Electronic Supplementary Information

Hydrothermal Synthesis of Vanadium Nitride and Modulation of Its Catalytic Performance for Oxygen Reduction Reaction

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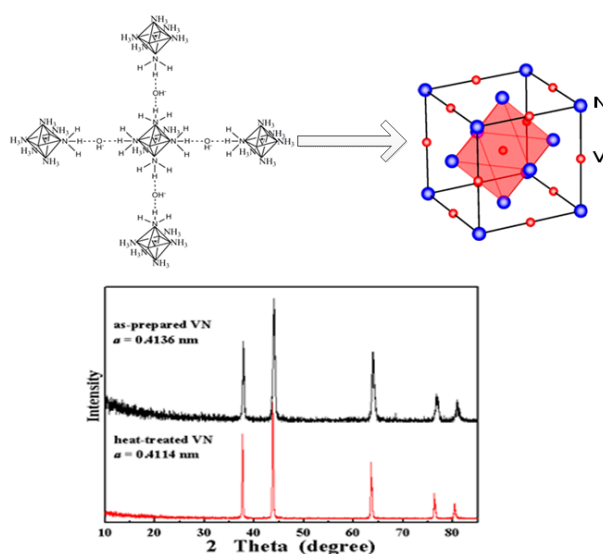
Methods

Sample preparation. VN was prepared by a simple hydrothermal method. In a typical procedure, 0.2 g VCl_3 was first dissolved into 40 ml DI water and 8 ml ammonia solution (30 wt.%) was added into the VCl_3 solution. Then the solution was treated with ultrasonication until the solution reached limpidity. The limpid solution was transferred into an autoclave for a hydrothermal reaction at 200 °C for 20 hours. The obtained black powder was VN. The VN powders were annealed at 750 °C in an ammonia gas flow (0.5 lpm, quarter inch tube) for two hours to improve the VN crystalline structure. The graphene-supported V_2O_3 was prepared by a hydrothermal method using VCl_3 as the precursor. First, 0.2 g VCl_3 (97%, Aldrich) and 8.0 ml graphene oxide (GO) (10 mg/ml in DI water, ACS Materials) were mixed with ultrasonication for 30 minutes. Then hydrothermal reaction occurred at 200 °C for eight hours and the obtained precipitation was washed with a large amount of DI water and dried at 80 °C for four hours. The obtained graphene-supported V_2O_3 was reduced at 1000 °C in a hydrogen and ammonia gas flow (0.5 lpm, quarter inch tube) for two hours to obtain VC and V(C, N), respectively.

Characterization. The morphology of the as-prepared samples, the selected area electron diffraction (SAED) pattern, the energy-dispersive X-ray spectrum (EDS), and the elemental mapping were obtained by using a Hitachi (H 9000 NAR) transmission electron microscope (TEM) and a Hitachi (S-4800) scanning electron microscope (SEM) equipped with an energy-dispersive spectroscopy analyzer. Powder X-ray diffraction (XRD) was performed on a Scintag XDS 2000 X-ray powder diffractometer with monochromatized CuKα radiation (λ=1.5418 Å); the data were collected between scattering angles (2θ) of 10° and 80°. Based on the XRD results, the corresponding cell parameters of each sample were calculated by using the Jade software. X-ray photoelectron spectroscopy (XPS) was conducted by using an HP 5950A ESCA spectrometer with an Mg Kα source. N_2 adsorption–desorption measurements were carried out at 77 K using a Quantachrome Autosorb gas-sorption system to determine the specific surface area of VN..

Electrochemical testing. The electrochemical characterization was carried out in 1M KOH at room temperature by using a CHI 760E electrochemical workstation (CHI Inc., USA). The three-electrode cell consisted of an Ag/AgCl electrode as the reference electrode, Pt as the counter-electrode, and a

glassy carbon electrode with catalysts as the working electrode. To prepare the working electrode, 5.0 mg catalyst was mixed with a 50 μl Nafion solution (5.0 % Nafion in ethanol) and 450 μl DI water. The mixture was sonicated and 5.0 μl suspension was dropped onto a glassy-carbon electrode with a diameter of 3 mm and then fully dried. Before electrochemical tests, the working electrode was kept in an Ar-saturated electrolyte by cycling the potential from 0.2 to -0.8 V at a scan rate of 0.1 V/s until reproducible results were obtained. Thereafter, the electrolyte was saturated with oxygen and cyclic voltammogram tests were carried out and recorded for ORR from 0.2 to -0.8 V at scanning rates of 0.01 V/s. Linear-sweep voltammograms (LSVs) were conducted from 0 to -0.4 V at the sweep rate of 0.005 V/s. The Tafel tests were conducted at the sweep rate of 0.005 V/s. The rotate disc electrocatalysis tests were conducted from -0.05 V to -0.45 vs. Ag/AgCl by an RDE-3A electrode at a sweep rate of 0.005 V/s in oxygen-saturated 1.0 M KOH solution. CV results are influenced by the activated state and the surface condition of the catalyst. Catalysts should be fully activated and the surface contaminants, e.g., surface oxygen, should be removed before the true CV is obtained. The activating process is usually conducted by CV tests (1-10 cycles). The typical first ten cycles of CVs of VN for ORR with Pt and graphite as the counter electrode are shown in Electronic Supplementary Information, Figs. S5c and d.


Fig. S1. Schematic of hydrothermal synthesis of VN and XRD results of as-prepared and heat-treated VN.

Fig. S1 illustrates the synthesis process of VN by the hydrothermal method and the corresponding XRD patterns of as-prepared and heat-treated VN. The coordination compound of ammonia and vanadium ions forms VN during the hydrothermal treatment. The XRD patterns of as-prepared and heat-treated VN are quite similar, which means that there are no phase changes during the heat treatment. The X-ray diffraction peaks of the heat-treated VN are slight narrower than that of as-prepared VN, suggesting the structure of as-prepared VN is improved during the heat treatment. The

crystal cell parameters of as-prepared and heat-treated VN in Fig. S1 suggest that the crystal cell parameters slightly decrease after the heat treatment. This is due to the perfection of VN crystalline structure.
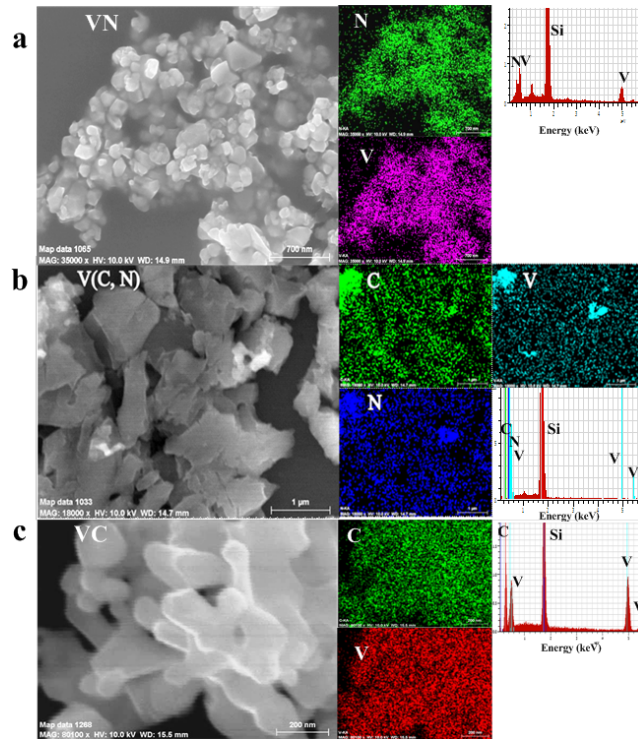

Fig. S2. SEM images and elemental mappings of (a) VN, (b) V(C, N), and (c) VC.
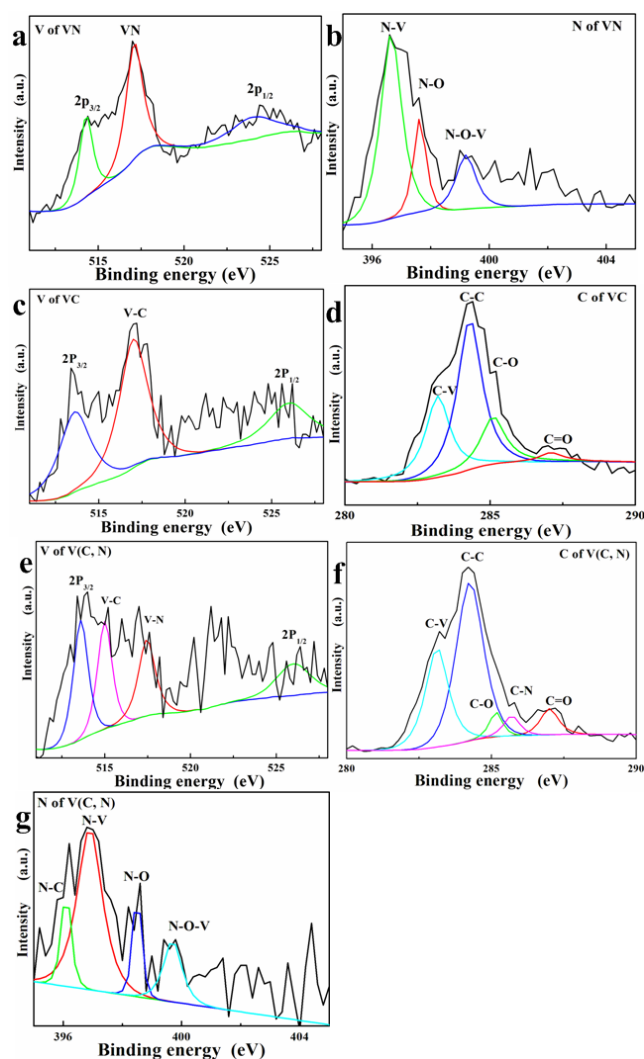
Fig. S3. (a), (c), and (e), high-resolution V2p XPS spectra of VN, VC, and V(C, N), respectively. (b) and (g), high-resolution XPS spectra of N 1s in VN and V(C, N). (d) and (f), high-resolution XPS spectra of C1s in VC and V(C, N).

Fig. S3 shows the electronic states of V, C, and N in VC, VN, and V(C, N). Comparison of Fig. S3a, c, and e clearly shows that $2P_{3/2}$ and $2P_{1/2}$ are the main states of V cations in VC, VN, and V(V, N). Carbon, as the source of VC and V(C, N) and support, are detected in both VC and V(C, N) (Fig. S3b and f) and the strongest C-C bond is originated from graphene. The N-V bond is the major state of N in both VN and V(C, N). V-C, V-N, and C-N bonds coexist in V(C, N), which is consistent with the elemental mapping results, which indicates the doped nitrogen reacted with both carbon and vanadium in the VC.
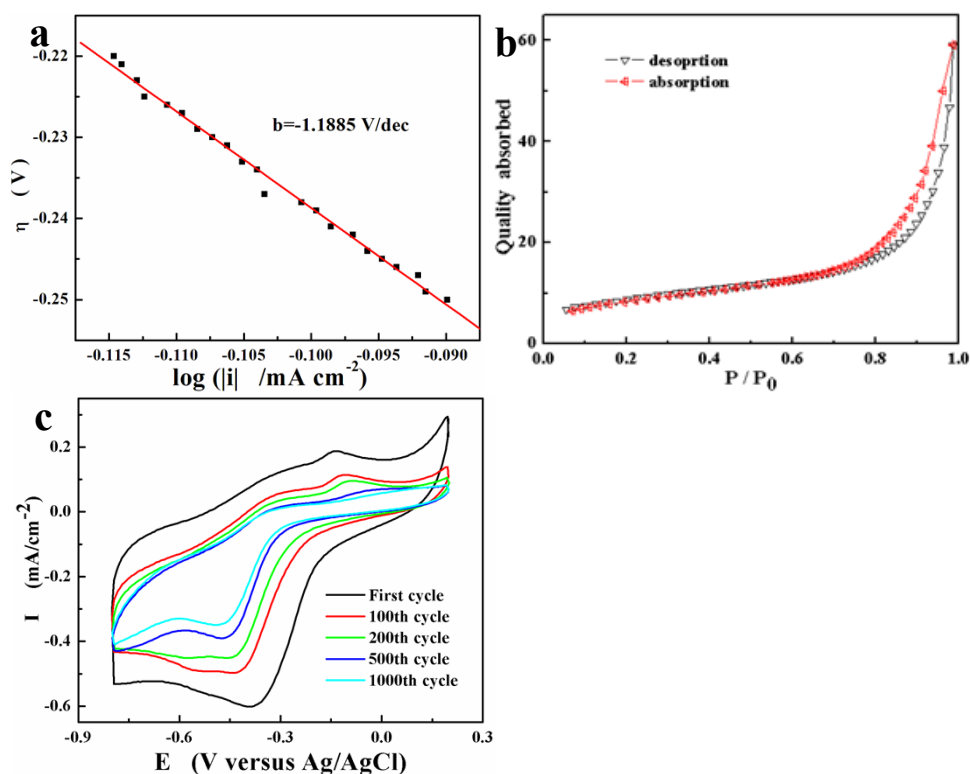
Fig. S4. (a) Tafel plot of Pt/C at the sweep rate of 0.05 V/s. (b) Nitrogen adsorption-desorption isotherms of VN catalysts. The specific surface area of VN is 30.6 m²/g. (c) Cyclic tests of VN at the sweep rate of 0.05 V/s.

Fig. S4c shows the cyclic characteristics of VN at a sweep rate of 0.05 V/s. It is clearly shown that with the proceeding of cycles, the ORR catalytic performance slightly decreased. Both the ORR peak voltage and the peak current decreased. The peak position shifted from -0.4 V to -0.46 V and the peak current intensity decreased from 0.61 mA/cm² to 0.35 mA/cm². The decrease may result from the oxidation of VN or the decrease of the oxygen concentration in the electrolyte during the tests.
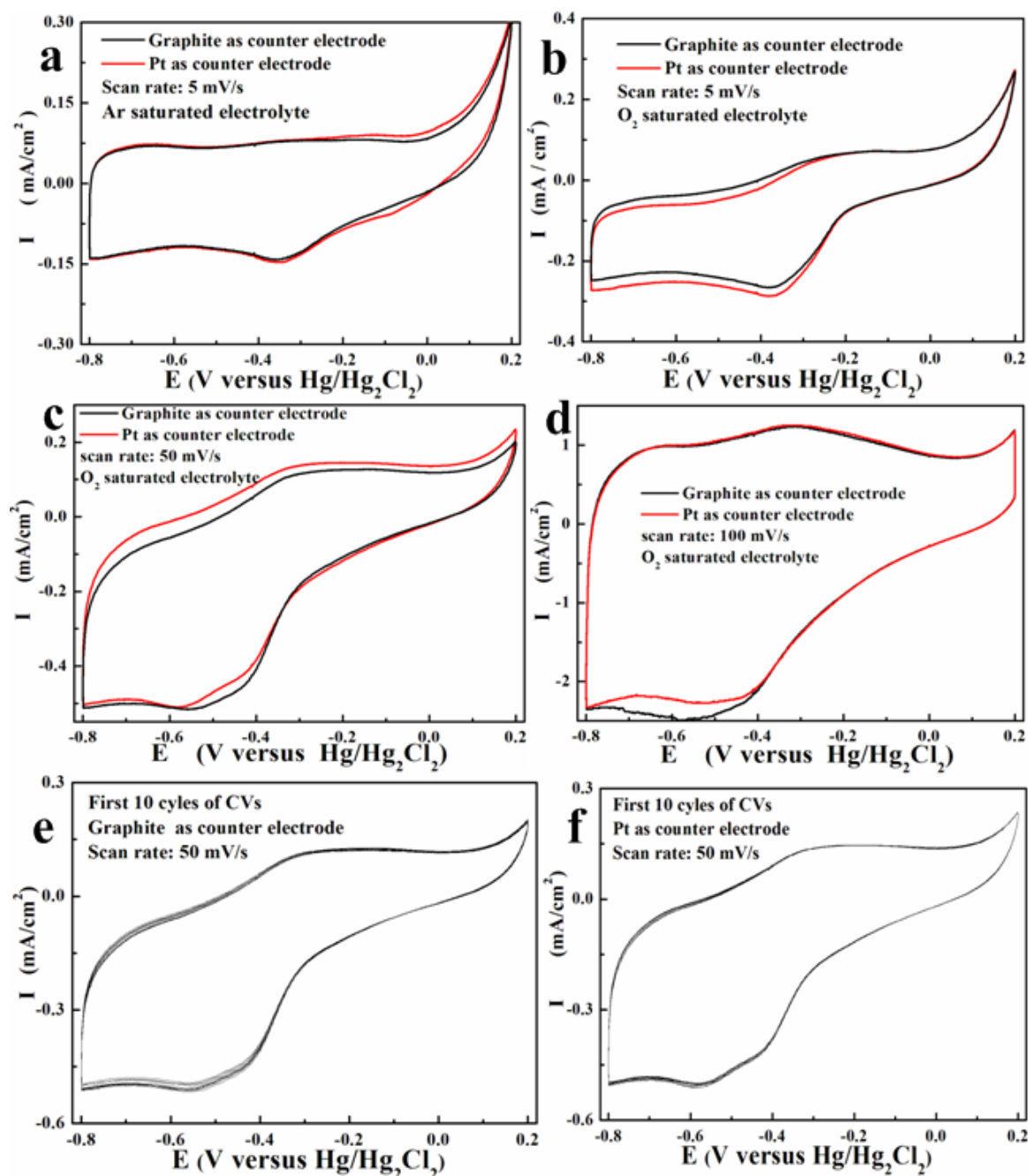
Fig. S5. ORR characteristics of VN in both (a) Ar and O_2-saturated KOH solutions with Pt and graphite as the counter electrode at different scan rates: (b) 5 mV/s, (c) 50 mV/s, and (d) 100 mV/s. First ten cycles of CVs of VN with (e) Pt and (f) graphite as the counter electrode in an O_2-saturated KOH solution.

We have examined the ORR characteristics of VN in both Ar and O_2-saturated KOH solutions with Pt and graphite as the counter electrode. Graphite is also a commonly used counter electrode for electrochemical test due to its high conductivity and stability in electrolyte. Fig. S5a clearly shows that there is almost no difference in the onset potential and peak potential of the ORR with Pt and

graphite as the counter electrode. The ORR current densities with Pt wire as the counter electrode are slightly higher than that with graphite as a counter electrode at a scan rate of 5 mV/s (Fig. S5b) and are smaller than that with graphite as a counter electrode at scan rates of 50 and 100 mV/s (Fig. S5c and d). Therefore, based on the results, there is no evidence that the Pt has deposited on the working electrode during the test. In addition, since all the electrochemical tests in this study were carried out with the Pt wire as the counter electrode, the evaluation of the catalysts performance and the comparison with the commercial Pt/C catalyst are fair and reliable. The typical first ten cycles of CVs of VN for ORR with Pt and graphite as the counter electrode are shown in Figs. S5c and d. During the pre-cycling, the differences in the CVs become smaller and smaller, and finally reach a stable status, after which the CV shows no change in the following test. And we use the CV after pre-cycling as the representative CV to study the catalyst performance.