Supplementary Information

1. Experimental methods

Preparation of the TNFs: TNFs were first prepared by a two-step thermal treatment of the electrospun polyvinylpyrrolidone (PVP)/titanium tetraisopropoxide $Ti(O^iPr)_4$ composite nanofibers which were made via electrospinning process. For the precursor, a solution containing 2 g PVP (MW ≈ 1,300,000), 4 ml of acetic acid and 2 ml $Ti(O^iPr)_4$ were added to 14 ml ethanol and stirred until completely dissolved. The solutions were degassed by sonication for 5 min and then mixed together. Briefly, the electrospinning process was performed in an electric field of 200 kV m^{-1}, generated by application of 20 kV voltage to a 10 cm gap between the spinneret and the collector.

Then, the prepared PVP/$Ti(O^iPr)_4$ composite nanofibers were heat-treated in a high-temperature furnace by the following steps: 1) annealing in air for 1h at 700°C for the shape stabilization of nanofibers and complete oxidation of the polymer PVP, 2) heating up to 900°C in NH_3 at a rate of 5°C min^{-1} for the nitridation, and then cooling down to room temperature in Ar.

Preparation of Pt catalysts: To apply the prepared TNFs to PEMFC electrocatalyst, we decorated the prepared TNFs with Pt NPs. Pt NPs were prepared by polyol method. 0.0332 g of $H_2PtCl_6 \cdot H_2O$ was dissolved in ethylene glycol. The TNFs support was dispersed in ethylene glycol and then mixed by adding metal salt solution with vigorous stirring. Afterwards, sodium hydroxide (NaOH) was added to control the size of Pt NPs by adjusting the pH of solution (>12). The solution was stirred well before heating at 160°C for 3 h in an Ar atmosphere under refluxing conditions. The solution was stirred overnight at room temperature and washed with copious amount of distilled water. The prepared electrocatalyst was dried in air at 40°C for 12 h and then calcined in air at 200°C for 1 h to remove any organic residues.

Preparation of electrocatalysts ink: In a typical procedure, 0.05 mL of Pt/TNF in isopropylalcohol was dispersed in a mixture containing 0.45 mL of isopropylalcohol, (0.5 mL of water), and 5 μL of Nafion solution (5 wt%, Aldrich). This mixture was then sonicated for 10 min. The amount of Pt in Pt/TNF samples was determined using inductively coupled plasma (ICP) analysis. The solid content of Pt/TNF in ethanol was quantified using a thermo gravimetric analyzer (TGA) from TA Instrument, Inc. (model SDT Q600). To prepare catalyst membrane, a specific volume of the above mixture of Pt/TNF was measured and drop-cast onto a glassy carbon electrode (5 mm in diameter) and dried gently under airflow. The Pt/C catalyst (20 wt% Pt on carbon black, Tanaka) was prepared using the same procedure as that for the Pt/TNF samples.

Electrochemical measurements: Electrochemical measurements were carried out in a half-cell using an AutoLab PGSTAT 302N potentiostat and rotating disk electrode (RDE) system with conventional three-electrode configuration at room temperature. All of the electrochemical measurements, except for oxygen reduction reaction (ORR) with RDE configuration, were performed in Ar saturated 0.1M $HClO_4$ solution at a scan rate of 20 mV s^{-1}. For ORR experiment, 99.99% of oxygen was bubbled to the electrolyte for 20 min before every measurement. The RDE rotating rate was 1600 rpm and sweep rate was 5 mV s^{-1}. A saturated calomel electrode and Pt wire were used as a reference and a counter electrode, respectively. All of the potentials, however, were related to reversible hydrogen electrode (RHE). Durability of catalysts was tested by cycling the potentials over 0.6-1.1 V in O_2-saturated 0.1M $HClO_4$ solution.

2. Density functional theory (DFT) calculation

Computational Methodology (DFT) – Spin-polarized density functional theory calculations were performed using the Vienna *ab initio* Simulation Package (VASP)[1-4] with the projector-augmented wave (PAW)[5, 6] method. Electron exchange-correlation functionals were represented with the generalized gradient approximation (GGA), and the model of Perdew, Burke and Ernzerhof (PBE)[7] was used for the nonlocal corrections. A kinetic energy cutoff of 400 eV was used with a plane-wave basis set. Orthorhombic supercells of 8.51 × 8.51 × 22.0 Å and 9.87 × 8.55 × 17.1 Å with periodic boundary conditions were used for the TiN-supported and graphene-supported six Pt atom cluster (Pt_6–TiN and Pt_6–graphene) systems, respectively. The vacuum spaces were larger than 12.0 Å and 6.0 Å for Pt_6–TiN and Pt_6–graphene, respectively. The TiN system consists of 32 Ti and 32 N atoms and the graphene system consists of 32 carbon atoms as described in Figure 1 (A) and (B), respectively.

The Brillouin zone integrations for both systems were conducted using 4 × 4 × 1 Monkhorst-Pack grid[8], with the Gamma (Γ)-point included and the first-order Methfessel-Paxton smearing[9] with a width of 0.1 eV. All atoms were fully relaxed and optimized until the total energy change upon two steps of the electronic self-consistent loop less than 10^{-4} eV. E_{Pt6} is calculated in a 15 Å cubic box with only the Γ-point. The adsorption energies (E_{ads}) of Pt_6 cluster on the surface systems are defined as:

$$E_{ads} = E_{substrate + Pt6} - E_{substrate} - E_{Pt6}$$

where $E_{substrate + Pt6}$, $E_{substrate}$ and E_{Pt6} are the total energies of Pt_6–TiN (or Pt_6–graphene), TiN (or graphene), and Pt_6 cluster, respectively. A negative adsorption energy indicates that adsorption is exothermic with respect to the free Pt_6 cluster.

DFT Results: adsorption of Pt_6 cluster – The adsorption energies (E_{ads}) of Pt_6 cluster were –6.91eV at a hollow site of TiN(100) and –0.82eV at a bridge site of graphene (Table S1). The more negative E_{ads} represents the stronger binding of Pt_6 on the surface. The stronger binding of Pt_6 on TiN(100) is attributed to the stronger interaction between Pt and Ti rather than Pt and N on the surface. As Pt_6 adsorbs on TiN, Pt_6 is strongly distorted due to the significant interaction between Pt and Ti. On the other hand, graphene without any defect shows weak interaction toward Pt.

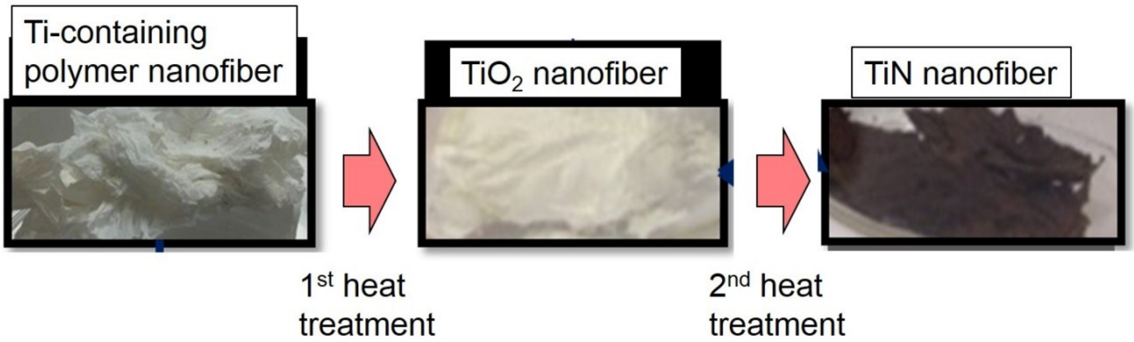

Figure S1. Photographs of as-prepared Ti-containing polymeric electrospun nanofibers, the first heat-treated in 700°C in air for 1h, and the second heat-treated in 900°C in NH_3 for 1h.

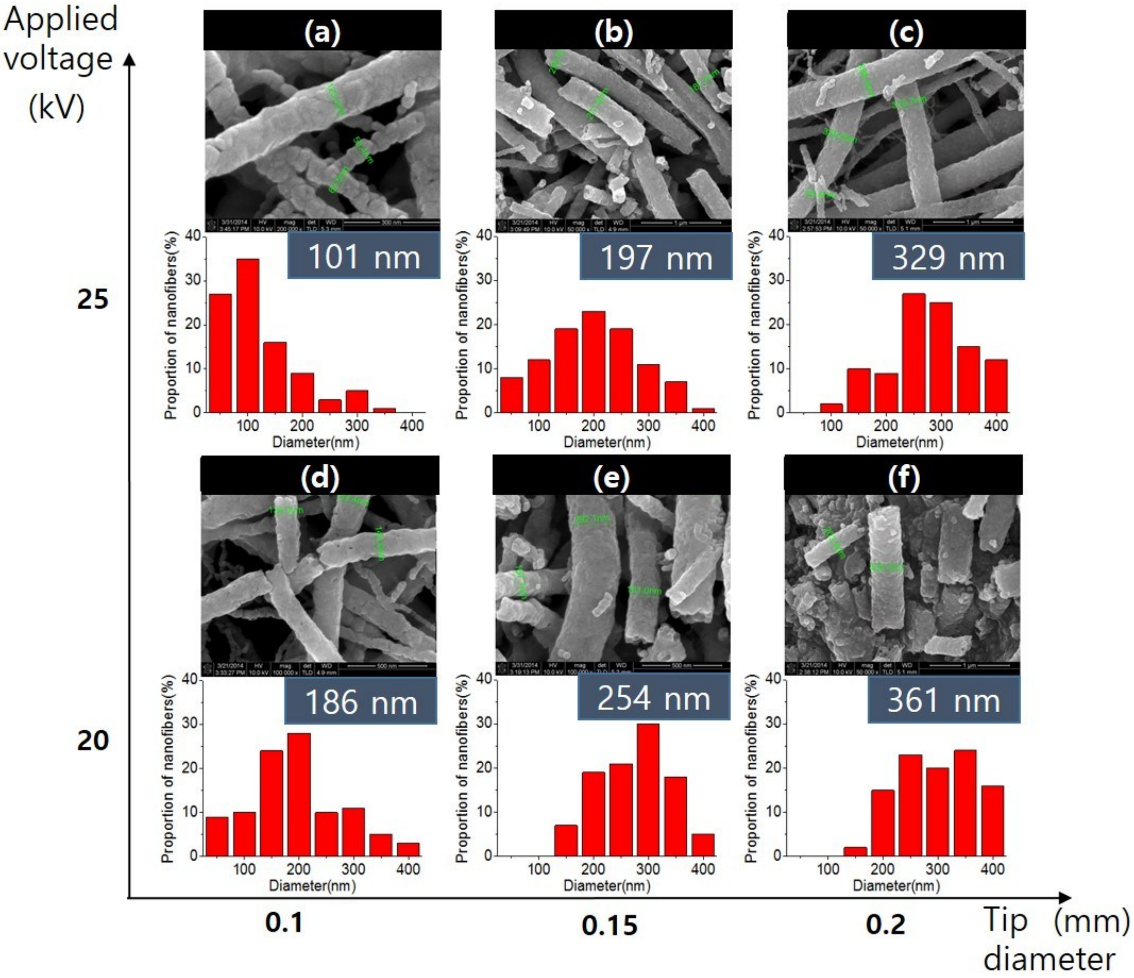

Figure S2. Results showing the dependence of the electrospun nanofiber diameter on the applied voltage and tip diameter: (a) 25 kV, 100 μm, (b) 25 kV, 150 μm, (c) 25 kV, 200 μm, (d) 20 kV, 100 μm, (e) 20 kV, 150 μm, (f) 20 kV, 200 μm. The diameter distribution was obtained from the SEM images of ~ 100 nanofibers.

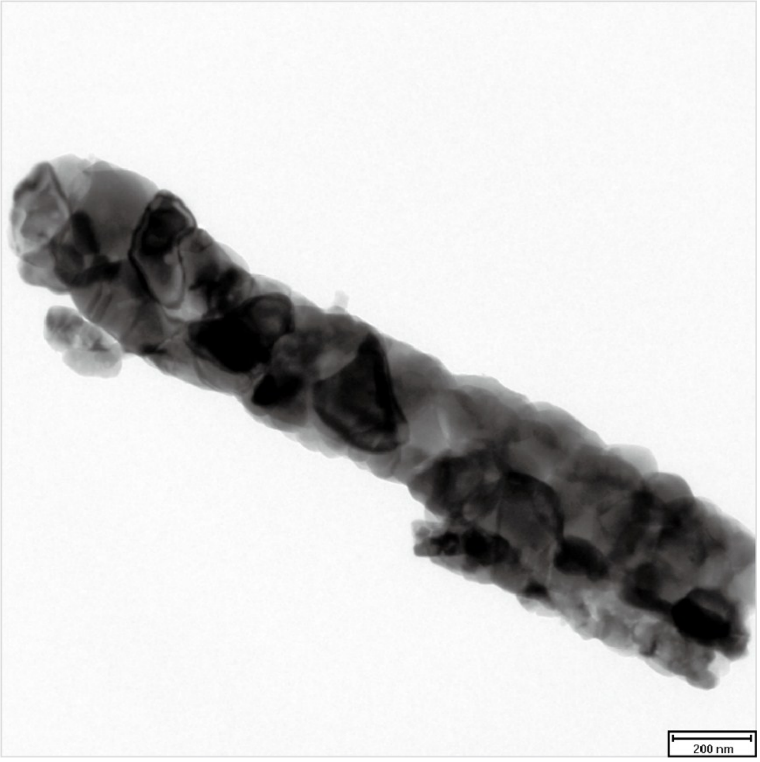

Figure S3. TEM image of TNF.

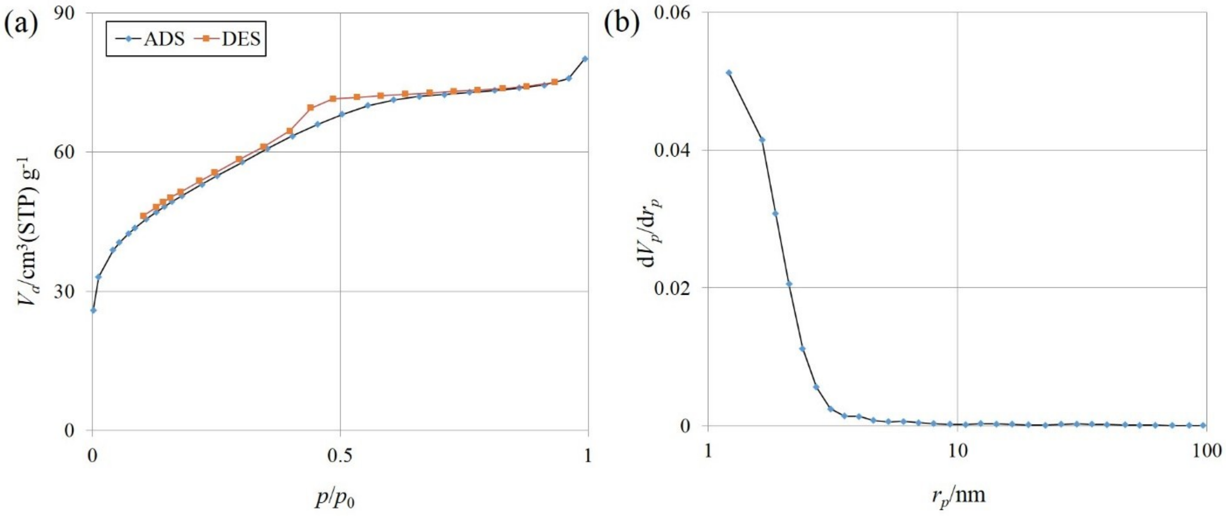

Figure S4. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of the prepared TNF.

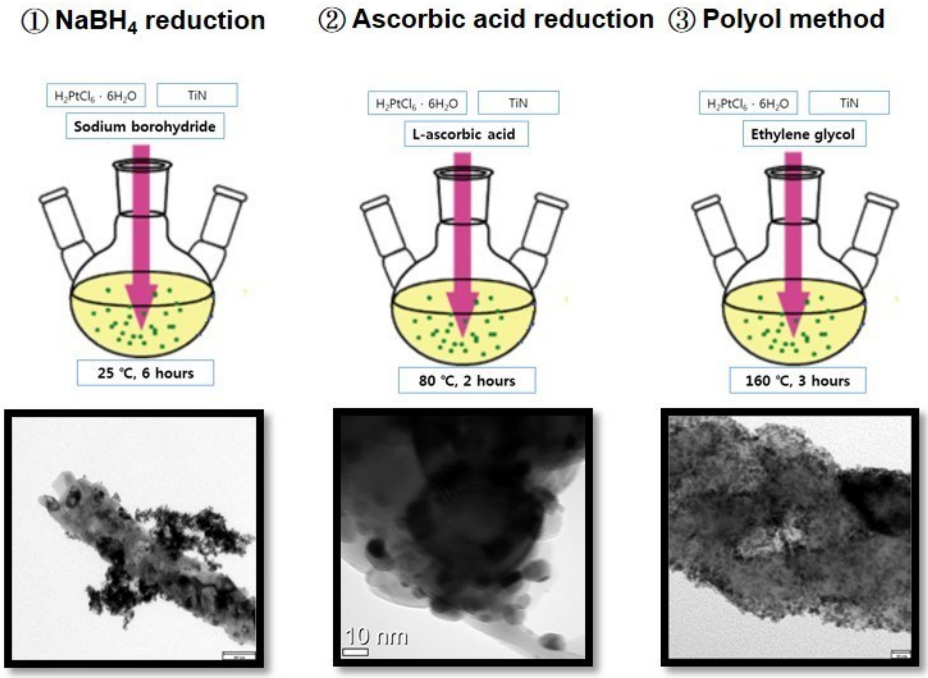

Figure S5. Results depicting the dependence of the Pt NP size/distribution on TNF structure on the used synthetic approach. Among the studied NP synthetic methods, polyol method showed more uniform size distribution and optimal catalyst dispersion of Pt NPs on TNFs than those of other methods.

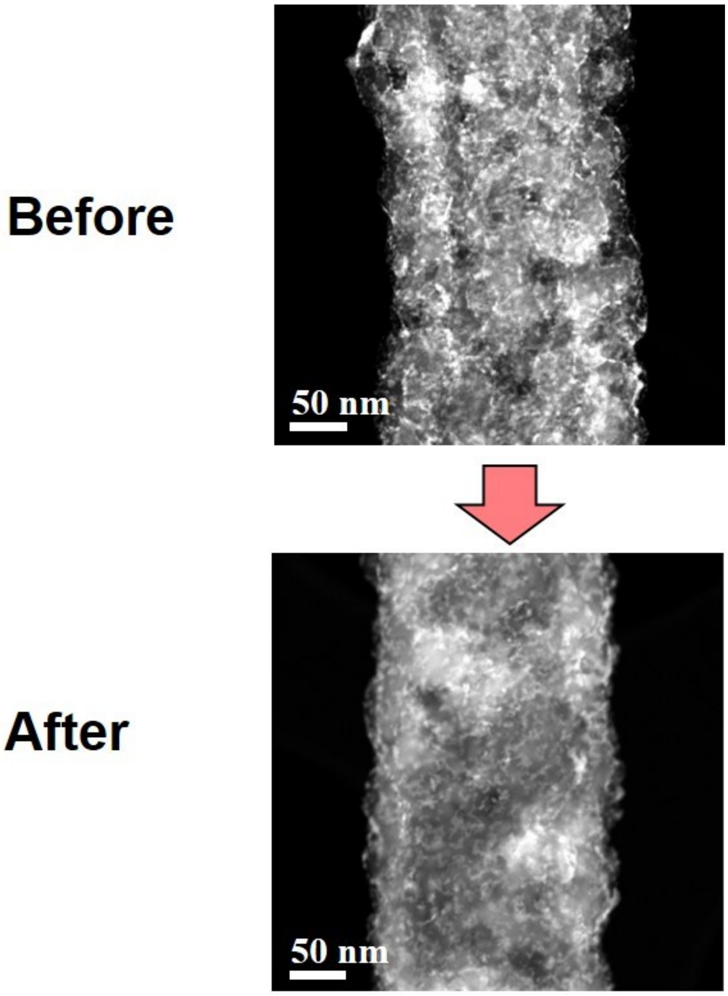

Figure S6. ADF images of Pt/TNF obtained before and after the ADT test.

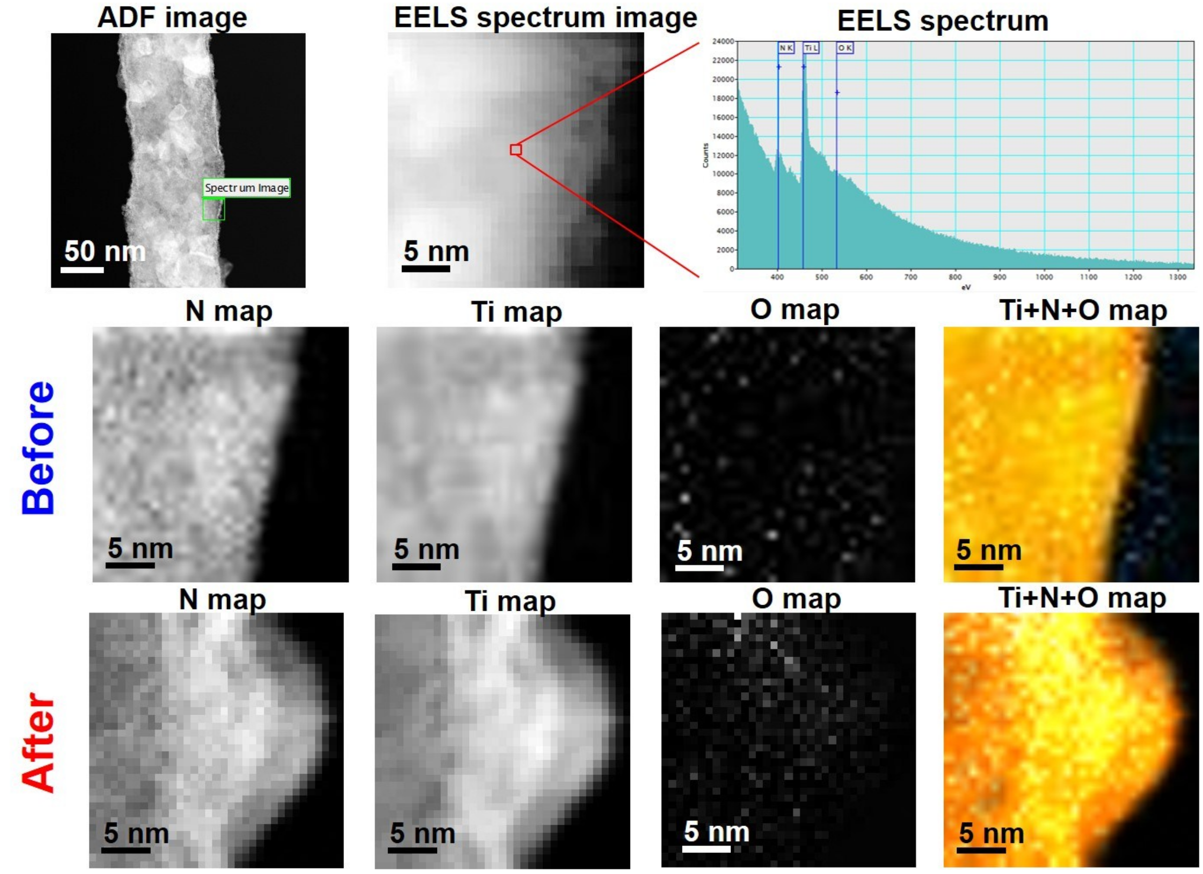

Figure S7. ADF-STEM images and EELS elemental mapping images of Pt/TNF obtained before and after the ADT test. The N K- and Ti L-edge peaks are observed from the EELS signal of the prepared TNF samples, whereas no O K peak was observed. Small white spots shown in O elemental map may originate from some noise signal (e.g. background) near O K region (~530 eV), leading to artifact in data processing of the EELS signal extraction.

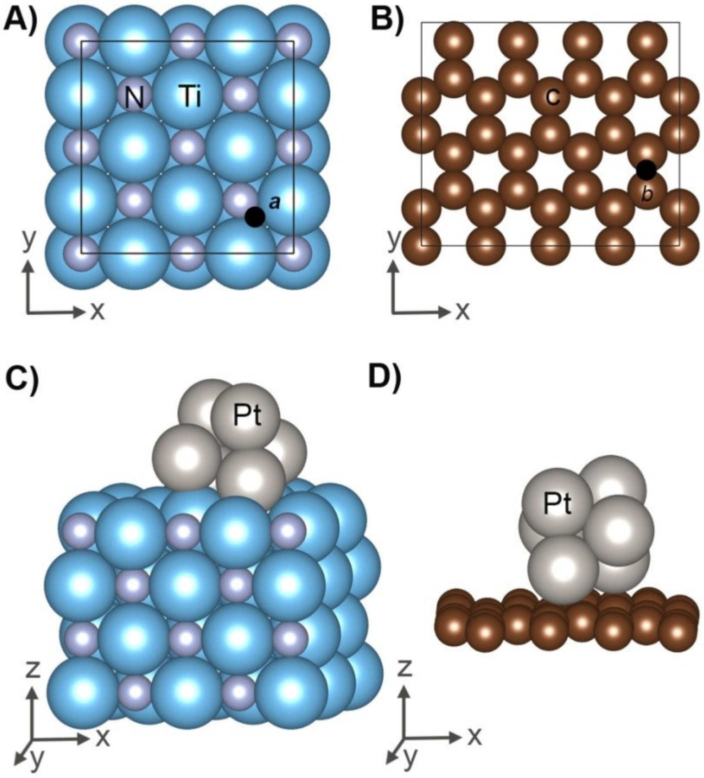

Figure S8. Top views of TiN system (a) and graphene system (b). Side views of optimized Pt_6–TiN (c) and Pt_6–graphene (d). Large cyan, small silver, small brown, and large gray spheres represent Ti, N, C, and Pt, respectively. Filled black circles (a and b) indicate the adsorption site of Pt_6 on TiN and graphene, respectively.

Table S1. Electrical resistance test of the studied samples by four-point probe method.

Sample	Electrical resistance (Ohm square^{-1})
Vulcan carbon	53.98
TiO_2 nanofiber	Not detectable
TiN nanofiber	0.5483

Table S2. BET surface area and pore characteristics of the prepared TNFs.

Sample	Surface area (m^2 g^{-1})	Average pore diameter (Å)	Total pore volume (cm^3 g^{-1})
TiN nanofiber	181.44	27.15	0.1232

Table S3. Adsorption energies (E_{ads}) of Pt_6 cluster on TiN and graphene.

Supporting Materials	E_{ads} (eV)
TiN	–6.91
Graphene	–0.82

References

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