## **Supporting Information**

## Ultrafine NiO Nanosheets Stabilized by TiO<sub>2</sub> from Monolayer

## NiTi-LDH Precursors: An Active Water Oxidation Electrocatalyst

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c. School of Chemical Sciences, The University of Auckland, Auckland 1142, New Zealand d. Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Mansfield Road, Oxford OX1 3TA, United Kingdom *Chemicals:* Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, TiCl<sub>4</sub>, NiO (Product #39923 with a particle size of several micrometers for extended X-ray absorption fine structure (EXAFS) experiments, Product #63730 with a particle size of ~30 nm for water oxidation experiments), anatase TiO<sub>2</sub>, urea, sodium dodecyl sulfate (SDS) and isooctane were purchased from Sigma-Aldrich Co. and used without further purification.



**Figure S1.** (A) HRTEM image, (B) XRD pattern, (C) AFM image and (D) the corresponding height profile of monolayered NiTi-LDH nanosheets.



**Figure S2**. (A) TGA analysis for Mono-NiTi-MMO; (B) XRD pattern of the products from calcination of Mono-NiTi-MMO at 800 °C.

Figure S2B shows that calcination of the NiTi-LDH nanosheets at 800 °C resulted in the formation of NiTiO<sub>3</sub> as the main reaction product. The co-existance of NiO is due to the excess molar ratio of Ni/Ti in LDH precursor. He and co-workers previously reported that calciation of NiTi-LDH at temparature below 600 °C results in the formation of NiO and TiO<sub>2</sub>, whereas calcination at temparature between 600-700 °C leads to the appearance of a Ni<sub>2</sub>TiO<sub>4</sub> spinel phase with a concomitant decrease in the NiO and TiO<sub>2</sub> content. At calcination temperature higher than 800 °C, the NiTiO<sub>3</sub> phase was produced.<sup>1</sup> Results here are thus in good accord with this prior study.<sup>1</sup>



**Figure S3**. (A) XRD patterns and (B) N<sub>2</sub> adsorption-desorption isotherms and the corresponding pore diameter distributions (inset) of (a) Mono-NiTi-MMO, (b) NS-NiO, (c) Bulk-NiTi-MMO and (d) NiO.

The XRD pattern for Mono-NiTi-MMO (Figure S3Aa) shows characteristic reflections for the (101) plane of anatase TiO<sub>2</sub>, as well as the (111), (200) and (220) reflections of NiO. It should be noted that the anatase (200) is weaker than expected, which may be ascribed to the lower TiO<sub>2</sub> crystallinity, preferential orientation in the anatase crystallites, or possible distortions arising from the nearby (200) reflections peak of NiO (the corresponding peak has been marked with a red line).

The Mono-NiTi-MMO, NS-NiO, Bulk-NiTi-MMO and commercial NiO were further characterized by  $N_2$  adsorption/desorption measurements to determine their specific surface area and pore size distribution, both of which affect their electrocatalytic performance. Figure S3B shows that all the samples showed type IV isotherms with a H3-type hysteresis loop, indicating the existence of interparticle mesoporosity and macroprous. The NS-NiO, Bulk-NiTi-MMO and commercial NiO samples possessed a broad pore diameter distribution of 2-20, 9-30 and 20-50 nm, respectively. In contrast, Mono-NiTi-MMO gave a bimodal pore diameter distribution comprising a mesopore (~4 nm) and a broad mesopore (20-50 nm). The BET specific surface areas of Mono-NiTi-MMO, NS-NiO, Bulk-NiTi-MMO and NiO were 165.8, 127.9, 98.1 and 147.1 m<sup>2</sup> g<sup>-1</sup>, respectively.

Table S1. A su	ummary of the X	K-ray diffraction	data for Mono-	NiTi-MMO.

Sample		Position $2\theta$ (°)	d (Å)	FWHM (°)	Calculated Size (nm)	Measured Size (nm)
Mono-NiTi-MMO	NiO	43.15	2.095	1.07	7.78	4.0
	TiO <sub>2</sub>	25.33	3.513	0.63	12.7	11.0

FWHM = full width at half maximum, Scherrer equation  $(D = K\lambda(\beta \cos\theta)^{-1})$ , K = 0.89.



**Figure S4**. (A) HRTEM image, (B) FFT pattern of the corresponding  $TiO_2$  area in Mono-NiTi-MMO showing the {001}surface and inset shows the geometrical model of anatase  $TiO_2$  nanocrystal. (TEM image and FFT pattern in Figure S4 of a single sheet of anatase  $TiO_2$  show the diffraction spots of the [001] zone and a {200} plane with a spacing of 0.19 nm.)<sup>2-3</sup>



Figure S5. A schematic illustration of atomic structure of  $\{110\}$  facet-exposed NiO and  $\{001\}$  facet-exposed TiO<sub>2</sub> from (A) top and (B) side view.



**Figure S6**. (A, B) TEM, (C) HRTEM images and (D) FFT pattern of NS-NiO in the corresponding square area.



Figure S7. EDX spectrum of Mono-NiTi-MMO.



**Figure S8**. (A) TEM image; (B, C, D) HRTEM images for Bulk-NiTi-MMO. The inset in C shows the FFT pattern of NiO in Bulk-NiTi-MMO. (E) AFM image and (F) the corresponding height profile of Bulk-NiTi-MMO.



Figure S9. (A) TEM and (B) HRTEM images for commercial NiO.

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Sample	Shell	$N^{[a]}$	$R [Å]^{[b]}$	$\sigma^2 [\text{\AA}^2]^{[c]}$	$\Delta E_0 \left[ \mathrm{eV} \right]^{\mathrm{[d]}}$	
NiO <sup>[f]</sup>	Ni-O	6.00 <sup>[e]</sup>	2.08	0.005	2.71	
	Ni-Ni	12.00	2.95	0.006	0.63	
Bulk-NiTi-MMO	Ni-O	6.00	2.08	0.005	0.45	
	Ni-Ni	12.00	2.96	0.009	0.38	
Mono-NiTi-MMO	Ni-O	5.70	2.05	0.006	0.47	
	Ni-Ni	7.70	2.98	0.012	1.50	

Table S2. Local structure parameters around Ni estimated by EXAFS analysis

[a] N = coordination number; [b] R = distance between absorber and backscatteratoms; [c]  $\sigma^2 = \text{Debye-Waller factor}$ ; [d]  $\Delta E_0 = \text{energy shift}$ ; R-space fit,  $\Delta r = -0.06 - 0.15$  Å; [e] Fixed to 6 for the first NiO<sub>6</sub> shell. [f] NiO with a particle size of several micrometer was treated as a reference sample.



**Figure S10.** (A) Ti K-edge XANES spectra, and (B) magnitude of  $k^2$ -weighted Fourier transforms of the Ti K-edge XANES spectra for Bulk-NiTi-MMO and Mono-NiTi-MMO.



**Figure S11**. (A) ESR spectra and (B) Ti 2p XPS spectra of (a) Bulk-NiTi-MMO and (b) Mono-NiTi-MMO at 110 K under Ar atmosphere; (C) Ni 2p XPS spectra of (a) NiO, (b) Bulk-NiTi-MMO, (c) NS-NiO and (d) Mono-NiTi-MMO.



**Figure S12**. (A) TOF with respect to Ni atoms at different overpotentials; (B) Electrocatalytic efficiencies of Mono-NiTi-MMO in alkaline media towards OER.

	Mono-NiTi-MMO	Mono-NiTi-LDH	NS-NiO	NiO	Bulk-NiTi-MMO
Loading amount (mg)	0.024	0.024	0.024	0.024	0.024
Mass (g mol <sup>-1</sup> )	200	227	75	75	200
Active site of Ni ions (µmol)	0.192	0.169	0.320	0.320	0.192
TOF (s <sup>-1</sup> ) Overpotential (V)					
0.3	0.006	0.003	0.001	0.0003	6E-05
0.35	0.016	0.005	0.001	0.001	0.0005
0.4	0.030	0.006	0.002	0.001	0.001
0.45	0.048	0.008	0.003	0.002	0.002
0.5	0.068	0.009	0.005	0.002	0.003

**Table S3.** The number of active sites and the TOF values for various Ni-containing

 electrocatalysts synthesized in this work.

The TOF value is calculated from equation:<sup>4</sup>

 $TOF = J^*A/(4^*F^*m)$ 

Where J is the current density (A cm<sup>-2</sup>), and A refers to the area of electrode, F is the Faraday constant (96485.4 C mol<sup>-1</sup>), and m means the moles of the active catalysts. Since the active site in the NiO-TiO<sub>2</sub> nanosheet is Ni ions, the TOF was calucated based on the amount of Ni ions.



**Figure S13**. (A) TEM, (B) HRTEM images, (C) XRD patterns and (D) ESR spectrum of Mono-TiO<sub>2</sub> obtained from HNO<sub>3</sub> treatment of Mono-NiTi-MMO.

As shown in Figure S13,  $TiO_2$  nanosheets obtained from acid treatment of Mono-NiTi-MMO retained the anatase form as evidenced by HRTEM and XRD pattern. From ESR spectrum, the  $Ti^{3+}$  defect sites around 1.996 can also be clearly observed in the obtained  $TiO_2$  nanosheets, which is accordance with the data presented in Figure S11A, B.

During the calcination process in the presence of Ti cations, the stabilized ultrafine highly reactive  $\{110\}$ -faceted NiO with defects as well as the existence of abundant heterostructure interfaces between NiO and TiO<sub>2</sub> phases and the Ti<sup>3+</sup> sites facilitate electron transfer, resulting in the promoted OER activity.



**Figure S14**. (A) TEM, (B) HRTEM images of anatase TiO<sub>2</sub>; (C) XRD patterns, (D) ESR spectra and electrochemical impedance spectra of TiO<sub>2</sub> and Mono-TiO<sub>2</sub> on a glassy carbon working electrode (E) and  $(1 \text{ cm} \times 1 \text{ cm})$  ITO substrates (F).

Figure S14 shows the reference anatase  $TiO_2$  with particle size of 40 nm. Compared to the XRD pattern of Mono-TiO<sub>2</sub>, the TiO<sub>2</sub> sample shows much more intense and sharper peaks, indicating better crystallinity. No obvious defects were seen by ESR (Figure S14D). EIS shows that Mono-TiO<sub>2</sub> gave a smaller resistance compared with defect-free TiO<sub>2</sub>. The decreased resistance of Mono-TiO<sub>2</sub> is due to its intrinsic good conductivity and the efficient charge transfer originating from the effect of Ti<sup>3+</sup> defects.<sup>5</sup> It should be noted that the severely decreased resistance of TiO<sub>2</sub> with and without defects on ITO substrates can be well understood by the increased area of

electrode area and the good conductivity compared to glassy carbon electrode. The above results indicate the introduction of  $Ti^{3+}$  can significantly improve the electrical conductivity and charge transfer efficiency at  $TiO_2$  catalysts/electrolyte interfaces.

Catalyst	Size	Electrolyte Solution	Current density (j)	Overpotential at the corresponding j	Onset potential	Reference
NiO-TiO <sub>2</sub> nanosheet	4 nm size * 1.1 nm thick	1 M KOH	10 mA/cm <sup>2</sup>	320 mV (220 mV at 0.5 mA/ cm <sup>2</sup> )	190 mV	This work
Ni/NiO(OH) /nitrogen doped carbon	15 nm for Ni/NiO(OH) nanoparticle	0.1 M KOH	10 mA/cm <sup>2</sup>	390 mV	330 mV	
Ni@C		0.1 M KOH	$10 \text{ mA/cm}^2$	420 mV	360 mV	<i>Adv. Energy Mater.</i> <b>2015</b> , <i>5</i> , 1401660
Ni@BP2000		0.1 M KOH	$10 \text{ mA/cm}^2$	460 mV	380 mV	
20% Pt/C		0.1 M KOH	$10 \text{ mA/cm}^2$	580 mV		
IrO <sub>2</sub>		0.1 M KOH	$10 \text{ mA/cm}^2$	350 mV	260 mV	
NiFe-LDH nanosheet	1 nm thickness	1 M KOH	$10 \text{ mA/cm}^2$	300 mV	/	
NiCo-LDH nanosheeet thickness	1 nm	1 M KOH	$10 \text{ mA/cm}^2$	330 mV	/	Nature Commun. <b>2014</b> , 5, 4477
CoCo-LDH nanosheets thickness	1 nm	1 M KOH	$10 \text{ mA/cm}^2$	350 mV	/	
NiFe-LDH Bulk	20 nm thickness	1 M KOH	$10 \text{ mA/cm}^2$	350 mV	/	

**Table S4**. Comparison of the electrocatalytic performance of a selection of Ni-containing electrocatalysts

NiO QDs	3.3 nm	0.5 M KOH	10 mA/cm <sup>2</sup>	320 mV	~290 mV	<i>Adv. Funct. Mater.</i> <b>2014</b> , 24, 3123
NiO QDs	3.8 nm	0.5 M KOH	$10 \text{ mA/cm}^2$	325 mV	310 mV	ACS Nano <b>2015</b> , 9, 5180
NiO film	8 nm thickness	0.1 M KOH	10 mA/cm <sup>2</sup>	540 mV	300 mV	Adv. Energy Mater. 2015, 5, 1500412
NiO/Fe		0.1 M KOH	$10 \text{ mA/cm}^2$	480 mV	1	
NiO/FeNC nanosheet		0.1 M KOH	$10 \text{ mA/cm}^2$	390 mV	240 mV	Angew. Chem. Int. Ed. <b>2015</b> , 54, 10530
IrOx		0.1 M NaOH	10 mA/cm <sup>2</sup>	320 mV	1	J. Am. Chem. Soc. <b>2013</b> , 135, 16977; J. Phys. Chem. Lett. <b>2011</b> , 2, 402
NiCeO <sub>x</sub>		1 M NaOH	$10 \text{ mA/cm}^2$	420 mV	/	J. Am. Chem. Soc. <b>2013</b> , 135, 16977
Amorphous NiO <sub>x</sub>		0.1 M KOH		250 mV at j=0.5 mA/cm <sup>2</sup>	190 mV	_
Amorphous CoO <sub>x</sub>		0.1 M KOH		$260 \text{ mV at } j=0.5$ $\text{mA/cm}^2$	210 mV	Science <b>2013</b> , 340, 60.
Amorphous FeO <sub>x</sub>		0.1 M KOH		$400 \text{ mV at } j=0.5$ $\text{mA/cm}^2$	320 mV	_



**Figure S15**. TEM and HRTEM images for Mono-NiTi-MMO after being used for 250 min (A, B) and after stability test (C, D) in OER. (The images clearly show that the faceted NiO still retained its morphology and exposed {110} facets after OER stability test.)



**Figure S16**. Supercell model of (A) {110} facets exposed NiO, (B) calculated final geometry of water adsorption on the NiO {110} surface; (C)  $V_{Ni}$ -doped NiO (the vacancy is indicated by the yellow indicate), (D) Calculated final geometry of water adsorption on the  $V_{Ni}$ -doped NiO {110} surface with 5×5×4 rhombohedral lattice; (E)  $V_{Ni}$ -doped NiO/TiO<sub>2</sub> heterojunction structure; (F) Calculated final geometry of water adsorption on the NiO/TiO<sub>2</sub> heterostructure.  $V_{Ni}$ -doped NiO/TiO<sub>2</sub> heterojunction structure with {110} surface of NiO and exposed {001} facet of TiO<sub>2</sub>. (G)  $V_{Ni}$ -doped NiO/V<sub>O</sub>-doped TiO<sub>2</sub> heterojunction structure; (H) Calculated final geometry of water adsorption on the  $V_{Ni}$ -doped TiO<sub>2</sub> heterostructure. (Blue: Ni; Grey, Ti; Red: O; White: H).



Figure S17. Charge density distribution of NiO- $V_{Ni}$ /TiO<sub>2</sub>- $V_O$  heterostructure.

The red area around the inferfaces of NiO- $V_{Ni}/TiO_2$ - $V_O$  heterostructure allowed for much faster electron transport, which was further confirmed by the obviously smaller charge transfer resistance of Mono-NiTi-MMO shown in Figure 3C, and thus improved OER activity.



Figure S18. Charge density distribution for the valence band maximum of  $TiO_2$ - $V_0$ .

## References

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