Supplementary Information

Revealing the Local Oxygen Transport in Ionomer Films on Multidimensional Nanoscale Catalysts in Fuel Cells

Yumeng Zhou[1], Linhao Fan[1*], Jiaqi Wang[1], Qing Du[1], Kui Jiao[1,2*]

1.State Key Laboratory of Engines, Tianjin University, 135 Yaguan Rd, Tianjin 300350, China.

2. National Industry-Education Platform for Energy Storage, Tianjin University, 135 Yaguan Rd, Tianjin 300350, China.

Email: lhfan@tju.edu.cn (LF); kjiao@tju.edu.cn (KJ)

Supplementary Note 1

To obtain the platinum (Pt) nanosphere structure, we first construct a spherical space with a diameter of ~3.8 nm, and then fill the space with Pt atoms which have a face-centered cubic (fcc) lattice with a lattice parameter of 0.392 nm. Finally, a nanosphere structure containing 1911 Pt atoms is obtained.

To obtain the core-shell structure, we first construct a dodecahedral space A with a height of ~2.3 nm as the core, which is filled with Pt-Co alloy that has $L1_0$ lattice with a lattice parameter of 0.378 nm. Then we construct a dodecahedron space B with a height of ~3.7 nm at the same position of the space A, and then fill the space both inside the space B and outside the space A with Pt atoms using a fcc lattice parameter of 0.392 nm. Finally, we get a core-shell structure containing 1586 Pt atoms and 469 Co atoms.

To obtain the Pt nanoframe structure, a rhombic dodecahedron space with a height of ~4nm is firstly constructed, which is filled with Pt atoms using a fcc lattice parameter of 0.392 nm. Then the Pt atoms near the edges of dodecahedron space are remained, while other Pt atoms are deleted to get a nanoframe with a hollow structure.

To obtain the Pt nanowire structure, the computational protocol developed by *Li et al.*[1] previously is extended. A $Pt_{15}Ni_{85}$ nanowire is restructured with a fcc lattice parameter of 0.392 nm firstly, where the Ni atoms are randomly distributed. Then Ni atoms are gradually removed, followed by a local relaxation using the reactive force field (ReaxFF) potential to simulate the de-alloying process through an electrochemical activation during experiments. 1 ns NPT simulation is performed at 353.15 K using the eam potential to obtain the final Pt nanowire with rich irregular surfaces, which has a diameter of ~2 nm and length of ~10 nm and contains 1988 Pt atoms. The final nanowire

with rich irregular surfaces has a diameter of ~2 nm and a length of ~10 nm and contains 1988 atoms. The one-dimensional nanowire has the similar Pt atom number with the nanosphere.

Supplementary Note 2

To obtain the equilibrium ionomer films on the carbon-supported catalysts, the following procedures are performed:

(a) 5 layers of graphene are reconstructed as the carbon support with an interval of 0.335 nm between each layer.

(b) The catalyst is placed on the middle of carbon support.

(c) 62 PFSA chains, 620 hydroniums, and 6200 water molecules are randomly inserted in the space on the carbon-supported catalyst.

(d) A virtual fixed wall is used to compress ionomer film to a thickness of 6.1 nm, making the ionomer density equal to that of the bulk ionomer.

(e) The L-J potential is reduced by two orders of magnitude during the 1 ns NVT simulation at 1000 K to make the PFSA chains relax sufficiently.

(f) The L-J potential is returned to a normal value and the temperature is decreased from 1000 K to 353 K for 1 ns.

(g) The temperature is changed repeatedly between 1000 K and 353 K for 4 times to reduce the system potential energy.

(h) The fixed wall is lifted to a height of ~15 nm from the carbon support, and another 5 ns NVT simulation is performed at 353 K to obtain an equilibrium configuration. The radial distribution functions (RDFs) between Pt and PFSA and between Pt and water are computed at 2-3 ns, 3-4 ns, and 4-5 ns, respectively. As shown in Fig. S9, the RDFs keep unchanged at different time to ensure that the ionomer films reach equilibrium.

Then, 1800 oxygen molecules are inserted into the gas region above the equilibrium ionomer films to analyze the oxygen transport through the ionomer films. A NVT simulation is performed for 10 ns at 353 K to ensure a steady-state oxygen transport process, and another NVT simulation is performed for 15 ns at 353 K to collect data for analysis. During the molecular dynamics simulation, the oxygen molecules that reach the catalyst surface will be removed to represent the consumption of oxygen and other oxygen molecules are added to the simulation system to keep the constant oxygen number.

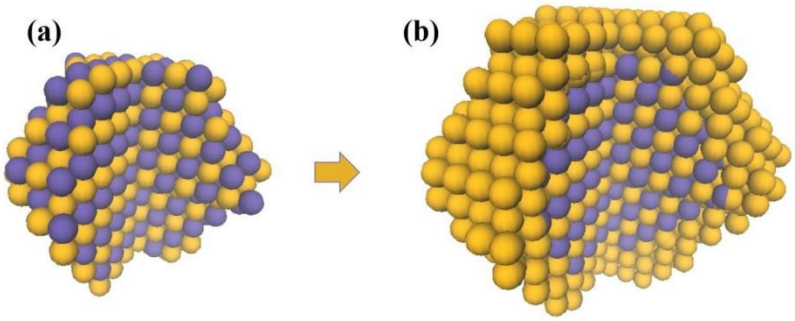

Figure S1. Reconstruction of core-shell catalyst. (a) Core of catalyst: Pt-Co alloy with $L1_0$ lattice. (b) Core-shell catalyst. The orange and purple beads represent the Pt and Co atoms, respectively.

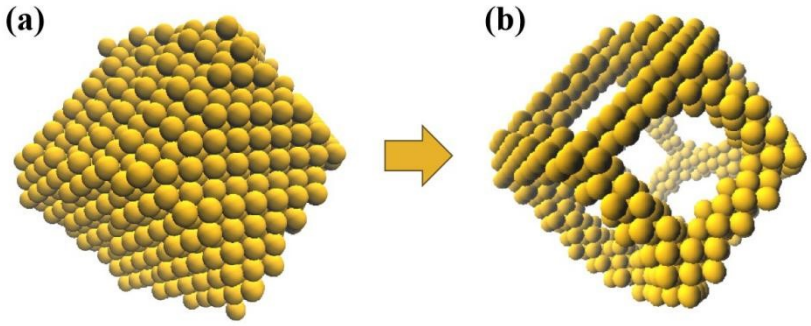

Figure S2. Reconstruction of nanoframe catalyst. (a) A rhombic dodecahedron full of Pt atoms with fcc lattices. (b) Nanoframe structure by deleting Pt atoms inside the body and at the center of surfaces.

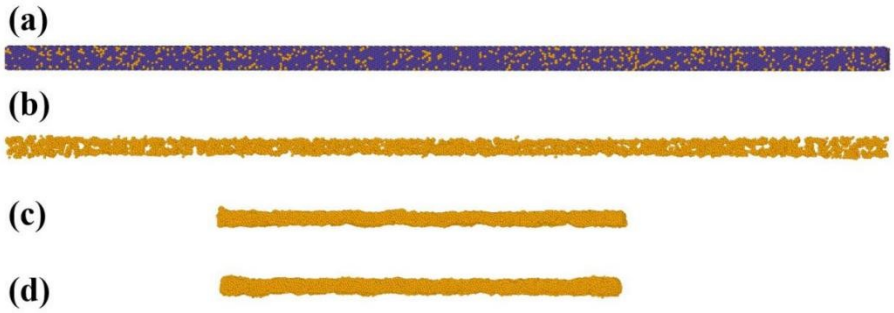

Figure S3. Reconstruction of nanowire catalyst. (a) A $Pt_{15}Ni_{85}$ nanowire. (b) Removing all Ni atoms. (c) Nanowire structure after NPT simulation using eam potential. (d) Final nanowire catalyst. The orange and purple beads represent the Pt and Ni atoms, respectively.

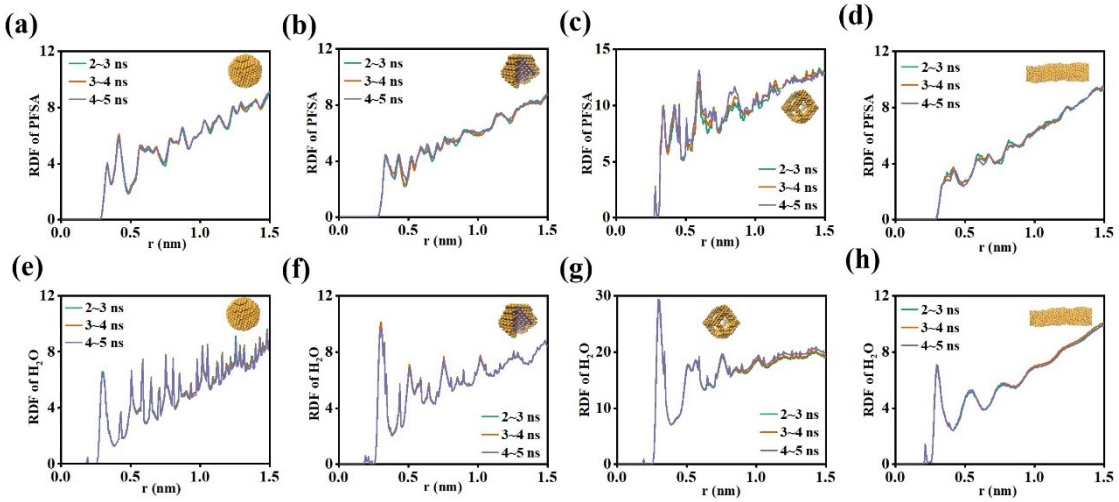

Figure S4. Radial distribution functions (a, b, c, and d) between Pt and PFSA and (e, f, g, and h) between Pt and water at different simulation time.

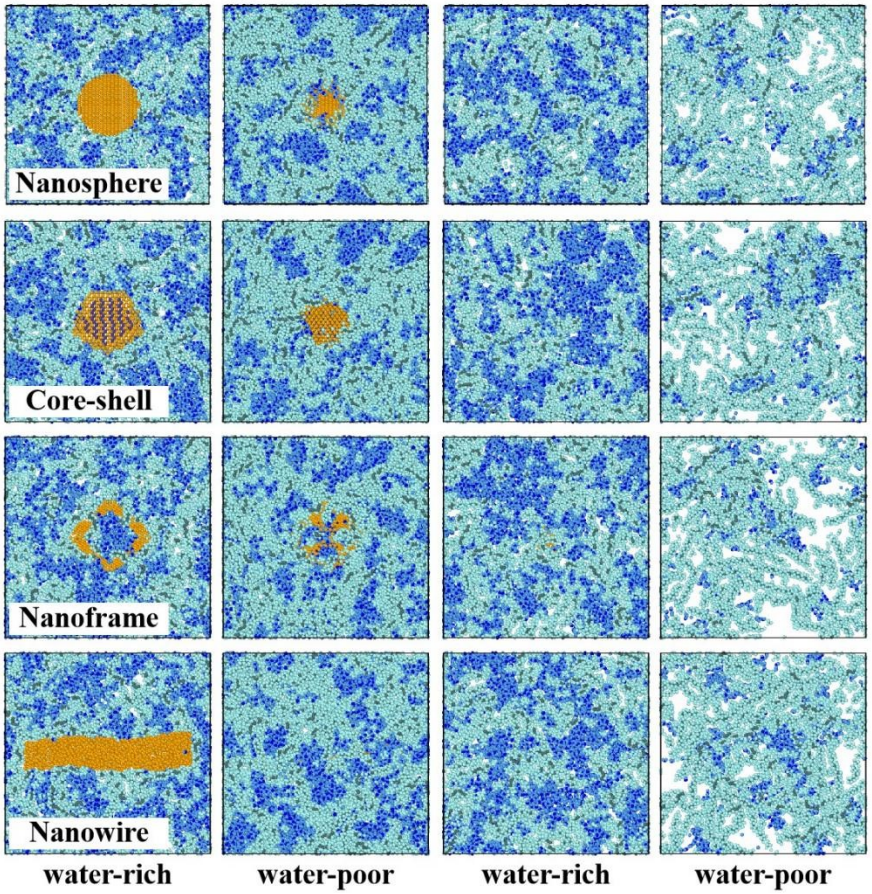

Figure S5. Snapshots on the X-Y plane for different layers in ionomer films.

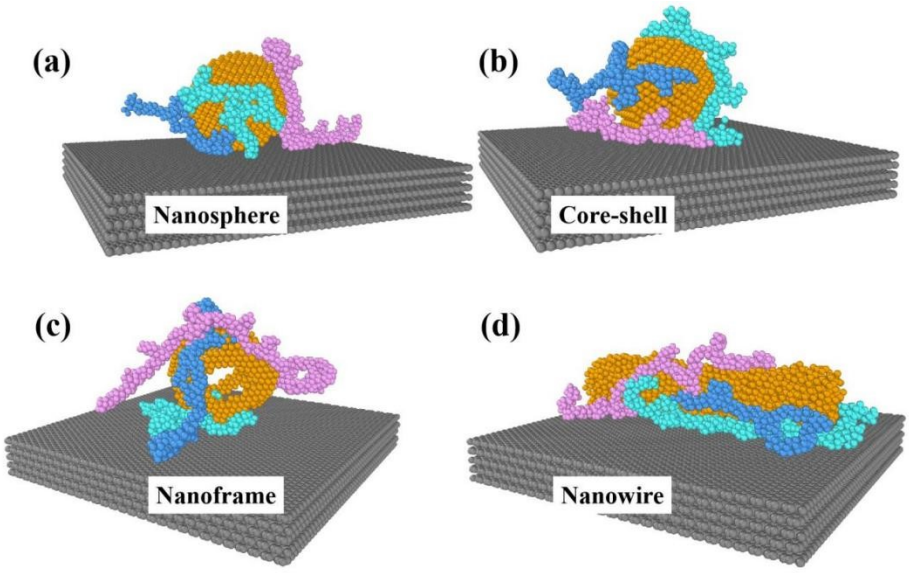

Figure S6. PFSA chains around (a) nanosphere, (b) core-shell, (c) nanoframe and (d) nanowire. The yellow beads represent catalysts, while other beads with different colors represent the different PFSA chains.

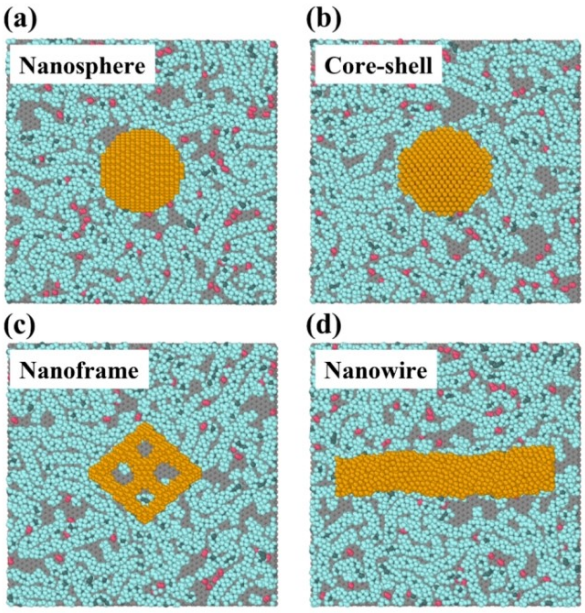

Figure S7. Snapshots in the regions within 0.73 nm from the carbon support for (a) nanosphere, (b) core-shell, (c) nanoframe, and (d) nanowire, respectively. The gray, orange, dark green, cyan and pink beads represent the carbon support atoms, Pt atoms, carbon atoms in PFSA, sulfur/oxygen/fluorine atoms in PFSA, oxygen molecules, respectively.

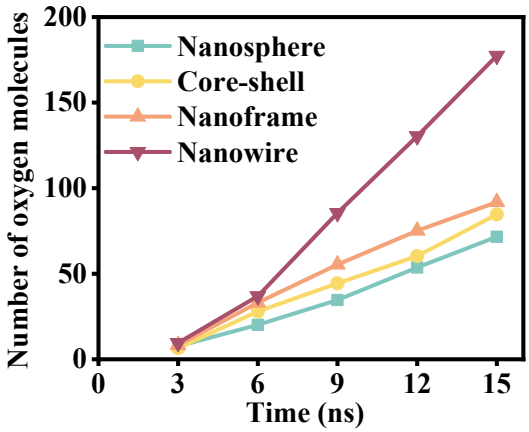

Figure S8. Number of oxygen molecules that reach catalyst surfaces.

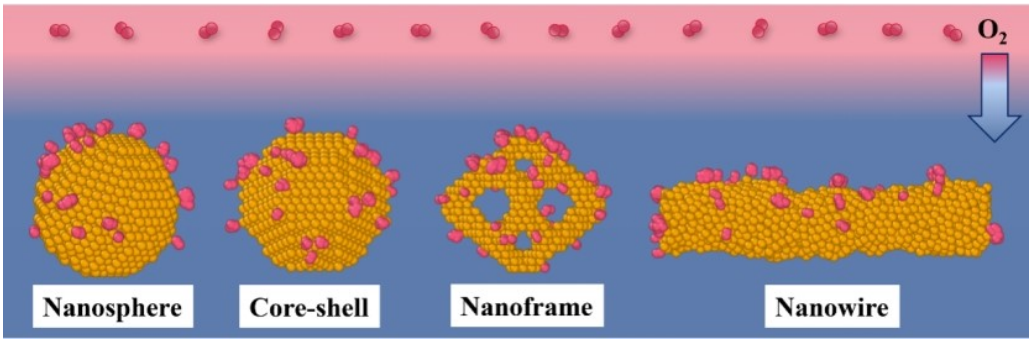

Figure S9. Snapshots of oxygen molecules that reach catalyst surfaces.

References

(1) M. F. Li, Z. P. Zhao, T. Cheng, A. Fortunelli, C. Y. Chen, R. Yu, Q. H. Zhang, L. Gu, B. V. Merinov, Z. Y. Lin, E. B. Zhu, T. Yu, Q. Y. Jia, J. H. Guo, L. Zhang, W. A. Goddard, Y. Huang and X. F. Duan, *Science*, 2016, **354**, 1414-1419.