Supporting Information

In Search of the Active Site in Nitrogen-Doped Carbon Nanotube Electrodes for the Oxygen Reduction Reaction

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1. Synthesis of vertically aligned carbon nanotubes by alumina template technique

To prepare vertically aligned non-N-doped and N-doped carbon nanotubes without any impurities, a variety of polymer precursors; PPA - polyphenylacetylene, P4VP - poly(4-vinylpyridine), PMPy – poly(3-methylpyrrole), PMVI – poly(2-methyl-1-vinylimidazole) and PPP – poly(p-pyridazine-3,6-diyl) having different nitrogen contents were taken in a template technique. CNTs are prepared from P4VP, PMPy, PMVI and PPP for the first time.

1.1. Synthesis of CNTs from polyphenylacetylene (PPA), poly(4-vinylpyridine) (P4VP), poly(2-methyl-1-vinylimidazole) (PMVI) and poly(p-pyridazine-3,6-diyl) (PPP)

PPA, PMVI, and PPP polymers are prepared according to the methods described in reference 1, 2, and 3 respectively. P4VP is purchased from Aldrich and used as-received.

CNTs are prepared from polyphenylacetylene (PPA) in a template technique according to the reference 4. Stock polymer solutions are prepared by dissolving appropriate amount (3 to 5 wt.%) of the polymer in a suitable solvent (PPA in dichloromethane, P4VP in ethanol, PMVI in methanol and PPP in N,N'-dimethylacetamide). In a typical synthesis procedure, polymer solution is impregnated directly into the pores of the alumina template (AAO, Whatman, Anodisc47, nanopore diameter of ~100 nm and length of ~60 μm) by applying vacuum from the bottom. The solvent was evaporated slowly, and the membrane was dried in a vacuum at 343 K. The polymer/alumina composite was then polished with fine alumina powder to remove the surface layers and ultrasonicated for 20 min to remove the residual alumina used for polishing. Then the membrane was placed in a quartz tube kept in a tubular furnace and carbonized at 1173 K for 2 h under inert gas atmosphere. The resulting carbon/alumina composite was then treated with 6 M NaOH to dissolve alumina template and free the carbon nanotubes. Finally, carbon nanotubes are washed with de-ionized water and dried.

1.2. Synthesis of CNTs from poly(3-methylpyrrole) (PMPy):

Poly(3-methylpyrrole) is coated on the pore walls of alumina membrane by the electrochemical oxidation of 3-methylpyrrole monomer according to the procedure described in reference 5. Electrochemical polymerization was carried out galvanostatically in a one-compartment cell under argon atmosphere. The concentrations of the monomer and Et_4NPF_6/propylene carbonate electrolyte are 0.11 and 0.05 M, respectively. Platinum sheets are used as the working and auxiliary electrodes. Ag/AgCl electrode is used as reference electrode. The monomer solution was de-aerated by

bubbling dry nitrogen gas for 30 min before electrochemical polymerization. Then electrochemical polymerization is carried out by applying current density of 0.15 mA/cm^2 for 15 min. It leads to a coating of polymer on the pore walls of alumina template. The resulting polymer/alumina composite is washed with hexane and dried. After that the composite is heat-treated at 1173 K for 2 h to decompose the polymer and form carbon/alumina composite. This was followed by the same procedure as described above to remove the alumina template. The carbon material was then washed with distilled water to remove the residual impurities and dried.

2. Scanning electron microscopic (SEM) images of the CNT samples

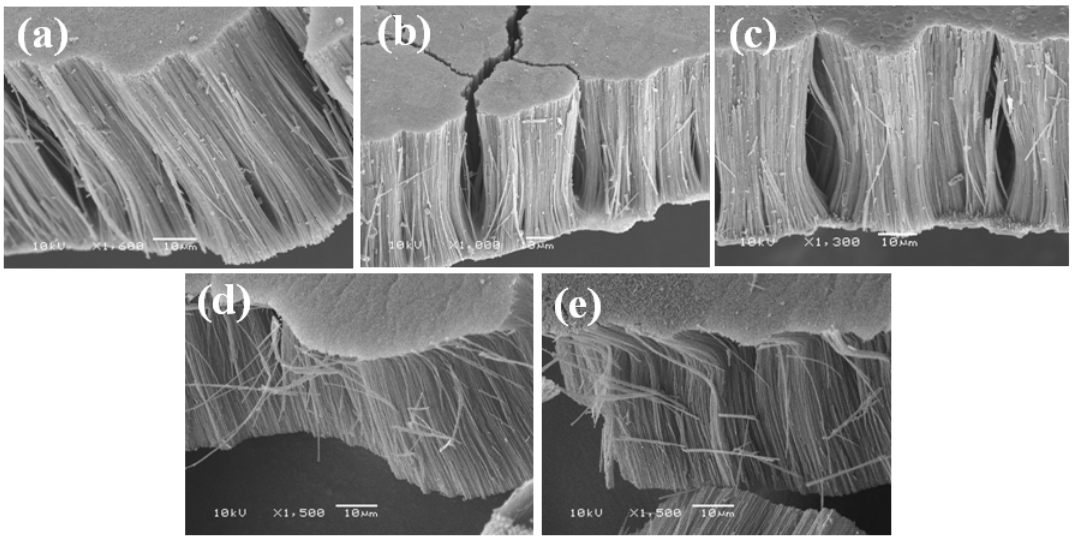

Figure S1. Low-magnification SEM images of (a) CNT_{PPA} (b) CNT_{P4VP} (c) CNT_{PMPy} (d) CNT_{PMVI}, and (e) CNT_{PPP}

Figure S1 shows the uniform, cylindrical and vertically aligned nanotubes distributed in a regular array with an outer diameter of 100 nm and length of 60 μm that almost matches

the pore dimensions of alumina template. In the case of CNT_{PMVI} and CNT_{PPP} samples, the regularity of the CNTs was slightly distorted at the open end of tubes. This may be due to the introduction of C-N bonding, which is shorter than the C-C bonds.

3. X-ray photoelectron survey scan spectra

XPS survey-scan spectra show predominant C1s peak around 284 eV in the non-N-doped CNTs, while the C1s and N1s peaks appear around 284 and 400 eV in the nitrogen-containing CNTs (Figure S2). The observed C1s peak mainly represents graphitic carbon. The spectra also show the presence of very small amount of surface adsorbed oxygen.

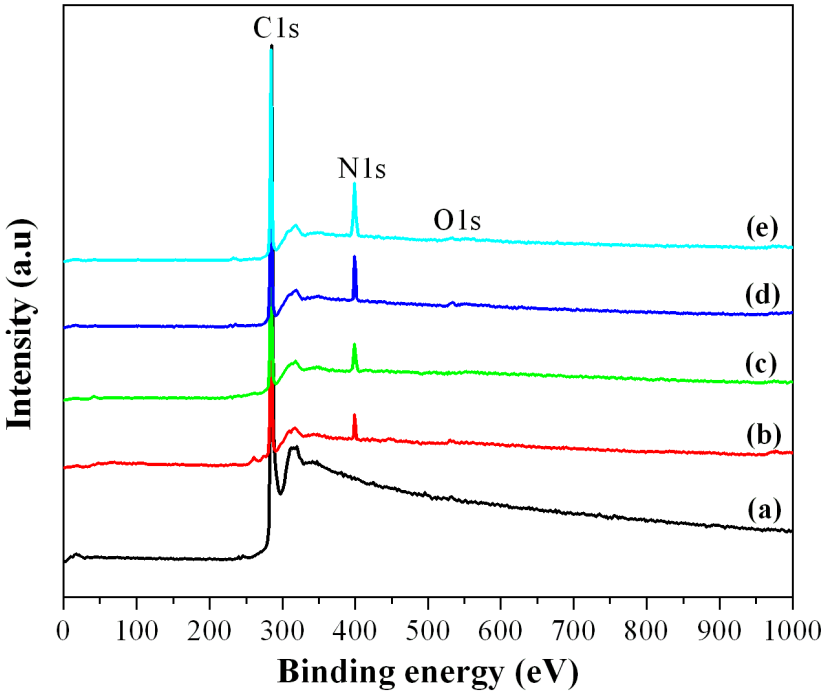

Figure S2. X-ray photoelectron survey scan spectra for (a) CNT_{PPA} (b) CNT_{P4VP} (c) CNT_{PMPy} (d) CNT_{PMVI}, and (e) CNT_{PPP}

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