Electronic Supplementary Information

Mesoporous vanadium nitride as a high performance catalyst support for formic acid electrooxidation

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Experimental

Preparation of mesoporous VN: $Zn_3V_2O_8$ was prepared by a solid state reaction of the stoichiometric mixture of ZnO (99.99%, Aldrich) and V_2O_5 (99.6%, Alfa Aesar) which were ground together and then heated for 4 hr in air at 500 °C. The temperature was subsequently increased to 750 °C and heated for 40 hr with intermediate regrindings. 2-3 g of $Zn_3V_2O_8$ was placed in an alumina boat. The boat was then placed in a silica tube with air tight silica end caps that had welded valves and connections to input and output gas lines. All gases were purified to remove trace amounts of oxygen or water using pellet copper, nickel, palladium and platinum with zeolites as support. The silica tube was then placed in a split tube furnace and the appropriate connections to gas sources made. Argon gas was passed over the sample for 15 min to expel air before establishing a flow of ammonia gas (Anhydrous, Air Gas). The sample was heated to 600 °C at 150 °C/hr. After treatment for 12 hr, the furnace power was turned off and the product cooled to room temperature in ~ 4 hr under an ammonia flow. Before the silica tube was taken out of the split tube furnace, argon gas was flowed through the tube to expel the ammonia gas. The silica tube was left in lab for 24 hr with one valve open in order to expose the ammonolysis product to air slowly. This latter procedure resulted in the formation of only a very thin oxide on the nitride surface.

Deposition of Pd nanoparticle on mesoporous VN and XC-72 carbon black: Firstly, 50 mg of mesoporous VN (or CNTs) was suspended in 50 ml of ethylene glycol solution, and an appropriate amount of $PdCl_2$ solution was added. Then the mixture was heated at 150 °C for 3 h. Subsequently, the

suspension was filtered and washed with deionized water, and then dried at 80 $^{\circ}$ C for 6 h to obtain the Pd /VN catalysts (or Pd/C).

Physicochemical characterization: Nitrogen adsorption/desorption isotherms were measured at -196 ^oC using a Micromeritics ASAP 2020 system. The samples were degassed at 200 ^oC for 24 hr on a vacuum line. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were performed with a LEO-1550 field emission SEM (FSEM). The size and morphology of Pd/VN catalyst and Pd/C catalysts were characterized by FEI T12 Spirit TEM STEM. X-ray diffraction spectra were measured with a Rigaku Ultima VI powder X-ray diffractometer (PXRD) with Cu K_α radiation (K_{α1}, $\lambda = 1.5406$ Å and K_{α2}, $\lambda = 1.5444$ Å). X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Kratos XSAM-800 spectrometer with an Mg Kα radiator.

Electrochemical Measurements: Electrochemical measurements were carried out with a potentiostat/galvanostat (WaveNano USB Potentiostat) and a conventional three-electrode test cell. The catalyst ink was prepared by ultrasonically dispersing the mixture of 5 mg catalysts, 1 mL ethanol, and 50 μ L 5 wt. % Nafion solutions. 10 μ L catalyst inks was pipetted and spread on the glassy carbon disk. A Pt foil and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. For Polarization current vs. time the potential was fixed at 0. 2 V.

Results



Fig. S1 EDX of Pd on mesoporous VN.



Fig. S2. Isotherm plot of N₂ absorption at 77 K for mesoporous VN for the BET surface area study.



Fig. S3 The histograms of Pd particle diameters of Pd/VN (A) and Pd/C (B).



Fig. S4 Cyclic voltammograms recorded in $0.5M H_2SO_4$ solution at a scan rate of 20 mV s⁻¹.



Fig. S5. Linear sweep voltammograms of Pd/C ormed in electrolytes of 0.5 M H_2SO_4 and 1 M HCOOH at a scan rate of 20 mV s⁻¹.