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TITLE:

Applying Dynamic Strain on Thin Oxide Films Immobilized on a Pseudoelastic Nickel-Titanium Alloy

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SUMMARY:

Dynamic, tensile strain is applied on TiO₂ thin films to study the effects of strain on electrocatalysis, specifically proton reduction and water oxidation. TiO₂ films are prepared by thermal treatment of the pseudo-elastic NiTi alloy (Nitinol).

ABSTRACT:

Direct alteration of material structure/function through strain is a growing area of research that has allowed for novel properties of materials to emerge. Tuning material structure can be achieved by controlling an external force imposed on materials and inducing stress-strain responses (i.e., applying *dynamic strain*). Electroactive thin films are typically deposited on shape or volume tunable elastic substrates, where mechanical loading (i.e., compression or tension) can affect film structure and function through imposed strain. Here, we summarize methods for straining n-type doped titanium dioxide (TiO₂) films prepared by a thermal treatment of a pseudo-elastic nickel-titanium alloy (Nitinol). The main purpose of the described methods is to study how strain affects electrocatalytic activities of metal oxide, specifically hydrogen evolution and oxygen evolution reactions. The same system can be adapted to study the effect of strain more broadly. Strain engineering can be applied for optimization of a material function, as well as for design of adjustable, multifunctional (photo)electrocatalytic materials under external stress control.

INTRODUCTION:

The ability to alter the surface reactivity of catalytic materials by introducing strain has been widely recognized¹⁻³. Effects of strain in crystalline materials can be introduced either by adjusting material architecture (*static strain*) or by applying a variable external force (*dynamic strain*). In crystalline materials, static strain can be introduced by doping⁴, de-alloying^{5,6}, annealing⁷, epitaxial growth on a mismatched crystal lattice² or size confinement^{2,3}. In polycrystalline materials, strain can occur within grain boundaries due to crystal twinning⁸. Determining the optimal degree of static strain with material architectures requires designing a new sample for each discrete level of strain, which can be time consuming and expensive. Furthermore, introducing static strain often introduces chemical or ligand effects^{9,10}, making it difficult to isolate the strain contribution. Applying a dynamic strain precisely controlled by an external force allows systematic tuning of a material's structure/function relationship in order to explore a dynamic range over the strain space without introducing other effects.

To study the effects of dynamic strain on electrocatalysis, metals or metal oxides are deposited on elastic shape or volume tunable substrates, such as organic polymers¹¹⁻¹⁵ or alloys^{16,17}. Applications of mechanical, thermal or electrical loading results in bending, compression, elongation or expansion of an elastic substrate, further inducing a stress-strain response on the deposited catalytic material. So far, catalyst engineering through dynamic strain has been exploited to tune electrocatalytic activities of various metallic and semiconducting materials. Examples include i) the hydrogen evolution reaction (HER) on MoS₂, Au, Pt, Ni, Cu, WC¹¹⁻¹⁴, ii) the oxygen evolution reaction (OER) on NiO_x¹⁶, nickel-iron alloys¹⁸ and iii) the oxygen reduction reaction (ORR) on Pt, Pd^{12,15,19,20}. In most of these reports, organic polymers, such as polymethyl methacrylate (PMMA), were used as elastic substrates. We previously demonstrated the application of elastic metallic substrates, such as stainless steel¹⁶ and a superelastic/shape-memory NiTi alloy (Nitinol^{17,21}) for strain studies. Nitinol has also been used as an elastic substrate for deposition of platinum films for ORR¹⁹ and deposition of battery cathode materials for energy storage^{22,23}. Due to its shape memory and pseudoelastic properties, NiTi alloys can be deformed by applying moderate heat¹⁹ or mechanical strain¹⁷, respectively. In contrast to organic elastic substrates, metallic substrates typically do not require deposition of adhesion promoters, are highly conductive and can easily be functionalized. Nitinol is used as a more elastic alternative to stainless steel (SS). While SS can be reversibly strained up to 0.2%, nitinol can be reversibly strained up to 7%. Nitinol owes its unique properties to a martensitic solid state crystal transformation that allows for large elastic deformations^{24,25}. Both materials are commercially available in different geometries (e.g., foils, wires, and springs). When shaped into elastic springs, metallic substrates can be used to study effects of dynamic strain on electrocatalysis without the need for expensive instrumentation¹⁶; however, defining the stress-strain response is more challenging than for other geometries.

In previous experimental studies with transition metal catalysts, changes in activities of catalytic surfaces under strain have been attributed to changes in the energetics of the d orbitals colloquially known as d-band theory²⁶. In contrast, the effects of strain on metal oxides is significantly more complex, as it can effect bandgap, carrier mobility, diffusion and distribution of defects and even direct/indirect transitions^{21,27-31}. Herein we provide detailed protocols for the

preparation and characterization of n-type doped TiO₂ thin films, as well as protocols to study electrocatalytic activities of these films under tunable, tensile strain. The equivalent system can be applied to study electrocatalytic activities of different materials as a function of dynamic strain.

PROTOCOL:

1. Preparation of NiTi/TiO₂ electrodes

1.1. Chemical and mechanical polishing of NiTi substrates

1.1.1. Cut the superelastic NiTi foil (0.05-mm thickness) into 1 cm x 5 cm strips.

1.1.2. Polish sample using 320-, 600- and 1200-grit sandpaper, and then rinse with ultrapure water (18.2 MΩ).

1.1.3. Polish sample with 1 μm diamond, 0.25 μm diamond, and 0.05 μm alumina polish.

1.1.4. After polishing, sonicate for 5 min in sequential baths of ultrapure water (18.2 MΩ), isopropanol, ethanol, ultrapure water (18.2 MΩ), and then dry under nitrogen (used organic solvents were reagent grade).

CAUTION: Organic solvents are flammable, can irritate skin and eyes, poisonous if ingested. Use with caution in well ventilated areas.

NOTE: Foils should be treated gently. Repeated bending or twisting can result in nano-to-micro sized fissures, which will affect its elastic properties decreasing the effects of strain on the electrocatalytic activities.

1.2. Preparation of TiO₂ films

1.2.1. Oxidize NiTi foils by placing foils in a 500 °C oven under aerobic conditions (**Figure 1**).

1.2.2. For preparation of 50 nm thick rutile TiO₂ films, heat NiTi foils for 30 min at 500 °C. Longer heating will result in thicker TiO₂ films. Heating will cause a change in the surface color from gray to blue/purple (**Figure 2**).

1.3. Applying tensile stress on NiTi/TiO₂

1.3.1. Gently clamp foil (1 cm x 5 cm strip) in a mechanical tester (**Table of Materials**) with 1 cm of foil exposed at each end.

1.3.2. Strain the NiTi/TiO₂ samples at a rate of 2 mm/min. Keep the strain at desired level (0-3%).

NOTE: Extension of the available 3 cm NiTi/TiO₂ lengthwise from 0.0 to 2.1 mm is considered straining from 0 to 7%, which can be calculated by simple equation $\text{strain} = (l - l_0)/l_0$, where l_0 is initial and l final length of foil exposed to tensile strain. Typical stress-strain curve is shown in **Figure 3**.

1.4. To start electrochemical measurements, pre-strain the foil to 5 N (taken as 0% strain).

NOTE: The slight pre-straining of the foil leads to more reproducible results.

2. Conducting electrochemical measurements under strain

2.1. Applying tensile stress on working electrode

2.1.1. To conduct electrochemical experiments under applied strain, assemble the custom-made electrochemical cell (**Figure 4** and **Figure 5**) loosely around the NiTi/TiO₂ foil. Ensure that the center of the NiTi/TiO₂ foil is exposed by carefully positioning the cell in the middle (**Figure 5**).

2.1.2. Tighten the cell gently onto the sample to create a solution-tight cell for the electrochemical measurements.

2.1.3. Fill up with an electrolyte and purge the solution gently with nitrogen.

2.1.4. Increase strain to specific levels, typically 0 to 3% in 0.5% increments and conduct electrochemical experiments for each discrete strain value.

2.1.5. Before each strain adjustment, loosen the electrochemical cell around NiTi/TiO₂ foil, so that the sample can move freely. Then realign the cell by gently tightening back onto the sample and refill the electrolyte for the next electrochemical measurements.

NOTE: Tightening and untightening the cell around the NiTi/TiO₂ foil is obviously more laborious and time consuming than working with a continuously tightened cell through the experiments. Nevertheless, this approach minimizes possible wrinkling of NiTi/TiO₂ foil leading to the most reproducible results and the highest effects of strain.

2.2. Electrochemical characterization of strained working electrode

2.2.1. As an initial experiment, conduct cyclic voltammetry (CV) or linear sweep voltammetry (LSV) measurements (**Figure 6A**). Further characterization could include impedance, electrolysis, chronoamperometry, etc.

2.2.2. Collect electrochemical measurements with samples exposed to discrete, increasing levels of strain (e.g., from 0 to 3% in 0.5% increments), followed by gradual decreasing of applied strain (e.g., from 3 to 0% in 0.5% increments).

2.2.3. Collect data for multiple experimental cycles (0%→3%→0%) to test the system mechanical stability and data reproducibility.

2.2.4. Alternatively, keep the foil strained at a discrete amount of strain for prolonged time periods (e.g., hours or days) and conduct electrochemical experiments periodically (e.g., voltammetry) or continuously (e.g. electrolysis).

2.3. HER experiments

2.3.1. Use 0.5 M sulfuric acid as the electrolyte, Ag/AgCl (1 M NaCl) as the reference electrode, and a coiled platinum wire (0.5 mm diameter by ~10 cm length) as the counter electrode.

CAUTION: Sulfuric acid causes severe skin burns and eye damage. Do not breathe mist, vapors, or spray. Wear protective gloves, protective clothing, eye protection, and face protection. Immediately wash exposed skin with copious amounts of water if exposed.

2.3.2. Scan the potentials between the open-circuit voltage (OCV) to -0.8 V vs RHE, starting with the highest potential value with scan rate 5-50 mV/s (**Figure 6A**).

2.4. OER experiments

2.4.1. Use 1 M sodium hydroxide as the electrolyte, Hg/HgO (1 M NaOH) as the reference electrode, and a coiled platinum wire (0.5 mm diameter by ~10 cm length) as the counter electrode.

CAUTION: 1 M sodium hydroxide can cause skin burns and eye damage. Do not breathe mist, vapors, or spray. Wear protective gloves, protective clothing, eye protection, and face protection. Immediately wash exposed skin with copious amounts of water if exposed.

2.4.2. For OER experiments, scan the potential between OCV to 2 V vs RHE, starting with the lowest potential value, with scan rate 5-50 mV/s (**Figure 6B**).

2.5. Impedance

2.5.1. Carry out electrochemical impedance spectroscopy (EIS) measurements at frequencies ranging from 1 Hz-100 kHz at a potential where no Faradaic process is observed (OCV) (**Figure 6C**).

2.6. Analyzing time profile, system stability and products

2.6.1. To test the stability of the system and measure products (e.g., H₂ and O₂), conduct electrolysis experiments.

2.6.2. For amperometric i-t measurements, choose the most suitable potential based on CV or LSV results (e.g., -0.25 V vs RHE for HER).

2.6.3. Alternatively, for chronopotentiometry experiments, choose the most suitable current density based on CV results.

2.6.4. If gas chromatograph is available, measure in-line hydrogen (from HER) or oxygen (from OER) gas produced electrochemically.

NOTE: These are examples of electrochemical analyses. Electrochemical characterization can be tailored for a specific study.

3. Controls

3.1. Capacitance measurements

3.1.1. To determine if increases in HER activities are simply due to increases in electroactive surface, conduct capacitance measurements at different strain values.

3.1.2. Run CV experiments at different scan rates (e.g., 1 and 500 mV/s) at a potential range where Faradic currents are negligible, so that currents represent only the charge/discharge of the electric double layer (e.g., 0 to 0.1 V vs RHE).

3.1.3. Plot scan rates versus currents (**Figure 7A**).

3.1.4. Compare increases in capacitance with strain with increases in electrocatalytic activities (e.g., HER or OER) with strain (**Figure 7A**).

NOTE: If increases in electrocatalytic activities are higher than increases in capacitance, it can be concluded that simple increase in grain separation and electroactive surface is not the only contributor to the increase in electrocatalytic activities.

3.2. Characterization of cracked films

3.2.1. Purposely crack NiTi/TiO₂ foil by keeping the foil strained at 7% for 30 min or longer for 50 nm TiO₂ films (**Figure 8**). Thicker TiO₂ films (100 nm) can be cracked at lower strains (3% strain).

3.2.2. Analyze the surface for cracking by scanning electrochemical microscopy (SEM), or other surface analysis methods, as described below.

3.2.3. Conduct electrochemical measurements as described above with pristine and purposely cracked TiO₂ films at different incrementally increased and then decreased strain values from 0%→3%→0% (**Figure 6D**). NiTi/TiO₂ foils with 50 nm thick TiO₂ films that were never strained pass 3% are considered pristine, *elastic*.

NOTE: Determine the specific “elastic limit”: the maximum stress that can be applied on a material before the onset of an irreversible deformation (e.g., grain rearrangement or even film cracking). Elastic range depends on film type, thickness and deposition method. For example, we show that 100 nm thick TiO₂ films crack at lower strains than 50 nm thick TiO₂ films.

3.3. Characterization of NiTi foils (i.e., unoxidized foils)

3.3.1. Polish NiTi foils as described in step 1.1, but do not thermally treat them.

3.3.2. Run all the electrochemical experiments, as described above, with NiTi foils that were not thermally treated as a control.

4. Surface characterization

4.1. Sample preparation

4.1.1. Cut and pretreat NiTi/TiO₂ as described in steps 1.1 and 1.2.

NOTE: The size of the sample foil depends on the size of the sample holder, which depends on a specific instrumentation used for the surface characterization.

4.1.2. Wash samples with water to remove any residual salt if used in electrochemical experiments before the characterization.

4.1.3. Assemble NiTi/TiO₂ foil in the tensile stretcher and strain to a desired level as described in section 1.3.

4.1.4. Assemble the custom-made sample holders around the strained sample and gently tighten the screws (**Figure 9**).

4.2. Surface characterization

4.2.1. To check film quality and changes in film topology with strain, collect scanning electrochemical microscopy (SEM) images.

4.2.2. Use other available surface analysis methods to monitor changes in surface chemical composition, grain rearrangements and exposed crystal lattices (e.g., Raman spectroscopy, XPS or XRD experiments) (**Figure 10**).

4.2.3. To check if a sample holder kept constant strain during the surface characterization experiments untighten the sample from the sample holder and look for any curl in the sample between the strained portion under the clamp and the unrestrained portion that was previously in the tensile tester.

REPRESENTATIVE RESULTS:

Pre-treated NiTi foils are oxidized at 500 °C under aerobic conditions (**Figure 1**). Due to the oxophilic nature of titanium, calcination at elevated temperatures results in a surface layer of rutile TiO₂. The thickness of the layer and degree of n-type doping are affected by annealing time and temperature, which is reflected in color change from gray (untreated sample) to uniform blue/purple after 20 min heating (**Figure 2**). Longer heating time results in thicker TiO₂ films (60 min for 100 nm films) and is accompanied by gradual loss of blue/purple color. Thicker TiO₂ films show analogous electrochemistry but are more prone to surface fissuring and therefore loss in film elasticity.

[Figure 1]

[Figure 2]

Nitinol behavior under thermal and mechanical stress reflects reversible solid-state phase transformation known as a martensitic transformation, between two different martensite crystal phases, making it a *pseudo-elastic* rather than an *elastic* material. A typical stress-strain curve of NiTi/TiO₂ samples is given in **Figure 3**. Note that the shape of the foil is rectangular and not specifically shaped for mechanical testing, which could result in nonuniform stress distribution from the center of the sample to the clamped sample section. Nevertheless, electrochemical characterization of strained foils is conducted with only a small section of NiTi/TiO₂ foil positioned in the middle (see further text). An assumption is made that within this small surface applied stress is uniform.

[Figure 3]

For measuring effects of strain on electrocatalytic properties of different materials, single or double compartment electrochemical cells are custom-built. **Figure 4** shows the electrochemical cell with both the cathode and anode compartment. If focus is only on the electrochemical characterization rather than the product (H₂ and/or O₂) collection, double compartment cells and membrane separation are not necessary for HER and OER experiments. The size of the cathode is limited by an opening in the electrochemical cell (**Figure 5**) that allows exposure of NiTi/TiO₂ foil to the electrolyte. Therefore, even though a large fraction of NiTi/TiO₂ foil is exposed to strain, only a small circle (i.e., 5 mm diameter) in the middle of the foil undergoes electrocatalysis. The working electrode volume should be kept relatively small relative to the surface of a counter electrode to minimize the effects of solvent resistance.

[Figure 4]

[Figure 5]

Typically, first experiments include CV or LSV (**Figure 6A,B**). These experiments are important for understanding the electrochemical system, such as Faradic versus non-Faradic ranges. Further electrochemical characterization can include electrochemical impedance to study changes in electrode surface reactivities with strain (**Figure 6C**). Amperometry or chronoamperometry can

be used to study system stability and accumulated products. Gas chromatography can be used to detect produced H₂ (cathode) or O₂ (anode).

[Figure 6]

Applying mechanical stress that exceeds a material elastic limit leads to grain rearrangements and cracking of the material's surface, which could increase electrocatalytic activities simply by increasing the overall electroactive surface or by exposing more catalytically active crystal facets or defects³². In these cases, dynamic strain would only affect grain rearrangement, which is different than actual changes at atomic or nanoscale material architecture. To rule out *nonelastic* effects on electrocatalytic activities, various control experiments are performed. First, to determine if increases in HER and OER activities are simply due to increases in electroactive surface, capacitance measurements are done at different strain values. Based on Randles-Sevcik expression³³, the plots of *scan rates vs currents* are linear and the slopes correspond to capacitance of the double layer. If an increase in the electroactive surface from capacitance data is significantly smaller than increases in HER or OER electrocatalytic activities, an assumption can be made that simple surface fissuring due to grain rearrangement is not the only (if any) contributor to the strain effects on electrocatalytic activities. Representative capacitance results and analysis are given in **Figure 7**.

[Figure 7]

To further determine if the changes in electroactivities with strain are due to elastic or inelastic deformation under applied tensile stress, experiments are conducted with pristine and purposely cracked TiO₂ films. When 7% strain is imposed on NiTi/TiO₂ films, surface fissures are clearly visible on SEM images (**Figure 8**). Films that were intentionally cracked did not show appreciable changes in electrochemical activity with increasing strain, likely due to the loss in elastic properties (**Figure 6D**). Samples that were purposely cracked show only small increases in HER activities within the 0-3% strain range, and these increases are irreversible, while pristine samples show significantly larger and reversible effects within the 0-3% strain range.

[Figure 8]

When surface characterization experiments are done with instrumentation that require sample enclosure (i.e., vacuum is required), the tensile stretcher cannot be directly connected to the sample in order to keep it under a defined strain. In these cases, custom-made sample holders are used, where the size and geometry are adapted for different instrumentation (**Figure 9**).

[Figure 9].

Thermal treating on nitinol typically leads to rutile TiO₂ structure. Raman and XPS spectroscopy show characteristic signals for rutile TiO₂ thin films^{34,35} as shown in **Figure 10**. Specifically, for the highly n-type doped TiO₂ films, 0-5% strain primarily effects distribution of oxygen vacancies rather than TiO₂ crystal structure, which does not lead to significant changes in XPS spectra²¹.

[Figure 10].

FIGURE AND TABLE LEGENDS

Figure 1. Scanning electrochemical microscopy images of polished (left) and oxidized (right) NiTi films.

Figure 2. NiTi foil heated at 500 °C in air for different time periods. Figure shows characteristic color changes.

Figure 3. Typical stress-strain curve for NiTi/TiO₂ foil (1 cm x 5 cm strip)

Figure 4. Two compartment cell. A) The scheme showing the individual components. **B)** The cell assembled into the tester for applying tensile strain. The cell was installed in proximity to the gas chromatograph for analysis of gaseous products. This figure illustrates how the tester can be easily assembled to work in conjunction with other instrumentation.

Figure 5. The single compartment cell used for HER and OER experiments.

Figure 6. Representative LSV and EIS data. A) LSV experiments showing HER on NiTi/TiO₂ films in 0.5 M sulfuric acid at a scan rate of 50 mV/s. **B)** LSV experiments showing OER on NiTi/TiO₂ films in 1 M sodium hydroxide at a scan rate of 50 mV/s. **C)** Electrochemical impedance at -0.38 V vs. RHE from 1 Hz to 100 kHz (Nyquist plots). **D)** LSV experiments in 0.5 M sulfuric acid at a scan rate of 50 mV/s with the purposely cracked TiO₂ films. This figure has been modified from Benson et al¹⁷.

Figure 7. Capacitance measurements. A) Plot of current vs scan rate from cyclic voltammograms collected within 50 mV of the OCV for TiNi/TiO₂ electrodes strained from 0 to 7%, where the slope represents the capacitance of the double-layer. **B)** Plot shows changes in capacitance with strain.

Figure 8. SEM image of the purposely cracked TiNi/TiO₂ foils

Figure 9. Sample holders used to “lock” NiTi/TiO₂ foil under strain for surface characterization experiments. Figure shows different sizes and geometries.

Figure 10. Surface characterization of TiO₂ thin films. A) Raman peaks characteristic for Rutile TiO₂. **B)** XPS measurements showing spectra for oxygen and titanium surface atoms. This figure has been modified from Benson et al.²¹.

DISCUSSION

Nitinol is a suitable elastic substrate for applying mechanical stress on thin films. It is commercially available, highly conductive and can be easily functionalized. Preparation of rutile

TiO₂ thin films by thermal treatment of nitinol, results in highly n-type doped TiO₂. It is important to emphasize that NiTi/TiO₂ is a unique system where TiO₂ films are prepared by thermal treatment of NiTi rather than a deposition method. Our previous publications have shown that strain applied on NiTi/TiO₂ primarily effects distribution, diffusion and energy of oxygen vacancies rather than TiO₂ crystal structure itself²¹. Currently reported studies on strained NiTi/TiO₂ are incomplete^{17,21} as they include only effects of tensile and not compressive strain. Compressive and tensile strain imposed on a catalyst structure often have opposite effects on electroactivities and therefore analyzing both is especially interesting for mechanistic studies. Instrumentation and methods presented here have not been tested for compression studies, as it can be challenging to prevent the foil wrinkling upon compression. Compression-tension studies with Nitinol substrate can be conducted using its shape-memory properties, where changes in sample geometry are induced through applied heat as demonstrated previously¹⁹.

The described methods can be used to study the effects of dynamic strain on electroactivities of thin films made from different materials and deposited by various methods (e.g., physical or chemical vapor deposition, atomic layer deposition, electrodeposition). For example, dynamic strain applied on copper films deposited on NiTi could be used to tune product selectivity for CO₂ electroreduction, as previously demonstrated with Cu films under static strain imposed either by alloying⁴ or through epitaxial growth³⁶. For each system, the characteristic elastic limit for a deposited film should be determined to achieve reproducible results and high effects of strain. The film elasticity will likely depend on multiple factors: deposited material, deposition method and film thickness as well as film crystallinity and grain structure. Determining an elastic limit can be challenging. For example, surface analysis using SEM does not have high enough resolution to detect nano-scale cracks and/or grain rearrangements; therefore, electrochemical or gas adsorption measurements are more appropriate. Purposely cracked films can be used as a control. Previous studies showed that increases in activities with strain for cracked films were not as significant as with pristine films and effects of strain were irreversible, suggesting that true elastic deformation causes high electroactivities^{16,17}. Interaction between the elastic substrate and a film (adhesiveness) and chemical compatibility are also important. The film deposition method can have significant effect on interaction between the elastic substrate, the adhesion promoter (if any) and thin films. As an alternative to Nitinol, stainless steel could be used as an elastic substrate, where large elasticity range is not required. Stainless steel is chemically compatible with metallic films that can allow good adhesion, especially due to high (~20%) chromium content.

A relatively simple electrochemical cell can be constructed to study effects of strain on various electrochemical systems. Photoelectrochemical experiments with a light-harvesting material deposited on an elastic substrate can also be conducted using the same system when an optically transparent material is placed as the cell window. Effects of strain on photoelectrochemical activities of organic dyes or polymers covalently attached to elastic substrates could also be investigated.

We show that tuning a dynamic strain with a relatively simple experimental setup can be used to find an optimal material structure with improved target activities as well as for tuning

electrocatalytic properties in situ. For example, we demonstrate 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 strained by 3%¹⁷. By applying an external mechanical stress, it could be possible to create a precisely controlled, multifunctional catalysts or electro-strain sensors for a range of applications.

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DISCLOSURES:

The authors declare no competing interests.

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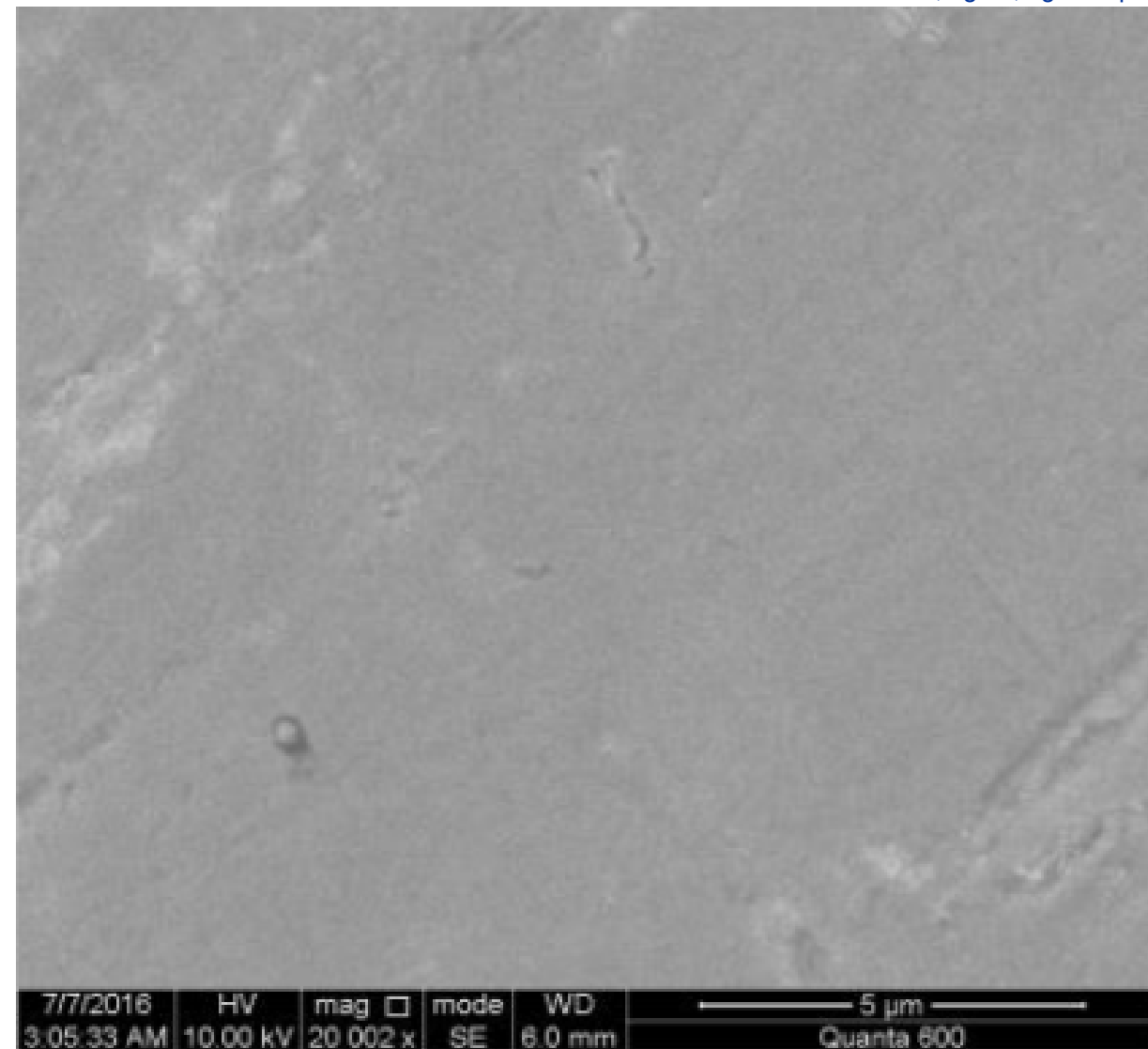
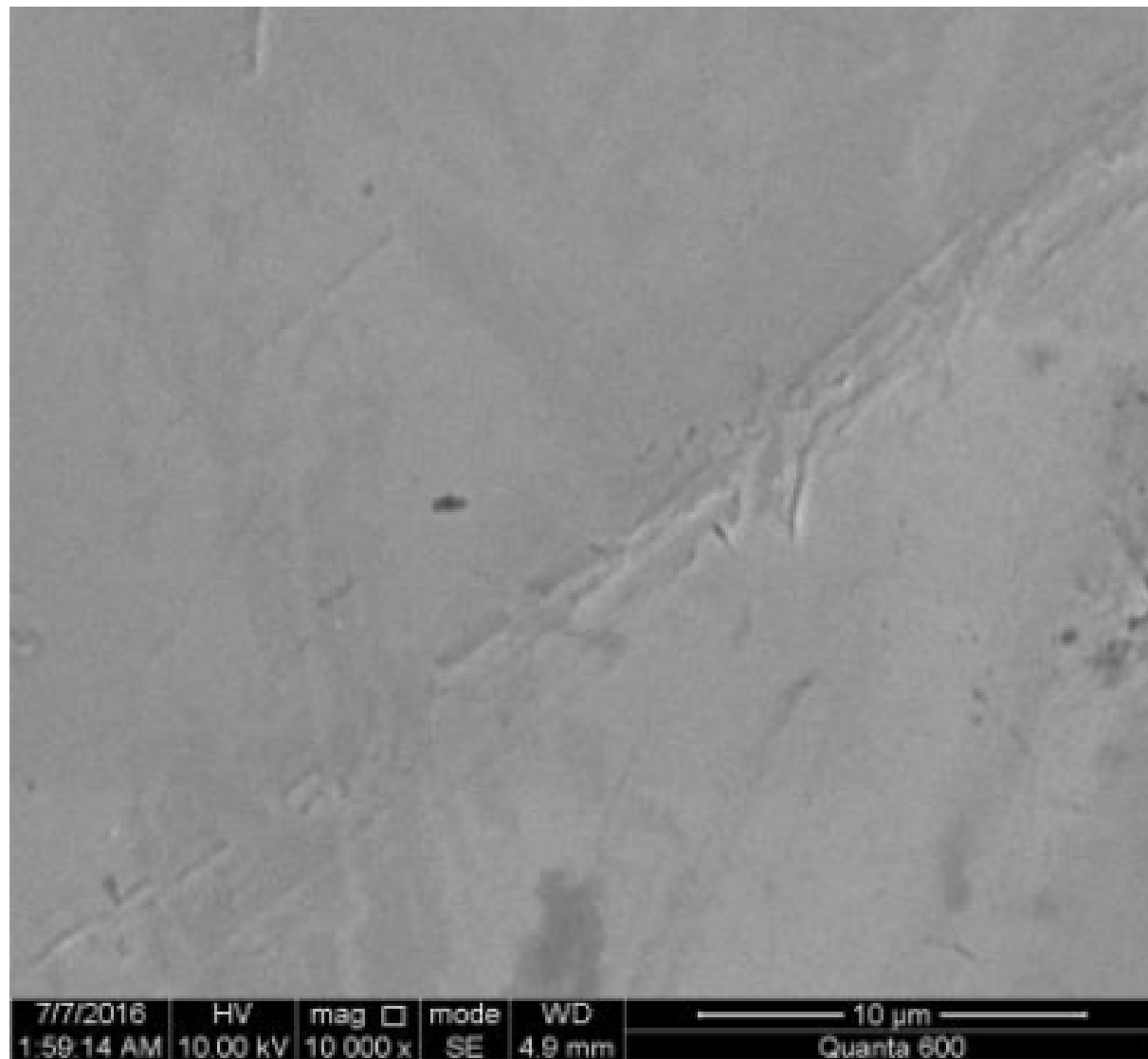
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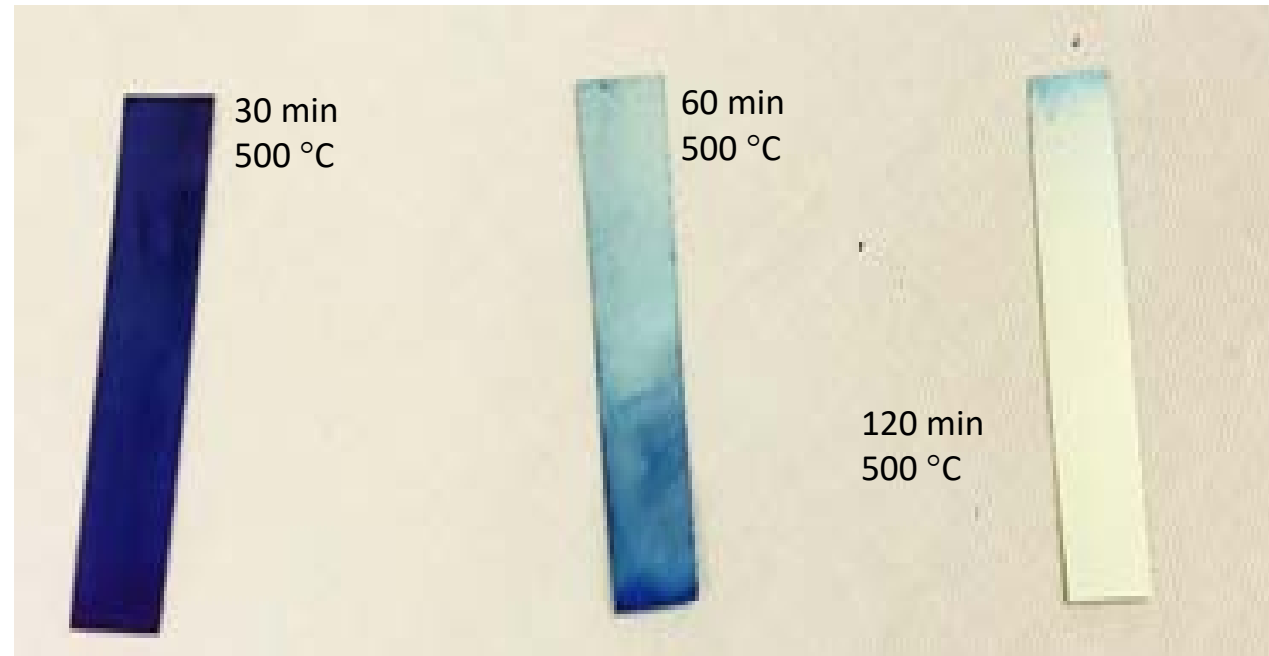
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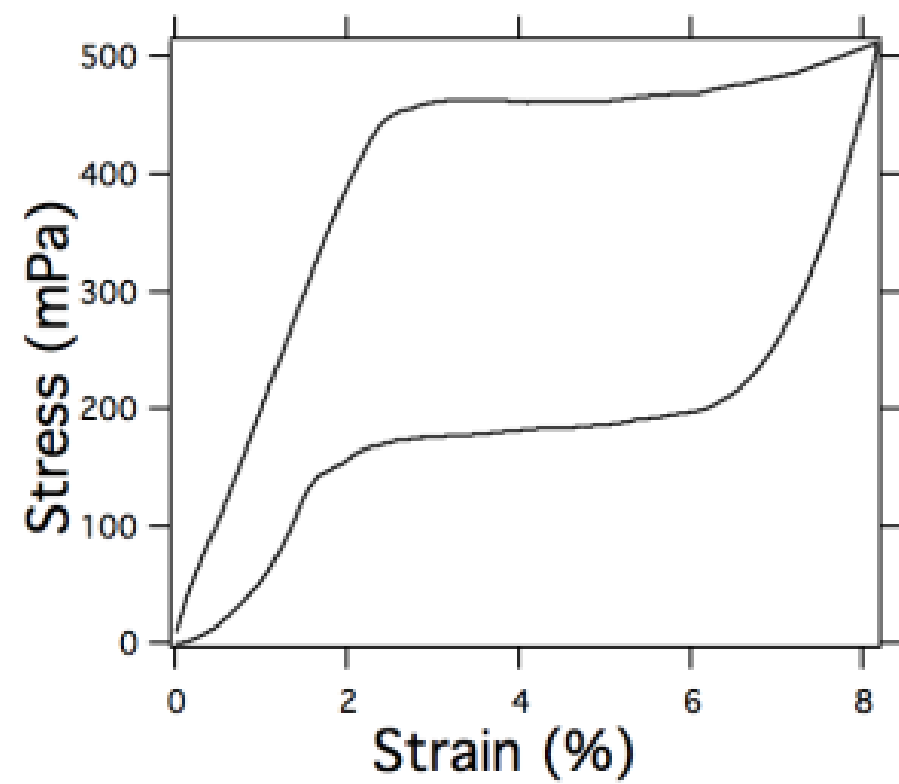
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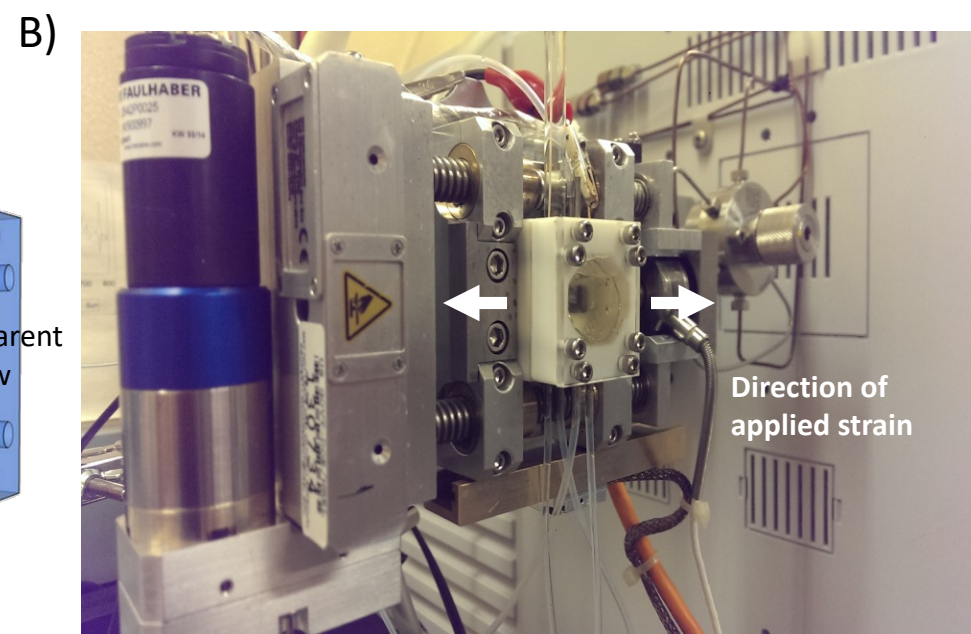
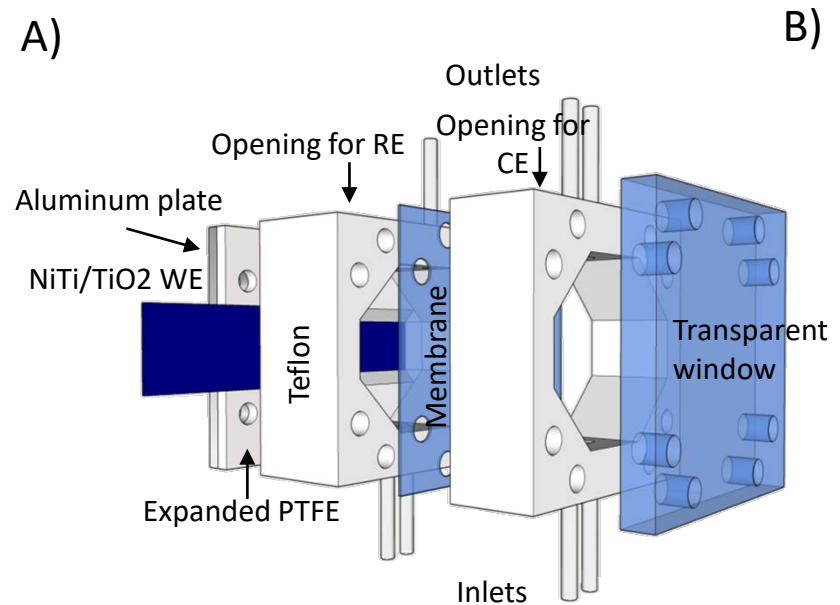
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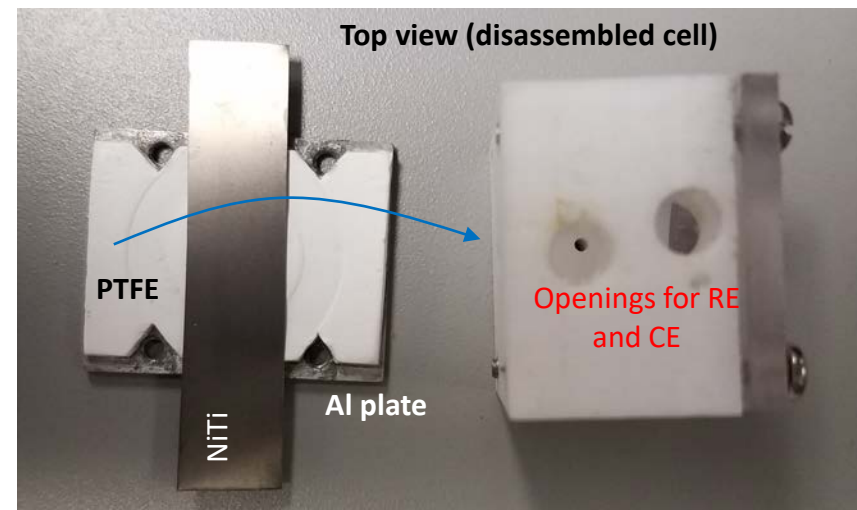
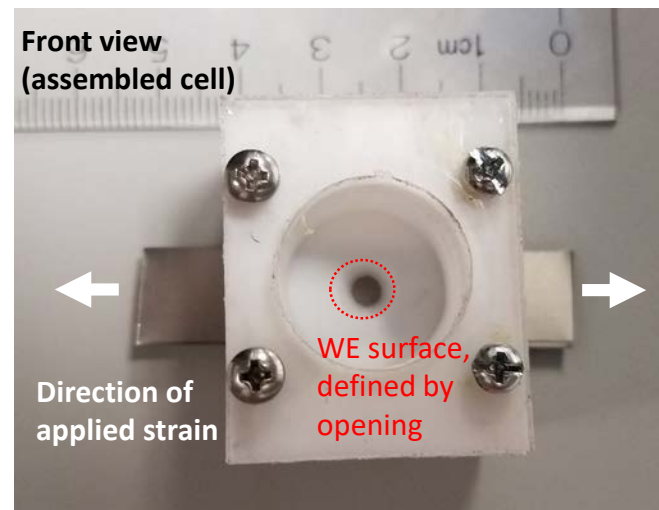
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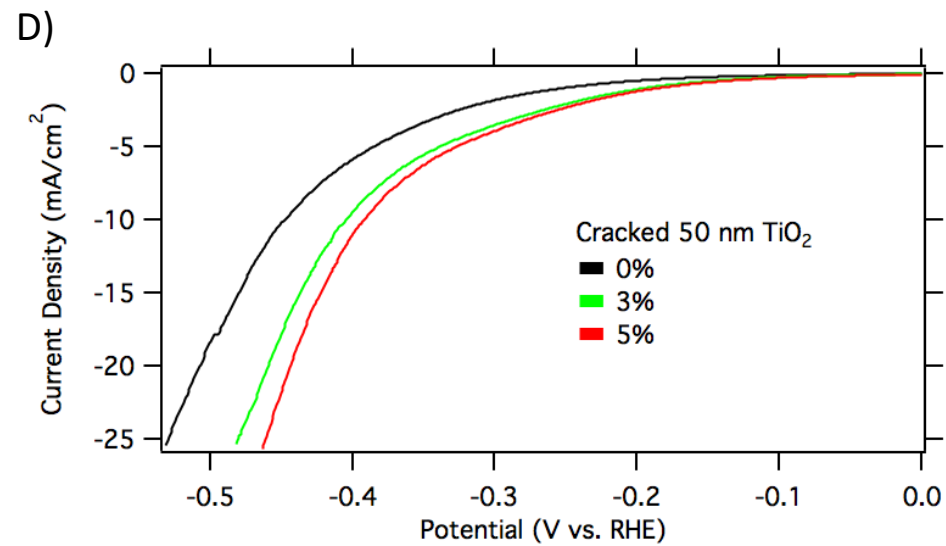
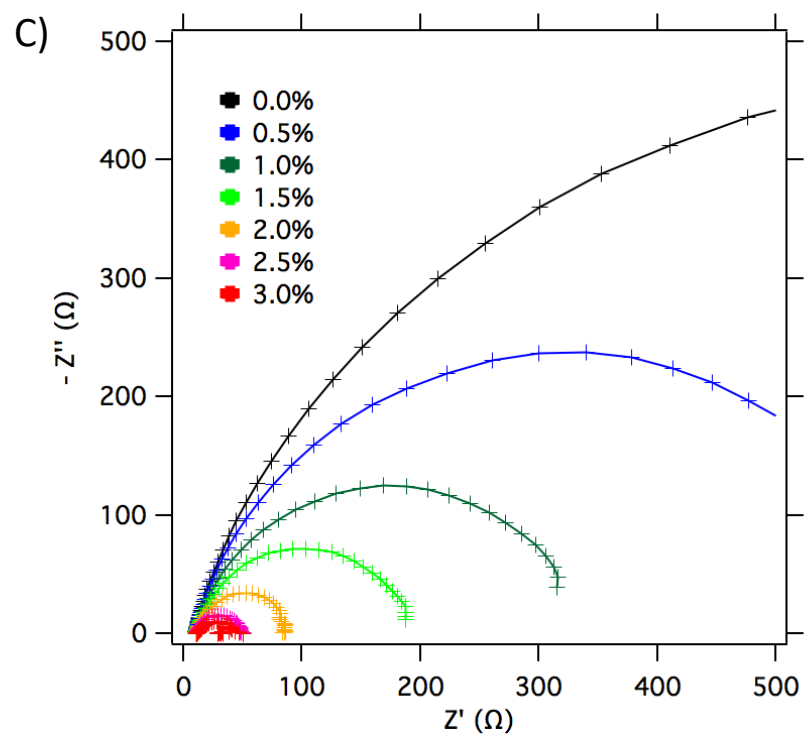
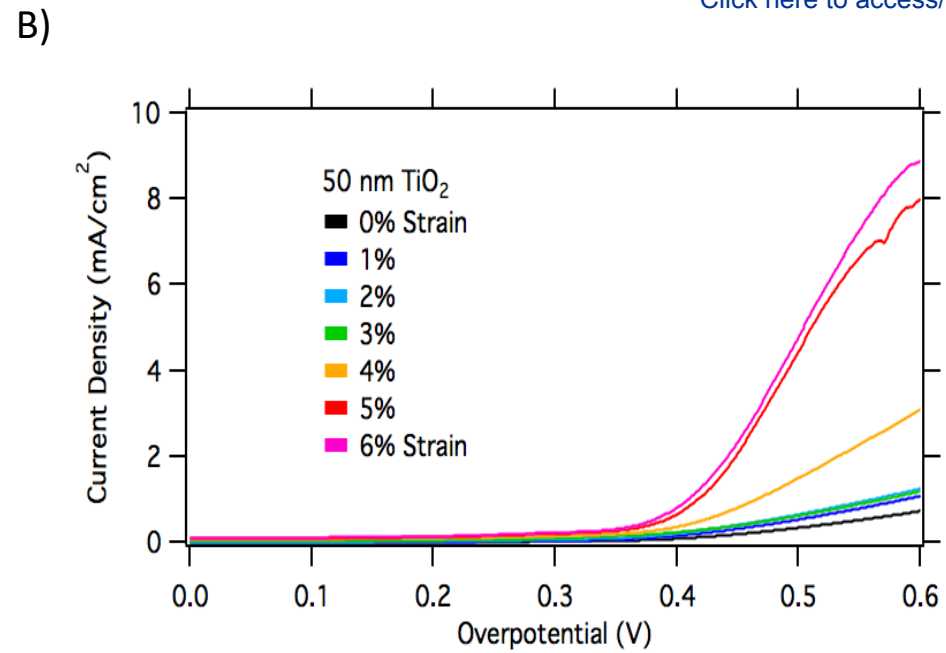
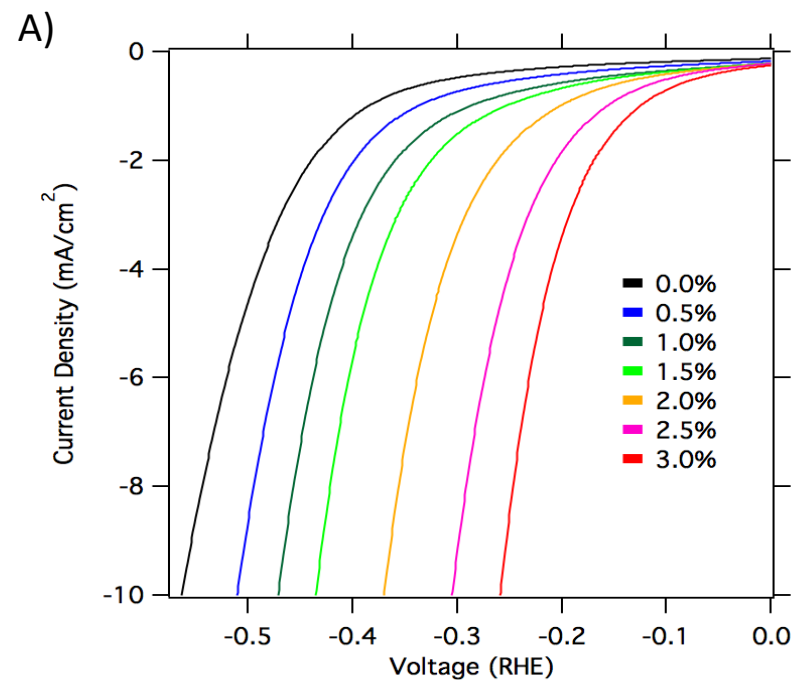


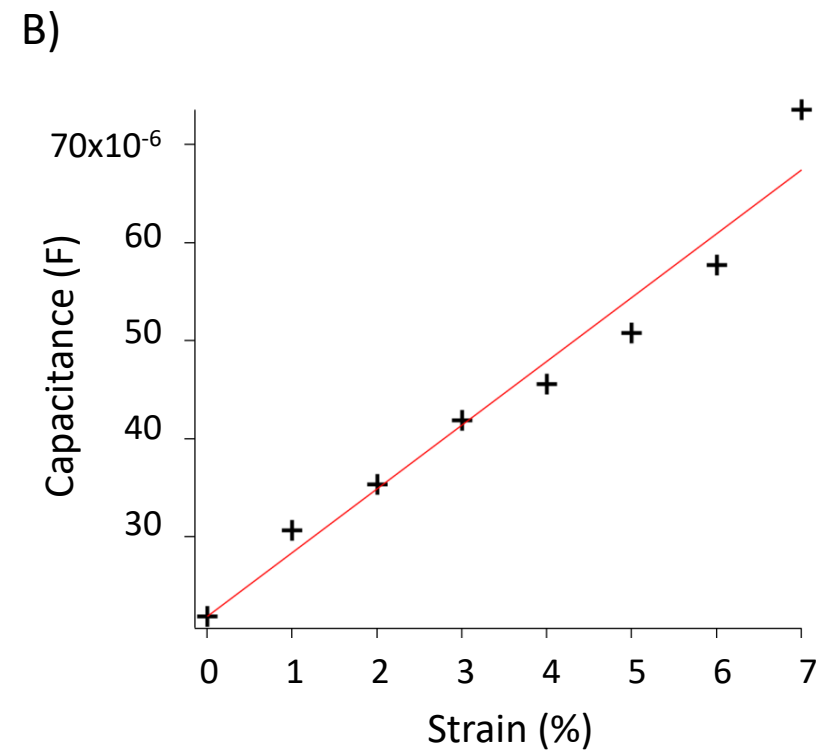
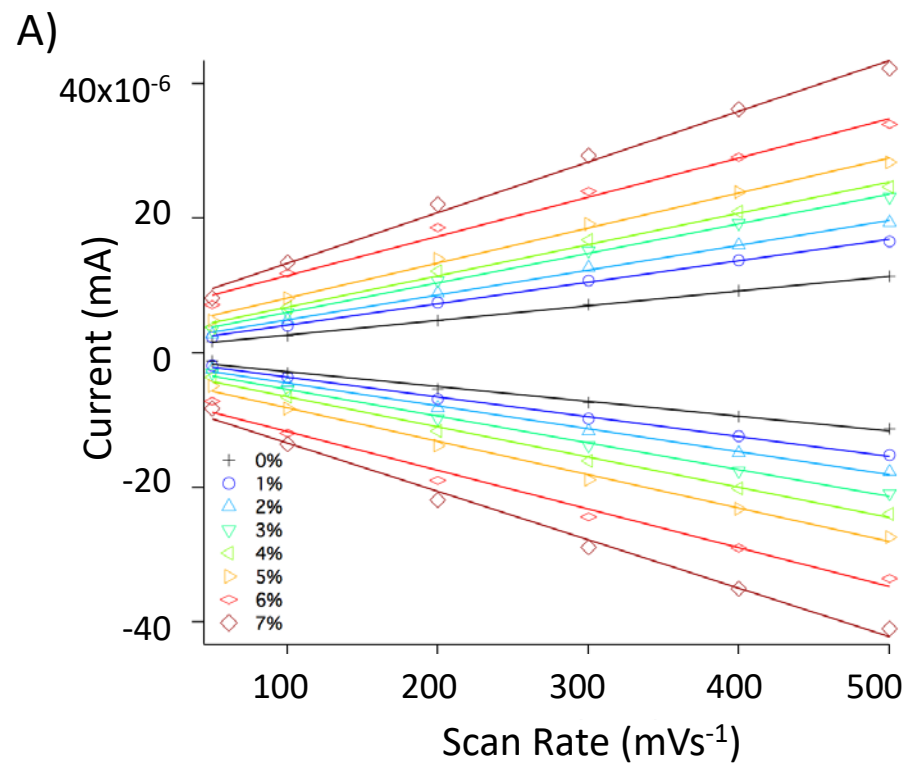












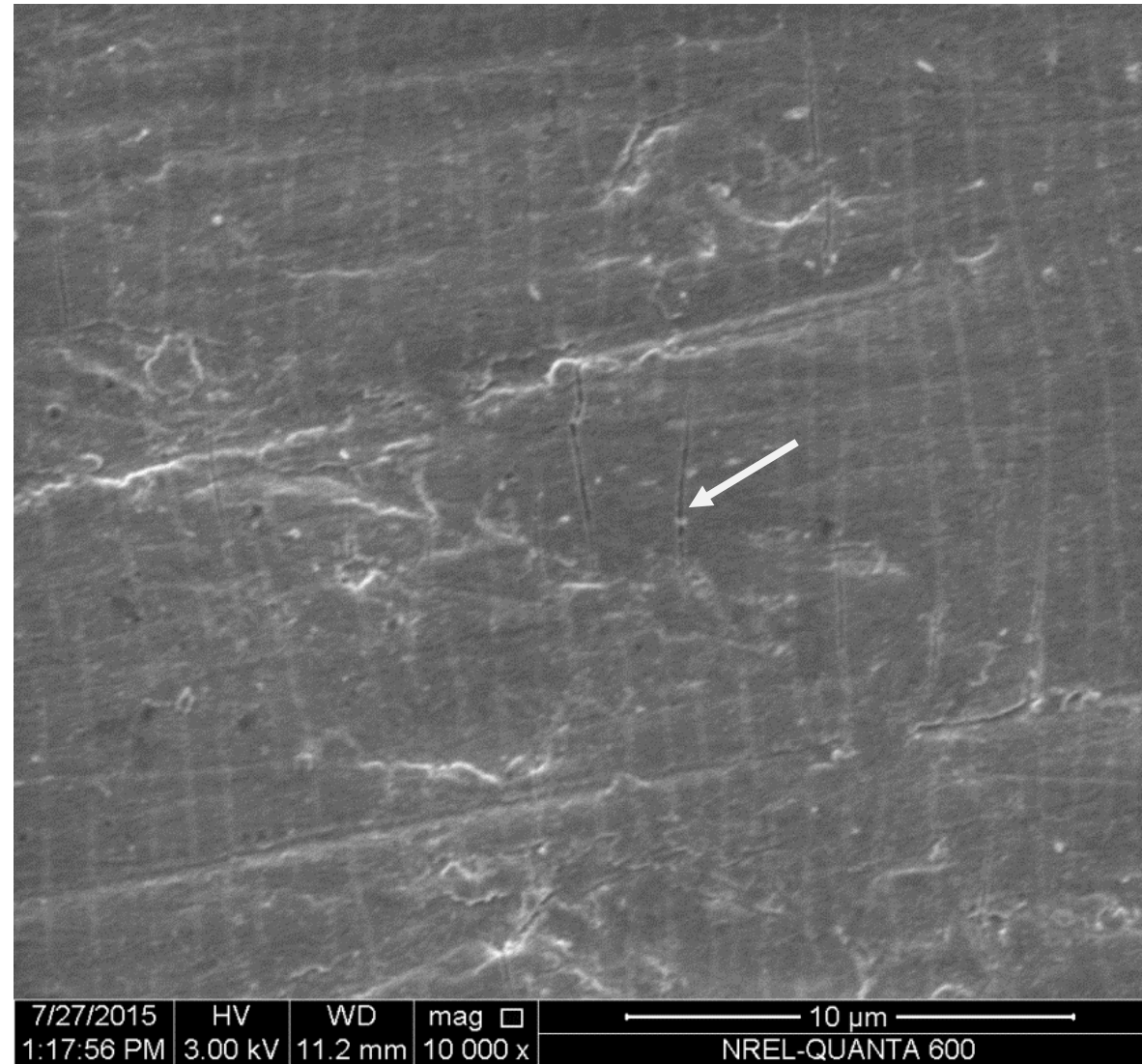
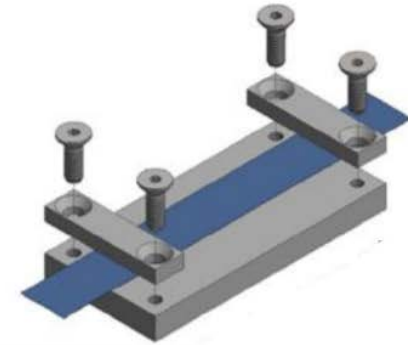
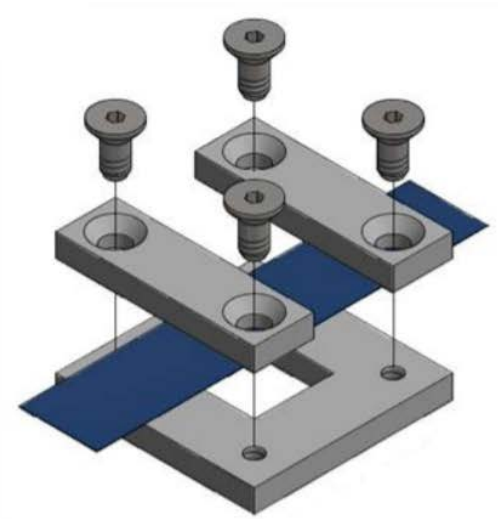
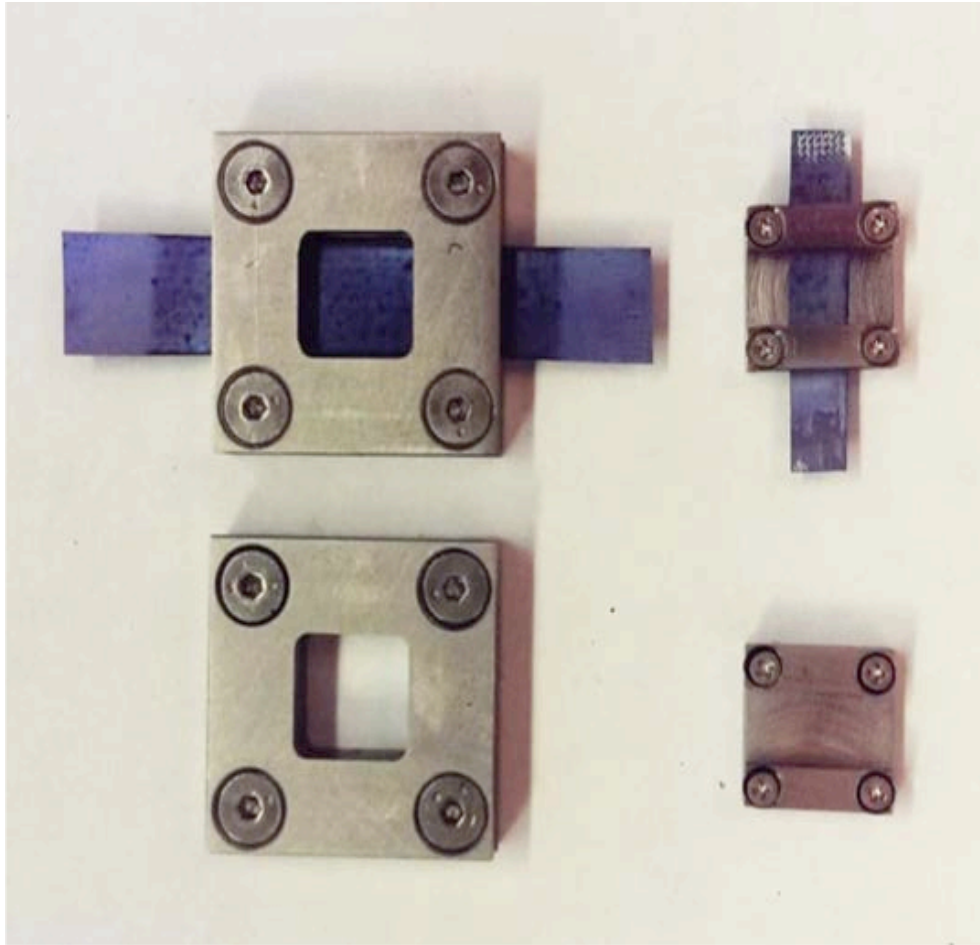
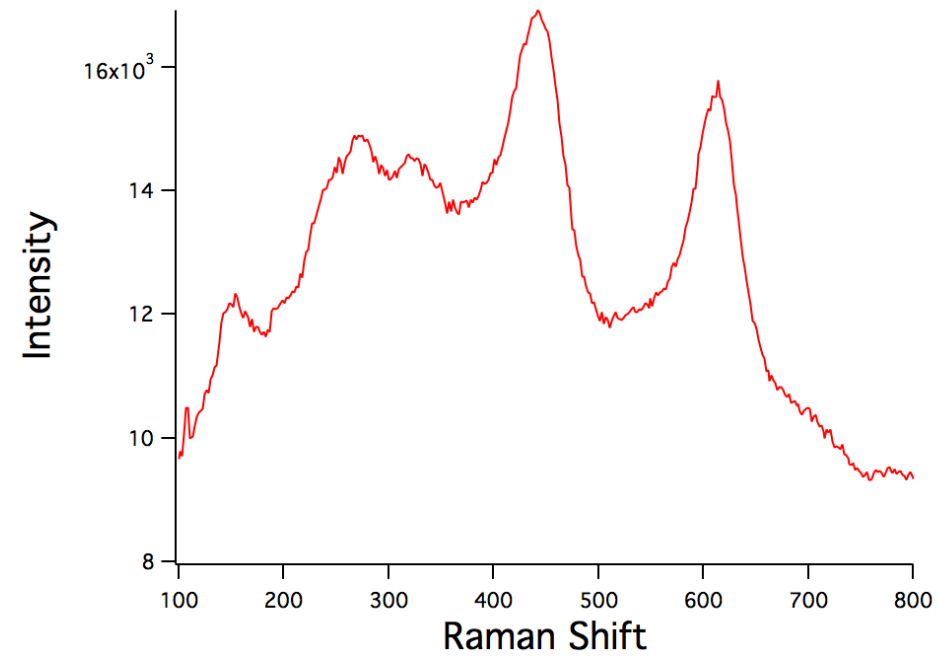


Figure 9

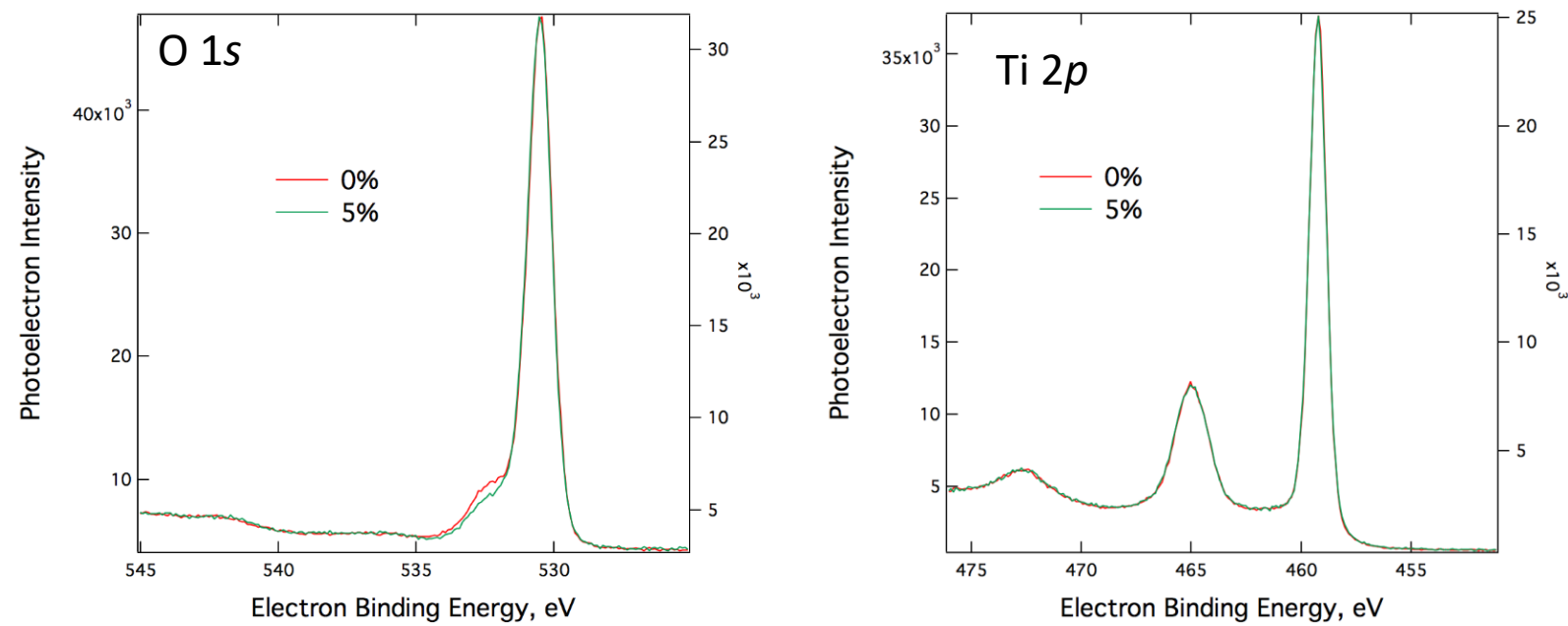
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A)



B)



Name of Material/ Equipment	Company	Catalog Number	Comments/Description
2-Propanol	Sigma		
Ag/AgCl (3M NaCl) Reference Electrode	Aldrich	109634	
Alkaline Reference Electrode	BASi	MF-2052	
Ethyl alcohol, Pure, 200 proof, anhydrous, =99.5%	Basi	EF-1369	
	Sigma		
	Aldrich	459836	
	MTI		
MT II / Full am SEMTester Series	Instrumen		
Nitinol foil, 0.05mm (0.002in) thick, superelastic, flat annealed, pickled surface	Alfa Aesar	45492	
PK-4 Electrode Polishing Kit	BASi	MF-2060	
	CHI		
Potentiostat 600D	instrumen		
	ts	600D	
Pt wire	Sigma		
	Aldrich	267228-1G	
Sodium hydroxide	Sigma		
	Aldrich	221465	
	Sigma		
Sulfuric acid	Aldrich	30743	

We appreciate the thoughtful comments by the editor and reviewers. Please see below our responses.

Editorial comments:

Changes to be made by the Author(s):

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version.

We did as requested.

2. Please sort the Materials Table alphabetically by the name of the material.

Completed as requested.

3. JoVE cannot publish manuscripts containing commercial language. This includes trademark symbols (™), registered symbols (®), and company names before an instrument or reagent. Please remove all commercial language from your manuscript and use generic terms instead. All commercial products should be sufficiently referenced in the Table of Materials and Reagents.

Completed as requested

4. Please ensure that all text in the protocol section is written in the imperative tense as if telling someone how to do the technique (e.g., “Do this,” “Ensure that,” etc.). The actions should be described in the imperative tense in complete sentences wherever possible. Avoid usage of phrases such as “could be,” “should be,” and “would be” throughout the Protocol. Any text that cannot be written in the imperative tense may be added as a “Note.” However, notes should be concise and used sparingly. Please include all safety procedures and use of hoods, etc.

We made changes in the text as requested.

5. The Protocol should be made up almost entirely of discrete steps without large paragraphs of text between sections. Please simplify the Protocol so that individual steps contain only 2-3 actions per step and a maximum of 4 sentences per step.

We made changes in the text as requested.

6. Please discuss limitations of the procedure in the Discussion.

Limitations of the procedure are discussed in the text:

Lines 374-376 “It is important to emphasize that NiTi/TiO₂ is a unique system where TiO₂ films are prepared by thermal treatment of NiTi rather than a deposition method.”

Lines 378-379 “Currently reported studies on strained NiTi/TiO₂ are incomplete^{17,21} as they include only effects of tensile and not compressive strain...”

Lines 391-394 “For each system, the characteristic elastic limit for a deposited film should be determined to achieve reproducible results and high effects of strain, which can be challenging...”

Reviewers' comments:

Reviewer #1:

Manuscript Summary:

The manuscript describes the use of NiTi shape memory alloy for applying controlled strains on oxide films for the purpose of modifying electrocatalytic behavior. Application of strain engineering principles to electrochemical system is a nascent field and this article certainly adds to the field.

The experimental set up and methodology are well represented and would be of interest to the community.

However, prior work describing the same method of strain application on metal oxide thin films needs to be referenced in this work as well as the authors need to address a few comments related to how robust their methodology is.

The manuscript therefore needs a minor revision before publication.

We have referenced our previous manuscripts (references 17, 21) related to strain studies with NiTi elastic substrates as well as studies by others (references 19, 22, 23).

(a) Can the opposite type of strain be applied to the surface coating? Is it possible to apply both compressive and tensile strains on the surface coating?

This is a good suggestion, as studies of both compression and tension is important for complete understanding of strain phenomena. Nevertheless, our system is not suitable for the compression studies. It could be potentially adapted, but because we didn't actually try it in the lab we didn't include it in the methods manuscript. Current version addresses compression studies in the text:

Lines 377-384 "Currently reported studies on strained NiTi/TiO₂ are incomplete^{17,21} as they include only effects of tensile and not compressive strain. Compressive and tensile strain imposed on a catalyst structure often have opposite effects on electroactivities and therefore analyzing both is especially interesting for mechanistic studies. Instrumentation and methods presented here have not been tested for compression studies, as it can be challenging to prevent the foil wrinkling upon compression. Compression-tension studies with NiTi substrates can be conducted using its shape-memory properties, where changes in sample geometry are induced through applied heat as demonstrated previously.¹⁹

(b) Referencing the following articles would enable a more thorough description of prior art for the same methodology: Scientific Reports volume 6, Article number: 27542 (2016), ACS Nano 2017, 11, 6, 6243-6251

We have included these references in the current version of the manuscript (ref 22, 23). Initially they were left out because we wanted to narrow the focus on electrocatalysis. Nevertheless, reviewer is right, these references are very important for this methods paper.

(c) The authors should comment on the critical crack density of the surface film. What is the maximum strain beyond which further cracking is not observed for these films? A good reference can be: Journal of Applied Physics 109, 084305 (2011); <https://doi.org/10.1063/1.3567912>

Determining the exact crack density as in the reference above is difficult for our system. We have determined empirically that NiTi/TiO₂ deformation up to 3% appears to be elastic, at 7% cracks are clearly visible on SEM images, while the cracks for the deformations between 3 and 7% were not visible on SEM images but electrochemical characterizations suggested some nonelastic deformations.

(d) the authors should discuss the ways in which this methodology can be applied to other types of metal oxide, metal and organic coatings

We wanted to limit the discussion on already published work. Nevertheless, we discussed in the text some other potential applications:

Lines 385-390 The described methods can be used to study the effects of dynamic strain on electroactivities of thin films made from different materials and deposited by various methods (e.g., physical or chemical vapor deposition, atomic layer deposition, electrodeposition). For example, dynamic strain applied on copper films deposited on NiTi could be used to tune product selectivity for CO₂ electroreduction, as previously demonstrated with Cu films under static strain imposed either by alloying⁴ or through epitaxial growth.³⁶

Lines 407-411 Photoelectrochemical experiments with a light-harvesting material deposited on an elastic substrate can also be conducted using the same system when an optically transparent material is placed as the cell window. Effects of strain on photoelectrochemical activities of organic dyes or polymers covalently attached to elastic substrates could also be investigated.

(e) What are the limitations of this technique?

Limitations of the procedure are discussed in the text:

Lines 374-376 "It is important to emphasize that NiTi/TiO₂ is a unique system where TiO₂ films are prepared by thermal treatment of NiTi rather than a deposition method."

Lines 378-379 "Currently reported studies on strained NiTi/TiO₂ are incomplete^{17,21} as they include only effects of tensile and not compressive strain..."

Lines 391-394 "For each system, the characteristic elastic limit for a deposited film should be determined to achieve reproducible results and high effects of strain, which can be challenging..."

Reviewer #2:

The manuscript gives a clear background introduction and a protocol on fabricating TiO₂ thin film with a commercial available NiTi foil and the electro-chemical characterisations. The results and discussion are impressive and would be helpful in pushing this research field forward. I recommend the publication of this manuscript.

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Author: Eric E. Benson, Elisa M. Miller, Sanjini U. Nanayakkara, et al.

Publication: Chemistry of Materials

Publisher: American Chemical Society

Date: Mar 1, 2017

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