

A Highly Active and Durable Co-N-C Electrocatalyst Synthesized Using Exfoliated Graphitic Carbon Nitride Nanosheets

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Synthesis of g-C₃N₄ and g-C₃N₄-NS

The g-C₃N₄ material was prepared according to a recent literature. Dicyandiamide was placed in a crucible with a lid and heated to 550 °C for 4 h with a ramp rate of 5 °C·min⁻¹ to give g-C₃N₄. The as-prepared g-C₃N₄ (2.0 g) was added to the concentrated sulfuric acid (50 ml), and the mixture was stirred at room temperature for 2 h. Then, the resulting solution was slowly added to a 1L beaker containing distilled water (100 mL), which then ultrasonicated for 1 h at room temperature. The solution was filtered, and the obtained products were dried at 80 °C to give g-C₃N₄-NS as colorless powders.

Synthesis of Co-N-C and Co-N-C-NS

The desired Co-N-C and Co-N-C-NS electrocatalysts were prepared by the following sequential processes: (i) Co adsorption to g-C₃N₄, (ii) addition of carbon black to Co adsorped g-C₃N₄ and following pyrolysis. In a typical experiment, g-C₃N₄ (or g-C₃N₄-NS, 400 mg) was added to an aqueous solution (20 mL) containing CoCl₂·6H₂O (12 mg). The mixture was heated for 4 h at 100 °C upon stirring until water was completely evaporated, producing Co-adsorped blue powders. Carbon black (400 mg) with distilled water (20 mL) was then added to the obtained blue powders. With the resulting heterogeneous mixture, we repeated the same drying procedure described as above. Resulting material was ground and pyrolyzed at 700 °C with a heating rate of 5 °C·min⁻¹ for 4 h under N₂ atmosphere to give final products Co-N-C (or Co-N-C-NS).

Characterization of catalysts

The particle size and height of both g-C₃N₄ and g-C₃N₄-NS were measured using atomic force microscope (AFM, XE-100, Park Systems) in the noncontact mode. Ultra violet experiments was conducted in reflection mode on diffuse reflectance ultraviolet visible spectrometer (UV-Vis spectrometer, Cary 5000, Varian) and the obtained data was transformed into absorption by Kubelka-Munk equation [$F(R)=(1-R)^2/2R$ (where R represents the absolute reflectance)].¹ In addition, band gaps of graphitic carbon nitrides were calculated from the Tauc plot as reported elsewhere.² Interlayer stacking of materials were confirmed by X-ray diffraction (XRD, Rigaku Mini Flex II) using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Surface area and gas adsorption properties of a catalyst were measured by N₂ adsorption/desorption isotherm measurement at 77 K (ASAP 2000). Morphology of a catalyst was determined by high resolution transmission electron microscope (HRTEM) and high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM, FEI Titan at 200 kV). Ratios of different nitrogen species presented at an electrocatalyst were analyzed by curve fitting of N 1s X-ray photoelectron spectra (XPS, PHI 50000 Versa Probe) from Al K α -ray (1486.6 eV) in 6.7×10^{-8} Pa.

Electrochemical measurements

An Autolab PGSTAT20 potentiostat (Metrohm Autolab B.V.) was used in all electrochemical measurements. The experiments were conducted in a standard three-compartment electrochemical cell with temperature control and a rotating disk electrode (RDE) system (Eco Chemie B.V.). A saturated calomel electrode (SCE) and a Pt wire were used as the reference and counter electrodes, respectively. However, all potentials were calibrated using a homemade reversible hydrogen electrode (RHE) and reported with respect to the RHE. A catalyst-coated glassy carbon (GC) electrode (5 mm in diameter) was used as the working electrode. The GC electrode was successively polished with slurries of 0.05 μm Al₂O₃ (Buehler) and washed ultrasonically with water before every use.

Rotating ring-disk electrode measurements (RRDE, 5.61 mm in diameter) were conducted using an AFMSRCE advanced electrochemical system (Pine Instrument Co., USA). A three-electrode cell system was employed: (i) a working electrode consisted of a rotating glass carbon disk and a platinum ring electrode (Pine Instrument Co., USA), (ii) a SCE electrode as a reference electrode, and (iii) a Pt wire as a counter electrode. Note that the electrocatalyst was loaded on the rotating glass carbon disk. The experiments were carried out in O₂-saturated 0.1 M KOH solution for the ORR.

Ink slurry was prepared by mixing Co catalyst, 5 wt % Nafion solution (Aldrich), and 2-propanol. The amount of the ink slurry ($0.464 \text{ mg}\cdot\text{cm}^{-2}_{\text{geo}}$ of Co catalyst on the working electrode) was carefully controlled and deposited on the GC electrode, then dried at $70 \text{ }^{\circ}\text{C}$ for 5 min to prevent loss of the catalyst. To measure the current of the ORR, linear sweep voltammetry (LSV) was conducted in an O_2 -saturated 0.1 M KOH solution. The stability of prepared catalysts was examined by repeating 10000 potential cycles between 0.6 V and 1.0 V (vs. RHE) at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ in O_2 saturated 0.1 M KOH solution.

Reference

1. A. A. A. Ahmed, Z. A. Talib, M. Z. bin Hussein and A. Zakaria, *J. Alloys Compound*, 2012, **539**, 154-160.
2. S. J. Hong, S. Lee, J. S. Jang and J. S. Lee, *Energy Environ. Sci.*, 2011, **4**, 1781-1787.

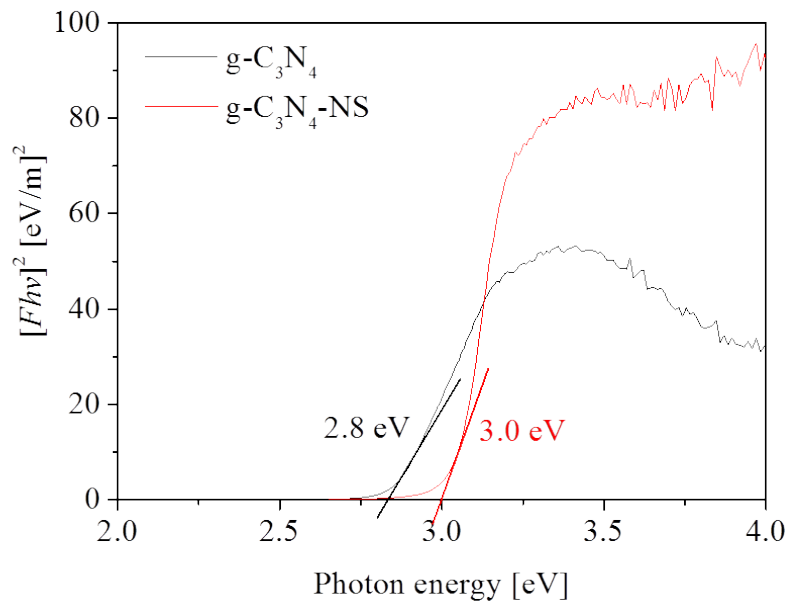


Fig. S1 Tauc plots of g-C₃N₄ and g-C₃N₄-NS, numbers indicate the band gaps of materials.

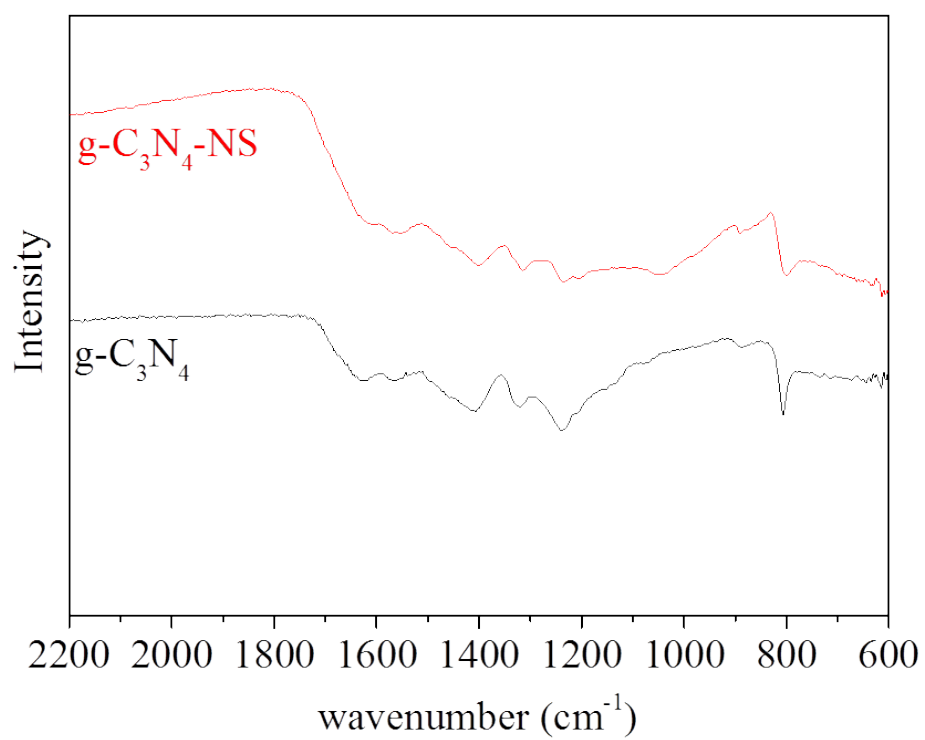


Fig. S2 IR spectra of $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4\text{-NS}$.