

Supporting Information

Cobalt/Titanium Nitride@N-doped Carbon Hybrid for Enhanced Electrocatalytic Hydrogen Evolution and Supercapacitance

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Table S1 the content molar ratio of Ti and Co in the Co-TiN@NG-x/CC from ICP results.

$n_{\text{Ti}}: n_{\text{Co}}$	Co-TiN@NG-1/ CC	Co-TiN@NG-2 /CC	Co-TiN@NG-4 /CC	Co-TiN@NG- 8/CC
Theoretical result	1:1	2:1	4:1	8:1
ICP result	1.05:1	2.03:1	4.05:1	8.06:1

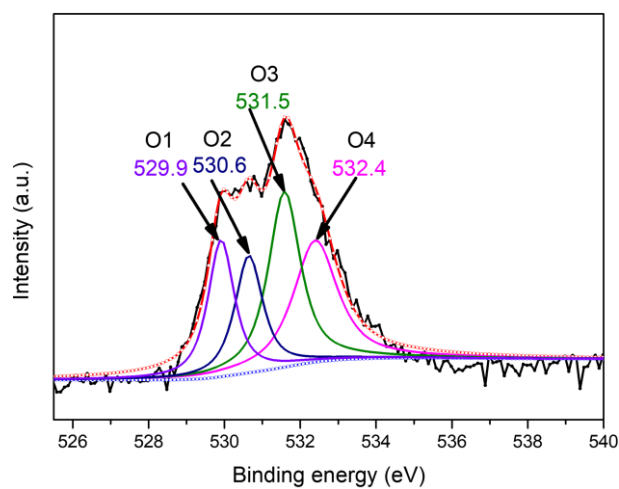


Fig. S1 XPS spectra of O 1s species on the surface of Co-TiN@NG-2/CC.

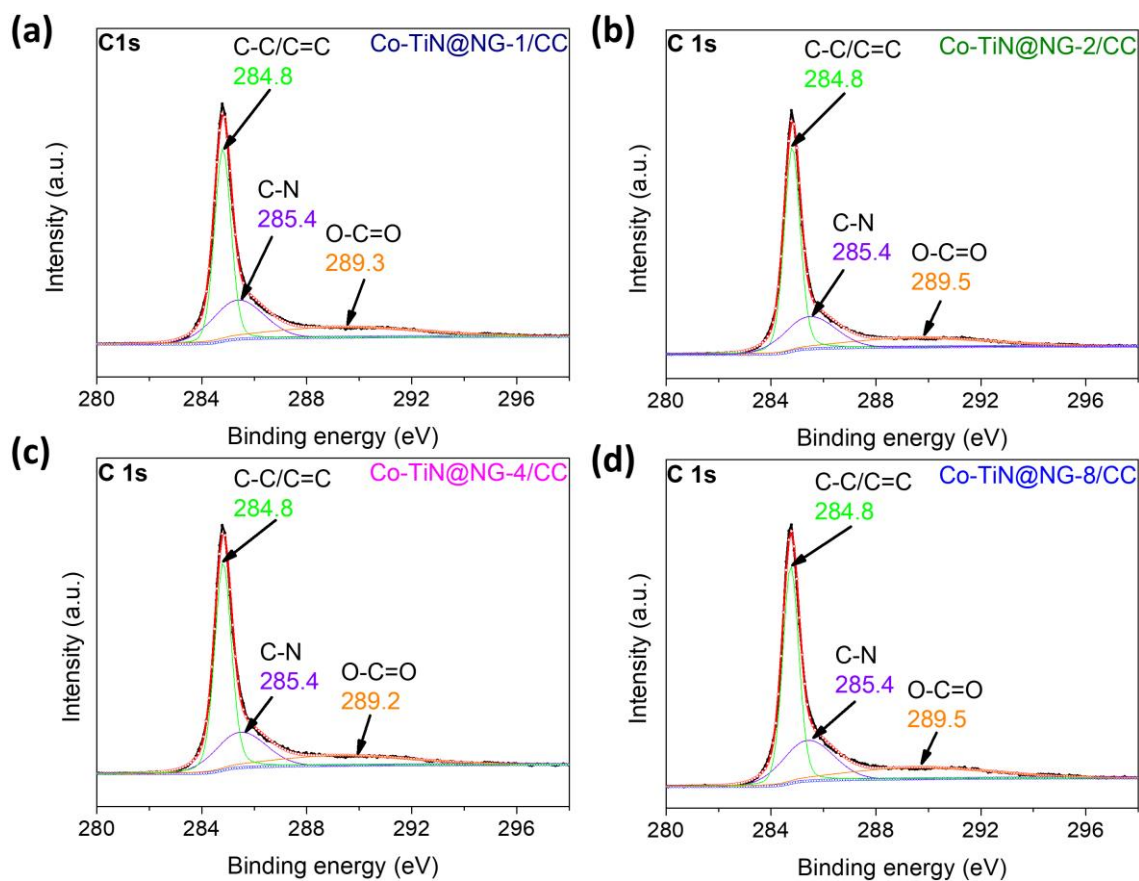


Fig. S2 High-resolution XPS spectra of C 1s of (a) Co-TiN@NG-1/CC, (b) Co-TiN@NG-2/CC, (c) Co-TiN@NG-4/CC and (d) Co-TiN@NG-8/CC

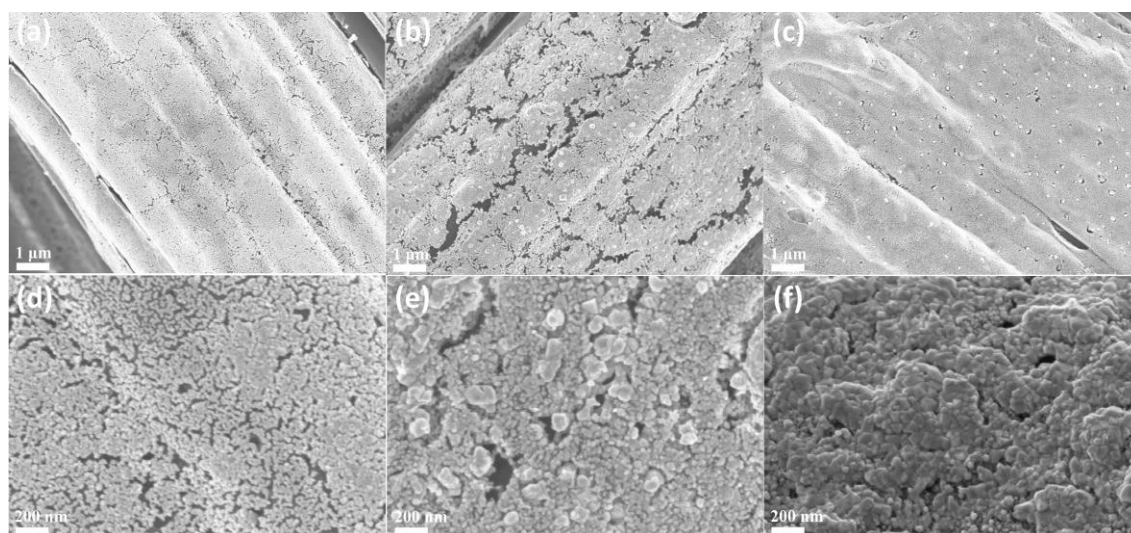


Fig. S3 FESEM images for (a) Co-TiN@NG-8/CC, (b) Co-TiN@NG-4/CC and (c) Co-TiN@NG-1/CC in low magnification, and (d) Co-TiN@NG-8/CC, (e) Co-TiN@NG-4/CC and (f) Co-TiN@NG-1/CC in high magnification.

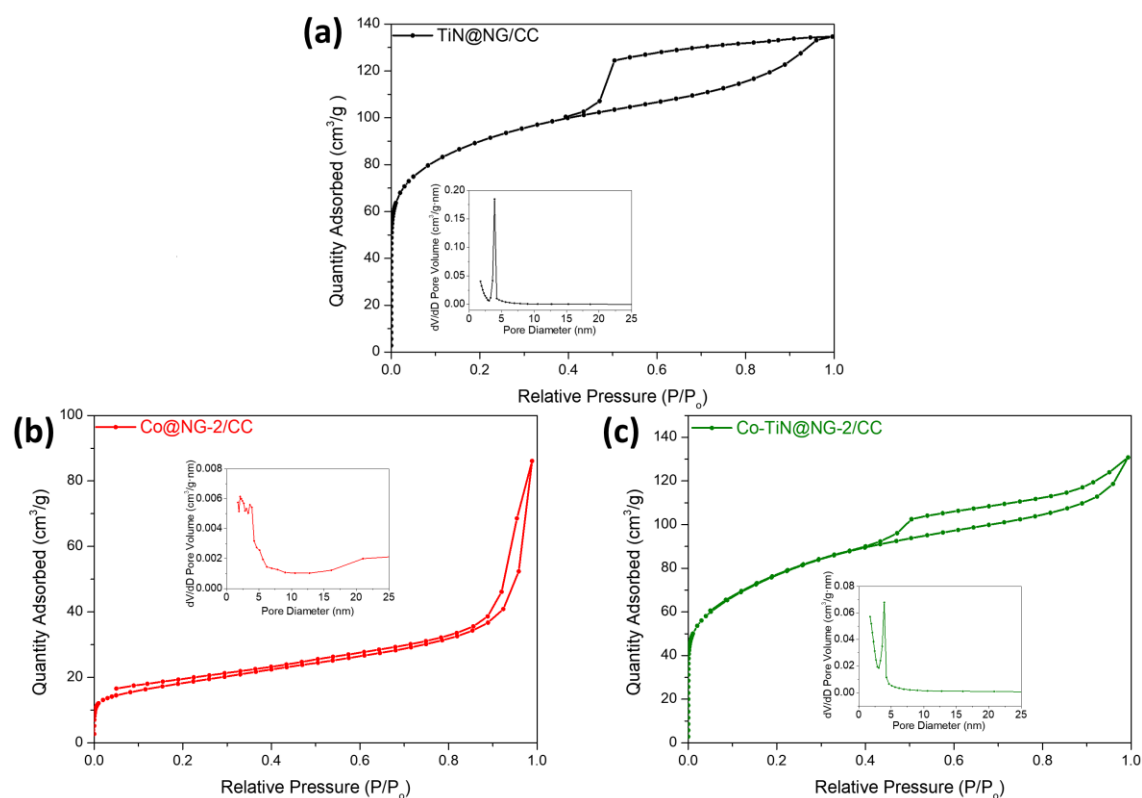


Fig. S4 N₂ adsorption/desorption isotherms and (inset) corresponding pore size distributions of (a) TiN@NG/CC, (b) Co@NG-2/CC and (c) Co-TiN@NG-2/CC

Table S2 Comparisons of HER electrocatalytic activity of Co-TiN with recently reported noble metal-free catalysts under alkaline conditions.

Catalyst	Substrate	Overpotential at 10 mA/cm ⁻² (mV)	Stability Time/CV cycles	Electrolyte	Reference
Co-TiN@NG-2/CC	CC	208	24 h/1000 cycles	1 M KOH	This work
MoS ₂ /MoSe ₂	GCE	235	3 h	1 M KOH	4
Co-BDC/MoS ₂	GCE	248	15 h/2000 cycles	1 M KOH	5
Ni(OH) ₂ /MoS ₂	GCE	227	1000 cycles	1 M KOH	6
CoSe ₂ /MoSe ₂	GCE	218	1000 cycles	1 M KOH	7
MoSe ₂ @Ni _{0.85} Se	NF	117	20 h/1000 cycles	1 M KOH	8
Ni-Mo _x C	GCE	183	24 h/1000	1 M KOH	9

Fe-Ni ₃ C	GCE	292	10 h/1000	1 M KOH	10
			cycles		
Co ₂ P/WC@C	GCE	180	12 h/1000	1 M KOH	11
			cycles		
Fe ₃ C-Mo ₂ C/NC	GCE	180	-	1 M KOH	12
			cycles		
HNFs					
WC@CNS	NF	220	5 h	0.1 M KOH	13
TaC@CNS	NF	250	-	0.1 M KOH	13
NbC@CNS	NF	240	-	0.1 M KOH	13
Co _{1.11} Te ₂ /C	GCE	178	20 h/1000	1 M KOH	14
			cycles		

Table S3 Mass activity (MA) and turnover frequency (TOF) of HER electrocatalysts in 1 M KOH.

Catalysts	Mass activity (mA·mg ⁻¹)	TOF (s ⁻¹)
TiN@NG/CC	1.64	0.00049
Co@NG/CC	1.48	0.00044
Co-TiN@NG-8/CC	4.06	0.0012
Co-TiN@NG-4/CC	5.12	0.0015
Co-TiN@NG-2/CC	5.95	0.0018
Co-TiN@NG-1/CC	3.78	0.0011

Table S4 Fitting results of Nyquist plots for all the samples.

Sample	R_s (Ω)	R_{ct} (Ω)
TiN@NG/CC	2.568	139.3
Co@NG/CC	2.664	20.07
Co-TiN@NG-8/CC	2.377	4.999
Co-TiN@NG-4/CC	2.474	4.837
Co-TiN@NG-2/CC	2.289	3.4
Co-TiN@NG-8/CC	3.736	5.583

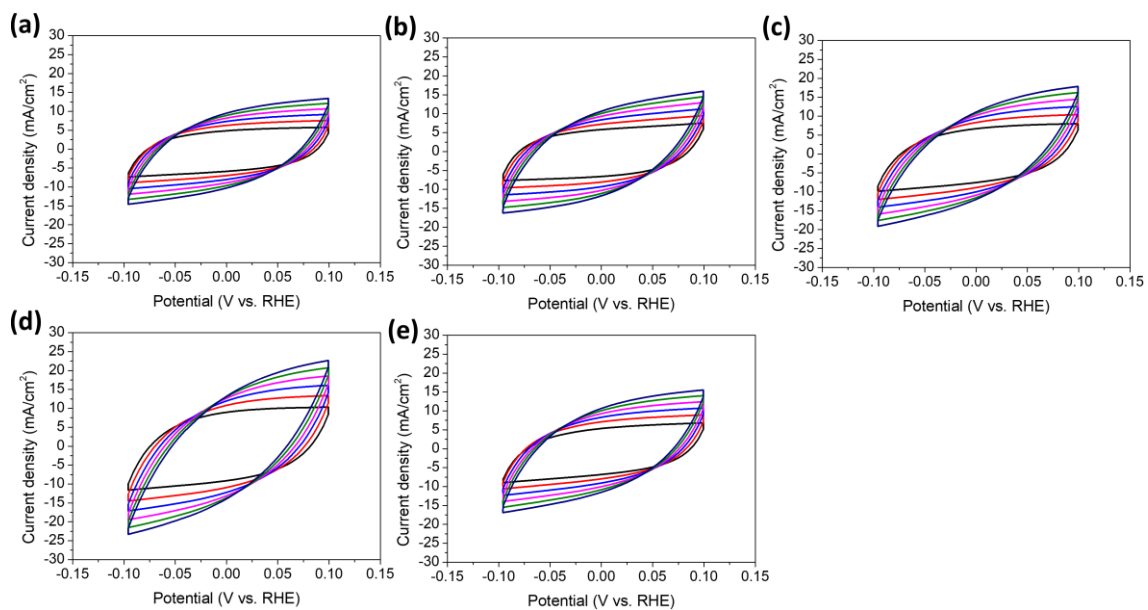


Fig. S5 CV curves at various scan rates for the determination of C_{dl} for sample (a) TiN@NG/CC, (b) Co-TiN@NG-8/CC, (c) Co-TiN@NG-4/CC (d) Co-TiN@NG-2/CC and (e) Co-TiN@NG-1/CC.

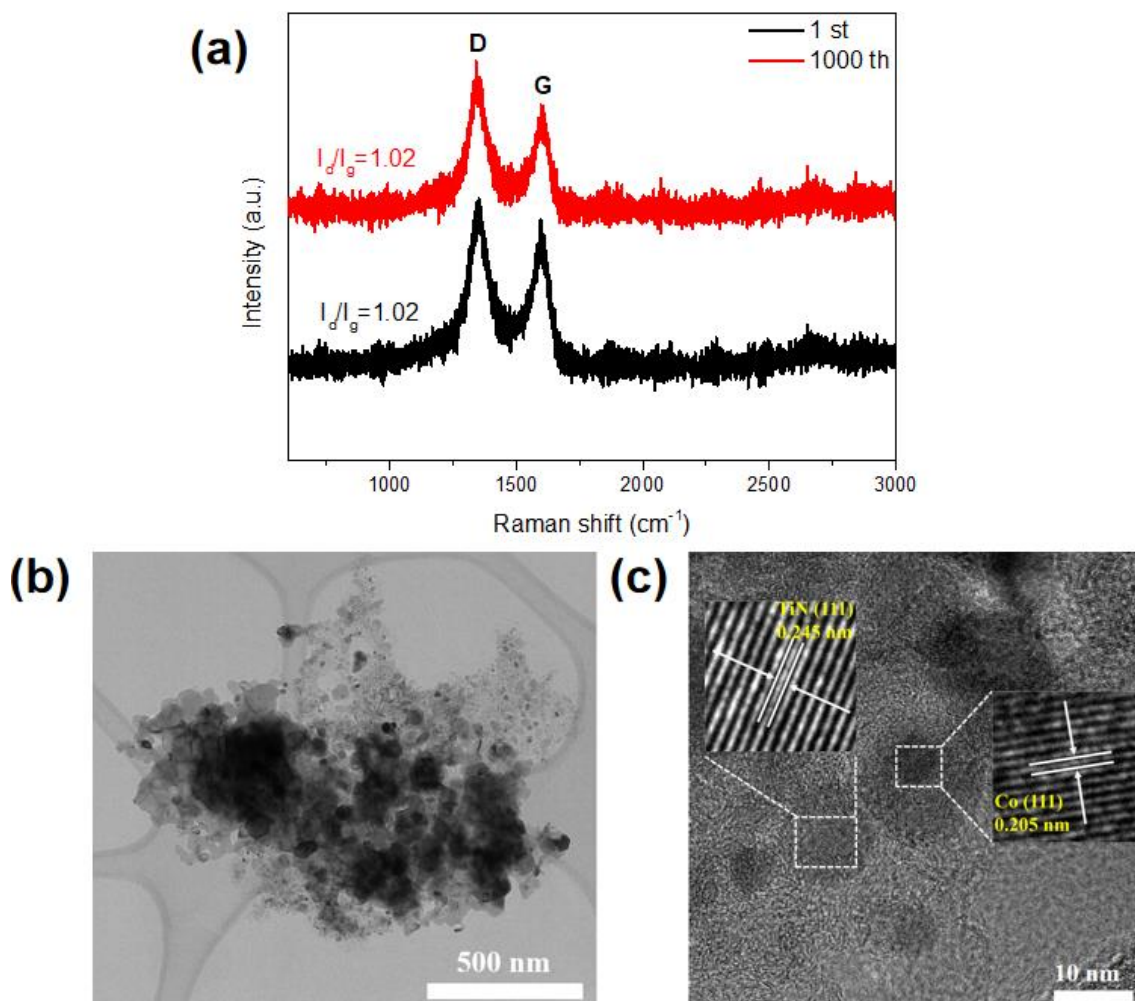


Fig. S6 (a) Raman spectra, (b) TEM image and (c) HRTEM image of Co-TiN@NG-2/CC catalyst after the continuous scanning test.

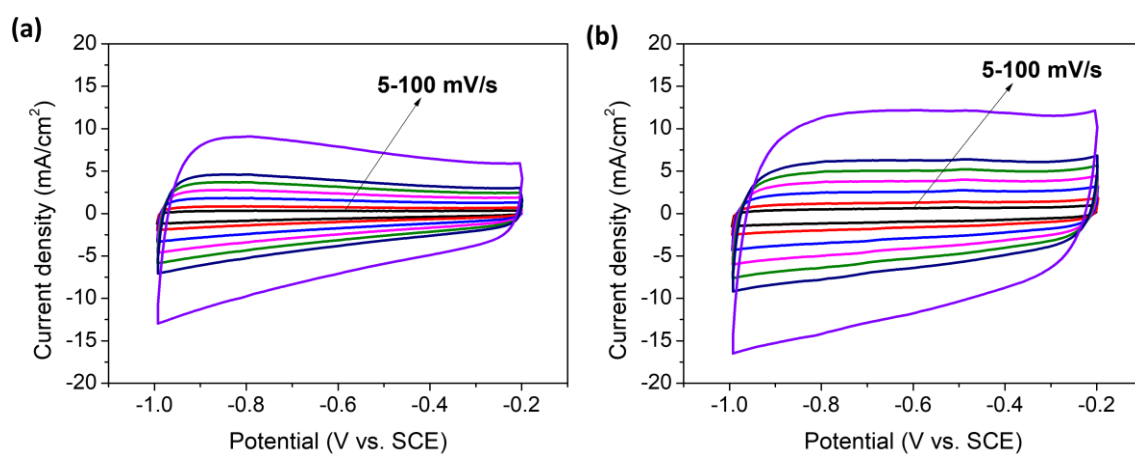


Fig. S7 CV curves of (a) TiN@NG/CC and (b) Co-TiN@NG-2/CC at different scanning rates from 5 to 100 mV/s.

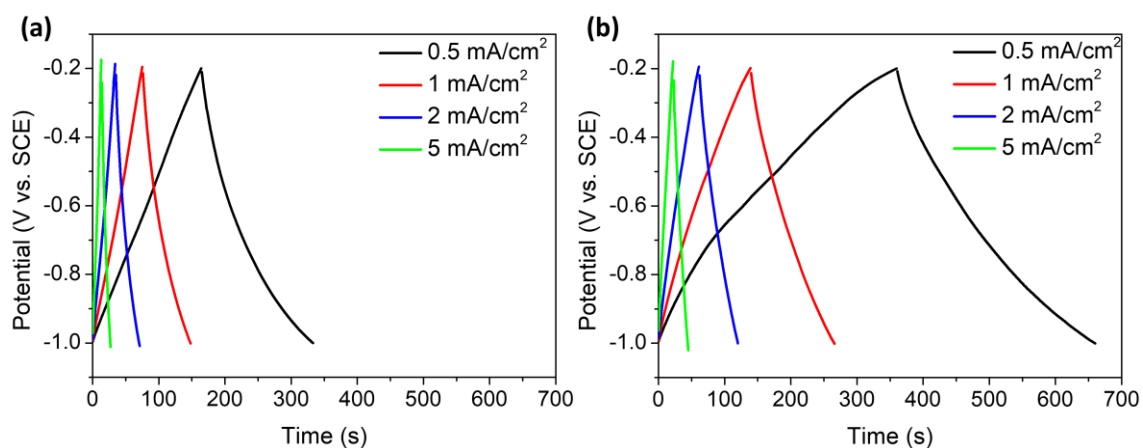


Fig. S8 GCD curves of (a) TiN@NG/CC and (b) Co-TiN@NG-2/CC at different current densities from 0.5 to 5 mA/cm² in 1 M KOH.

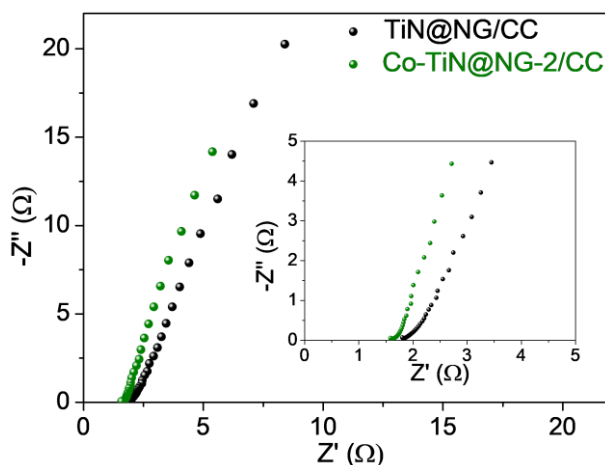


Fig. S9 EIS test of TiN@NG/CC and Co-TiN@NG-2/CC at an open-circuit potential in 1 M KOH.

Table S5 Comparison the capacitance performance of Co-TiN with other metal nitrides that have been reported recently.

Electrodes	Potential Range	Electrolyte	Capacitance	Reference
Co-TiN@NG-2/CC	-1.0 to -0.2 V (Vs. SCE)	1.0 M KOH	88.5 F/g (148.6 mF/cm ²) at 2 mA/cm ²	This work
Si@Ti@TiN thin film array	0 to 0.8 V (Vs. Ag/AgCl)	0.5 M H ₂ SO ₄	43.8 mF/cm ² at 1.0 mA/cm ²	6
TiN	-0.8 to 0.2 V	2.0 M KOH	38.5 F/g at 40 mV/s	7

	(Vs. SCE)			
TiN/CNT	-0.6 to 0.25 V	7.5 M KOH	89.96 F/g at 10 mV/s	8
	(Vs. SCE)			
MoN _x /TiN NTA	-1.2 to -0.6 V	1.0 M LiOH	121.50 mF/cm ² at 0.3 mA/cm ²	9
	(Vs. SCE)			
TiN@C	-1 to 0 V (Vs. SCE)	1.0 M KOH	11.15 mF/cm ² at 10 mV/s	10
	(Vs. SCE)			
TiN/C	-1.2 to 0.4 V	1.0 M KOH	102.6 F/g at 1 A/g	11
	(Vs. SCE)			
TiN/C	-1.0 to 0 V (Vs. SCE)	1.0 M KOH	159.0 F/g at 0.5 A/g	12
	(Vs. SCE)			
Nb ₄ N ₅ @NC	0 to 0.6 V (Vs. Ag/AgCl)	1.0 M KOH	243.6 mF/cm ² at 0.5 mA/cm ²	13
	(Vs. Hg/Hg ₂ SO ₄)			
GaN	-0.5 to 0.4 V (Vs. Hg/Hg ₂ SO ₄)	1.0 M H ₂ SO ₄	24 F/g at 0.5 mA/cm ²	14
	(Vs. Ag/AgCl)			
CrN	0 to 0.8 V (Vs. Ag/AgCl)	0.5 M H ₂ SO ₄	12.8 mF/cm ² at 1 mA/cm ²	15