Electronic Supplementary Information (ESI)

A highly efficient transition metal nitride-based electrocatalyst for oxygen reduction reaction

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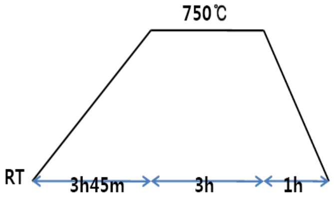
Synthesis of TMNs by urea-glass route

Five TMNs were synthesized by urea-glass route. The 1g of metal chloride precursor was dispersed in 2.53ml of ethanol under stirring. This reaction should be carried out in the hood because the metal precursor reacts with ethanol vigorously (especially $TiCl_4$), releasing HCl vapor. After clear solution was obtained, appropriate amount of urea, as a nitrogen source instead of NH_3 gas, was added to the solution (Table S1). After 1h stirring, a viscous metal-urea complex was moved to alumina boat and calcined in a tubular furnace under N_2 with a flow rate of 100 sccm. Detailed heat treatment conditions were shown in Table S1. Only for Ta_3N_5, the maximum temperature was 700℃.

In case of NbN, passivation process is required prior to taking out the sample from the furnace to prevent rapid oxidation of the catalyst surface. Without passivation process, NbN catalyst burned like charcoal in the atmospheric condition. Passivation was performed using mixed gas consists of 1% O_2/He gas and pure N2 gas after the furnace cooled down to room temperature. At first, 10 sccm of 1% O_2/He and 30 sccm of N_2 flowed through the furnace for 10 minutes. During the next 10 minutes, 20 sccm of 1% O_2/He and 20 sccm of N_2 flowed. In this manner, 30 sccm of 1% O_2/He and 10 sccm of N_2 passed the furnace followed by 40 sccm of 1% O_2/He without $N_{2.}$

Table S1. Detailed synthetic conditions of five different TMNs.

Precursor	urea (mg)	R[a)]	Heat treatment condition	Post treatment
$MoCl_5$	220	1		X
WCl_4	184	1		X
$NbCl_5$	1509	5		○ (passivation)
$TiCl_4$	1583	5		X
$TaCl_5$	1111	9	Max. Temperature: 700℃	X

[a)] R: molar ratio of urea to metal precursor

Fig. S1. a) XRD patterns of synthesized TMNs and SEM images of b) Mo_2N, c) W_2N, d) NbN, e) Ta_3N_5, and f) TiN.

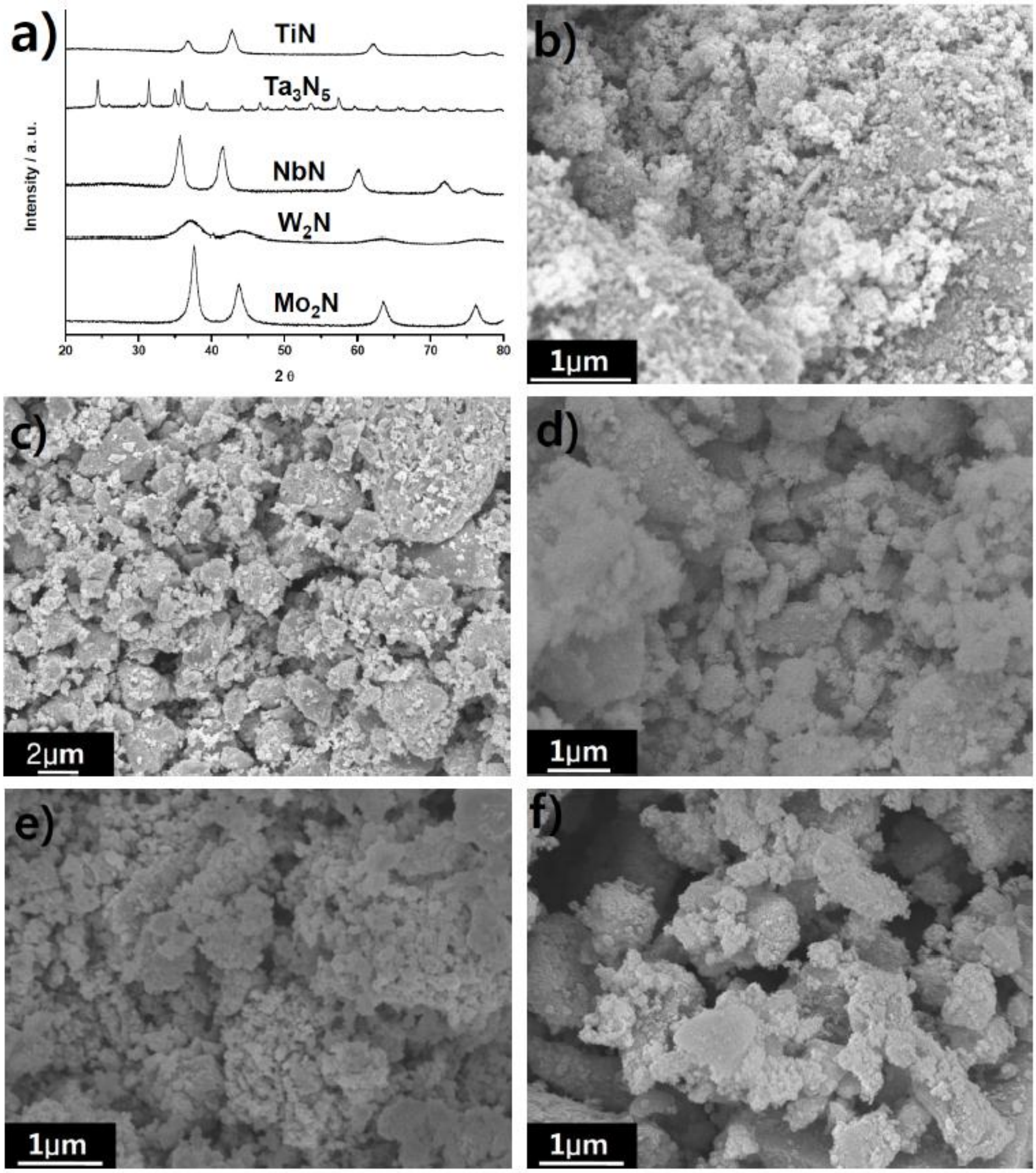


Fig. S2. a) XRD patterns of synthesized TiN-based catalysts. Vertical lines indicated reference pattern of TiN (JCPDS No. 38-1420), b) Magnified XRD patterns taken from the areas marked with red circle in a).

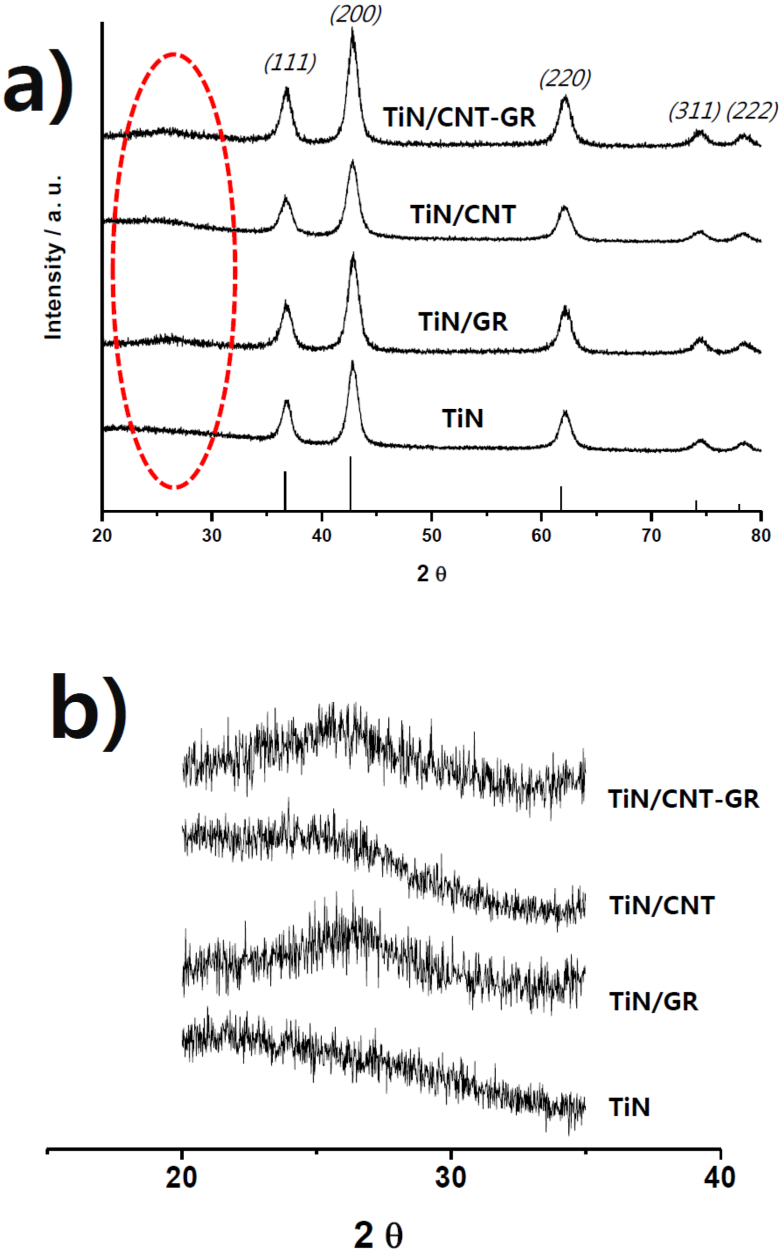


Fig. S3. Enlarged images of insets in Fig. 4. a) TiN, b) TiN/GR, c) TiN/CNT, and d) TiN/CNT-GR.

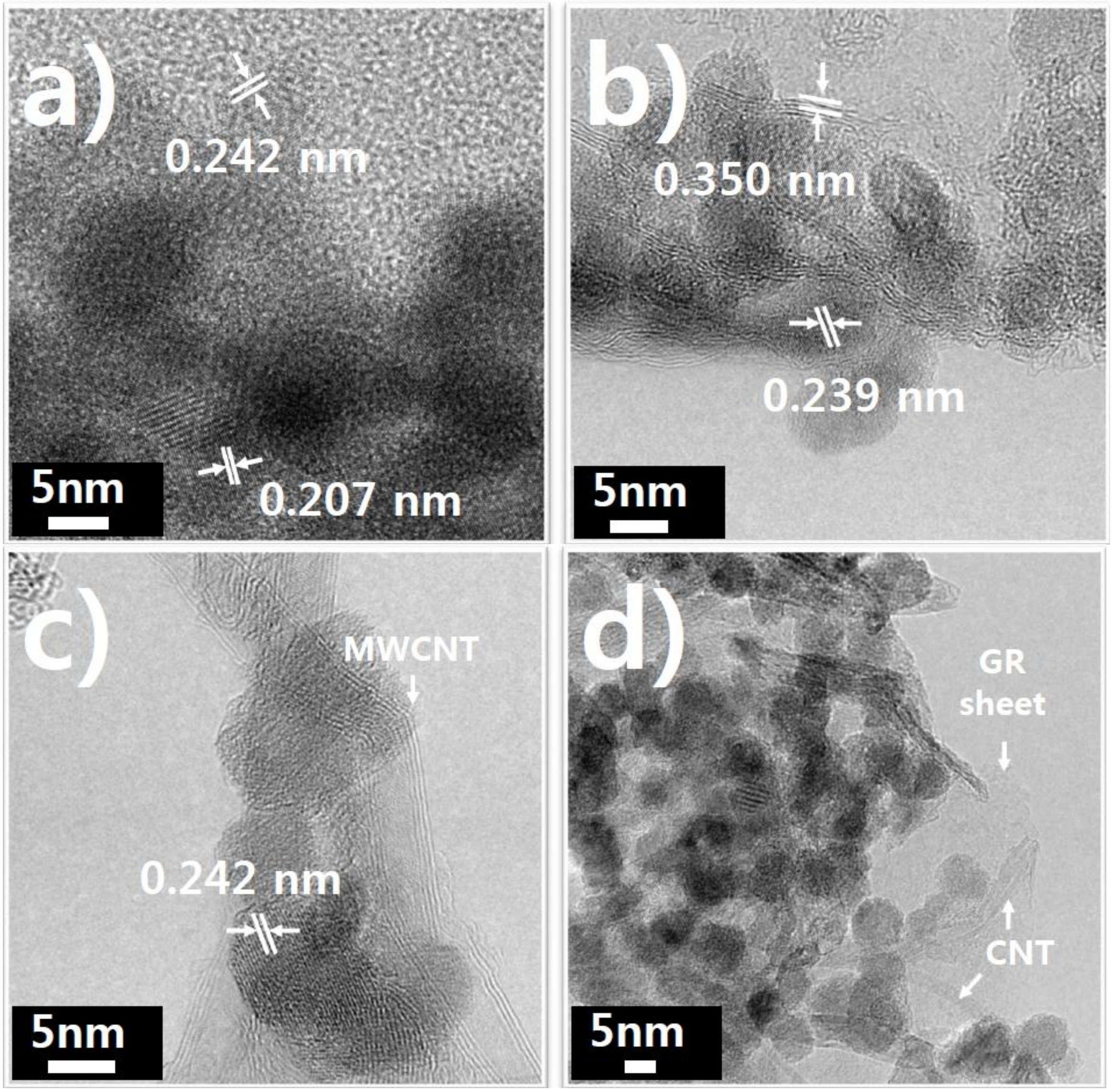


Fig. S4. SEM images of a) TiN/CNT and b) TiN/CNT-GR focused on morphology of CNT.

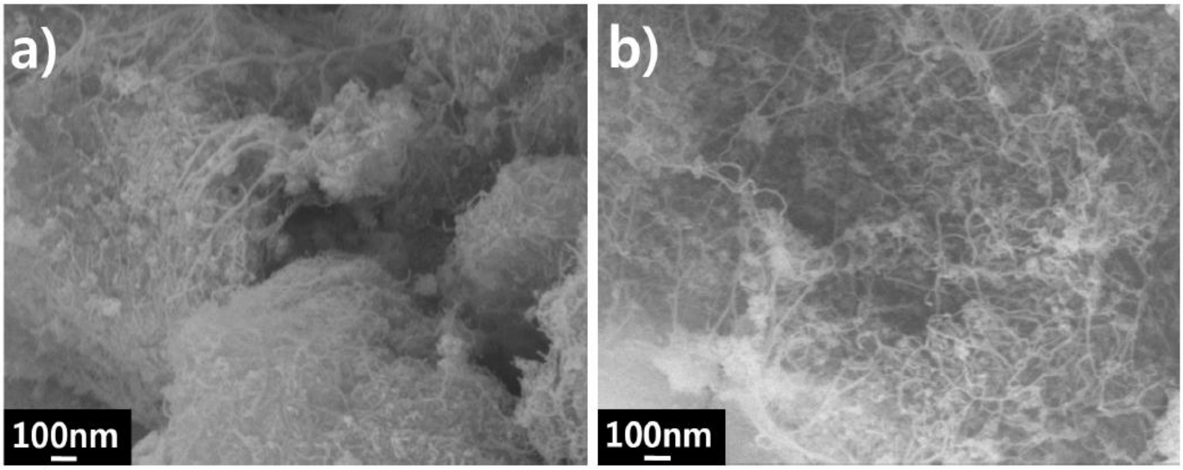


Fig. S5. Low magnification TEM images of a) TiN/GR, b) TiN/CNT, and c) TiN/CNT-GR.

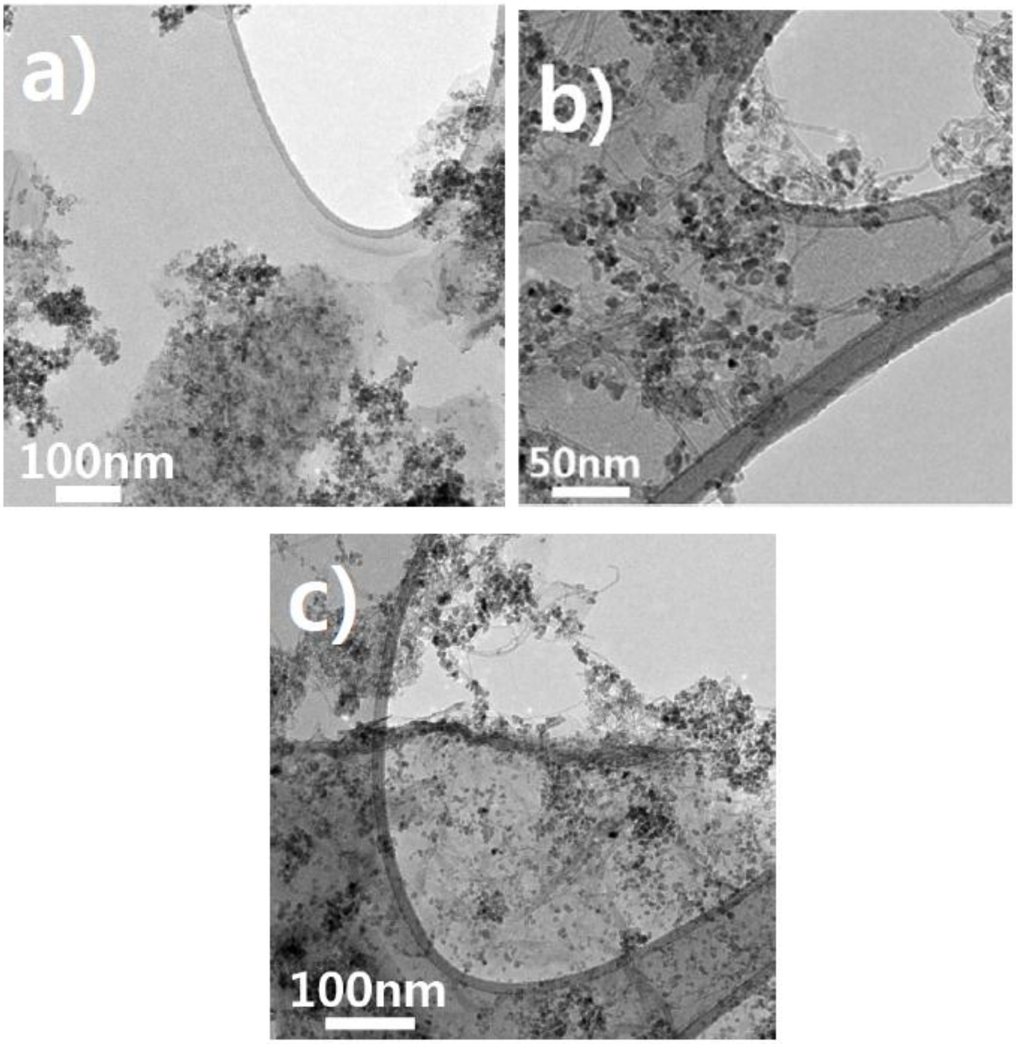


Fig. S6. a) X-ray absorption near edge structure (XANES) spectra of Ti K-edge, b) Fourier-transforms of Ti K-edge EXAFS for supported and bare TiN catalysts.

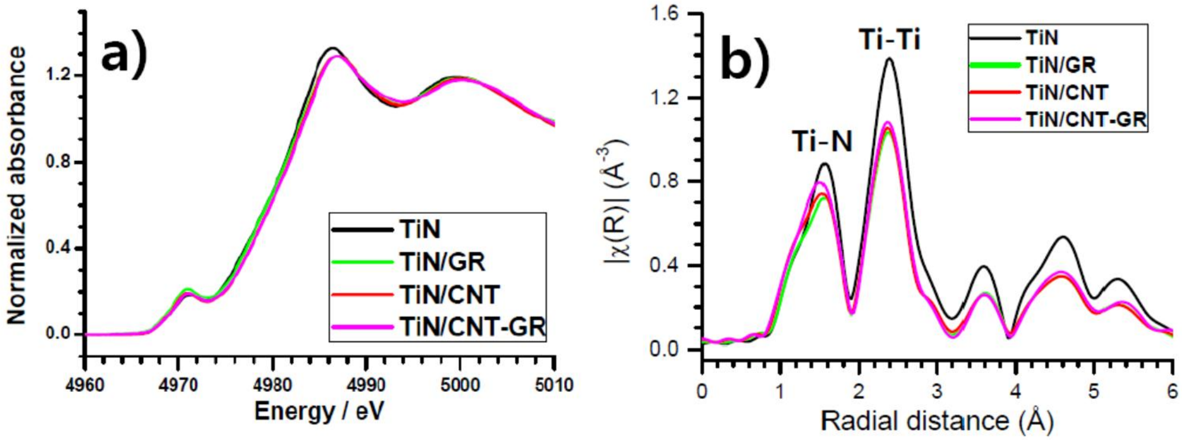


Table S2. Structural parameters calculated from Ti K-edge EXAFS fits for supported and bare TiN NPs.

Catalysts	$N_{Ti\text{-}N}$^{a}	$N_{Ti\text{-}Ti}$$^{a)}$	$R_{Ti\text{-}N}$$^{b)}$ (Å)	$R_{Ti\text{-}Ti}$$^{b)}$ (Å)	$\sigma^2_{Ti\text{-}N}$$^{c)}$ ×10^3 (Å^2)	$\sigma^2_{Ti\text{-}Ti}$$^{c)}$ ×10^3 (Å^2)	R factor$^{d)}$
TiN`	3.4	5.4	2.111	2.986	7.4	6.4	0.0293
TiN/GR	3.3	4.6	2.105	2.978	10.0	8.1	0.0257
TiN/CNT	3.8	4.9	2.103	2.974	12.1	8.6	0.0262
TiN/CNT-GR	3.6	5.2	2.104	2.976	10.6	9.0	0.0216

$^{a)}$coordination number (max. ±0.5); $^{b)}$bond distance (max. ±0.003), $^{c)}$Debye-Waller factor (max. ±0.002); d)a sum-of-squares measure of the fractional misfit.

Table S3. The activities of nitride-based materials for ORR.

Catalyst	Onset potential (V vs RHE)	Activity @ 0.7V (mA/cm^2)	Reference
Mo_2N/C	0.7	0	14
W_2N/C	0.6	0	15
TaON	0.8	-0.005	7
Zr,Nb,Ta-CNO	above 0.85	-0.1	13
TiN/CB	0.84	-0.6	12
TiN/CNT-GR	0.83	-1.4	present work

Fig. S7. a) LSV results of synthesized TiN-based catalysts with commercial Pt/C (E-TEK) catalyst, b) LSV results of TiN/CNT-GR catalyst before and after 500 cycles of potential sweep between 0.6~1.0 V at 50mVs^{-1}.

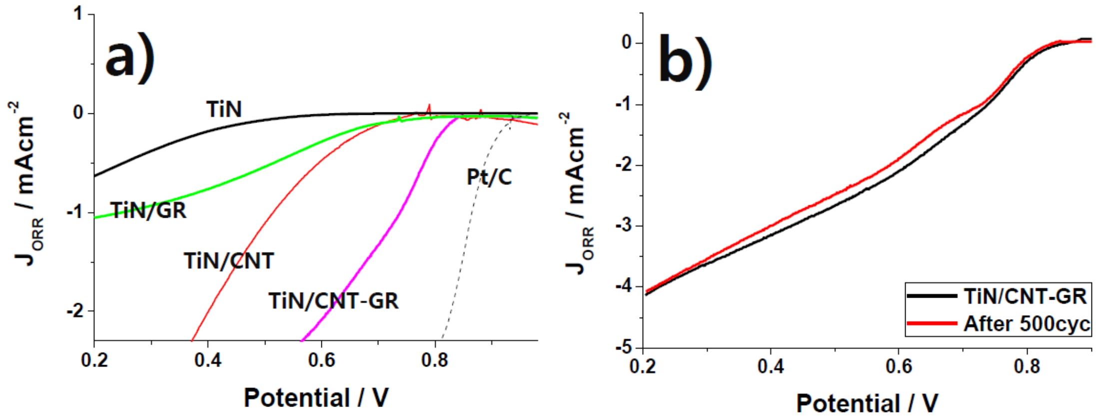


Fig. S8. LSV results of a) TiN, b) urea/CNT-GR (nitrogen-doped carbon), and c) physically mixed TiN with CNT-GR (TiN-CNT-GR) in 0.5 M H_2SO_4. (Dotted lines under O_2; solid lines under N_2.)

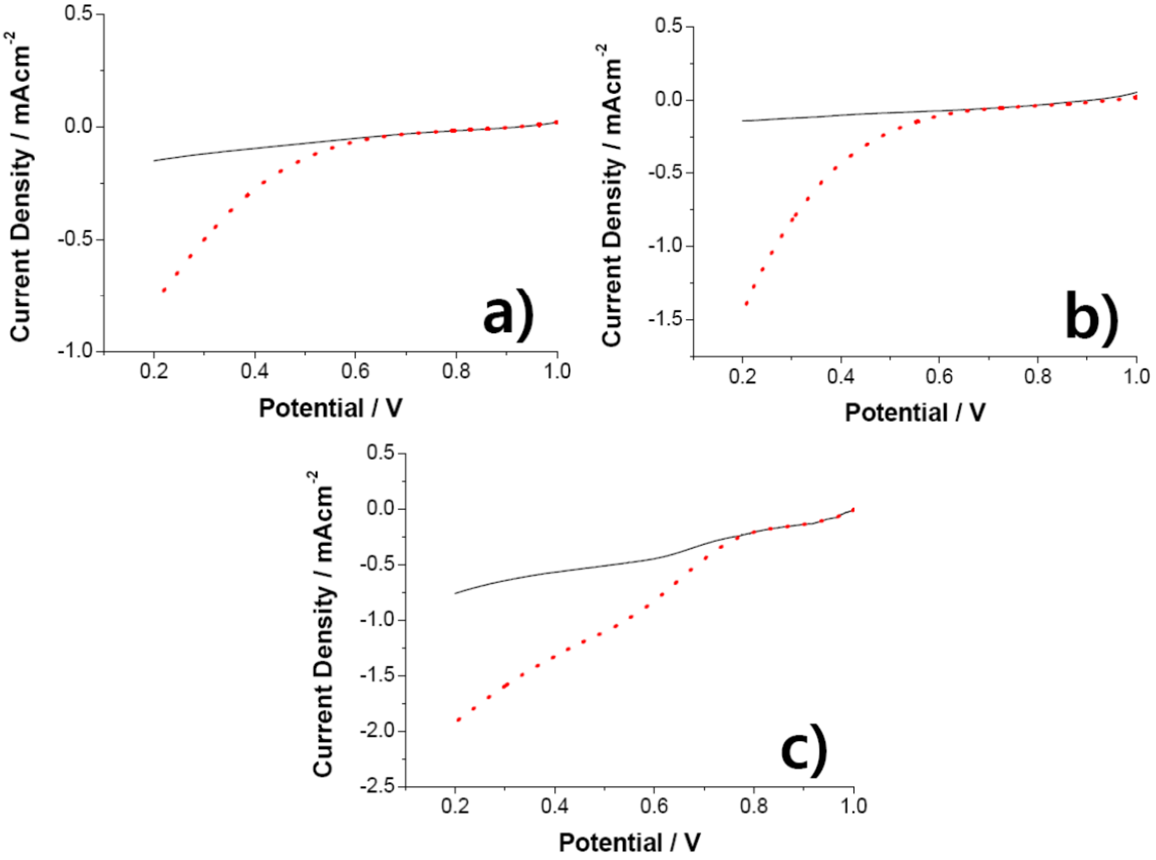


Fig. S9. LSV results of a) TiN, b) urea/CNT (nitrogen doped carbon), and c) physically mixed TiN with CNT (TiN-CNT) in 0.5 M H_2SO_4. (Dotted lines under O_2; solid lines under N_2.)

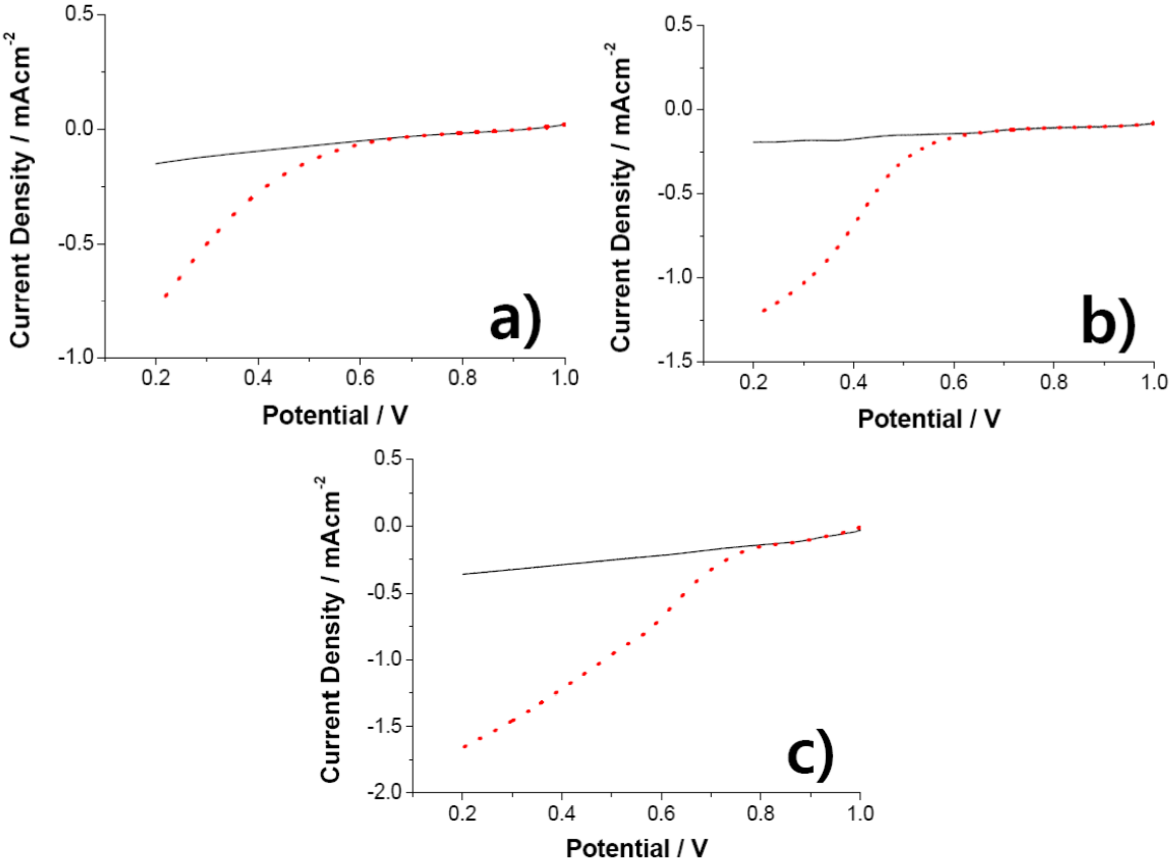


Fig. S10. LSV results of a) TiN, b) urea/GR (nitrogen doped carbon), and c) physically mixed TiN with GR (TiN-GR) in 0.5 M H_2SO_4. (Dotted lines under O_2; solid lines under N_2.)