Supplementary information

Nickel telluride as a bifunctional electrocatalyst for efficient water splitting in

alkaline medium

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Electrodeposition of RuO₂ on Au-glass ^{S1}:

Electrodeposition of RuO_2 on Au-glass substrate was carried out from a mixture of $RuCl_3$ (0.452 g) and KCl (2.952 g) in 40 ml of 0.01M HCl by using cyclic voltammetry from 0.015 to 0.915 V (vs. Ag|AgCl) for 100 cycles at a scan rate of 50 mV s⁻¹. Finally heated at 200 °C for 3 h in presence of Air.

Electrodeposition of Ni₃S₂ on Au-glass S2a

The Ni₃S₂ films were deposited on to the Au-glass substrate by deposition bath containing 50 mM NiCl₂ \cdot 6H₂O and 1 M thiourea. Electrodeposition of Ni₃S₂ on Au-glass substrate was conducted within the potential range between –1.2 V and 0.2 V vs. Ag |AgCl at a scan rate of 5 mV s⁻¹ for 6 sweep cycles.

Electrodeposition of Ni₃Se₂ ^{S2b}

Ni₃Se₂ was electrodeposited on the substrate by a controlled-potential deposition at -0.80 V (vs. Ag/AgCl) for 300 s from an aqueous solution containing 10 mM Ni(CH₃CO₂)₂·4H₂O, 10 mM SeO₂ and 25 mM LiCl at 25 °C. The pH of the electrolytic bath was adjusted with dilute HCl to be 2.5. After electrodeposition, the substrates were washed with deionized water in order to remove impurities and adsorbents from the surface.

Calibration of Ag|AgCl:

The Ag|AgCl|KCl(sat.) reference electrode was calibrated by measuring open circuit potential (OCP) at Pt wire in pure H2 saturated 1.0 M H2SO4 solution. A value of -0.197 V was obtained as the OCP which was used as the standard potential of Ag|AgCl in this article. The measured potentials vs the Ag/AgCl at any given pH is were converted to the reversible hydrogen electrode (RHE) scale via Nernst equation:

$$E_{\rm RHE} = E_{\rm Ag|AgCl} + 0.059 \rm pH + E_{\rm Ag|AgCl}^{\rm o}$$

Where ERHE is the converted potential vs. RHE, $E_{Ag|AgCl}$ is the experimentally measured potential against Ag|AgCl reference electrode, and $E^{o}_{Ag|AgCl}$ is the standard potential of Ag|AgCl at 25 °C (0.197 V).

KOH Electrolyte Purification^{S3}

1 M KOH electrolyte was purified following a reported procedure.⁵³ In a H₂SO₄-cleaned 50 mL polypropylene centrifuge tube, ~2 g of 99.999% Ni(NO₃)₂·6H₂O was dissolved in ~4 mL of 18.2 M Ω ·cm H₂O. 20 mL of 1 M KOH were added to precipitate high-purity Ni(OH)₂. The mixture was shaken and centrifuged, and the supernatant was decanted. The Ni(OH)₂ then underwent three washing cycles by adding ~20 mL of 18.2 M Ω ·cm water and ~2 mL of 1 M KOH to the tube, redispersing the solid, centrifuging, and decanting the supernatant. Finally, the tube was filled with 50 mL of 1 M KOH for purification. The solid was redispersed and mechanically agitated for at least 10 min, followed by at least 3 h of resting. The mixture was centrifuged, and the purified KOH supernatant was decanted into a H₂SO₄-cleaned polypropylene bottle for storage.



 $\textbf{Fig.S1} \ \ \text{Raman spectrum of the Ni_3Te}_2 \ electrodeposited on Au substrate}$



Fig. S2 Cyclic voltammograms of Ni_3Te_2 electrodeposited on (a) Au glass (b) Ni foam in N_2

saturated 1M KOH solution.



Fig. S3 Cyclic voltammograms for OER of 1 st cycle and 100 th cycles for (a) unpurified 1 M KOH (b) purified 1 M KOH prepared as mentioned above.



Fig. S3c LSV measured in N2 saturated 1M KOH solution at hydrothermally synthesized

Ni₃Te₂ on Au electrode to check the Ni preoxidation peak.



Fig. S4 LSVs measured at Ni_3Te_2 @ Au for different electrodeposition times in N_2 saturated 1 M KOH solution at a scan rate of 0.01V s⁻¹



Fig.S5 OER activity of Ni₃Te₂ catalysts electrodeposited for 300 s on various substrates.

Comparison of Hydroxyl Attachment on Ni Sites (Catalyst Activation): Density Functional Theory (DFT) Calculations

The adsorption energy of the hydroxyl ion on the catalyst surface of NiO and Ni₃Te₂ was calculated by employing DFT calculations using projected augmented wave (PAW) method ⁵⁴, that are implemented in the Vienna Ab initio Simulation Package (VASP). ^{55,56} The exchange-correlation interaction was treated in the framework of generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional ⁵⁷ and ultrasoft potentials. ⁵⁸ Since the rotationally invariant version of the GGA+U method can give a good description of the cohesive energy, electronic structure, and mechanical and magnetic properties of bulk and surfaces of materials, the GGA+U method was used to study the adsorption energy of OH⁻ ion on various Ni sites of NiO and Ni₃Te₂. A plane wave cut-off of 400 eV was set up to ensure convergence in energy. The Brillouin zone was sampled using Mokhorst-Pack generated sets of K-points. ⁵⁹

The (001) surface of NiO, and (001) and (010) surfaces of Ni₃Te₂ were selected to estimate the favorable adsorption Ni sites of OH^- ion in the DFT calculations. K-point meshes of 5×5×1, 5×11×1 and 5×5×1 were found to be sufficient to a self-consistent field (SCF) convergence criterion of 1×10⁻⁴ eV for NiO (001) surface, Ni₃Te₂ (001) surface and Ni₃Te₂ (010) surface, respectively. Free surfaces of NiO and Ni₃Te₂ were simulated using a slab model with 1×1×2 super cells (or 1×2×1, depending on the orientation of free surface), as shown in Fig. S6a and Fig. S7a, respectively. A relatively large vacuum gap of ~20 Å was set between free surfaces to prevent the interactions of the system and its periodically repeated images. Thus, dipole corrections were applied perpendicular to the surface plane. As sown in Fig. S6a and Fig. S7a,

the bottom lattice of the model was fixed at the ground-state bulk distances, while the top lattice was set to be free to move in all directions.

The OH⁻ adsorption energy (E_{ad}) was calculated from equation 1 as shown below:

$$E_{ad} = E_{NiX-OH} - [E_{clean} + E_{OH}]$$
⁽¹⁾

where, E_{clean} is the internal energy of the slab models for Ni₃Te₂ and NiO (see Figs. S6 & S7), E_{OH}^{-} is the internal energy of the isolated OH⁻ ion, and E_{NiX-OH}^{-} is the total formation energy of NiX surface with bound OH⁻ (X = O or Te) (see Figs.S8, S9, and S10).

By adapting the quasi-Newton scheme as the convergence criterion, the relaxation was first carried out to reconstruct the free surfaces of the slab model, as well to obtain the clean internal energy: E_{NiX} . Thereafter, an OH⁻ ion was placed on the top of the active Ni site (on the relaxed free surface) at a distance of 1.86 Å ^{S10} to calculate the total formation energy E_{NiX-OH} .

For the Ni-oxide surface, the OH^- ion was placed right above one Ni-site on NiO (001) surface (Fig. S8a). It was observed that after relaxation the three Ni sites on (001) surface slightly move out of the initial plane due to the interaction with the more electronegative OH^- ion (Fig. S8b). Such displacement of the metal ions following binding with the hydroxyl anion has been observed previously.^{S11} The OH^- ion adsorption energy was calculated to be -1.608 eV using Eq. 1 as mentioned above.

On the other hand, owing to difference in coordinations, three distinct Ni sites on Ni₃Te₂ (two tetrahedral and one square pyramidal) on (001) and (010) surfaces, respectively, were selected to adsorb OH^- ions, as presented in Fig. S9a-c and Fig. S10a-c, respectively. These active Ni sites have been denoted as Ni(1), Ni(2) – tetrahedral sites on (001) plane; Ni(3) – square

pyramidal on (001) plane; Ni(4), Ni(5) – tetrahedral on (010) plane and Ni(6) – square pyramidal



Fig.S6 (a) 3-dimensional slab model of Ni_3Te_2 with lattices of 1×1×2; (b) (001) free surface (topview) of the 1×1×2 Ni_3Te_2 crystal structure; and (c) (010) free surface (side view) of the 1×2×1 Ni_3Te_2 crystal structure. The active Ni sites are denoted as Ni1, Ni2, Ni3, Ni4, Ni5 and Ni6.



Fig.S7 (a) 3-dimensional slab model of NiO with lattices of 1×1×2; (b) (001) free surface (topview) of NiO crystal structure. The active Ni site has been pointed out.

on (010) plane as shown in Figs. S9 and S10, respectively. It can be observed from Fig. S9a'-c' and Fig. S10a'-c' that after relaxation the coordination of OH^- ions and Ni sites, the angle of Ni-O-H, as well as the distance between OH^- ions and active Ni sites have changed owing to the

adsorption interaction.



Fig.S8 (a) Side view of the original crystal structure of NiO with an OH^- ion placed on the top of the active Ni site, which is located on (001) free surface. The original bond distances of Ni-O and O-H are set as 1.86 Å and 0.96 Å, respectively; (b) The relaxed structure after OH^- ion adsorbed on active Ni site.



Fig.S9 Side views of the original (a-c) and the corresponding relaxed (a'-c') crystal structures of Ni_3Te_2 with OH^- ions placed on the top of active Ni sites: Ni1, Ni2 and Ni3, which are located on (001) plane.



Fig.S10. Side views of the original (a-c) and the corresponding relaxed (a'-c') crystal structures of Ni_3Te_2 with OH^- ions placed on the top of active Ni sites: Ni4, Ni5 and Ni6, which are located on (010) plane.



Fig. S11 Comparison of (a) Ni 2p and (b) Te 3d and (c) O1s XPS spectra of Ni_3Te_2 catalyst (before and after) for 24 h of stability.



Fig. S12 SEM images and corresponding EDAX spectra of Ni_3Te_2 on Au substrate show the identical morphology and composition of catalyst before and after 24h of chronoamperometry



Fig.S13a Comparison of XRD patterns from the catalysts after 24 h of OER activity with as prepared Ni₃Te₂ catalyst synthesized from hydrpthermal methods.



Fig.S13b Comparison of XRD patterns from the catalysts after 24 h of OER activity with as prepared Ni_3Te_2 catalyst electrodeposited on Au glass.



Fig.S14 OER Tafel slope of Ni₃Te₂ electrodeposited on GC

Testing of evolved gas:

Rotating ring disk electrode (RRDE) set up was used in bipotentiostat mode to monitor the gas evolved at the anodic reaction. For this procedure Ni_3Te_2 was electrodeposited on GC disk electrode in a RRDE set-up and scanned at the anodic potential range while Pt ring was held a potential of 0.2 V (vs. RHE). The idea was to hold the Pt ring potential suitable for ORR such that if any O₂ was being produced at the disk electrode, it will be collected and reduced at the ring electrode resulting in an increase of the ring current. Both the ring current and disk current were measured as function of applied disk potential. Initially 1M KOH solution was purged with N₂ gas for 30 min before starting the reaction to remove dissolved O₂ and blanketed in N₂ atmosphere. The disk electrode was scanned from 1.0 to 1. 5 V (vs. RHE) at a scan rate of 10 mV s⁻¹ at 1600 rpm. Initially, the ring current was maintained at almost zero current when disk current was almost zero. As soon as the disk current started to increase, the ring current also increased, indicating that there was indeed oxygen reduction happening at the Pt ring electrode and this O₂ was being generated at the disk electrode (Fig. 6a). From this Fig. 6a the onset potential of OER was obtained as 1.36 V vs. RHE.

OER Faradaic Efficiency:

Prior to RRDE measurement, N_2 gas was purged in the cell for 30 min and then blanketed with N_2 during the experiment. The disk electrode was maintained at constant potential steps from 1.41 to 1.45 V (vs RHE) for consecutive periods of 1 min each, while being rotated at a 1600 rpm under a N_2 gas blanket. The ring electrode was held at 0.2 V (vs. RHE) throughout the experiment, which was sufficiently negative to reduce the collected oxygen rapidly. The Faradaic efficiency can be given as:

Faradaic Efficiency = $\frac{2i_r}{i_d N}$

where ir and id are the measured ring and disk currents, respectively, and N is the collection efficiency of RRDE, 0.17 in this work.

The OER faradaic efficiency of the catalyst was calculated from the ratio of ring and disk current and has been presented in Fig. 6b. The highest Faradaic efficiency was obtained to be about 99.8% at the applied disk potential of 1.41 V (vs. RHE), and decreased to 47.1% with the disk voltage increasing to 1.45 V (vs. RHE). The faradaic efficiency was also checked by using water displacement methods wherein, the efficiency of OER and HER catalyst is defined as the ratio of the amount of O₂ and H₂ evolved during the catalytic experiments to the amount of O₂ and H₂ expected based on theoretical considerations. The volumes of evolved O₂ and H₂ was estimated by collecting the evolved gases (at constant potential for 1h) in a graduated cylinder by water displacement method. The theoretical amount of O₂ and H₂ were then calculated by applying Faraday law. This process also shows almost 100% of efficiency of Ni₃Te₂ catalyst for OER reaction.

Collection Efficiency:

The measured ratio of the ring limiting current to the disk limiting current is known as the collection efficiency (N) of that RRDE electrode and it can be written as-



ⁱLimiting,Ring

Fig. S15 Rotating Ring-Disk voltammograms in N₂ saturated 0.001M K₃Fe(CN)₆ containing 1M KOH at 10 mV s⁻¹ at different rotation rate. Ring potential was held on 0.65 V vs. Ag/AgCl which is sufficient to oxidize the product rapidly at ring. (Here ring current was shown as a potential of disk electrode)

At disk electrode, the reduction of ferricyanide ($Fe(CN)_{6^{3-}}$) to ferrocyanide (($Fe(CN)_{6^{4-}}$) took place, on the other hand ferrocyanide is oxidized to ferricyanide at ring at positive potential (0.65 V vs. Ag/AgCl). The value of N was calculated and it was found to be 0.17.



Fig. S16 HER polarization curve of hydrothermally synthesized Ni_3Te_2 @ Au in N_2 saturated 1 M KOH solution at a scan rate of 10 mV s⁻¹



Fig. S17 Comparison of polarization curves for NiO_X, Ni₃S₂, Ni₃Se₂ and Ni₃Te₂.

Calculation of catalyst loading:

According to the Faraday's second law of electrolysis, the amount of a material deposited on an electrode is proportional to the amount of electricity used. Thus from the electrodeposition curve, the mass of catalyst can be calculated as-

Mass = (Molecular weight of Ni₃Te₂ × Charge)/ (No. of electron involved in process × Faraday Constant)

Here, we can get the total charge from the deposition curve at constant potential (-1.05 V vs. Ag|AgCl). As tellurium cation (Te^{4+}) is electrochemically reduced to Te^{2-} , thus the number of electron involved in the process is 6.



Fig. S18 Electrodeposition curve for nickel telluride.



Fig. S 19 (a) Experimental setup of OER process (b) Image shows experiment to detect production of gaseous oxygen

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