Dynamic Tuning of a Thin Film Electrocatalyst by Tensile Strain

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We report the ability to tune the catalytic activities for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) by applying mechanical stress on a highly n-type doped rutile TiO₂ films. We demonstrate through operando electrochemical experiments that the low HER activity of TiO₂ can reversibly approach those of the state-of-the-art non-precious metal catalysts when the TiO₂ is under tensile strain. At 3% tensile strain, the HER overpotential required to generate a current density of 1 mA/cm² shifts anodically by 260 mV to give an onset potential of 125 mV, representing a drastic reduction in the kinetic overpotential. A similar albeit smaller cathodic shift in the OER overpotential is observed when tensile strain is applied to TiO₂. Results suggest that significant improvements in HER and OER activities with tensile strain are due to an increase in concentration of surface active sites and a decrease in kinetic and thermodynamics barriers along the reaction pathway(s). Our results highlight that strain applied to TiO₂ by precisely controlled and incrementally increasing (i.e. dynamic) tensile stress is an effective tool for dynamically tuning the electrocatalytic properties of HER and OER electrocatalysts relative to their activities under static conditions.

The ability to alter a materials’ structure/function relationship by strain has been widely recognized. Electrocatalytic activities of heterogenous catalysts depend on the surface reactivities toward chemical species along a reaction pathway. Surface reactivities are highly dependent on the surface electronic state, crystal structure and concentration of accessible active sites, all of which can be modulated by surface strain. Several recent reviews summarize theoretical and experimental studies how strain affects electrocatalytic materials. Surface strain can be introduced either internally through material architecture (static strain) or by applying an external force (dynamic strain). Static strain in crystalline materials can be introduced by doping, de-alloying, annealing, epitaxial growth on a mismatched crystal lattice or by intrinsic surface-stress in 2D materials. In polycrystalline materials, strain naturally occurs within grain boundaries due to crystals twinning or edge defects. Due to the size confinement, nanomaterials are inherently strained, and that strain can be tuned by preparing nanoparticles with various shapes or sizes. For architecturally strained materials, it is often difficult to separate strain-induced effects from chemical or ligand effects.

Tuning static strain by varying material architecture is a rather laborious approach since it requires synthesis of a new sample for each discreet amount of strain. The ability to systematically measure materials’ structure/function relationship under precisely controlled and incrementally increasing strain allows one to explore a dynamic range over the strain space without introducing other effects. Experimental studies showing the effects of dynamic strain on electrocatalytic activities have emerged in the literature only recently. A comprehensive review of strained electrochemical systems was published recently. Examples of tunable substrates include elastic materials such as organic polymers and metallic materials such as stainless steel and pseudoelastic/shape-memory NiTi alloys. Alternatively, external forces have been applied by an atomic force microscopy tip, by introducing subsurface inert gas bubbles or by Li-ion intercalation/deintercalation in battery materials. Application of mechanical, thermal or electrical loading result in bending, compression or expansion of an elastic substrate, further inducing stress-strain response on the deposited material. Such catalyst engineering through dynamic strain has been shown for: i) HER on MoS₂, Au, Pt, Ni, Cu, WC, and nickel-iron alloys. The primarily focus of the previous studies was effects of strain on the catalytic activities of transition metals and the experimental results were consistent with d-band theory, described in the seminal work by Mavrikakis et al. In contrast, effects of strain on catalytic properties of materials with more complex chemical and electronic structures, such as metal oxides, remains poorly understood. In addition to d-band, strain can affect overlap of d and p orbitals from metal and oxygen atoms, respectively, thereby inducing M–O bond rearrangement and phase transitions. Strain can also affect formation energies and diffusion pathways.

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of oxygen vacancies ($V_O$), leading to changes in surface reactivities. While TiO$_2$ has been shown to split water under illumination, a co-catalyst (typically Pt) is used to promote catalysis. Although the stochiometric rutile TiO$_2$ surface has low reactivity toward water, theoretical studies suggested that the surface reactivity can be activated by tensile strain. Recently, scanning tunneling microscopy (STM) measurements showed increase in hydrogen (H*) adsorption energy on stochiometric rutile TiO$_2$(110) with increase in surface strain. Due to the complexity of the system, most of the previous studies were focused on theory and only specific aspects of TiO$_2$ reactivity with water as a function of strain. Considering that strain can affect simultaneously multiple aspects of TiO$_2$ electronic structure and reactivity, it can be expected that each step along a reaction pathway is affected to some degree by strain. Here we show and discuss the effects of dynamic tensile strain on TiO$_2$ HER and OER activities, based on both experiments and theory. The effects, reported here, are significantly larger than ones observed for transition metals catalysts and trend is reversed.

Results and Discussion

The experimental set-up used in this study was described in our preceding publication. Briefly, rutile TiO$_2$ thin films are thermally grown on a pseudo-elastic material Nitinol (NiTi intermetallic). Due to the oxophilic nature of titanium, thermal treatment of NiTi at elevated temperatures under aerobic conditions leads to a nickel-free surface of TiO$_2$. Oxidation of mechanically polished NiTi at 500 °C for 30 min results in a ∼50 nm thick films of rutile TiO$_2$(110), confirmed by XPS, XRD and Raman spectroscopies. In this work, we find that electrocatalytic results are the most reproducible and effects of strain highest for samples that are never stressed past 3%. For detailed experimental protocols describing sample preparation, application of tensile strain and electrochemical experiments see the Supplemental Information section. The strain applied to the thermally treated, TiO$_2$-coated NiTi foil is increased at 0.5% increments from 0 to 3% (% corresponds to an increase in electrode surface from its original dimensions). HER catalytic activities were evaluated by steady-state electrochemistry measurements in 0.5 M sulfuric acid aqueous solution with TiO$_2$ films under dynamic tensile strain a 0–3% (Fig. S1a,b). Linear sweep voltammetry (LSV) results are shown in Fig. 1a. A summary of the electrochemical parameters can be found in Tables 1 and S1. As the samples are strained, the overpotential (η), taken as the voltage required to pass 10 mA/cm$^2$ shifts anodically by a remarkable ∼320 mV (Fig. 1b). The TiO$_2$ under zero applied strain shows a large Tafel slope (173 mV/dec) at overpotentials where Tafel behavior is observed and a small exchange current
Table 1. HER electrochemical parameters measured for TiO$_2$ electrodes at 0–3% strain. More information is given in Table S1. HER activities are measured in 0.5 M H$_2$SO$_4$. EIS measurements are conducted in the frequency range 1 Hz to 100 kHz at −0.28 V vs RHE.

| Strain (%) | $\eta$ (mV) at 1 mA/cm$^2$ | $\eta$ (mV) at 10 mA/cm$^2$ | $j_0$ (A/cm$^2$) | Tafel slope (mV/dec) | $R_{CT}$ (Ω) | $C_a$ (μF) |
|------------|----------------|----------------|----------------|----------------|-------------|-------------|
| 0          | 385             | 565             | $7 \times 10^{-4}$ | 173             | 1108        | 4.1         |
| 1          | 289             | 472             | $9 \times 10^{-4}$ | 155             | 332         | 3.8         |
| 2          | 202             | 371             | $21 \times 10^{-6}$ | 137             | 88          | 5.1         |
| 3          | 125             | 260             | $97 \times 10^{-6}$ | 124             | 39          | 7           |

Volmer step: $\text{H}_2\text{O}^+ + e^- + \cdots \Rightarrow \text{H} + \text{H}_2\text{O}$ (1)

Heyrovsky step: $\text{H} + \text{H}^+ + e^- \Rightarrow \text{H}_2 + \cdots$ (2)

The higher Tafel slopes at low overpotentials are often observed for semiconductors, where charge transfer is mediated by surface states. We also conduct electrochemical impedance spectroscopy (EIS) measurements in the frequency range 1 Hz to 100 kHz at different strain conditions. Nyquist plots (Fig. 1d) show that the high frequency series resistance ($R_s$) (≈10 Ω) which is normally mostly determined by conduction in the electrolyte does not change significantly with strain, suggesting that strain has no significant effects on the reaction conditions. In contrast, the charge transfer resistance ($R_{CT}$) decreases systematically from $\sim$1 kΩ to $\sim$40 Ω for 0 to 3% strain, respectively. The decrease in $R_{CT}$ represents an improvement in the reaction kinetics between TiO$_2$ surface and reactants in solution. As can be expected, the observed decreases in $R_{CT}$ with strain are inversely proportional to the observed increases in $j_0$. Overall, the measured electrochemical parameters suggest that improved HER activities under strain are due to increased concentration of active surface sites (i.e. higher $j_0$) and consequently faster reaction kinetics (i.e. higher $\eta$, $j_0$, 1/$R_{CT}$). Interestingly, $j_0$ and 1/$R_{CT}$ do not linearly vary with strain and more significant changes in electrochemical parameters ($\eta$, $j_0$, $R_{CT}$) occur for strains above $\sim$1.5% (Fig. 1b, S2a–c). Electrochemical data are consistent with the results we reported previously, where strain raises the energy distribution of V$_{O}$ (n-type dopants) near the conduction band and causes an increase in carrier concentration density of surface states (SSDOS), with most significant increase between 1–2% (Fig. S2d). In sum, these electrochemical experiments show that straining a rutile TiO$_2$ film transforms it from a poor HER electrocatalyst to a facile one, with activities comparable to activities of other state-of-the-art earth-abundant metal catalysts. For example, the HER onset potential at 3% strain is comparable to these typically reported for molybdenum (MoS$_2$) and tungsten sulfides (WS$_2$) ($\sim$250 mV at 10 mA/cm$^2$), while exchange current densities ($\sim$10$^{-4}$ A/cm$^2$) are significantly higher.

Generally, the effects of mechanical strain on any solid material can lead to changes in grain reorganization and/or changes in crystal structure at atomic level. Effects, such as cracking and fissuring of the TiO$_2$ film could in theory improve HER activities by i) exposing more catalytically active TiO$_2$ crystal facets, edges or defects, ii) increasing the overall electroactive surfaces or iii) exposing the underlying NiTi substrate. We have explored each of these conceivable circumstances in more detail. First, we note that our prior work on thermally grown rutile TiO$_2$ on Nitinol foils showed elastic behavior, with no cracking at low tensile strain values of 0–5%. Here we confirm those results by imaging surface morphology with strain using scanning electron microscopy (SEM). SEM images were taken of polished samples, after oxidation at 500 °C, first strained multiple times to 3% (i.e. elastic range) and then to 7% (i.e. inelastic range). When strained to 3% no change in the TiO$_2$ surface morphology is observed (Fig. 2a, insert). However, when samples are strained up to 7% a change in the surface morphology (fissuring) is observed and large cracks in the surface are visible (Fig. 2b, insert). SEM findings are consistent with the electrochemical data. There are no significant changes in HER activities at 0% strain for samples that undergo multiple stretch-release cycles up to 3% and the effects of strain on HER activities were reversible (Fig. 2a). After the first strain-release cycle, small permanent increases in HER activity is observed, likely due to some surface activation process. For samples that are purposely cracked by straining past their elastic limit, some increases in HER activities with strain are observed (Fig. 2b). Nevertheless, increase in HER is less significant than ones presented in Fig. 1a and the effects are irreversible.

Additional evidence that the overall electroactive surface is not increasing significantly with strain is provided by electrochemical analysis. Double layer capacitance ($C_{dl}$) measurements show that $C_{dl}$ increase only 1.7-fold from 4.1 to 7.0 μF when strained from 0 to 3% (Table 1, Fig. S2b), which is significantly lower than changes in observed HER activities. LSV measurements also are conducted with NiTi substrates that were not thermally treated (i.e., simply the native oxide NiTiO$_x$ without a thermally grown rutile TiO$_2$ overlayer). For this control we observe a small, reversible increase in HER activities with strain, with about $\sim$10 mV cathodic shift in HER onset potential per 1% percentage strain (Fig. S4). Although relatively small, the effects of strain on HER activities for untreated NiTi are still significant and comparable to previous reports on strain-induced changes in HER activities for metallic substrates ($\sim$30 mV/strain). For comparison, we see about $\sim$100 mV change...
in onset potential per 1% strain for thermally grown 50 nm thick TiO\(_2\) film. Other electrochemical parameters for untreated NiTiO\(_x\) also are inconsistent with those measured for TiO\(_2\) (Table S1). These data make clear that exposure of the NiTiO\(_x\) underlayer via cracking cannot explain increases in TiO\(_2\) HER activities. In total, these results strongly suggest that i) opening and closing of surface fissures and exposure of the NiTiO\(_x\) substrate does not explain large improvements in HER activities we have observed; and ii) a continuous TiO\(_2\) film is required to observe large, reversible effects of strain suggesting an elastic deformation.

In addition to HER, we also examine the effects of tensile strain (0–3%) on the rutile TiO\(_2\) activity for the OER. LSV measurements in 1 M NaOH are conducted with 50 nm thick TiO\(_2\) rutile thermally grown on NiTi (Fig. 3a). The LSV curves show large onset potentials (\(\eta\), defined as the potential at an OER current density of 1 mA/cm\(^2\)) (Table 2) in comparison to other OER catalysts\(^{48,49}\). The \(\eta\) required to pass 1 mA/cm\(^2\) shifts cathodically 89 mV from 0 to 3% strain. In comparison to HER activities presented in this work, the observed increases in OER activities with strain are more moderate, but nevertheless comparable to the previous studies on strain-induced effects on OER for different materials\(^{6,22,32,38}\). Tafel analysis shows increase in Tafel slope with 0–3% strain suggesting strain effects OER mechanism (Table 2, Fig. 3b). Significant increases in exchange current densities (\(j_0\)) with increased strain (Table 2, Fig. 3b) are consistent with increased concentration of surface active sites and faster reaction kinetics. Similar to HER results, OER data are consistent with our previous study, where strain raises the energy distribution of VOs (n-type dopants) near the conduction band and causes an increase in carrier concentration density of surface states (SS\(_{D\text{ev}}\))\(^{39}\). Interestingly, Liu et al. observed an opposite trend with pervoskite cobaltite thin films, where OER activities decrease under applied static tensile strain or with introduction of oxygen vacancies\(^{50}\). Further increases in OER activities above 3% strain (Fig. S6) are due to some TiO\(_2\) film fissuring. This can be expected considering that surface fissuring exposes Ni, which in its oxidized form (NiO\(_x\)) is a better
OER catalyst than TiO$_2$ in the alkaline electrolyte investigated here. As with the HER results, for cracked TiO$_2$ surface effects of strain on OER activities are irreversible.

Theory. In our preceding study with n-doped TiO$_2$ films we showed that the tensile strain applied on 50 nm rutile TiO$_2$ primarily affects the spatial and energetic distribution of oxygen vacancies (VOs)\textsuperscript{39}. Therefore strain-induced changes in the HER and OER catalytic activities are associated with the changes in V Os. This is consistent with previous reports showing that bridging VOs are primary active sites for dissociative water adsorp-
tion\textsuperscript{51–54}. Water dissociation is followed by proton transfer to nearby bridging oxygen atom (OH$_b$) forming two hydroxyl groups for each V O, and finally diffusion of OH$_b$ away from the original binding site\textsuperscript{53}. In contrast to defective TiO$_2$, the surface of stochiometric TiO$_2$ (s-TiO$_2$) is considered unreactive toward water molecules. However, tensile strain can increase water reactivity on s-TiO$_2$ by increasing the energy gain upon water adsorp-
tion and by decreasing its dissociation barrier\textsuperscript{37}.

For most transition metal oxides, the first step in HER mechanism (Eq. 1) is considered a facile chemical reaction. Typically, the common descriptor for HER activities is hydrogen adsorption free energy ($\Delta G_H^*$), with the most efficient HER catalysts having $\Delta G_H^*$ approaching 0 (i.e., Sabatier principle). Tensile strain can increase or decrease H$^*$ binding in a manner that depends on a catalyst electronic state (d-band theory for transition metals)\textsuperscript{33,55}, as well as an applied overpotential\textsuperscript{16}. A previous study with cobalt(II) oxide nanorods, where strain was imposed through nanostructuring, showed that an increase in tensile strain from 0 to 4% leads to an increase in $\Delta G_H^*$ from negative to positive values, with optimal $\Delta G_H^*$ around 0 eV achieved at 3% strain\textsuperscript{40}. To study H$^*$ adsorption for our system, we performed Plane-Wave Density Functional Theory (PW-DFT) calculations for strained rutile TiO$_2$ (110) surfaces (both stochiometric and defective TiO$_2$). Detailed description of the com-
putational methods is given in the Supplemental Information section. Calculations show that the adsorption strength of H$^*$ is weakened in the presence of an VO (Table S3,S5) with the local minima of H$^*$ configurations choosing bridging oxygen sites in the row opposite of the VO (Supplemental Information Fig. S9, Table S6 is less stable by >0.3 eV). In sum, we found that tensile strain imposed on TiO$_2$ increases both H$^*$ binding (i.e. more negative $\Delta G_H^*$) and HER activities measured experimentally. This trend is opposite from the one observed for CoO nanorods described above, as well as the trend for transition

| Strain (%) | $-\eta$(mV) at 1 mA/cm$^2$ | $j_a$(A/cm$^2$) | Tafel slope (mV/dec) |
|-----------|-----------------|----------------|--------------------|
| 0         | 1.89            | $6.5 \times 10^{-9}$ | 59                 |
| 1         | 1.82            | $1.7 \times 10^{-8}$ | 68                 |
| 2         | 1.79            | $6.6 \times 10^{-7}$ | 87                 |
| 3         | 1.80            | $4.5 \times 10^{-6}$ | 102                |

Table 2. OER electrochemical parameters measured for TiO$_2$ electrodes at 0–3% strain. OER activities are measured in 1 M NaOH.
metal catalysts where excessive H* binding impedes HER activities\textsuperscript{17-19}. Tafel slopes between 173 and 120 mV/dec measured in this work (Table 1) are higher than ones reported for CoO nanorods\textsuperscript{39,49} as well as most of other transition metal catalysts\textsuperscript{39,56}. Higher Tafel slopes suggest different HER mechanism, possibly one with more significant impact of the first Volmer step (Eq. 1). Hypothetically, more negative \( \Delta G_{\text{OH}} \) can improve HER activities by decreasing activation barrier or by improving thermodynamics for H* formation (Eq. 1, Fig. S10). Alternatively, overall HER rates could be limited by a modest reactivity of water molecules on TiO\textsubscript{2} surface, and not H* binding. Both hypotheses are consistent with higher Tafel slopes determined experimentally and presented computational results. More comprehensive understanding how strain affects HER and OER catalytic mechanisms requires additional computational studies for the entire reaction profile, especially looking at interaction of water molecules with V\textsubscript{O}\textsubscript{8}. Such calculations are rather complex and would exceed the scope of this publication.

It is important to recognize that effects of strain on TiO\textsubscript{2} HER activities are very complex. Relatively simple theoretical model with single V\textsubscript{O} and single H* is presented here. Previous reports show that applied strain effects diffusion pathways and overall distribution of H* on rutile TiO\textsubscript{2}\textsuperscript{39,56}. Strain also affects formation, diffusion and energy of V\textsubscript{O}\textsubscript{8}, as discussed throughout the text. Our calculations show that the formation energy required to create an V\textsubscript{O} decreases with increasing tensile strain from 2.86 eV (unstrained) to 2.51 eV (strained at 3%) (Table S2). Therefore, it is likely that strain influences the mechanism of water splitting leading to \( \text{H}_2 \) evolution in more complex ways than simply changing the adsorption strength of H*. Effects of strain on V\textsubscript{O}\textsubscript{8} will lead to considerable effects on reaction barriers and pathways to water splitting, where the optimum pathway might differ depending on strain.

Conclusions

We showed that dynamically straining a thin film of n-doped rutile TiO\textsubscript{2} up to 3% tensile strain using an elastic NiTi substrate significantly increases both HER and OER activities. Significant improvements in HER activities with tensile strain are likely due to an increase in surface active sites and a decrease in kinetic and thermodynamics barriers along the reaction pathway(s). In our preceding work\textsuperscript{39}, we showed that tensile strain increased density of surface accessible V\textsubscript{O}\textsubscript{8}, which is consistent with improved HER and OER activities. We calculate a lower activation barrier for V\textsubscript{O} formation and a stronger binding of the H* intermediates with strain. This study demonstrates that application of mechanical stress may be a general method for tuning dynamically the catalytic properties of metal oxides.

Methods

In this work we followed the procedures we published earlier\textsuperscript{39}. Briefly, superelastic NiTi foil (0.05 mm thickness) was obtained from Alpha Aesar and cut into \( \sim 1 \times 5 \text{ cm} \) samples. The foils were then oxidized at 500°C under aerobic conditions for 30 minutes. Oxidized NiTi samples were loaded into an MTII/Pulliam SEMTester equipped with a 450 N capacity load cell and controlled using MTTESTQuattro control software. Samples were strained at a rate of 2 mm/min. Electrochemical measurements were controlled by a CH Instruments 600D potentiostat using a custom-built single compartment cell with an Ag/AgCl reference electrode and platinum counter (Fig. S1a). We have described in our previous publication\textsuperscript{39}. For a typical experiment, the cell is loosely assembled around the NiTi and then the cell is tightened onto the sample to create a solution tight cell for electrochemical measurements. To strain the working NiTi electrode, the electrolyte is drained and the cell loosened so that the sample can move freely, and then the strain is adjusted (2 mm/min) under software control. The cell is then re-aligned, gently tightened back onto the sample, and the electrolyte is replaced for further measurements. This procedure is repeated at each strain value (Fig. S1b). We observed that electrochemical results were the most reproducible and effects highest for samples that was never stretched pass 3%. To make sure that observed increases in hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) were not due to the electro-deposition of trace amount of platinum on the working electrode from counter Pt electrode, we run control with carbon felt electrode. Silver/silver chloride and mercurous oxide were used as a reference electrode for HER or OER measurements respectively.

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References

1. Li, J., Shan, Z. & Ma, E. Elastic strain engineering for unprecedented materials properties. \textit{MRS Bulletin} \textbf{39}, 108–114, \url{https://doi.org/10.1557/mrs.2014.3} (2014).
2. Luo, M. & Guo, S. Strain-controlled electrocatalysis on multimetallic nanomaterials. \textit{Nature Reviews. Materials} \textbf{2}, 17059, \url{https://doi.org/10.1038/s41578-017-0022-y} (2017).
3. Yang, S., Liu, F., Wu, C. & Yang, S. Tuning Surface Properties of Low Dimensional Materials via Strain Engineering. \textit{Small} \textbf{2016}, 4028–4047 (2016).
4. Chen, R.-S., Korotov, A., Huang, Y.-S. & Tsai, D.-S. One-dimensional conductive IrO2 nanocrystals. \textit{Nanotechnology} \textbf{17}, R67 (2006).
5. Clark, E. L., Hahn, C., Jaramillo, T. F. & Bell, A. T. Electrochemical CO2 Reduction over Compressively Strained CuAg Surface Alloys with Enhanced Multi-Carbon Oxygenate Selectivity. \textit{Journal of the American Chemical Society} \textbf{139}, 15848–15857, \url{https://doi.org/10.1021/jacs.7b08607} (2017).
6. Liu, Z. \textit{et al}. Electrochemical tuning of layered lithium transition metal oxides for improvement of oxygen evolution reaction. \textit{Nature Communications} \textbf{8}, 4345, \url{https://doi.org/10.1038/ncomms5345}, \url{https://www.nature.com/articles/ncomms5345#supplementary-information} (2014).
7. Sethuraman, V. A. \textit{et al}. Role of Elastic Strain on Electrocatalysis of Oxygen Reduction Reaction on Pt. \textit{The Journal of Physical Chemistry C} \textbf{119}, 19042–19052, \url{https://doi.org/10.1021/acs.jpcc.5b06096} (2015).
8. Gu, J. \textit{et al}. A graded catalytic–protective layer for an efficient and stable water-splitting photocathode. \textit{Nature Energy} \textbf{2}, 16192, \url{https://doi.org/10.1038/nenergy.2016.192}, \url{https://www.nature.com/articles/nenergy2016192#supplementary-information} (2017).
27. Potapenko, D. V., Gomes, G. T. & Osgood, R. M. Correlation of H Adsorption Energy and Nanoscale Elastic Surface Strain on Rutile.
26. Li, Z., Potapenko, D. V. & Osgood, R. M. Controlling Surface Reactions with Nanopatterned Surface Elastic Strain.
24. Muralidharan, N., Carter, R., Oakes, L., Cohn, A. P. & Pint, C. L. Strain Engineering to Modify the Electrochemistry of Energy Storage Electrodes. Scientific Reports 6, 27542, https://doi.org/10.1038/srep27542, http://www.nature.com/articles/srep27542 supplementary-information (2016).

Braghuraman, S., Soleymaniha, M., Yu, Z. & Felt, J. R. The role of mechanical force on the kinetics and dynamics of electrochemical redox reactions on graphene. Nanoscale 10, 17912–17923, https://doi.org/10.1039/C8NR03968B (2018).
Li, Z., Potapenko, D. V. & Osgood, R. M. Controlling Surface Reactions with Nanopatterned Surface Elastic Strain. ACS Nano 9, 82–87, https://doi.org/10.1021/acsnano.9b00150 (2015).
Potapenko, D. V., Gomes, G. T. & Osgood, R. M. Correlation of H Adsorption Energy and Nanoscale Elastic Surface Strain on Rutile TiO2(110). The Journal of Physical Chemistry C 120, 21373–21380, https://doi.org/10.1021/jpc.c605129e (2016).
Gsell, M., Jakob, P. & Menzel, D. Effect of Substrate Strain on Adsorption. Science 280, 717–720, https://doi.org/10.1126 science.280.5364.717 (1998).

Wang, H. et al. Direct and continuous strain control of catalysts with tunable battery electrode materials. Science 354, 1031–1036, https://doi.org/10.1126/science.aaf7680 (2016).
Lu, Z., Jiang, K., Chen, G., Wang, H. & Cui, Y. Lithium Electrochemical Tuning for Electrochemical Stabilization. Advanced Materials 30, 1800978–1800986 (2018).
Wang, H. et al. Electrochemical tuning of vertically aligned MoS2 nanoflakes and its application in improving hydrogen evolution reaction. Proceedings of the National Academy of Sciences 110, 19701–19706, https://doi.org/10.1073/pnas.1316792110 (2013).
Wang, A. et al. Tuning the oxygen evolution reaction on a nickel–iron alloy via active straining. Nanoscale 11, 426–430, https://doi.org/10.1039/C8NR08879A (2019).

Mavrikakis, M., Hammer, B. & Norskov, J. K. Effect of Strain on the Reactivity of Metal Surfaces. Physical Review Letters 81, 2819–2822 (1998).
Kushima, A., Yip, S. & Yildiz, B. Competing strain effects in reactivity of LaCoO3 with oxygen. Physical Review B 82, 115433, https://doi.org/10.1103/PhysRevB.82.115433 (2010).

Muralidharan, N. et al. Tunable Mechanochemistry of Lithium Battery Electrodes. ACS Nano 11, 6243–6251, https://doi.org/10.1021/acsnano.7b02404 (2017).
Shu, D.-j., Ge, S.-T., Wang, M. & Ming, N.-B. Interplay between External Strain and Oxygen Vacancies on a Rutile TiO2(110) Surface. Physical Review Letters 101, 116102 (2008).
Yang, L., Shu, D.-j., Li, S.-C. & Wang, M. Influence of strain on water adsorption and dissociation on rutile TiO2(110) surface. Physical Chemistry Chemical Physics 18, 14833–14839, https://doi.org/10.1039/c6cp01066c (2016).
Petrie, J. R., Jeen, H., Barron, S. C., Meyer, T. L. & Lee, H. N. Enhancing Perovskite Electrocatalysis through Strain Tuning of the Chemical Properties of Bimetallic Surfaces. Journal of Physical Chemistry C 120, 7252–7255, https://doi.org/10.1021/acs.jpcc.7b00281 (2016).

Benson, E. E. et al. Semiconductor-to-Metal Transition in Rutile TiO2 Induced by Tensile Stress. Chemistry of Materials 29, 2173–2179, https://doi.org/10.1021/acs.chemmater.6b04881 (2017).
Ling, T. et al. Activating cobalt(ii) oxide nanorods for efficient electrocatalysis by strain engineering. Nature Communications 8, 1509, https://doi.org/10.1038/s41467-017-01872-y (2017).
Wang, Z.-w., Shu, D.-j., Wang, M. & Ming, N.-B. Strain effect on diffusion properties of oxygen vacancies in bulk and subsurface of rutile TiO2. Surface Science 606, 186–191, https://doi.org/10.1016/j.susc.2011.09.014 (2012).
Zheng, Y.-f., Chen, S., Yang, J.-H. & Gong, X.-G. Polarorn-enhanced giant strain effect on defect formation: The case of oxygen vacancies in rutile TiO2. Physical Review B 99, 014113, https://doi.org/10.1103/PhysRevB.99.014113 (2019).
Shi, Y. et al. Role of Surface Stress on the Reactivity of Anatase TiO2(001). The Journal of Physical Chemistry Letters 8, 1764–1771, https://doi.org/10.1021/acs.jpclett.7b00181 (2017).

Shinagawa, T., Garcia-Esparza, A. T. & Takahara, K. Insight on Tafel slopes from a microkinetic analysis of aqueous electrocatalysis for energy conversion. Scientific Reports 5, 13801, https://doi.org/10.1038/srep13801 (2015).
Vandermolen, J., Gomes, W. P. & Cardon, P. Investigation on the Kinetics of Electroreduction Processes at Dark TiO2 and SrTiO3 Single Crystal Semiconductor Electrodes. Journal of The Electrochemical Society 127, 324–328, http://doi.org/10.1149/1.2129664 (1980).
46. Salvador, P. & Gutiérrez, C. Mechanisms of Charge Transfer at the Semiconductor-Electrolyte Interface: I. Kinetics of Electroreduction at Dark of and in Aqueous Solution on a Sintered Nb-doped Electrode: Influence of pH. *Journal of The Electrochemical Society* 131, 326–336, https://doi.org/10.1149/1.2115569 (1984).

47. McCrorry, C. C. L. et al. Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *Journal of the American Chemical Society* 137, 4347–4357, https://doi.org/10.1021/ja510442p (2015).

48. Seh, Z. W. et al. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* 355, eaad4998, https://doi.org/10.1126/science.aad4998 (2017).

49. Roger, I., Shipman, M. A. & Symes, M. D. Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. *Nature Reviews Chemistry* 1, 0003, https://doi.org/10.1038/s41570-016-0003 (2017).

50. Liu, X. et al. Uncovering the Effect of Lattice Strain and Oxygen Deficiency on Electrocatalytic Activity of Perovskite Cobaltite Thin Films. *Advanced Science* 6, 1801898, https://doi.org/10.1002/advs.201801898 (2019).

51. McCrory, C. C. L. et al. Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *Journal of the American Chemical Society* 137, 4347–4357, https://doi.org/10.1021/ja510442p (2015).

52. Seh, Z. W. et al. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* 355, eaad4998, https://doi.org/10.1126/science.aad4998 (2017).

53. Roger, I., Shipman, M. A. & Symes, M. D. Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. *Nature Reviews Chemistry* 1, 0003, https://doi.org/10.1038/s41570-016-0003 (2017).

54. Liu, X. et al. Uncovering the Effect of Lattice Strain and Oxygen Deficiency on Electrocatalytic Activity of Perovskite Cobaltite Thin Films. *Advanced Science* 6, 1801898, https://doi.org/10.1002/advs.201801898 (2019).

55. Schaub, R. et al. Oxygen Vacancies as Active Sites for Water Dissociation on Rutile TiO₂(110). *Physical Review Letters* 87, 266104, https://doi.org/10.1103/PhysRevLett.87.266104 (2001).

56. Lu, G., Linsebigler, A. & Yates, J. T. Ti³⁺ Defect Sites on TiO₂(110): Production and Chemical Detection of Active Sites. *The Journal of Physical Chemistry* 98, 11733–11738, https://doi.org/10.1021/j10006a017 (1994).

57. Lun Pang, C., Lindsay, R. & Thornton, G. Chemical reactions on rutile TiO₂(110). *Chemical Society Reviews* 37, 2328–2353, https://doi.org/10.1039/B719085A (2008).

58. Pan, X., Yang, M.-Q., Fu, X., Zhang, N. & Xu, Y.-J. Defective TiO₂ with oxygen vacancies: synthesis, properties and photocatalytic applications. *Nanoscale* 5, 3601–3614, https://doi.org/10.1039/C3NR00476G (2013).

59. Hammer, B. & Nørskov, J. K. Electronic factors determining the reactivity of metal surfaces. *Surface Science* 343, 211–220, https://doi.org/10.1016/0039-6028(96)80007-0 (1995).

60. Flupfer, A. J., Monakhov, E. V., Svensson, B. G., Chaplygin, I. & Lavrov, E. V. Hydrogen motion in rutile TiO₂. *Scientific Reports* 7, 17065, https://doi.org/10.1038/s41598-017-16660-3 (2017).

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**Competing interests**

The authors declare no competing interests.

**Additional information**

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