Electronic Supplementary Information

Influence of carbon doping concentration on photoelectrochemical activity of

TiO₂ nanotube arrays under water oxidation

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Fig. S1 TEM images of (a) undoped TNAs, (b) 2 h treated CTNAs, (c) 4 h treated CTNAs.



Fig. S2 EDX spectra of (a) undoped TNAs and (b) 16 h treated CTNAs



Fig. S3 Raman spectra of undoped TNAs and various CTNAs using 514 nm radiation. (a) Anatase TNAs have E_g modes at 144, 196, and 638.5 cm⁻¹, a doublet of A_{1g} and B_{1g} modes at 517 cm⁻¹, and B_{1g} at 395 cm⁻¹. (b) Raman spectra of the carbon D band at 1376 cm⁻¹ and the D' band at 1666 cm⁻¹.



Fig. S4 (a) XPS survey spectra of undoped TNAs and CTNAs photoelectrodes and (b) C/Ti atomic ratio (%)



Fig. S5 X-ray photoelectron spectroscopy of (a) carbon 1s and (b) oxygen 1s.



Fig. S6 Photographs of (a) the undoped TNAs, (b) 2 h treated CTNAs, (c) 4 h treated CTNAs, and (d) 8 h treated CTNAs that were anodized on Ti foil.



Fig. S7 (a) Photograph of CTNAs that were anodized on quartz. The opaque portion surrounded by the red dotted rectangle is the TNA. (b) Scanning electron microscopy image of TNAs on quartz.



Fig. S8 Photoconversion efficiency of each sample at an external potential of 1.5 eV versus RHE while under 100 mW cm⁻² of white light. Cyclic voltammetry (CV) was run at a scan rate of 1 mV s⁻¹, and the average of the two potentials at the point where the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reaction.



Fig. S9 Photoconversion efficiency of each sample at an external potential of 1.5 eV versus RHE while under 100 mW cm⁻² of white light.

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Sample	Carbon contents (wt.%)
Undoped CTNAs	0.056
2 hour CTNAs	0.170
4 hour CTNAs	0.172
8 hour CTNAs	0.208
16 hour CTNAs	0.319

Table S2 Atomic % ratio of Ti, O, and C in the XPS spectrum and % area carbonates (O–C–O and O–C=O) calculated from the C1s peak.

Sample	Atomic % of Ti (Ti2p)	Atomic % of O (O1s)	Atomic % of C (C1s)	% area carbonates
Undoped CTNAs	28.07	62.18	9.75	43.9
2 hour CTNAs	27.65	59.53	12.82	48.8
4 hour CTNAs	26.59	58.61	14.80	51.78
8 hour CTNAs	24.92	55.27	19.81	55.91
16 hour CTNAs	23.72	53.29	22.99	62.49