Supporting Information

Myriophyllum-like Hierarchical TiN@Ni_3N Nanowire Arrays for Bifunctional Water Splitting Catalyst

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Experimental Section

Ti foil (thickness: 100 μm)，sodium hydroxide (NaOH), ethanol, acetone, nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), concentrated ammonium hydroxide (25.0–28.0 wt%), concentrated HCl (36.0–38.0 wt%), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), ammonium fluoride (NH_4F), urea, potassium hydroxide (KOH), sulfuric acid (H_2SO_4) were of analytical grade and purchased from Shanghai Chemical Corp. All chemicals were used as received without further purification. Deionized (DI) water was used for all experiments.

Calculation of electrochemically active area ($R_f \times 10^3$):

The roughness factor ($R_f \times 10^3$) was evaluated from the double-layer capacitance (C_{dl}) charging curve using cyclic voltammetry in a narrow potential range (0.3–0.5 V) through the equation: $R_f \times 10^3 = C_{dl}/60$ μF·cm^{-2} (capacitance of a smooth surface),[13] in which $C_{dl} = I_{cap}/(dE/dt)$, where I_{cap} is the capacitive current at the midpoint of the scan range and dE/dt is the scan rate.

Calculation of turnover frequency (TOF):

The TOF values of TiN@Ni3N and Ni3N electrode were calculated according to equation:[S1, S2] $TOF = j \times A/(4 \times F \times m)$, among which j is the current density obtained at overpotential of 60 mV in A/cm^2, A is the surface area of the electrode, F is the Faraday efficiency (96,485 /mol), and m is the number of moles of the TiN@Ni_3N and Ni_3N deposited onto the electrodes.

Supporting Figures

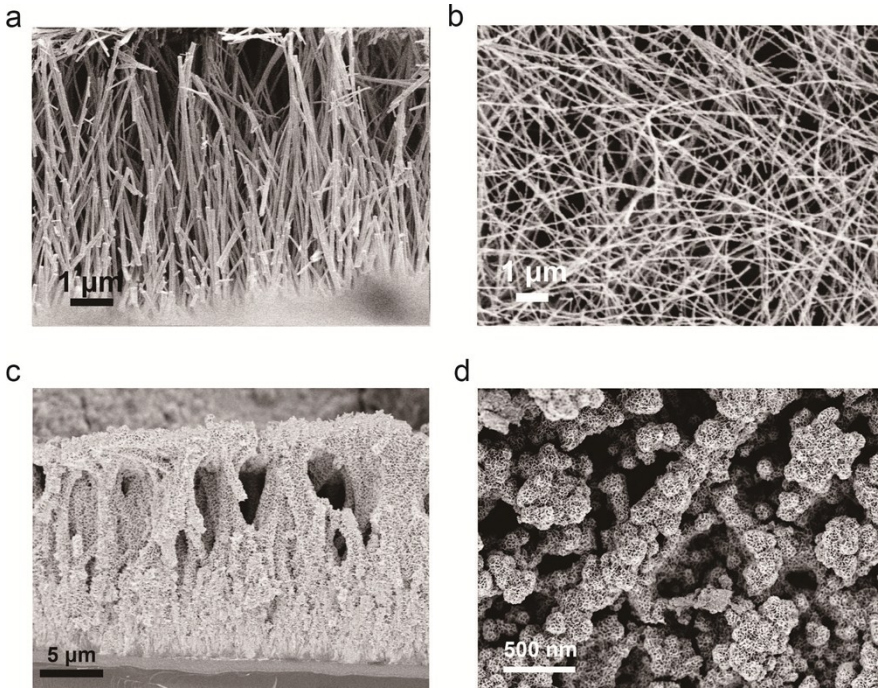

Figure S1. SEM images of (a, b) pure TiN nanowires and (c, d) TiN@NiO nanowires.

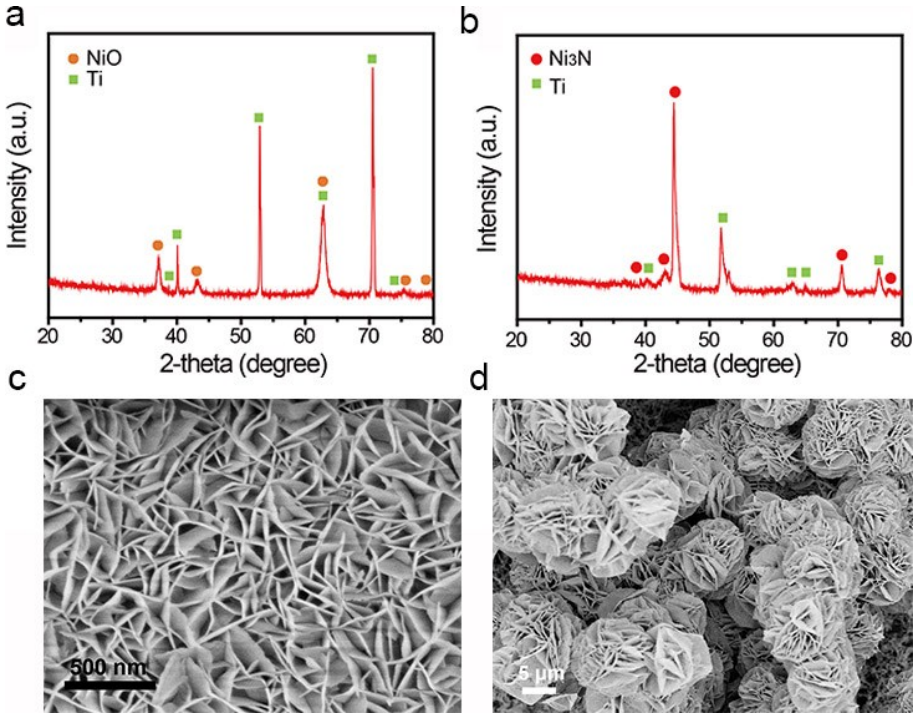

Figure S2. XRD patterns of (a) NiO nanosheets (PDF No. 71-1179) and (b) Ni_3N nanosheets (PDF No. 10-0280), along with the Ti foil substrate. SEM images of (c) NiO nanosheets and (d) Ni_3N nanosheets grown directly on Ti foil.

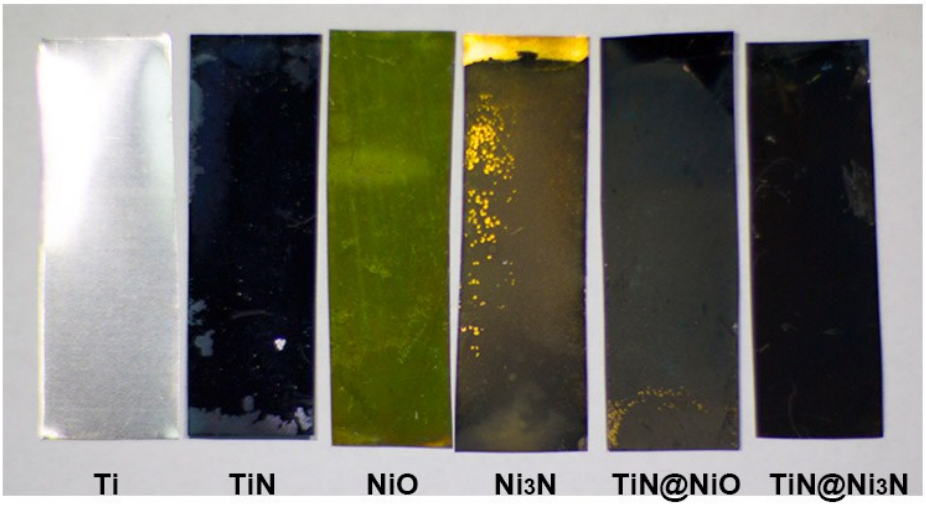

Figure S3. Photographs of the as-synthesized samples grown in Ti foils.

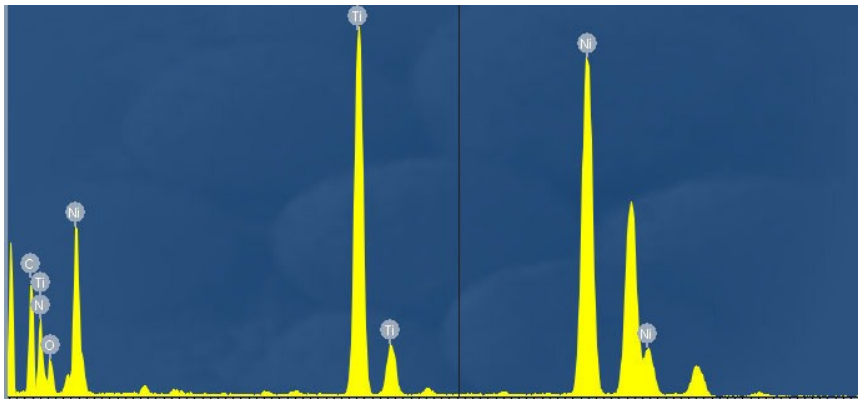

Figure S4. EDS spectrum of the TiN@Ni_3N nanowire arrays.

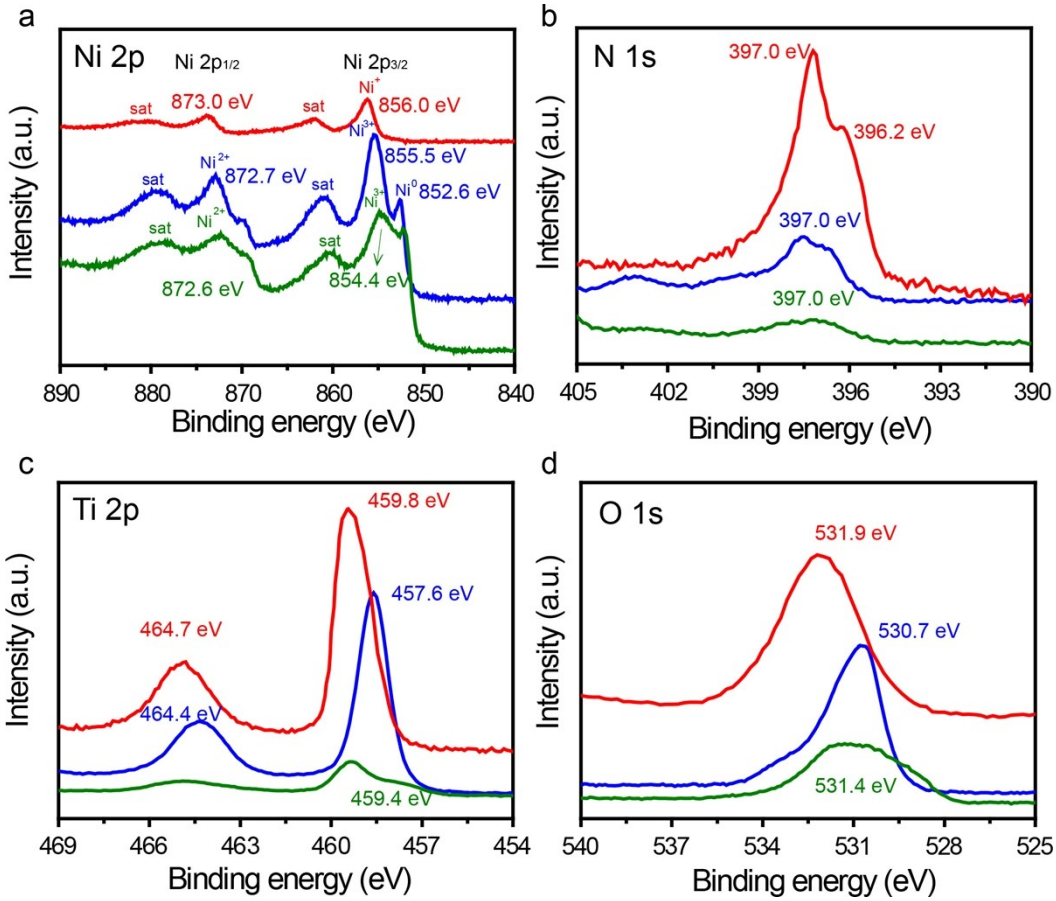

Figure S5. High-resolution XPS spectra of (a) Ni 2p, (b) N 1s, (c) Ti 2p and (d) O 1s. Red curves correspond to the as-prepared samples. Blue curve correspond to the post-HER samples. Green curves correspond to the post-OER samples.

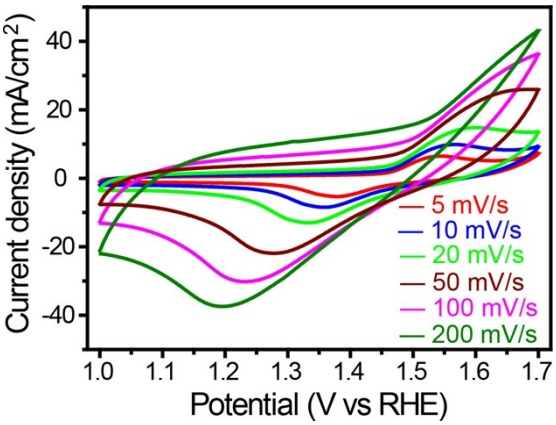

Figure S6. CV curves of TiN@Ni_3N between 1.0 and 1.7 V (vs. RHE) measured at a scan rate of 5 - 200 mV/s in 1 M KOH.

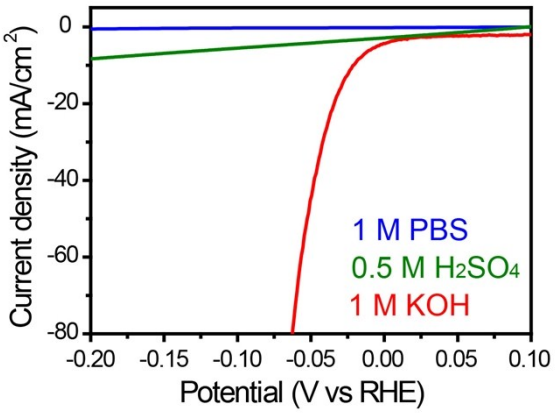

Figure S7. LSV curves of TiN@Ni_3N in neutral electrolyte (blue curve), acid electrolyte (green curve) and alkaline electrolyte (red curve).

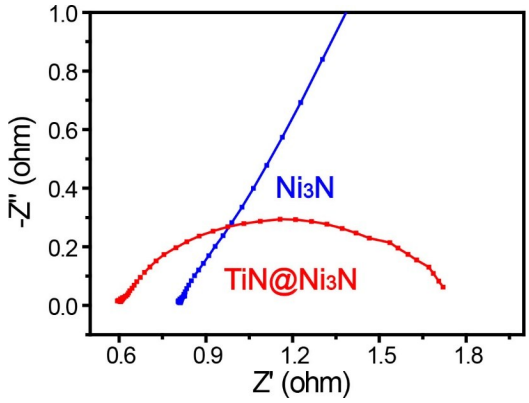

Figure S8. Nyquist plots of the TiN@Ni_3N nanowire arrays and the Ni_3N nanosheets with enlarged scale.

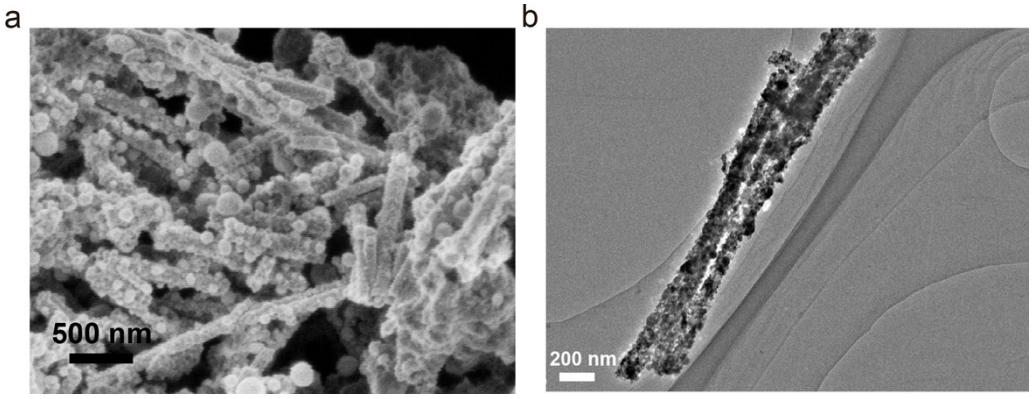

Figure S9. (a) SEM and (b) TEM images of the TiN@Ni_3N nanowires after 10 h of electrocatalytic reaction.

Table S1. Comparison of HER electrocatalytic performance between this work and previously reported materials.

Materials	**Electrolyte**	**Scan rate (mV/s)**	**Onset potential (mV)**	**Potential (vs RHE) at 80 mA/cm^2 (mV)**	**Tafel slope (mV/dec)**	**References (in the manuscript)**
TiN@Ni_3N	1 M KOH	5	15	–62	42.1	**This work**
Ni_3N/Ni-foam	1 M KOH	25	50	–290	60	**Ref.13**
$NiMoN_x$/C nanosheets	0.1 M $HClO_4$	2	78	/	35.9	**Ref.19**
Ni_2P nanosheets	0.5 M H_2SO_4	5	50	~ –200	68	**Ref.20**
$Ni_{0.33}Co_{0.67}S_2$ NWs	0.5 M H_2SO_4	5	52	–110	44.1	**Ref.21**
Ni_3S_2 Nanosheet Arrays	neutral media	50	170	>400	/	**Ref.25**
NiS/Ni foam	1 M KOH	5	150	220	83	**Ref.27**
CFP/$NiCo_2O_4$/CuS	0.5 M H_2SO_4	2	31	-110	41	**Ref.28**
Nickel phosphorus nanoparticles film	1 M KOH	2	98	-150	55	**Ref.29**
Ni_5P_4 films	0.5 M H_2SO_4	/	~120	>150	40	**Ref.30**
Ni_5P_4 films	1 M KOH	/	~115	>150	53	**Ref.30**

Table S2. Comparison of OER electrocatalytic performance between this work and previously reported materials.

Materials	**Electrolyte**	**Scan rate (mV/s)**	**Onset potential (V vs RHE)**	**Potential (vs RHE) at 50 mA/cm^2 (V)**	**Tafel slope (mV/dec)**	**References (in the manuscript)**
TiN@Ni_3N	1 M KOH	5	1.52	1.65	95.4	**This work**
Ni_3N nanosheets	1 M KOH	5	1.55	1.58	45	**Ref.7**
Ni_3N/Ni-foam	1 M KOH	25	1.60	1.68	120	**Ref.13**
NiS/Ni foam	1 M KOH	5	1.55	1.56	89	**Ref.27**
Nickel phosphorus nanoparticles film	1 M KOH	2	1.55	1.62	120	**Ref.29**
Ni_5P_4 films	1 M KOH	40	1.58	1.50	40	**Ref.30**
Fe-Ni-O*x*-NPs	1 M KOH	10	1.48	1.53	38	**Ref.31**
$Ni(OH)_2$/NiOOH	1 M KOH	100	1.56	/	54	**Ref.32**

References

S1. X. Lu and X. Zhao, *Nat. Commun.*, **2015**, 6, 6616.

S2. A.J. Esswein, M.J.McMurdo, P. N. Ross, A.T. Bell and T. D. Tilley, *J. Phys. Chem. C*, **2009**, 113, 15068-15072.