Supplementary information

Solid phase polymerization of phenylenediamine toward self-supported FeN_x/C catalyst with high oxygen reduction activity

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1. Catalyst synthesis: In a typical approach to the synthesis of PpPD-Fe-ZnO catalyst, 1 g p-phenylenediamine, 1 g zinc oxide nanoparticles, 1 g ammonium persulfate, and 0.2 g ferric chloride hexahydrate were ground together. Then the mixtures were transferred to hydrothermal synthesis reactor, which was heated to 150 ° C to allow phenylenediamine to fully polymerize and form poly-p-phenylenediamine(PpPD). The subsequent heat treatment was performed at 950 °C in a nitrogen-gas atmosphere for one hour. The heat-treated sample was then pre-leached in 0.5 M H_2SO_4 at room temperature for 24 hours, and then thoroughly washed in de-ionized water. In the final step, the catalyst was heat-treated again in nitrogen-gas atmosphere for two hours. The PpPD-Fe was prepared without adding zinc oxide nanoparticles. The PpPD-Fe-Al_2O_3 was prepared using Al_2O_3 nanoparticles as hard template.

2. Rotating disk electrode (RDE) measurements: RDE measurements were performed using a CHI Electrochemical Station (Model 760e) in a conventional three-electrode cell. A homemade reversible hydrogen electrode was used as a reference electrode. Performance data was recorded at a catalyst loading of 0.9 $mgcm^{-2}$ for non-precious samples in 0.1 M $HClO_4$ at a rotating disk speed of 900 rpm and room temperature. In RDE tests, ORR steady-state polarization curves were recorded with a potential step of 10 mV and a period time of 100 s from 1.0 to 0 V using a negative-going scan.

3. Fuel cell testing: Catalyst inks were prepared by ultrasonically mixing catalyst powders with Nafion® solution and ethanol. The inks were then applied to the gas diffusion layer, and the cathode catalyst loading was 2.4 $mgcm^{-2}$. A commercial Pt/C (JM, 60%) was used as the anode catalyst, and the loading of Pt was 0.8 $mgcm^{-2}$. Then, the MEA was prepared by hot-pressing, and Nafion 211 membrane was adopted. Fuel cell polarization curve was tested at 80 ° C, H_2 and O_2 flow rates were 300 $mLmin^{-1}$ at 100% RH, and no back pressure was applied.

4. TEM image: As shown in Figure S1, the morphology of ZnO nanoparticles is irregular.

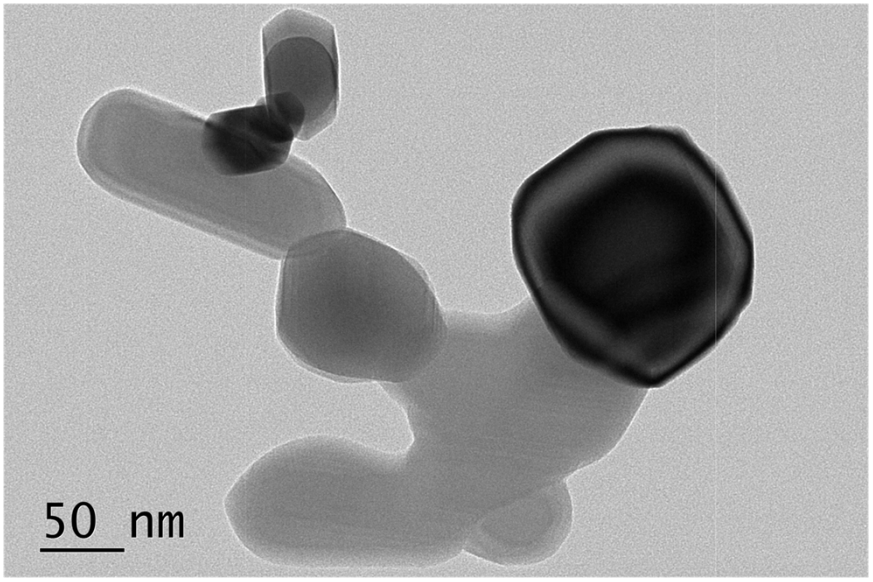

Figure S1. The TEM image of ZnO.

5. Elemental analysis by XPS: Elemental quantification of samples were performed using X-ray photoelectron spectroscopy (data shown in Table S1).

Table S1. Elemental quantification analysis of catalysts

	Atomic concentration, %						
	C 1s	**O 1s**	**N 1s**	**S 2p**	**Fe 2p**	**Zn 2p**	**Al 2P**
PpPD-Fe-ZnO	**92.67**	**2.67**	**2.77**	**0.87**	**0.28**	**0.23**	**0.51**
PpPD-Fe	**88.97**	**4.15**	**3.5**	**1.07**	**0.38**	**0.17**	**1.75**
PpPD-Fe-Al_2O_3	**65.57**	**17.7**	**1.53**	**0.53**	**0.3**	**0.25**	**14.13**