

Dopamine-induced Pt and N-doped carbon@silica hybrids as a high-performance anode catalyst of polymer electrolyte membrane fuel cell

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Experimental Section

Materials

Tetraethylorthosilicate (98%, TEOS, Sigma–Aldrich), ammonium hydroxide (28 ~ 29%, NH₄OH, Sigma–Aldrich), ethanol (Sigma–Aldrich), dopamine hydrochloride (DA, Sigma–Aldrich), tris(hydroxymethyl)aminomethane (TRIS, Sigma–Aldrich) and chloroplatinic acid hydrate (H₂PtCl₆•xH₂O, Sigma–Aldrich) were purchased. Deionized water (DI water) was used in this experiment.

Synthesis of silica

We fabricated silica with narrow size distribution by Stöber method. The method is well known strategy as simple and controllable in size of silica by adjusting concentration of TEOS, water, ethanol and ammonium. First, ethanol (250 mL) and DI water (8.7 mL) well mixed by stirring magnetic bar. And then, we added TEOS and ammonium hydroxide solution in the mixture. The solution was mildly stirred. After 3h, silica was centrifuged and washed several times using ethanol then dried in an oven (at 60 °C and for 24 h).

Formation of polydopamine on silica

The silica was well dispersed in Tris buffer solution (8.5 pH at 25 °C) for 30 min by sonication bath. Dopamine hydrochloride was added in the solution (2 mg/mL). The mixture was stirred with 250 rpm at room temperature for 6 h. Polydopamine coated silica was washed five times by DI water with centrifugation and dispersion.

Pt coating over PDA–silica and carbonization

The PDA–silica were dispersed in DI water by sonication for 30 min. Pt precursor was added in the solution and then heated in oil bath at 90 °C. After 12h, Pt deposited PDA–silica was separated by centrifugation. The composites were washed several times using DI water and ethanol. The Pt–PDA–silica was heated until 400 °C in a heating chamber at N₂ atmosphere (heating rate: 1 °C/min) and then kept the temperature at 400 °C for 2h. Additionally, the composite was heated reach 800 °C (heating rate: 5 °C/min) and then maintain the temperature at 800 °C for 3 h.

Characterization

200 kV Field-emission Transmission Electron Microscope (FE–TEM, JEM–2100F (HR), JEOL LTD.), Field-emission Scanning Electron Microscope (FE–SEM, S–4800, Hitachi), Fourier Transform Infrared Spectroscopy Microscope (FT–IR Microscope, BrukerOptiks), X–ray Photoelectron Spectroscopy (XPS, MultiLab 2000, Thermo), Thermogravimetry Analyzer (TGA, TG 209 F3, NETZSCH) and Manual Probe Station (SUMMIT 11862B, SASCAD) were used for characterizing and analyzing each step's product and reaction.

MEA fabrication with Pt and N-doped carbon@silica

The MEA with Pt and N-doped carbon@silica was fabricated by catalyst-coated membrane (CCM) method. Before utilized, Pt and N-doped carbon@silica was mixed with high-surface carbon black (VulcanXC-72) and thermally treated ($H_2/Ar=1/9$ in volume, 300 °C, 3 h). Pt and N-doped carbon@silica ink was prepared by ultrasonic mixing of 10 mg of the composite catalyst with perfluorosulfonic acid (PFSA) polymer dispersion (Nafion solution, 5 wt.% polymer content, DE520); 1 mL of isopropyl alcohol (IPA, JUNSEI) with 68 μ L of Nafion solution. Pt loading was $0.3\text{mg}_{Pt}\text{cm}^{-2}$. For cathode, commercial Pt/C (40 wt.% Pt, Johnson Matthey) was used with same preparation procedure, but $0.2\text{mg}_{Pt}\text{cm}^{-2}$ of Pt loading. Then, catalyst-coated membrane was sandwiched by the porous gas diffusion layers (GDL, 35BC from SGL with surface area of 6.25 cm^2). The MEA, fabricated with commercial Pt/carbon on both anode and cathode was also prepared accordingly for comparison.

Fuel Cell Test

The performances of the both MEAs were evaluated by integrated fuel cell station (custom-made, CNL). The experiment was performed in galvanostatic mode. The reactant gases were pure H_2 (100 sccm) and O_2 (200 sccm) for anode and cathode, respectively, and fed through humidifier. Each MEA was activated prior to the measurement (70 °C, 300 min), and the cell temperature was maintained at 70 °C during measurement. The non-humidified atmosphere was set by flowing fuel gases directly into cell.

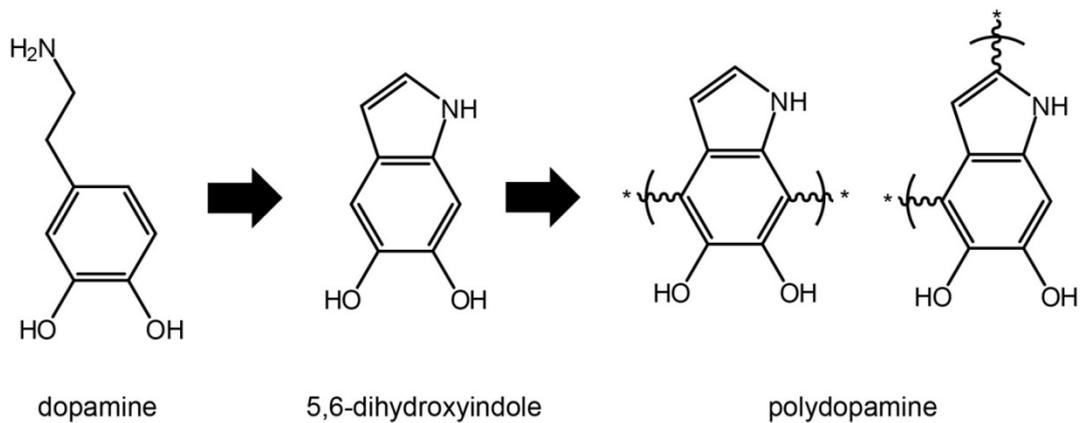


Fig. S1. Polymerization pathway of dopamine.

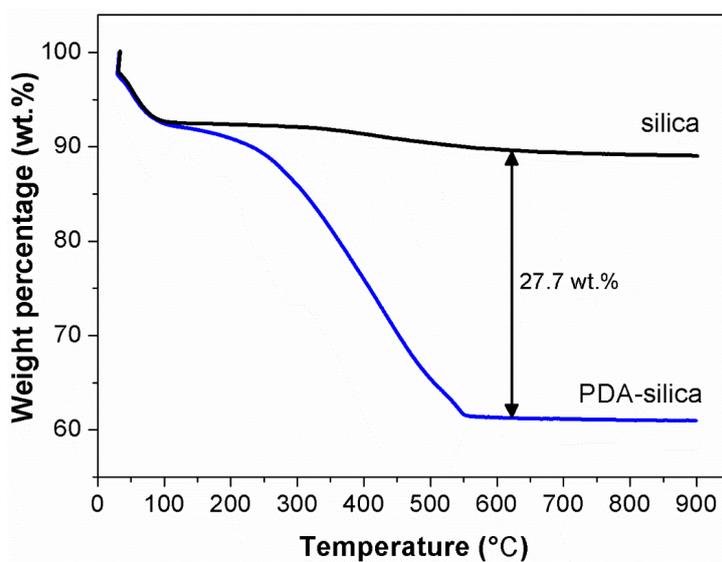


Fig. S2. TGA spectra of pristine silica and PDA-silica.

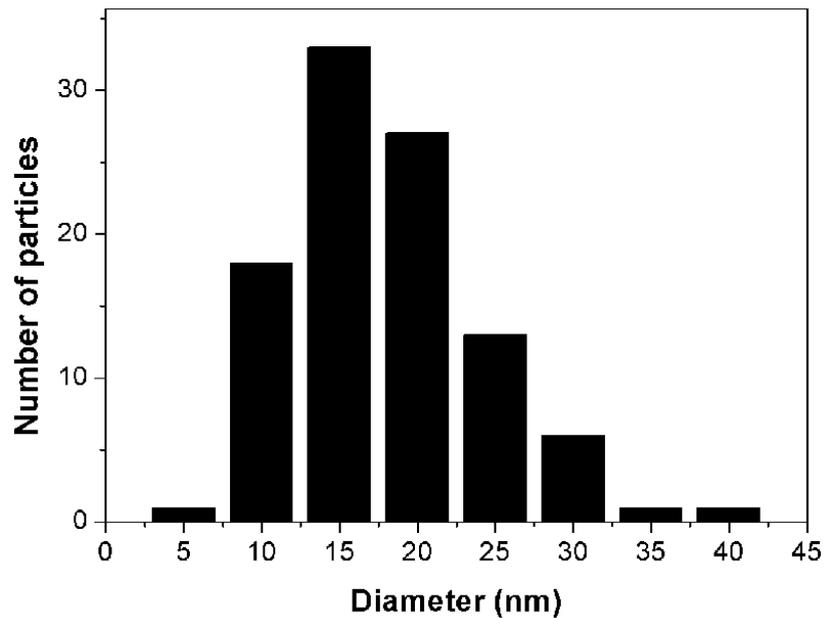


Fig. S3. Size distribution of Pt NPs over silica after carbonization of PDA.

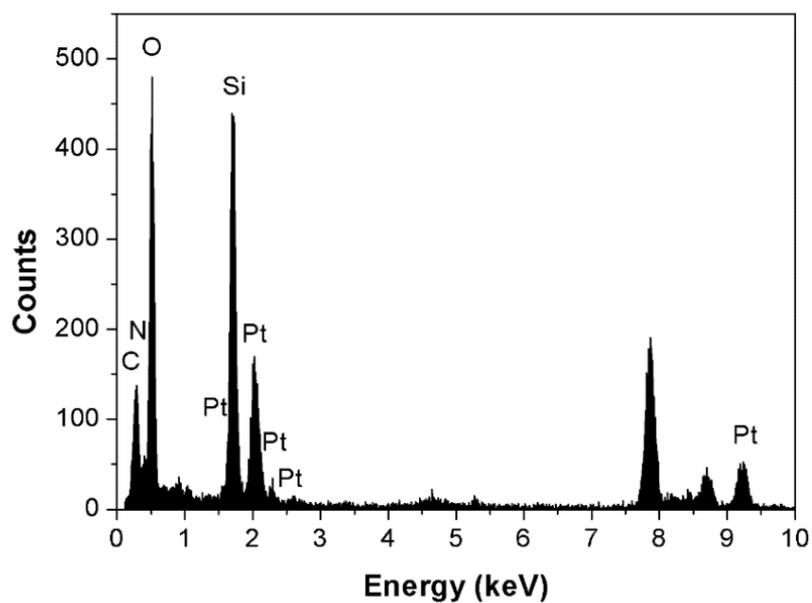


Fig. S4. Energy dispersive spectroscopy (EDS) of Pt and N-doped carbon@silica.

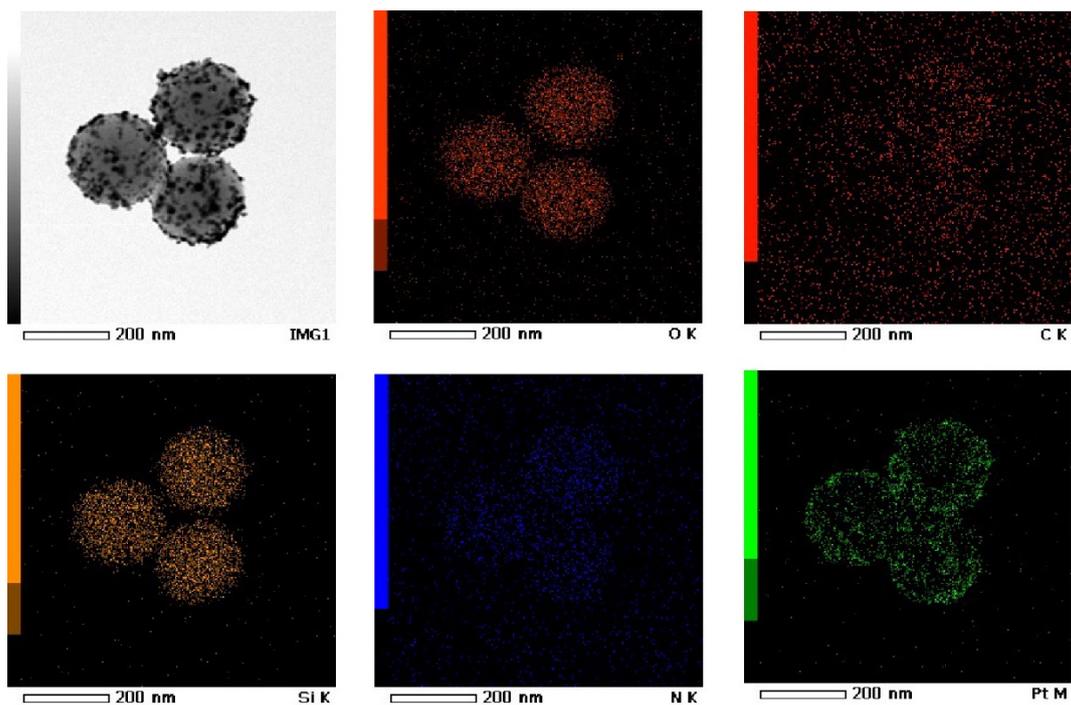


Fig. S5. Element mapping of oxygen (O), carbon (C), silicon (Si), nitrogen (N), and Pt of Pt and N-doped carbon@silica.

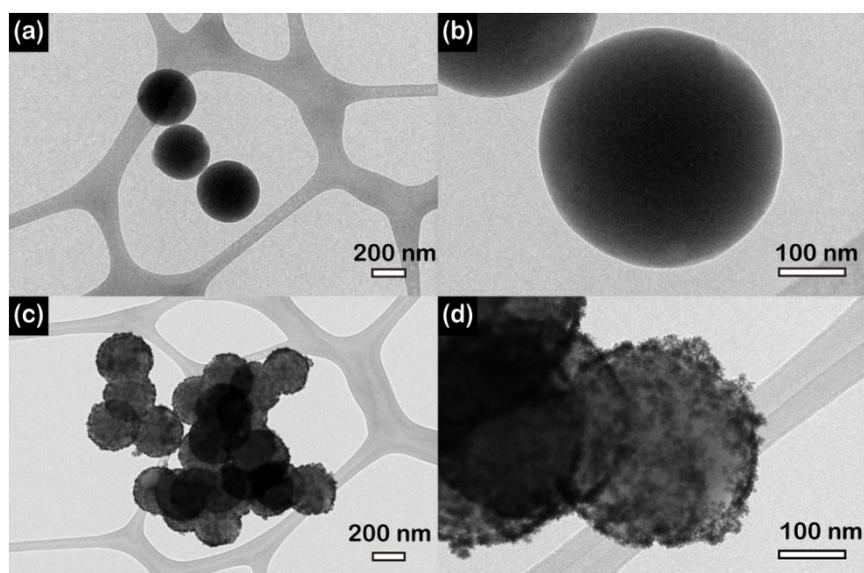


Fig. S6. TEM images of Pt unloaded silica (a,b) and Pt doped PDA-silica (c,d) under different magnification.

Pristine silica and PDA-silica were compared for Pt deposition under same experimental conditions to investigate the effects of PDA.

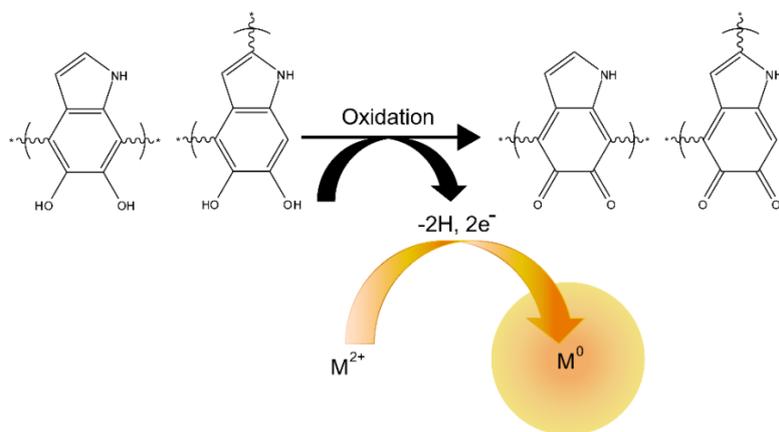


Fig. S7. Schematic illustration of reducing pathway from Pt ion into Pt NP using self-reducing ability of PDA.

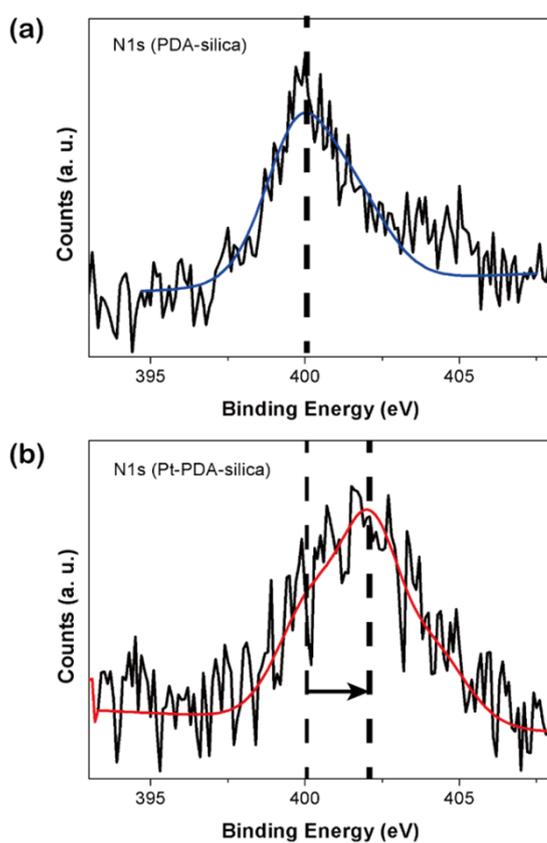


Fig. S8. High resolution XPS N1s diagram of (a) PDA-silica and (b) Pt-PDA-silica.

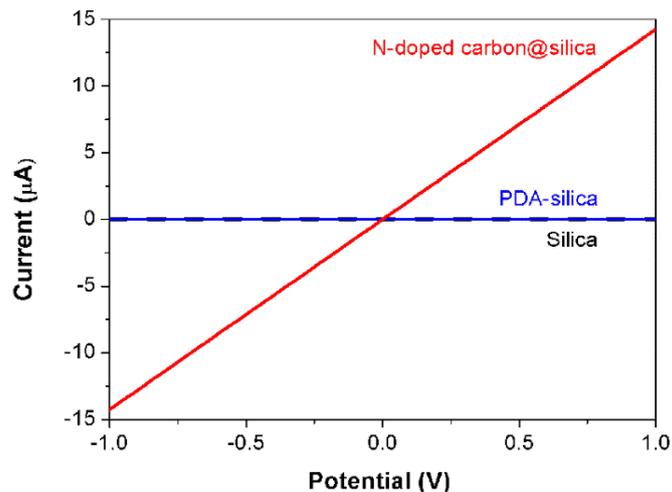


Fig. S9. I-V curves using manual probe station for the measurement of the electric current between gold electrodes linked with (black dash line) silica, (blue line) PDA-silica and (red line) N-doped carbon@silica at room temperature.

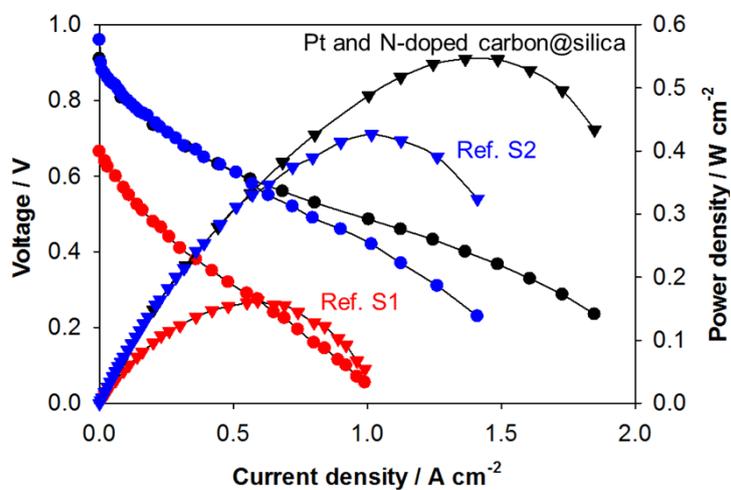


Figure S10. H₂/O₂-based single PEMFC performance comparison with non-humidified condition of Pt and N-doped carbon@silica and other composites from Ref. S1 and Ref. S2.

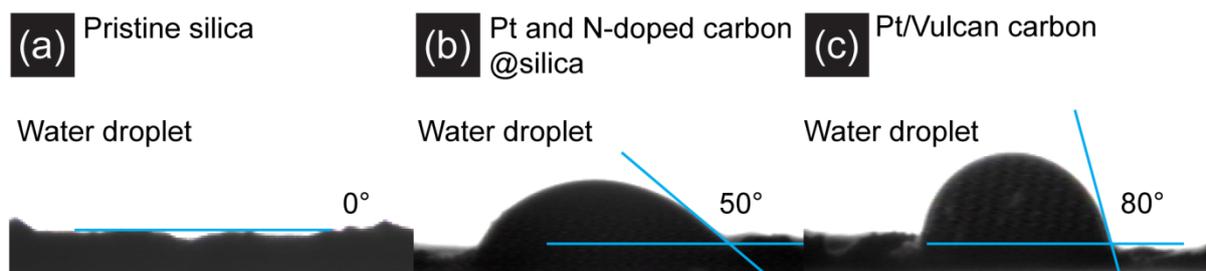


Figure S11. Contact angles (CA) of water droplets on prepared (a) pristine silica, (b) Pt and N-doped carbon@silica and (c) Pt/Vulcan carbon, measured by contact angle measurement (Phoenix 300 Plus, Surface Electro Optics).

The hydroscopic properties of silica and Pt and N-doped carbon@silica were investigated and compared with commercially available Pt/Vulcan carbon. The pristine silica and Pt and N-doped carbon@silica were more hydrophilic ($CA < 50^\circ$) than Pt/Vulcan carbon ($CA = 80^\circ$). This result indicated silica-based hybrid materials given hydroscopic benefit to increase the performance of anode catalyst in PEMFCs.

References

- [S1] W. -K. Chao, C. -M. Lee, D. -C. Tsai, C. -C. Chou, K. -L. Hsueh and F. -S. Shieu, *J. Power Sources*, 2008, **185**, 136.
- [S2] B. Yang, Y. Z. Fu and A. Manthiram, *J. Power Sources*, 2005, **139**, 170.