3-D N-doped porous graphene-like network and vanadium nitride co-promoted Pt electrocatalyst with high activity and stability for the oxygen reduction reaction

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Production of 3-D N-doped porous graphene-like network (3DNPG):

The 3DNPG were synthesized via a synchronous graphitization-activation combination method, by using an ion-exchange resin as carbon precursor, nickel acetate as catalyst precursor of graphitization and KOH as pore-forming agent, according to one of our previous work (Adv. Mater., 2013, 25, 2474-2480). Particularly, an additional reagent, melamine, is selected as the “nitrogen source” for the building of the new-style N-doped product of 3DNPG. Typically, the D113 macroporous acrylic type cation exchange resin (500 g) was impregnated in 5 L nickel acetate aqueous solution (0.1 mol L⁻¹) for 6 h. Afterwards, the resin was washed with deionized water and dried at 80 °C for 12 h. Then the Ni⁺-included resin (100 g) was added in a 1 L ethanol solution containing 200 g KOH and 20 g melamine, and stirred at 80 °C until the mixture solution became an ‘ink-paste’. After that, the mixture was dried in the vacuum condition at 80 °C for 48 h. Finally, the mixture was heated at 800 °C for 2 h with a heating rate of 2 °C min⁻¹ under N₂ atmosphere. After cooling, the resulting sample was added into 2 mol L⁻¹ HCl solution for more than 6 h with intensive sonication. Afterwards, the sample was repeatedly washed by deionized
water until a pH value of 7 was reached, dried at 80 °C in ambient for 24 h. In addition, the 3-D porous graphene-like network (3DPG) was also prepared without the use of “nitrogen source” melamine by above conditions.

**Production of 3DNPG/VN:**

The 3DNPG/VN is synthesized by the one-step sintering of 3DNPG with NH₄VO₃ and melamine. Typically, 5g 3DNPG was mixed with 2g NH₄VO₃ and 2g melamine in hot water of 80 °C by magnetic stirring, and the mixture solution was sequentially stirred at 80 °C until the mixture solution became an ‘ink-paste’. Afterwards, the mixture was dried in the vacuum condition at 80 °C for 48 h. Finally, the mixture was heated at 900 °C for 2 h with a heating rate of 2 °C min⁻¹ under N₂ atmosphere.

**Production of 3DNPG/VN/Pt:**

The 3DNPG/VN/Pt is synthesized by the Intermittent Microwave Heating (IMH) method. Appropriate amount of H₂PtCl₆ and 3DNPG/VN were mixed with ethylene glycol in an ultrasonic bath for 30 min. The mixture was subjected to microwave heating (5 s on and 5 s off for 20 cycles) using a homemade microwave oven (2,000 W, 2.45 GHz). The product was acidified, filtered, washed and dried at 80 °C for 12 h in vacuum. In addition, for the comparison of electrocatalytic performances, 3DNPG/Pt and 3DPG/Pt were also synthesized by the same method. The projected contents of Pt in 3DNPG/VN/Pt, 3DNPG/Pt and 3DPG/Pt all are 15 wt. %.

**Characterization of materials**

The X-ray diffraction (XRD) measurement was carried out with a Bluker D8-Advance diffractometer with Cu Kα radiation (λ= 1.5406 Å). The morphologies of the samples were examined by using a field emission scanning electron microscopy (SEM, Philips, FEI Quanta 200FEG) and a transmission electron microscopy (TEM, JEOL-2010). The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an XPS apparatus (ESCALAB 250). Nitrogen adsorption-desorption using an Surface Area Analyzer (ASAP 2420) were conducted to investigate the specific surface area and porosity of samples. The actual content of Pt in the 3DNPG/VN/Pt and 3DNPG/Pt is determined by the inductively coupled plasma atomic emission spectrometry (ICP-AES) technique.

**Electrochemical measurements**
The catalytic activities of the electrocatalysts for the ORR were evaluated by using a Rotating Ring Disc Electrode (RRDE) with a biopotentiostat (AFCBP1E, Pine Instrument Co., USA) at 25 °C with Pt foil as counter electrode and reversible hydrogen electrode (RHE) as reference electrode. A mixed solution of 5.0 mg electrocatalysts, 0.95 mL ethanol and 0.05 mL Nafion solution (0.05 wt %) was ultrasonicated for to form a well-dispersed ink. A certain amount of the ink was transferred onto the surface of the glass carbon in RRDE to be working electrodes. The value of geometric surface area of the rotating disc electrode is 0.2475 cm$^2$. An O$_2$-saturated 0.1 M HClO$_4$ aqueous solution was used as electrolyte for the ORR testing and N$_2$-saturated 0.1 M HClO$_4$ aqueous solution was used as electrolyte for the CV and continuous potential cycle testing.

Fig. S1 Nitrogen adsorption-desorption isotherm (A) and pore size distribution (B) of the 3DNPG sample.