Supporting Information for

## Defects tailoring $IrO_2$ (a) $TiN_{1+x}$ nano-heterojunction for superior water oxidation activity and stability

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Fig. S2 (a) TEM and (b) HRTEM images of  $IrO_2$ .



Fig. S3 EDS spectrum and the corresponding element contents of (a)  $IrO_2/TiN$  and (b)  $IrO_2/TiN_{1+x}.$ 



Fig. S4 EPR spectra of  $IrO_2/TiN$  and  $IrO_2/TiN_{1+x}$ .



Fig. S5 High-resolution of (a) Ir 4f, (b) Ti 1 s, (c) O1s and (d) N 1 s XPS spectra.



Fig. S6 CV curves of (a)  $IrO_2$ , (b)  $IrO_2$ @TiN, and (c)  $IrO_2$ @TiN<sub>1+x</sub> measured within the range of 0.87–0.97 V vs. RHE, (d) corresponding plots of the current densities at 0.919 V vs. RHE with the different scan rates.



Fig. S7 CV curves of (a) TiN, (b)  $TiN_{1+x}$  measured within the range of 0.87–0.97 V vs. RHE, (d) corresponding plots of the current densities at 0.919 V vs. RHE with the different scan rates.



Fig. S8 (a) Mass activity and (b) specific activity of the prepared samples.



Fig. S9 IrO<sub>2</sub>@TiN<sub>1+x</sub> at the current densities of 10, 50, 100 mA cm<sup>-2</sup> for 10 h.



Fig. S10 (a) TEM and (b) HRTEM of  $IrO_2@TiN_{1+x}$  after 100 h stability test.



Fig. S11 The optimized models of (a) IrO<sub>2</sub>@TiN and (b) IrO<sub>2</sub>@TiN<sub>1+x</sub>.