Electronic Supplemenary Information

Novel ordered nanoporous graphitic carbon nitride with C_3N_4 stoichiometry as a support for Pt-Ru anode catalyst in DMFC

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Survey scan XPS spectrum and deconvoluted C_{1S} and N_{1S} spectra are shown in Fig. S1. The carbon nitride sample contains carbon, nitrogen and small amount oxygen. Oxygen should be absorbed from the atmosphere during the survey scan. C_{1S} spectrum can be deconvoluted into two peaks. The major C peak at 288.1 eV is identified as sp^2-bonded carbon (C=N). The weaker C peak at 284.7 eV is assigned to graphitic carbon in good agreement with literature.[1,2] N_{1S} spectrum consists of four main contributions. The two main signals at 398.6 eV and 400.4 eV correspond to two types of sp^2 hybridized nitrogen[2] (N_α (bonded to two neighboring atoms) and N_β, (bonded to three neighboring atoms), respectively as labeled in Fig. S3). The two weakly deconvoluted signals at 401.7 and 404.6 eV are also observed and attributed to the $-NH_2$ or =NH groups, which correspond to uncondensed terminal amino groups. The peak area at 398.6 eV corresponding to N_α is about 3 times the total area of peaks at 404.6, 401.7 and 404.4 eV corresponding to N_β.

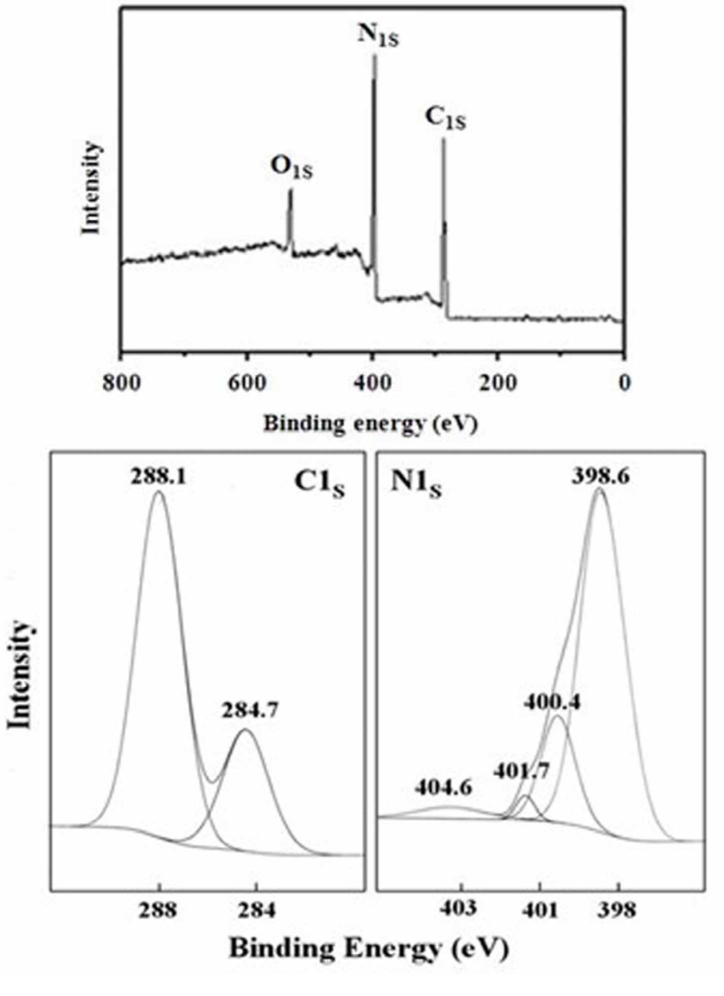

Fig. S1 XPS spectra of the carbon nitride.

Fig. S2 shows a Fourier-transform infrared (FT-IR) spectroscopic measurement, which implies the existence of condensed aromatic CN heterocycles. The overall features of the spectrum are similar to those of other g-C_3N_4 systems.[2,3] The absorption bands near at 1571 and 1630 cm^{-1} are attributed to C=N stretching, while the three bands at 1255, 1323 and 1428 cm^{-1} to aromatic C-N stretching. The peak at 809 cm^{-1} belongs to triazine ring mode, which correspond to condensed CN heterocycles.[1-3] A broad band near at 3150 ~ 3500 cm^{-1} corresponds to the stretching modes of $–NH_2$ or =NH groups, which are uncondensed amine groups, in agreement with the results from XPS measurement. In addition to FT-IR and XPS measurements, elemental analysis also showed that there is a small amount of hydrogen element (2.9 wt %) in the sample. This may be attributed to hydrogen attached to the uncondensed nitrogen atoms.

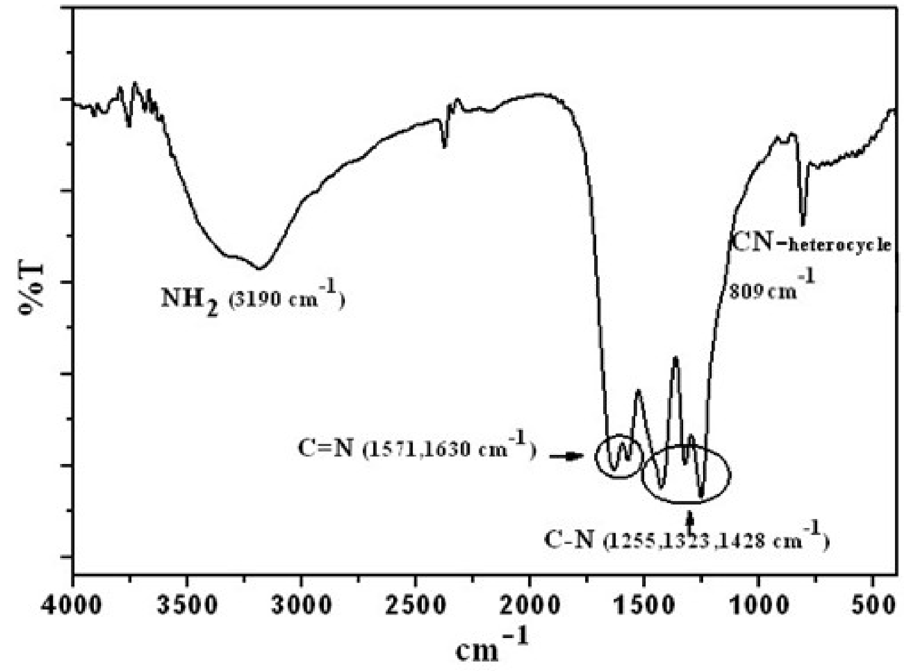

Fig. S2 FT-IR spectrum of the carbon nitride.

All the results from our XPS, FT-IR, and starting materials suggest that the resulting C_3N_4 network structure is made of novel tri-s-triazine rings (C_6N_7) cross-linked by trigonal N atoms as shown in Fig. S3. While N_α represents N atoms that connected to two neighboring carbon atoms in s-triazine rings, N_β indicates trigonal N atoms that make 3-fold coordination to 3 neighboring atoms.[4-6] The expected N_α/N_β atomic ratio of 3 is supported by XPS measurement in Fig. S1.

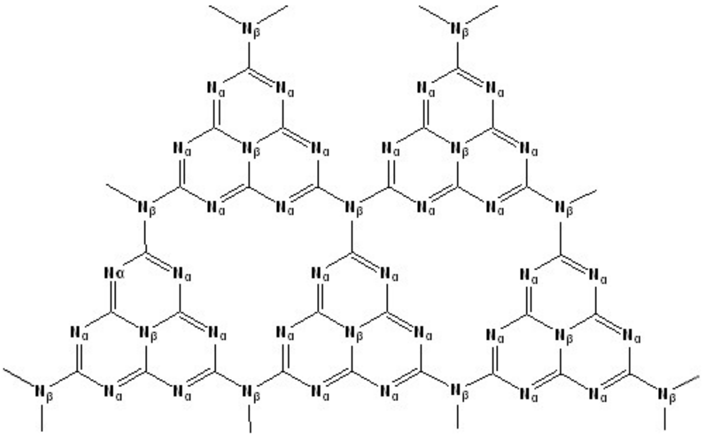

Fig. S3 Atomic structure of a graphitic-C_3N_4 single layer. Nitrogen atoms occupy two different types of positions in the layer, labeled α and β in the figure.

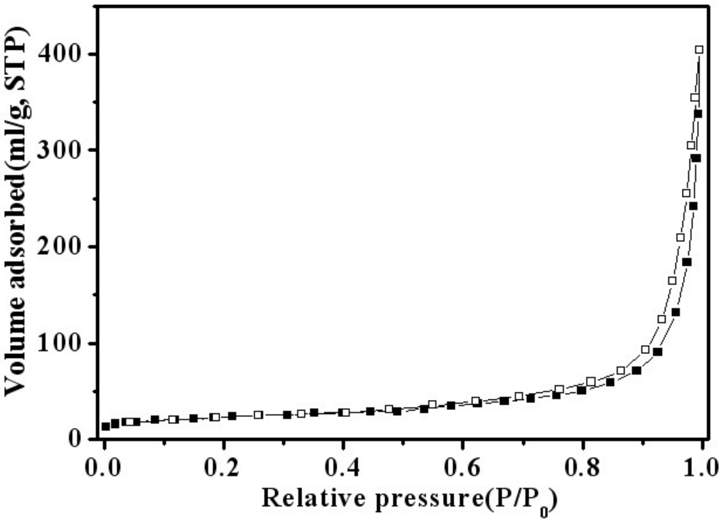

Fig. S4 Nitrogen adsorption-desorption isotherms at -196℃ for the graphitic carbon nitride.

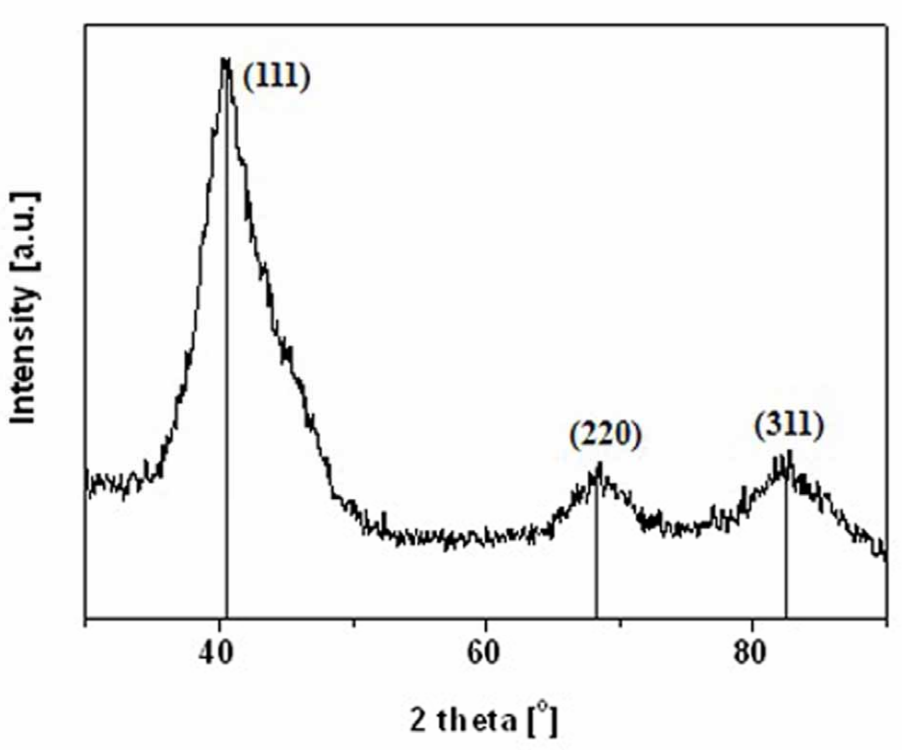

Fig. S5 XRD pattern for a PtRu/C3N4 catalyst.

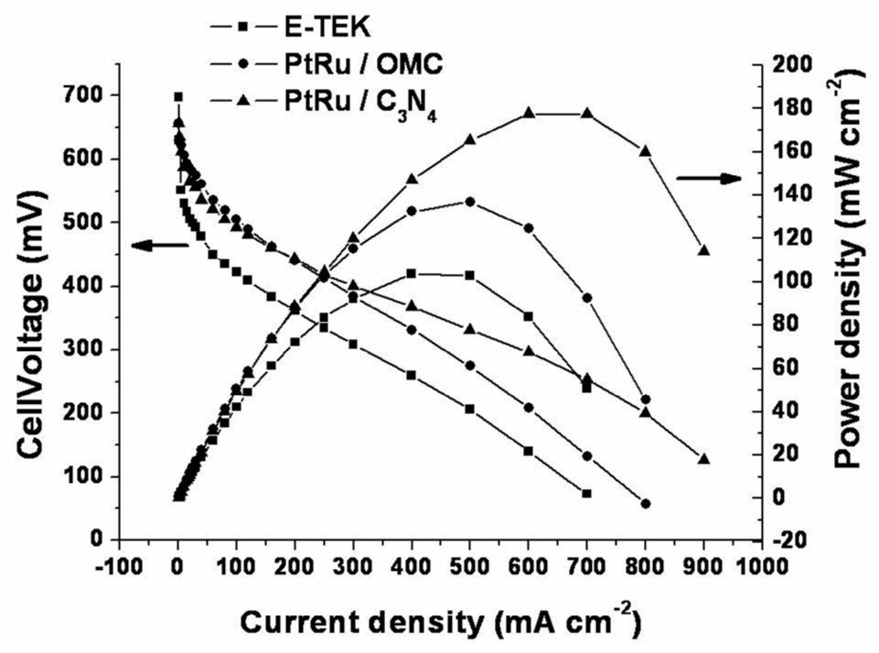

Fig. S6 The polarization and power density curves for direct methanol fuel cell using Pt-Ru/C_3N_4, Pt-Ru/OMC or a commercial Pt-Ru/E-TEK catalyst as an anode determined at 60 °C. Cathode: Johnson Matthey Pt black (5.0 mg/cm^2) with O_2-feeding mode.

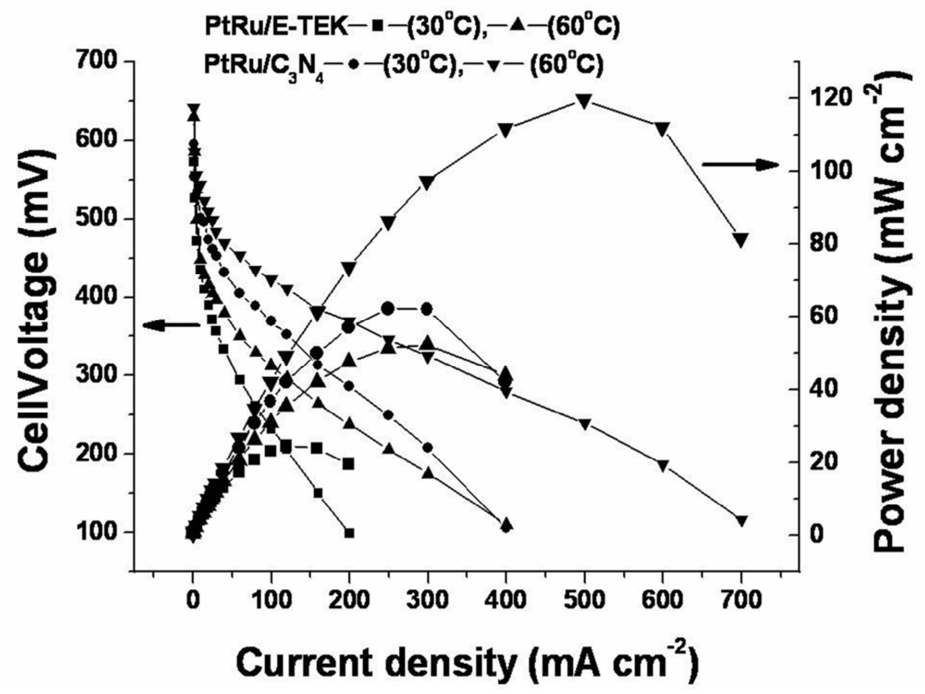

Fig. S7 The polarization and power density curves for direct methanol fuel cell using Pt-Ru/C_3N_4 or a commercial Pt-Ru/E-TEK catalyst as an anode determined at 30 °C and 60 °C. Cathode: Johnson Matthey Pt black (5.0 mg/cm^2) with air-breathing mode.

Experimental Section

Synthesis of the graphitic C_3N_4 structure: Close-packed well ordered silica colloidal crystalline was prepared according to the previous method.[7] The dried colloidal monolith was then sintered slightly at their points of contact by heating to 500–700 ^oC for 2 h in order to provide pore connectivity in the replica structure before precursor infiltration according to the previous work.[7] The cyanamide ($CN\text{-}NH_2$) was employed as a molecular precursor for graphitic C_3N_4 structure since its low melting point of 45 ^oC allowed facile nanocasting process at relatively low temperature. The synthesis of carbon nitride was carried out by incorporation of the liquid cyanamide into colloidal silica template under static vacuum at 70 ^oC, and the mixture was kept for 60 min in this condition according to the previous method.[6] The monolith was dried and then washed in ethanol solution to remove excessive precursor. The mixture was then annealed at 550 ^oC for 3 - 5 h with heating rate of 3 ^oC /min under Ar gas flow. For comparison, an ordered macroporous carbon (OMC) with similar pore size was synthesized using phenolic resin as a carbon precursor at 1000 ^oC with a similar colloidal crystal as template as described elsewhere.[7] The resulting silica-carbon composites were soaked in aqueous HF to dissolve the silica template, and resulting residue was filtered and washed with distilled water several times and then dried in oven at 70 ^oC.

Carbon treatment and catalyst preparation: Carbon nitride and OMC, each with 240 nm ordered macropores in size and Vulcan XC-72 were used as catalyst supports in this work. The activation of supporting carbon was performed based on slight modification of previously reported method.[8] Typically, 1.0 g of carbon was added to 100 ml HNO_3 (10% v/v) solution. The suspension was stirred for 48 h at room temperature and then filtrated to have an activated support.

Supported Pt_{50}-Ru_{50} catalysts were prepared by surfactant-stabilized method using chloroplatinic acid and ruthenium chloride as catalyst precursors, Pluronic L64 ($EO_{13}PO_{30}EO_{13}$) as surfactant and $NaBH_4$ as reducing agent.[9] Equi-molar $H_2PtCl_6{\cdot}6H_2O$ and $RuCl_3{\cdot}xH_2O$ were dissolved in deionized water and L64 was added by stirring for 1 h at ambient temperature. The required amount of the above-prepared activated carbon was suspended in DI-water and homogeneous carbon solution was obtained by stirring. Then this carbon solution was mixed with the metal salt solution. The mixture was adjusted to pH of 8 by dropwise addition of NaOH. The Pt-Ru/support reaction mixture was stirred 4 h for complete reduction of Pt and Ru ions by $NaBH_4$ solution, which was prepared by dissolving appropriate amount of $NaBH_4$ in deionized water. The Pt-Ru/support catalyst slurry was collected at the bottom. The catalyst slurry was then filtered, rinsed thoroughly with excessive amount of ethanol-water (50:50 = v/v) solution, deionized water, and dried in a vacuum oven at 70 ^{o}C. The Pt-Ru loading was controlled to have 60 wt % for fair comparison with commercial E-TEK Pt-Ru catalyst (60 wt %) supported on Vulcan XC-72.

Characterization: The scanning electron microscopy (SEM) images were obtained using a Hitachi S-4700 microscope operated at an acceleration voltage of 10 kV. Energy dispersive X-ray (EDX) analysis was performed to identify elemental composition of the sample in connection with SEM. The transmission electron microscopy (TEM) was operated on EM 912 Omega at 200 kV. Also, high resolution TEM image was obtained by using transmission electron microscope (JEOL FE-2010) operated at 200 kV. Nitrogen adsorption and desorption isotherms were measured at -196 ^{o}C using gas adsorption analyzer KICT-SPA 3000S. The specific surface areas were determined from nitrogen adsorption in the relative pressure range from 0.05 to 0.15 using the BET (Brunauer-Emmett-Teller) equation. The X-ray diffraction patterns were recorded by using a Rigaku diffractometer with Cu Kα radiation at a scan rate of 4 ^{o}/ min at 40 kV and 20 mA. Thermogravimetric analysis profile was obtained using TA Instrument TGA 2950. Infrared spectroscopy was recorded with Perkin-Elmer Fourier transform infrared spectrometer. X-ray photoelectron spectroscopy (XPS) was performed by an ESCALAB 250 x-ray photoelectron spectrometer using Al Kα x-ray as an excitation source. Elemental analysis was taken with an EA 1110 elemental analyzer. The electrical conductivity of porous carbons was measured by standard four-probe method at ambient condition. Silver paste was used to connect a copper probe with a sample and four probes were arranged by the van der Pauw's method which can rule out the anisotropic effect on conductivity of sample.[10]

Single cell test: Cell performance was evaluated using DMFC unit cell with a 2 cm^2 cross-sectional catalyst area and measured with a potentiometer work station (WMPG-1000) according to previous work.[7] The membrane electrode assembly (MEA) was made by hot-pressing (at 135 °C under the pressure of 2000 psi for 5 min) pretreated Nafion-115 membrane sandwiched by anode and cathode, which had been prepared by painting a desired amount of supported catalyst ink on a Teflonized carbon paper (TGPH-090) and dried in an oven at 70 ^{o}C for 1h. The catalyst ink was made by mixing 100 mg of catalyst with 0.763 ml of 5 wt% Nafion solution and stirred prior to use. Anode and cathode electrodes consisted of carbon paper and carbon-supported catalyst layer. The catalyst loadings at anode and cathode were 3.0 (based on Pt-Ru metal only) and 5.0 mg/cm^2 (unsupported Pt catalyst layer from Johnson Matthey), respectively. The Nafion-115 membrane was pretreated by first boiled in 3 wt % H_2O_2 for 1 h and then boiled in 0.5 M H_2SO_4 for 1 h. The single cell test fixture was composed of two steel end plates and two graphite plates with rib-channel patterns allowing the passage of methanol to the anode and oxygen gas to the cathode. A 2.0 M methanol solution was supplied to the anode at a flow rate of 1.5 mL/min by a Masterflex liquid micropump, while dry O_2 was fed to the cathode at a rate of 100 cc/min through a flowmeter. Another series of experiments were performed with air-breathing mode at cathode side instead of O_2 gas feeding mode, keeping other conditions identical in DMFC.

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