oxygen penetration into the FeO/Pt interface to form FeO₂, displaying an O–Fe–O trilayer structure. DFT calculations suggested that the FeO₂ phase was thermodynamically more stable than FeO on Pt(111) (ref. 32). The structural difference between FeO₂ and FeO could be easily distinguished in STM from their apparent heights, moiré patterns and atomic structures.

Interestingly, the oxidation kinetics of FeO NSs at 500 K or below were found to be strongly size-dependent. While most FeO islands were oxidized to FeO₂, small FeO islands remained the FeO phase. Figure 1e shows that the area of FeO₂ domains on an individual island increases with the increasing island size. No FeO₂ domains were observed on FeO islands with d < 3.2 nm (Supplementary Fig. 2). In situ STM images (Supplementary Fig. 2) show that FeO₂ domains were developed by oxygen penetration from the step edges of FeO NSs, as generally proposed in the oxidation of NSs. Assuming a uniform diffusion rate for oxygen insertion into the formation rate of FeO₂ domains should be proportional with the edge perimeters of FeO NSs and smaller FeO NSs should display a higher oxidation ratio (Supplementary Fig. 2c).

Size-dependent structural dynamics of supported FeO NSs in O₂. By examining the structure of FeO NSs and their interaction with O₂, we found the enhanced oxidation resistance of FeO NSs with d < 3.2 nm was caused by a dynamic size effect described below. As-prepared FeO NSs typically exhibit two types of step structures, exposing two-coordinated Fe or O atoms (Supplementary Figs 3 and 4). The steps terminated by Fe atoms, also known as coordinatively unsaturated ferrous (CUF) sites, are active sites for O₂ dissociation, whereas the steps terminated by coordinatively unsaturated oxygen (CUO) atoms and the surface plane of FeO were found inert to O₂ (ref. 16). For simplification, the two types of steps were termed as the CUF step or the CUO step, whose atomic structures could be viewed directly in STM images (Supplementary Fig. 4). A detailed structural analysis showed that the structure of the CUF step is independent on the island size. As manifested in Fig. 2, three triangular FeO islands expose exclusively CUF steps, which display the same structure and lattice constant.

Despite the same shape and structure, these triangular FeO islands exhibited a drastically different structural dynamics when exposed to O₂ at 270 K. Figure 3 shows O₂ dissociation at CUF sites of the Fe₇₈O₆₆ NS led to the spontaneous and complete reconstruction of NS, which was also the case for smaller FeO NSs (Supplementary Fig. 5). Element-specific STM images (Supplementary Note 1) have allowed us to reveal not only the number of Fe and O atoms, but also their relative positions. Upon O₂ exposure, 23 O atoms were added to the edges of Fe₇₈O₆₆ NS, accompanying a collective shift of all oxygen atoms to the adjacent 3-fold hollow sites of the Fe layer (Supplementary Note 2, Supplementary Figs 6 and 7). Consequently, all CUF sites at the edges could be saturated by two-coordinated oxygen atoms, forming the CUF steps rather than by dangling oxygen atoms as before reconstruction. The line profile of the CUF step appears inverted to that of the CUF step (Supplementary Fig. 7). DFT calculations show that, before reconstruction, dangling oxygen atoms bind weakly at the step edge, with the adsorption energy of 0.64 eV (Fig. 3g). The binding energy of O adatoms is increased to 1.26 eV by bonding with two neighbouring Fe atoms (Fig. 3h), though such a configuration is not stable and prefers to reconstruct. The
reconstruction shifts surface O atoms to the adjacent three-fold hollow sites of Fe lattice and results in the strong binding of edge O atoms with the adsorption energy of 2.14 eV (Fig. 3i).

Thus, all O adatoms were stabilized at the step edges by the spontaneous reconstruction of FeO NSs.

In contrast, a partial reconstruction was observed for larger NSs, such as Fe\textsubscript{210}O\textsubscript{190} and Fe\textsubscript{378}O\textsubscript{351}. Supplementary Figure 8 shows only a portion of surface oxygen atoms was shifted to the adjacent 3-fold hollow sites of Fe lattice, resulting in a reconstructed oxygen domain and oxygen dislocation lines at the boundary between reconstructed/unreconstructed domains. At the dislocation, Fe atoms were over-saturated with 4-fold oxygen coordination and appeared as protrusion lines running parallel to the steps (Supplementary Fig. 8)\textsuperscript{34}. The reconstructed domain was evidenced by the formation of CUO steps, while the edges of unreconstructed domain were terminated by either dangling or dislocated oxygen atoms\textsuperscript{19,34}.

The size-dependent structural dynamics of FeO NSs could be driven via different channels. DFT calculations on supported FeO clusters show that, while the energy released from oxygen adsorption increases with the size increasing from Fe\textsubscript{16}O\textsubscript{6} to Fe\textsubscript{28}O\textsubscript{21}, the driving force (or thermodynamic preference) associated with the shift of oxygen atoms to achieve a complete reconstruction decreases more rapidly (Supplementary Fig. 9). Both energy release and the driving force will eventually level off with increasing size. These results suggest that a complete structural reconstruction likely occurs in small NSs, which is in agreement with STM study. For example, although the energy release from oxygen adsorption at Fe\textsubscript{10}O\textsubscript{6}/Pt(111) is the smallest among the FeO clusters being calculated, its reconstruction is thermodynamically most favourable. On the other hand, with size increasing, the increment in the energy released from oxygen adsorption cannot match the decrease in the driving force from reconstruction (Supplementary Fig. 9), and thus a complete reconstruction becomes less favourable. Indeed, STM study shows...
that the reconstruction of larger FeO NSs is only partial with the formation of surface dislocations (Supplementary Fig. 8). The dynamic response of FeO NSs could be observed at even 15 K, upon the dissociative adsorption of oxygen at the CUF sites (Supplementary Fig. 10). The fact that an adsorption of several oxygen atoms at the edge of FeO NSs could induce locally the reconstruction of FeO NSs at such a low temperature suggests that the reconstruction could be initiated without thermal activation. However, DFT calculations show that, to initiate the reconstruction, diffusion of isolated oxygen atoms to adjacent 3-fold hollow sites of Fe needs to overcome a barrier \( E_d \) of \( \approx 0.33 \text{ eV/O atom} \) (Supplementary Fig. 11). Meanwhile, oxygen insertion into the FeO–Pt(111) interface, that is, the transition to FeO2, has an even higher energy barrier of 1.41 eV/O atom (Fig. 4a). Thus, the driving force for the reconstruction is unlikely to be limited to thermodynamics. Note that we have not taken into account the partitioning of the energy released from oxygen adsorption, which should be in the form of hot electrons\(^3\) and local atomic displacements. The energy channelling model requires that these energies are effectively used for the reconstruction, rather than generating thermal losses\(^3\). It is believed that hot electrons typically decay on the timescale of picoseconds. Such a fast timescale could in principle inhibit the channelling to take place, or alternatively be the reason why the reconstruction of smaller FeO NSs is complete but not the larger ones. In any case, the concerted reconstruction of NSs is a complex process; their activation energies depend on the density of the CUF sites (that is, the number of adsorbed oxygen atoms) and the size of the NSs (Supplementary Fig. 11). As such, we cannot rule out the possibility of barrierless channels upon saturation adsorption of oxygen at the CUF sites. This size-dependent structural dynamics warrants further exploration both experimentally and theoretically using time-dependent approaches to gain in-depth understanding.

The oxidation of FeO NSs determined by dynamic size effect. The dynamic size effect governs the oxidation kinetics of FeO NSs by tuning the stability of O atoms at the step edges. In situ
The enhanced oxidation resistance was also found for CoO NSs with \( d < 3 \) nm supported on Pt(111) and Au(111), whereas larger CoO NSs are susceptible for further oxidation (Supplementary Fig. 12). Thus, the enhanced oxidation resistance of smaller active NSs is not just a unique feature of the FeO/Pt(111) system, but could rather be observed in other supported NSs. We expect that the reconstruction mechanism discussed above could be transferred to supported active NSs with similar structural configuration. Indeed, a number of rocksalt-type oxides, such as FeO, CoO, NiO, MnO, VO and EuO, have been shown to exhibit similar structural configurations, when they were supported on different metal substrates, such as Pd, Rh, Pt, Au and Ag\(^{38-40}\). These supported oxide NSs are promising for a number of applications in catalysis, magnetic storage and material sciences\(^{21,24,39-41}\).

Oxides are usually considered as a rigid surface during the reaction at low temperatures\(^{42}\). We show that oxide NS can exhibit a rapid structural change at the elementary step. The triangular FeO NSs investigated above exhibit not only the same shape and structure, but also similar electronic properties and electrostatic potential (Supplementary Figs 9 and 13), which usually indicate their similar behaviour in oxidation. Instead, the dynamic size effect observed here manifests its dominant influence in the nanoscale chemistry. Although we have used a model system to illustrate the dynamic size effect, this effect should be somewhat general for active NS in exothermic reactions. Our results demonstrate how NS prevents the insertion of oxygen into the oxide–metal interface, which might be key to develop passivating coatings for metals.

In summary, we demonstrate a dynamic size effect that governs the oxidation of active FeO NSs. Even with the same structure, FeO NSs exhibited a size-dependent structural dynamics when reacting with O\(_2\). The structural dynamics is driven by the exothermic reaction between O\(_2\) and CUF sites. Since the density of active CUF sites decrease with the increasing size of NS, the reaction energies are only sufficient for the complete reconstruction of FeO NSs with \( d < 3.2 \) nm, but fall short for larger ones. As a result, FeO NSs with \( d < 3.2 \) nm could stabilize oxygen at the steps and passivate themselves from oxidation, whereas larger FeO NSs suffer deep oxidation due to the partial reconstruction and the development of dislocation lines. The same enhanced oxidation resistance was also observed for CoO NSs with \( d < 3 \) nm, indicating the dynamic size effect could be general in the oxidation of supported active NSs, at least for those with similar structural configurations. Therefore, our findings provide not only a general understanding for the enhanced oxidation resistance in nanomaterials, but also new routes for stabilizing active nanocrystals and developing oxidation-resistant coatings.

### Methods

**Experimental details.** The experiments were carried out in a combined ultrahigh vacuum (UHV) system equipped with Createc low-temperature scanning tunnelling microscope (LT-STM), XPS, UPS and the cleaning facilities. The STM and preparation chambers have a base pressures of \( 4 \times 10^{-10} \) mbar and \( 6 \times 10^{-11} \) mbar, respectively. The Pt(111) single crystal (Matek) was cleaned by cycles of Ar ion sputtering (1.5 keV, 10 \( \mu \)A) and annealing at 1,200 K. Nano-sized FeO islands were deposited onto Pt(111) by vapour deposition of Fe atoms in an
2. Valden, M., Lai, X. & Goodman, D. W. Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties. Nat. Mater. 12, 53–58 (2013).

3. Lauritzen, J. V. by counting nearest neighbors. J. Catal. 13, 577–588 (2015).

4. Calle-Vallejo, F. et al. Imaging single-molecule reaction intermediates stabilized by surface dissipation and entropy. J. Phys. Chem. Lett. 8, 1401–1405 (2017).

5. Sun, D. & Li, W. A first-principles study of the structure, electronic properties, and oxygen binding of FeO/Pt(111) and FeO2/Pt(111). Chin. J. Catal. 34, 973–978 (2013).

6. Yoshida, H. et al. Imaging water molecules interacting with supported nanoparticulate catalysts at reaction conditions. Science 335, 317–319 (2012).

7. Sprengel, W. in Oxide Materials at the Two-Dimensional Limit (ed. Schwertmann, U.) 285–288 (2008).

8. Leibbrandt, G. W. R., Grugone, S., Dupont, L. & Tarascon, J. M. Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries. Nat. Mater. 11, 4258–4263 (2010).

9. Mertz, L. R. et al. Correlating the catalytic performance of O–H groups on Pt(111) with the bond angle between the oxygen atom and the two Pt atoms. J. Catal. 215, 432–437 (2002).

10. Kresse, G. & Joubert, D. From ultracore pseudopotentials to the projector augmented wave method. Phys. Rev. B 59, 1758–1775 (1999).

11. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
Center for Functional Nanomaterials, a user facility at Brookhaven National Laboratory, and at the National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the U.S. DOE under Contract DE-AC02-05CH11231. We thank Dr Huanxin Ju and Prof Junfa Zhu from the BL11U beamline in NSRL for assistance with XPS measurements. We thank the fruitful discussions with Prof Miquel Salmeron, Prof Shengbai Zhang, Prof Jun Li, Prof Qiang Fu and Dr Jan Hrbek.

**Author contributions**

Y.L., Y.Z., Q.L., Y.N., H.C., W.H. and F.Y. carried out STM, STS and XPS experiments. J.X., L.Y., Z.Z. and P.L. performed DFT calculations. F.Y., Y.L. and X.B. analysed the data and wrote the paper. X.B. and F.Y. designed and supervised the work.

**Additional information**

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

**Competing financial interests:** The authors declare no competing financial interests.

**Reprints and permission** information is available online at http://npg.nature.com/reprintsandpermissions/

**How to cite this article:** Liu, Y. et al. Enhanced oxidation resistance of active nanostructures via dynamic size effect. *Nat. Commun.* **8**, 14459 doi: 10.1038/ncomms14459 (2017).

**Publisher’s note:** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s) 2017