

***Supporting information***

Nano-sized TiN on Carbon Black as an Efficient  
Electrocatalyst for the Oxygen Reduction  
Reaction Prepared using an mpg-C<sub>3</sub>N<sub>4</sub> Template

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## Experimental details

**Synthesis of mpg-C<sub>3</sub>N<sub>4</sub>/CB composite:** Uniformly-porous mpg-C<sub>3</sub>N<sub>4</sub> was first produced on CB (Vulcan XC-72R, Cabot Corp.) from cyanamide (CA; 99%, Aldrich) dissolved in a 40 wt% water dispersion of an aqueous silica solution composed of 12-nm silica spheres (Ludox HS-40, Aldrich). The weight ratio of CA to silica was kept at unity, and the ratio of (CA + silica) to CB was 10 wt% while maintaining the weight of CB at 2.0 g. After stirring the solution for 1 h, the mixture was heated to 343 K with stirring to ensure slow evaporation of the water. The resulting solid was heated in a closed ceramic crucible at a rate of 2.3 K min<sup>-1</sup> for 4 h to reach 823 K, and then held at this temperature for 4 h. Removal of the silica by washing with a 4 M NH<sub>4</sub>HF<sub>2</sub> solution yielded a mpg-C<sub>3</sub>N<sub>4</sub>/CB composite.

**Synthesis of TiN/CB:** Titanium (IV) chloride (1.08 g, Wako Chemicals) was slowly added to 2.0 g of ethanol. To this solution, 1.35 g of the prepared mpg-C<sub>3</sub>N<sub>4</sub>/CB was added. After 1 h, complete penetration of the solution into the mesoporous framework was assumed. The infiltrated mpg-C<sub>3</sub>N<sub>4</sub>/CB composite was collected by suction filtration and washed twice with ethanol. The resulting powder was heated at a rate of 3.25 K min<sup>-1</sup> over 4 h to 1073 K, and then kept at this temperature for 3 h under N<sub>2</sub> flow.

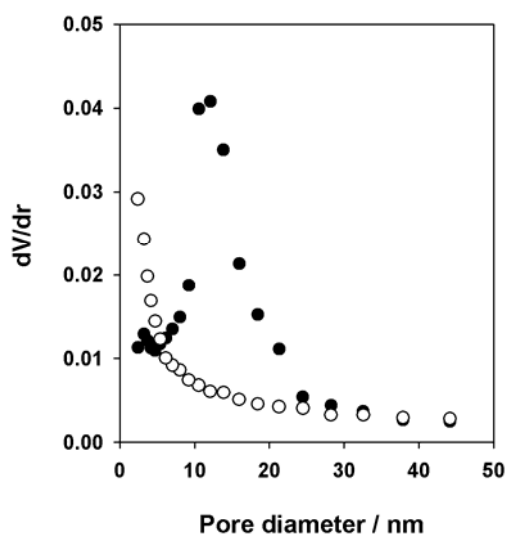
**Electrochemical measurement:** An ink of the powder catalysts was prepared as follows. The prepared catalyst (5 g) was suspended in a mixture of 1 mL of ethanol and 0.05 mL of 5% Nafion solution (Sigma-Aldrich) under ultrasonication for 15 min. A 50  $\mu$ L aliquot of the suspension was then dropped onto a hydrophobic carbon paper (10  $\times$  10 mm; TGP-H-120, Toray), used as received, and dried at 393 K under static air. Electrochemical measurements were conducted in 100 mL of 0.1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution at 303 K using a potentiostat (HSV-100 or HZ-5000, Hokuto Denko). A carbon sheet and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The Ag/AgCl electrode was calibrated using a reversible hydrogen electrode (RHE), which consisted of a Pt electrode and hydrogen gas at 1 atm, and all potentials are expressed against RHE in this paper. After bubbling with N<sub>2</sub> for 30 min to remove dissolved O<sub>2</sub>, cyclic voltammogram measurements were conducted between 0.11 and 1.26 V vs. RHE at a scan rate of 50 mV s<sup>-1</sup> and a temperature of 303 K. The oxidation and reduction cycles were repeated 10 times to ensure stabilization of the sample electrode. To examine ORR performance, slow-scan linear-sweep voltammograms were recorded from 1.26 V vs. RHE at a scan rate of -5 mV s<sup>-1</sup> after bubbling with N<sub>2</sub> or O<sub>2</sub> gas for 30 min.  $i_{\text{ORR}}$  denotes the difference in current under O<sub>2</sub> and N<sub>2</sub> atmospheres.

**Single-cell test:** A single cell (membrane-electrode-assembly, MEA) was prepared using TiN/CB and Pt/CB for the cathode and anode catalysts, respectively. The TiN/CB catalyst (2 mg cm<sup>-2</sup>) was loaded on a carbon sheet substrate (gas-diffusion layer) to a catalyst layer thickness of  $\sim$ 35  $\mu$ m. A Nafion 212 proton-membrane was employed, and the total electrode area of the MEA was 5 cm<sup>2</sup>. Pt/CB catalyst for the anode was obtained from Tanaka Kikinzo Kogyo (TEC10E50E, 50 wt% Pt, 0.3 mg-Pt cm<sup>-2</sup>). The temperature of the entire cell was maintained at 363 K and H<sub>2</sub> (anode)

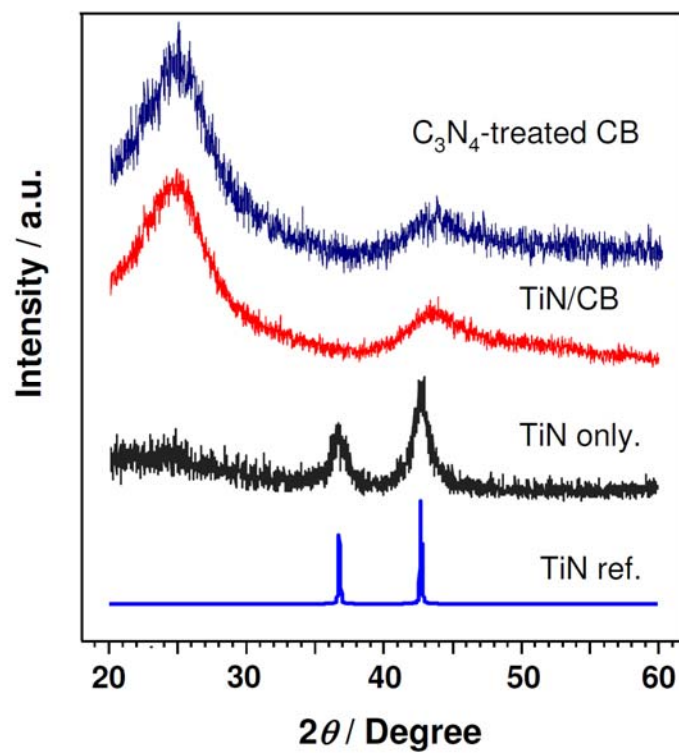
Supplementary Material (ESI) for Chemical Communications  
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and O<sub>2</sub> (cathode) flows, humidified at 363 K under backpressures of 0 and 0.3 MPa, were used at flow rates of 500 cm<sup>3</sup> min<sup>-1</sup>.

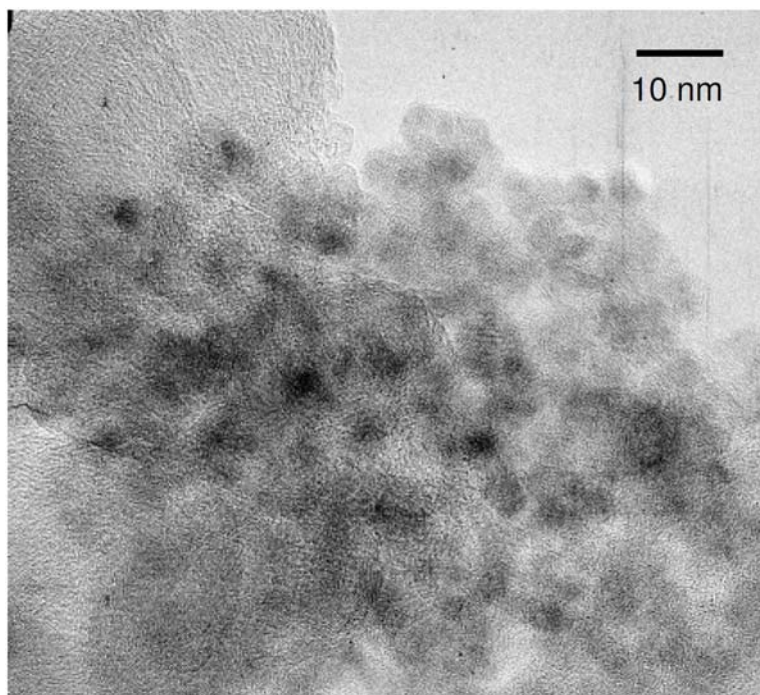
**Characterization:** Observation of samples was performed using a transmission electron microscopy (TEM; JEM-2010F, JEOL). The crystal structure of the sample was investigated by X-ray diffraction (XRD; RINT-Ultima III, Rigaku). Thermogravimetric analysis was carried out for the TiN/CB samples using a Rigaku Thermoplus TG8120 to obtain the loading amounts of Ti.



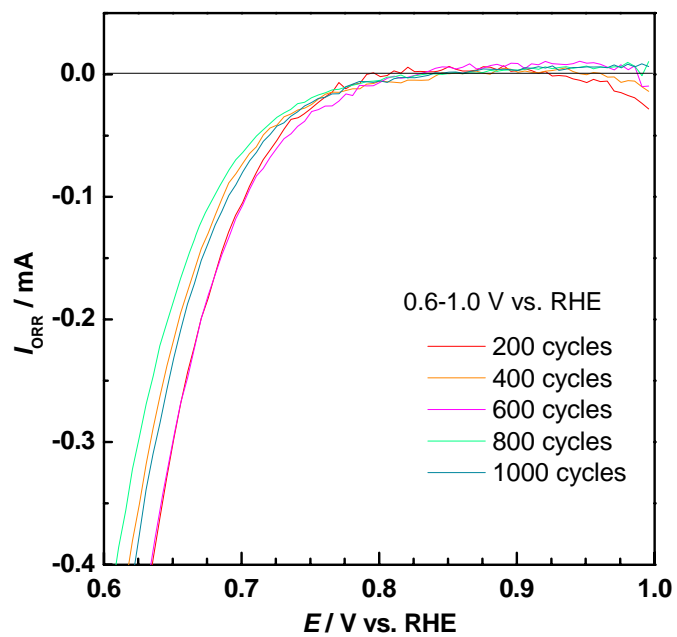
**Figure S1.** Pore size distribution of CB (open circles) and mpg-C<sub>3</sub>N<sub>4</sub>/CB composite (closed circles).



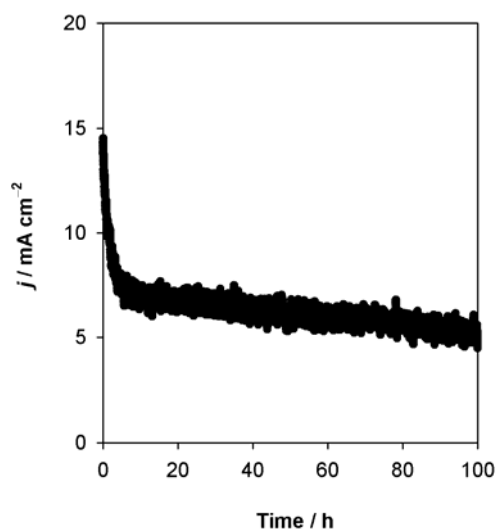
**Figure S2.** XRD patterns for TiN-nanoparticles, TiN/CB composite and C<sub>3</sub>N<sub>4</sub>-treated CB.



**Figure S3.** TEM image of TiN/CB composite prepared by impregnation of TiN nanoparticles on CB.



**Figure S4.** Voltammograms for the ORR on the TiN/CB sample, after charging-discharging cycles under  $\text{N}_2$  atmosphere between 0.6 and 1.0 V vs. RHE, in 0.1 M  $\text{H}_2\text{SO}_4$  at 303 K.



**Figure S5.** Potentiostatic coulometry using the single cell containing a TiN/CB cathode for durability test at 0.6 V. The cathode and anode catalysts were TiN/CB and Pt/CB, respectively. The temperature of the entire cell: 363 K; H<sub>2</sub> (anode) and O<sub>2</sub> (cathode) flows: 500 cm<sup>3</sup> min<sup>-1</sup>, humidified at 363 K under no backpressures.