

## Supplementary information

# Three-Dimensional Construction of Electrode Materials Using TiC Nanoarrays Substrates for Highly Efficient Electrogeneration of Sulfate Radicals and Molecular Hydrogen in a Single Electrolysis Cell

Sung-Woo Park,<sup>†<sup>a</sup></sup> Eun-Tae Yun,<sup>†<sup>a</sup></sup> Hyun Jung Shin,<sup>a</sup> Wooyul Kim,<sup>b</sup> Jaesang Lee<sup>a</sup> and Dong-Wan Kim<sup>\*a</sup>

<sup>a</sup>School of Civil, Environmental and Architectural Engineering, Korea University, Seoul 02841, South Korea

<sup>b</sup>Department of Chemical and Biological Engineering, Sookmyung Women's University, Seoul 04310, South Korea

\* Corresponding author. Tel.: +82 2 3290 4863; fax: +82 2 3290 5999; E-mail: dwkim1@korea.ac.kr (D.-W. Kim)

† These authors contributed equally to this article.

**Table S1.** Comparison of PDS generation capability of BDD@TiC NWs with recently reported BDD anodes.

Cell configuration					PDS generation			Ref.
Anode (dopant conc. / area)	Cathode	Electrolyte	pH	Volume (L)	Applied current density (mA cm <sup>-2</sup> )	PDS conc. (mol L <sup>-1</sup> )	Time	
BDD@TiC NWs (8,000 ppm / 1 cm <sup>2</sup> )	Platinum	0.1 M Na <sub>2</sub> SO <sub>4</sub>	6.5	0.05	44 (@ 4.5 V)	1.97	1 hour	This work
BDD (8,000 ppm / 1 cm <sup>2</sup> )					25 (@ 4.5 V)	0.45	1 hour	
BDD (8,000 ppm / 6 cm <sup>2</sup> )	Graphite	0.8 M Na <sub>2</sub> SO <sub>4</sub>	-	0.08	30	4 - 4.5	1 hour	S1
BDD (8,000 ppm / 7.5 cm <sup>2</sup> )	Platinum	0.1 M Na <sub>2</sub> SO <sub>4</sub>	3	-	20	0.15 - 0.2	10 min.	S2
BDD (- ppm / 7.065 cm <sup>2</sup> )	Titanium	0.4 M Na <sub>2</sub> SO <sub>4</sub>	9	0.15	30	21.25	5 hours	S3
BDD (- ppm / 12.5 cm <sup>2</sup> )	Platinum	0.1 M Na <sub>2</sub> SO <sub>4</sub>	5	0.1	30	1.4 - 1.6	3 hours	S4
BDD (- ppm / 63 cm <sup>2</sup> )	Zirconium	2.0 M H <sub>2</sub> SO <sub>4</sub>	-	1	40	0.15	5 hours	S5
BDD (- ppm / 10 cm <sup>2</sup> )	Titanium	0.03 M Na <sub>2</sub> SO <sub>4</sub>	5	0.16	10	0.25 - 0.3	40 min.	S6

Ref.

- S1. T. Niu, J. Cai, P. Shi and G. Zhao, *Chem. Eng. J.*, 2020, **386**, 123971.
- S2. L. Chen, C. Lei, Z. Li, B. Yang, X. Zhang and L. Lei, *Chemosphere*, 2018, **210**, 516-523.
- S3. F. Zhang, Z. Sun and J. Cui, *RSC Adv.*, 2020, **10**, 33928.
- S4. J. Cai, T. Niu, P. Shi and G. Zhao, *Small*, 2019, **15**, 1900153.
- S5. J. Cai, M. Zhou, Y. Liu, A. Savall, K. G. Serrano, *Chemosphere*, 2018, **204**, 163-169.
- S6. Y.-U. Shin, H.-Y. Yoo, Y.-Y. Ahn, M. S. Kim, K. Lee, S. Yu, C. Lee, K. Cho, H.-I. Kim, J. Lee, *Appl. Catal. B-Environ.*, 2019, **254**, 156-165.

**Table S2.** Comparison of HER activity of Pt@C@TiC NWs with recently reported Pt-based composite catalysts.

Catalyst	Electrolyte	Overpotential (mV)	Current density (mA cm <sup>-2</sup> )	Tafel slope (mV dec <sup>-1</sup> )	Pt in catalyst (wt. %)	Total Pt loading mass (mg cm <sup>-2</sup> )	Ref.
Pt@C@TiC NAs		33.1		31.2	-	0.029	This work
Pt@TiN NAs		39.7		38.6	0.087	-	S7
Pt/LSG	0.5 M H <sub>2</sub> SO <sub>4</sub>	131	10	72	20 - 23	0.04	S8
Pt/def- WO <sub>3</sub> @CFC		42		101	-	-	S9
Mo <sub>2</sub> C@NC@ Pt		27		28	7.49	-	S10
Pt/G <sub>5</sub> -(MoS <sub>2</sub> ) <sub>5</sub>		33		23	19.1	0.027	S11

Ref.

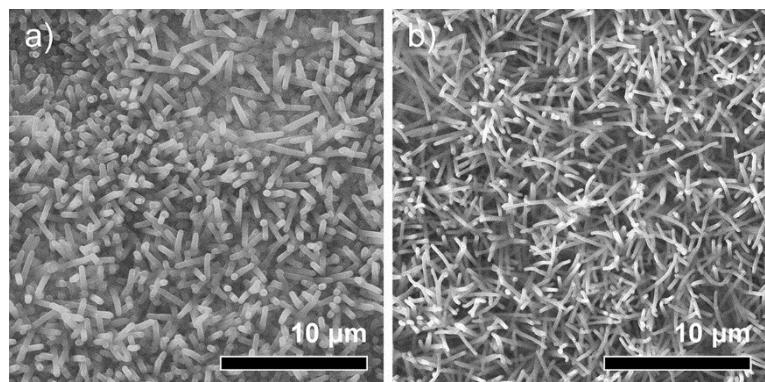
S7. C. Wang, H. Shi, H. Liu, J. Fu, D. Wei, W. Zeng, Q. Wan, G. Zhang and H. Duan, *Electrochim. Acta*, 2018, **292**, 727-735.

S8. P. Nayak, Q. Jiang, N. Kurra, X. Wang, U. Buttner and H. N. Alshareef, *J. Mater. Chem. A*, 2017, **5**, 20422.

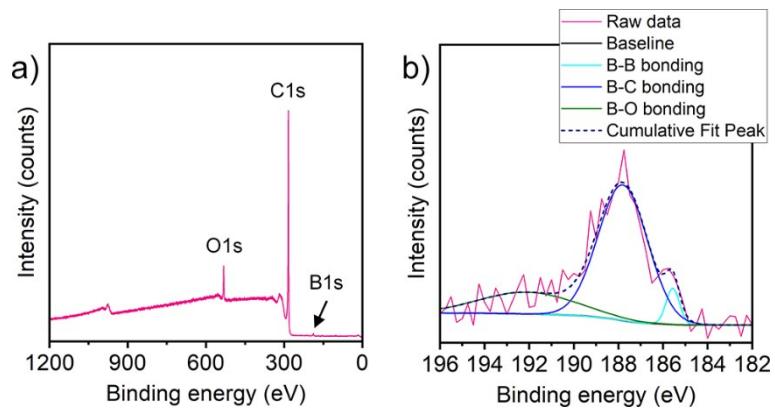
S9. H. Tian, X. Cui, L. Zeng, L. Su, Y. Song and J. Shi, *J. Mater. Chem. A*, 2019, **7**, 6285.

S10. J.-Q. Chi, J.-Y. Xie, W.-W. Zhang, B. Dong, J.-F. Qin, X.-Y. Zhang, J.-H. Lin, Y.-M. Chai and C.-G. Liu, *ACS Appl. Mater. Interfaces*, 2019, **11**, 4047-4056.

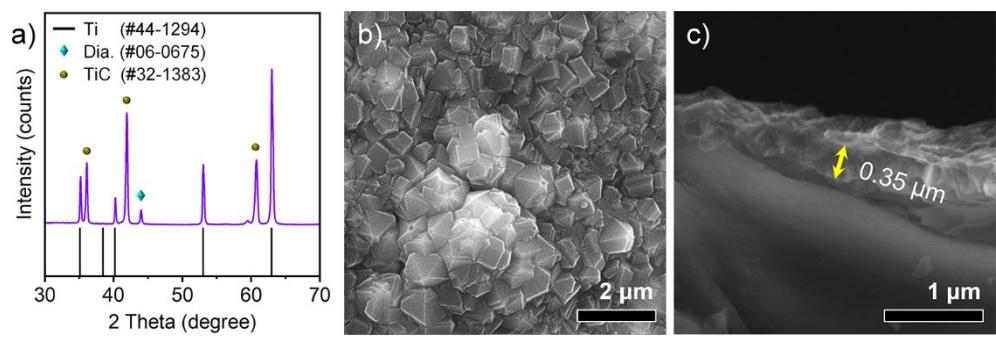
S11. Z. Gao, M. Li, J. Wang, J. Zhu, X. Zhao, H. Huang, J. Zhang, Y. Wu, Y. Fu and X. Wang, *Carbon*, 2018, **139**, 369-377.



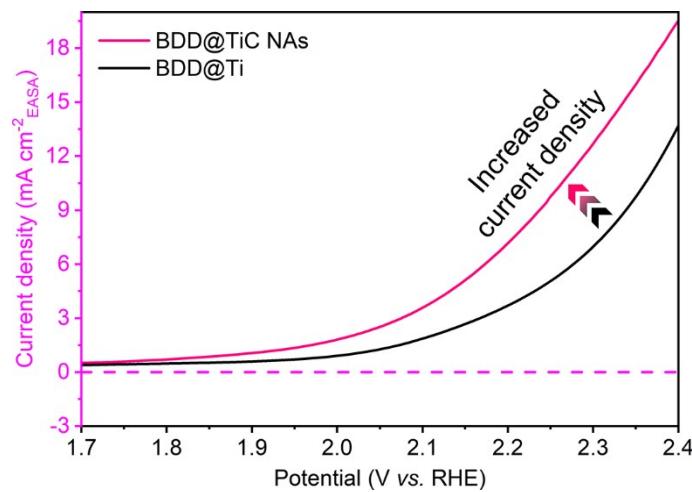
**Figure S1.** SEM images of C@TiC NAs prepared using a) N<sub>2</sub>-purged acetone and b) air-purged acetone.



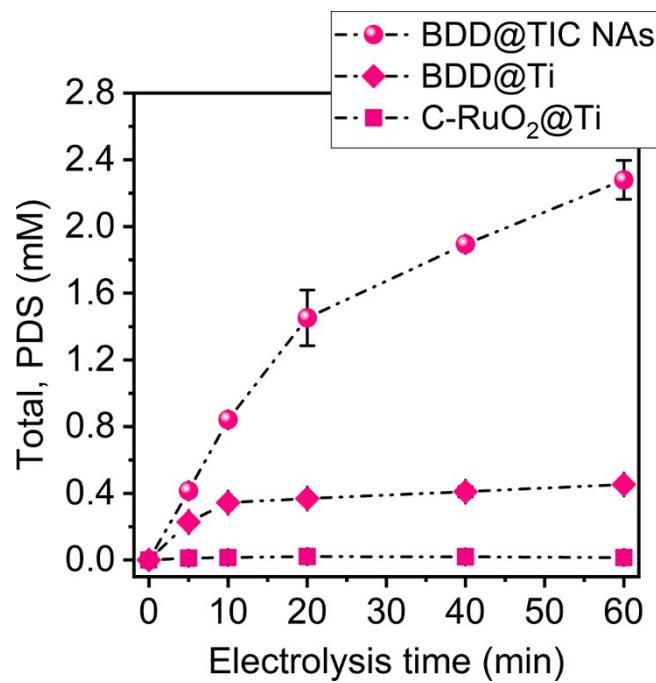
**Figure S2.** a) XPS survey spectrum and b) deconvoluted B1s narrow spectrum of BDD@TiC NAs.



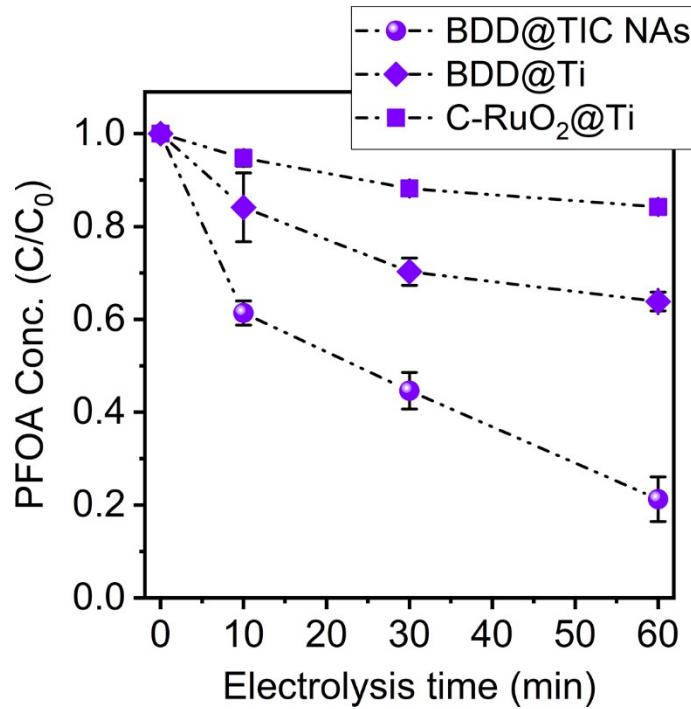
**Figure S3.** a) XRD pattern of flat BDD@Ti. b and c) Top-view and cross-section SEM images of BDD@Ti.



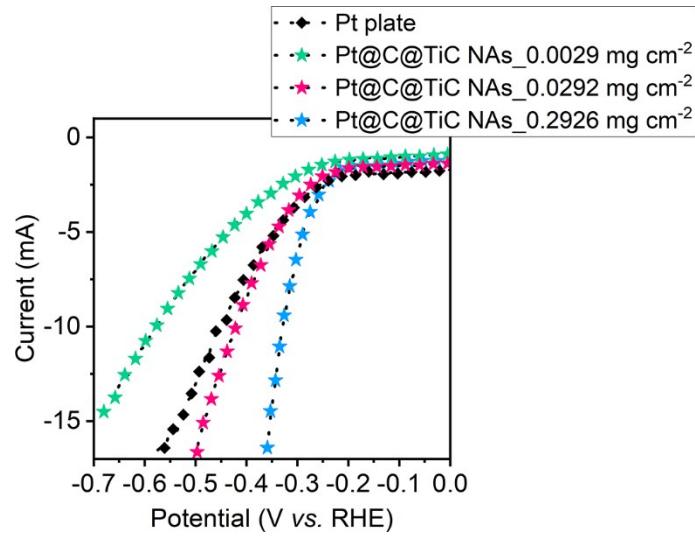
**Figure S4.** Magnified CV curves at initial OER step (current adjusted by ECSA).



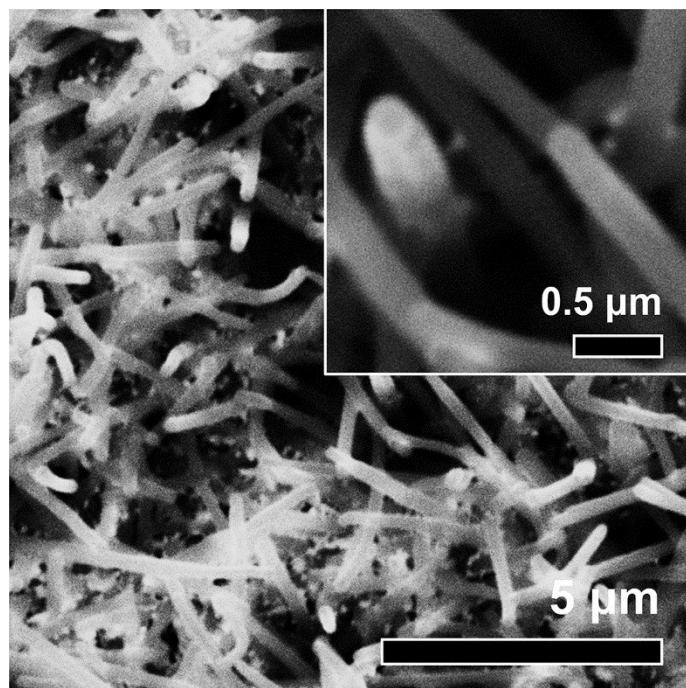
**Figure S5.** Time-dependent concentration profiles of PDS measured by ion chromatography.



**Figure S6.** Degradation efficiencies for PFOA at each electrode ( $[\text{Na}_2\text{SO}_4]_0 = 0.1 \text{ M}$ ,  $[\text{PFOA}]_0 = 0.1 \text{ mM}$ , [applied voltage] = 4.5 V).



**Figure S7.** LSV curves of each electrode measured in 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH = 6.5).



**Figure S8.** SEM images of Pt@C@TiC NAs\_0.29.