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Ethanol-tolerant polyethyleneimine functionalized palladium nanowires in alkaline media: The "molecular window gauze" induced the selectivity for the oxygen reduction reaction

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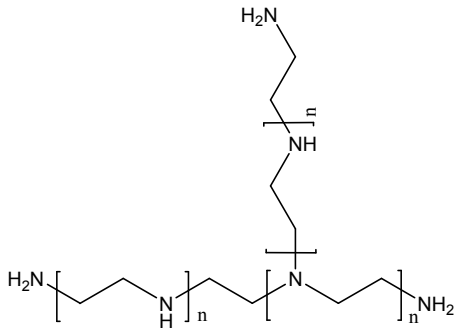
Molecular dynamics simulation

Molecular dynamics simulations with MM+ force field were carried out to understand the adsorption mechanism of PEI polymers on Pd (111) surface. The systems were built by putting 3 PEI polymers (each with 571~648 atoms, 3074~3490 Kg/mol in weight), in random orientation, above a double-layer, 20x20 atom Pd surface (800 atoms in total). Simulations were carried out in 300K and with time step of 2.0 fs. The trajectories were lasted at least 2 ns before being terminated. During simulation, atoms on Pd (111) layers were frozen. All the MD simulations were performed using the GROMACS package (version 5.0.5).[1-3]



Scheme S1 Molecular structure of PEI**.**

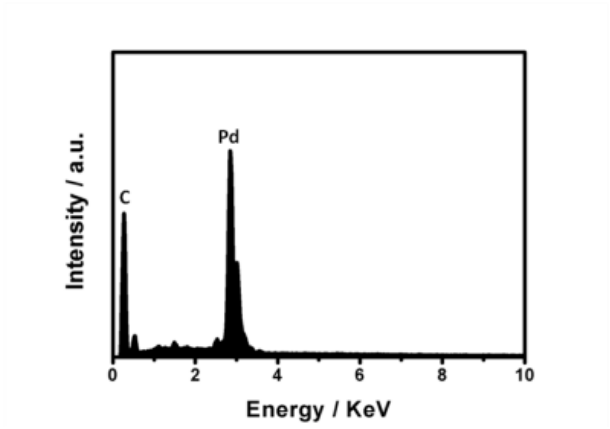


Fig. S1 EDX spectrum of Pd-NWs@PEI.

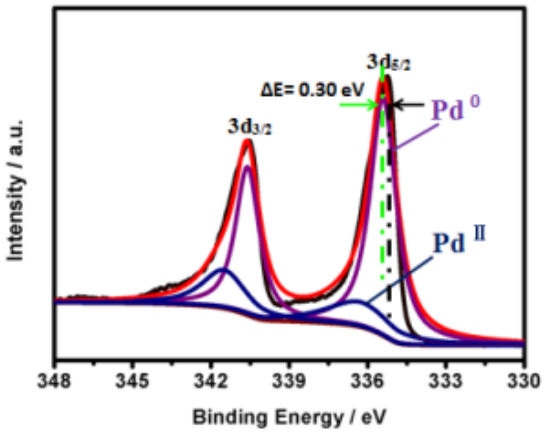


Fig. S2 Pd 3d XPS spectrum of Pd-NWs@PEI. The vertical black dotted lines represent the standard value of Pd 3d5/2.[4]

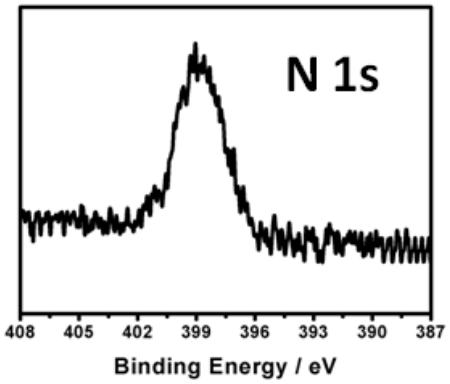


Fig. S3 N1s XPS spectrum of Pd-NWs@PEI.

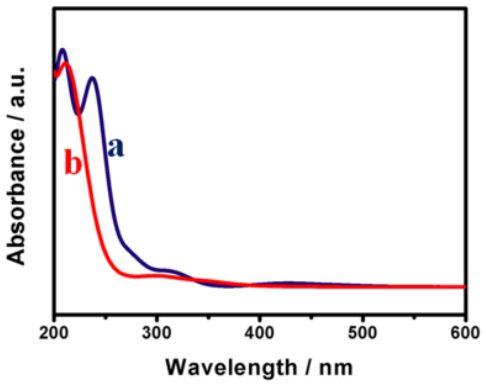


Fig. S4 UV–vis absorption spectra of (a) single-component K_2PdCl_4 solution and (b) the mixture solution of K_2PdCl_4 and PEI.

The UV−vis absorption peaks of single-component K_2PdCl_4 solution locate at 207 and 235 nm, which can be ascribed to ligand−to−metal charge transfer bands of $PdCl_3(H_2O)^-$ species.[5, 6] After adding PEI, the peaks at 208 and 237 nm disappear and a new peak at 211 nm appear, indicating that PEI can interact with K_2PdCl_4 to generate PEI-Pd^{II} complex.

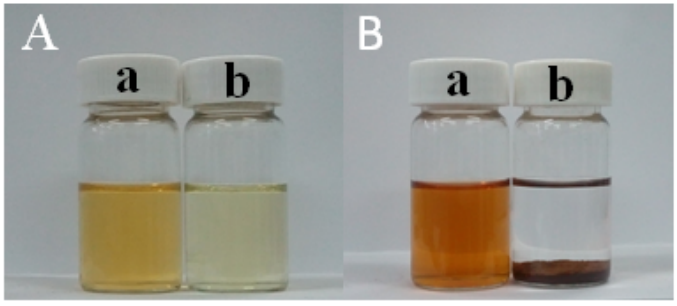


Fig. S5 Photographs of (A) the mixture solution of K_2PdCl_4 and PEI and (B) the single-component K_2PdCl_4 solution (a) before and (b) after adjusting the solution pH to 7.5.

When the pH of the mixture solution of K_2PdCl_4 and PEI is adjusted to 7.5, a light yellow solution is obtained (Fig.S5A-b). In a controlled experiment, a lot of red flocculent $PdO{\cdot}H_2O$ precipitation is generated immediately in a few seconds after adjusting the pH of single-component $PdCl_2$ solution to 7.5[7] (Fig.S5B-b). These above experimental phenomena further confirm that PEI can interact with K_2PdCl_4 to generate PEI-Pd^{II} complex via coordination interaction.

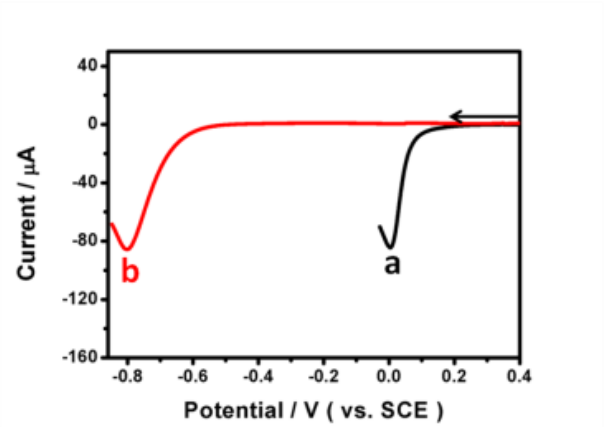


Fig. S6 Linear sweeping voltammograms of (a) the single-component K_2PdCl_4 solution and (b) the mixture solution of K_2PdCl_4 and PEI in 0.1 M KCl electrolyte (pH 2.0) at the glassy carbon at a scan rate of 100 mV s^{-1}.

As observed, the reduction peak potential of PEI-Pd^{II} complex negatively shifts ca. 800 mV compared to that of K_2PdCl_4.

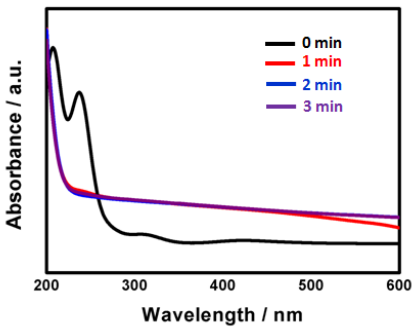


Fig. S7 Time-dependent UV−vis absorption spectra of the single-component K_2PdCl_4 solution after addition of $N_2H_4 \cdot H_2O$.

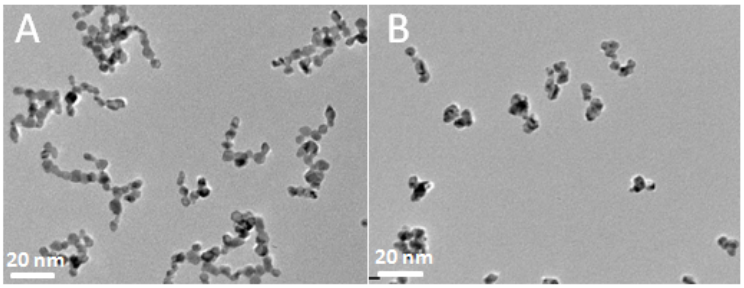


Fig. S8 TEM images of Pd-NWs@PEI synthesized at (A) pH 7.0 and (B) PH 3.0.

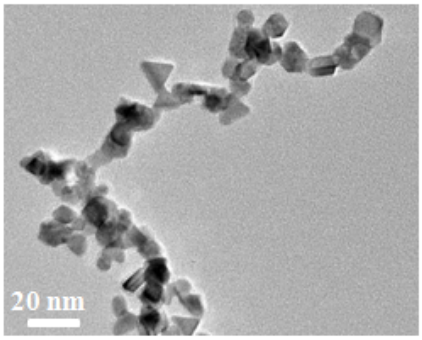


Fig. S9 TEM image of the obtained Pd nanonecklaces by increasing the amount of $N_2H_4 \cdot H_2O$ to 2.0 mL.

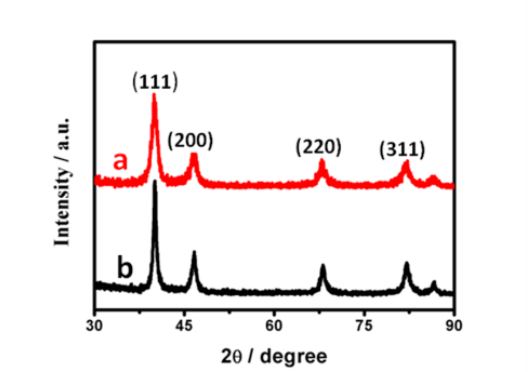


Fig. S10 XRD patterns of (a) Pd-NWs@PEI and (b) commercial Pd black.

According to the Scherrer formula, the average particle sizes of Pd-NWs@PEI and Pd black are calculated from the (111) diffraction peak to be ca. 4.7 and 19.1 nm, respectively.

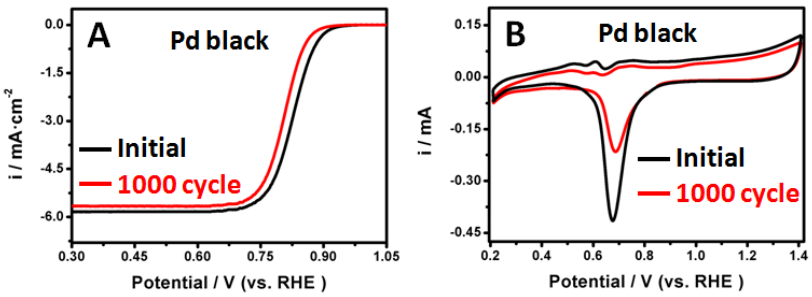


Fig. S11 (A) ORR polarization curves of commercial Pd black before and after 1000 potential cycles in O_2-saturated 0.1 M NaOH solution at a scan rate of 5 mV s^{-1} and rotation rate of 1600 rpm. (B) CV curves of commercial Pd black before and after 1000 cycles in N_2-saturated 0.1 M NaOH solution at a scan rate of 50 mV s^{-1}.

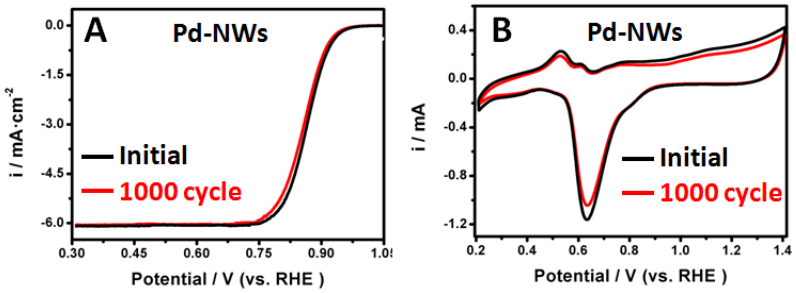


Fig. S12 (A) ORR polarization curves of Pd-NWs@PEI before and after 1000 potential cycles in O_2-saturated 0.1 M NaOH solution at a scan rate of 5 mV s^{-1} and rotation rate of 1600 rpm. (B) CV curves of Pd-NWs@PEI before and after 1000 cycles in N_2-saturated 0.1 M NaOH solution at a scan rate of 50 mV s^{-1}.

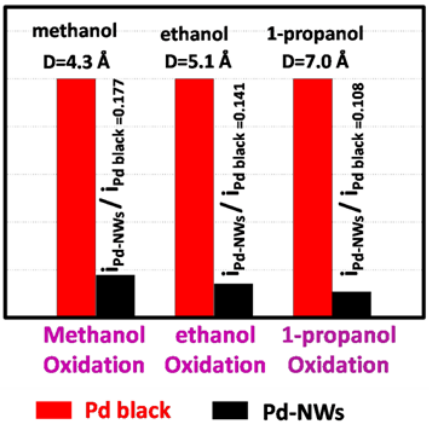


Fig. S13 The ratios of specific peak current densities of methanol, ethanol, and 1-propanol at Pd-NWs@PEI ($i_{Pd\text{-}NWs@PEI}$) to these at commercial Pd black (i_{Pd}). For convenience, the specific peak current densities of methanol, ethanol, and 1-propanol at Pd black were normalized to 1. A smaller value of the $i_{pdpt@ptpd}/i_{Pt}$ implies better alcohol tolerant ability. As observed, the value of the $i_{Pd\text{-}NWs@PEI}/i_{Pd}$ decreases with increasing molecule size of alcohol.

References

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