Electronic Supplementary Information for

Self-assembly of CNH Nanocages with Remarkable Catalytic Performance

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Materials and chemicals: Cyanuric chloride (99%, Aldrich), melamine (99%, Aldrich), dimethyl sulfoxide (DMSO) (>99.5%, Sinopharm Chemical Reagent Co, Ltd.), Pt-C catalyst (20% Pt on Vulcan XC-72R, Johnson Matthey, UK), 5% Nafion (45% H_2O_2, 50% ethanol, DuPont) and KOH (99%, Aldrich) were used without further treatment or purification.

Synthesis of the CNH nanocages: Melamine (0.315g, 2.5mmol) was suspended in 50mL DMSO. A solution of cyanuric chloride (0.461g, 2.5mmol) in 50mL DMSO was then added dropwise with stirring. Then, the system was heated to 160 ^oC for 10 h under nitrogen atmosphere. The flask was then cooled to room temperature and the precipitates in the reactor were collected by filtration. The product was washed with methanol three times, water three times, and then dried under vacuum at 80 ^oC.

Characterization: TEM images were taken on a JEM-2010 electron microscope, operated at 200 kV. The elemental mapping was achieved from electron energy loss spectroscopy (EELS) equipped on TEM. XPS analyses were performed using a Thermo ESCALAB 250 spectrometer, employing an Al-KR X-ray source with a 500 μm electron beam spot. A Micromeritics ASAP 2000 analyzer was employed to analyze the pore structure and surface area of the the product and the commercial Pt-C catalyst. Powder X-ray diffraction (PXRD) (D/MAX 2500, Rigaku) was used to analyze the microstructure of the product. Fourier transform infrared (FT-IR) spectroscopy (Nicolet 380, Thermo Scientific) and ultraviolet-visible (UV-Vis) spectroscopy (Shimadzu, UV-3600) were employed to analyze the chemical structure. The chemical composition was examined using an elemental analyzer (EA1110, CE Instrument). Thermo gravimetry (TG) analysis was implemented on STA 409 PC Luxx under nitrogen atmosphere.

Electrochemical tests: A GC electrode was carefully polished with gamma alumina powder until a mirror finish was obtained. Then the electrode was rinsed and fully sonicated with double distilled water to remove alumina residues. Finally, it was dried in vacuum. The CNHNC were used for catalysis tests and compared with a commercial Pt-C catalyst. In a mixture of 5% Nafion (50 μL) and ethanol (1mL), the catalysts (5 mg) were dissolved by sonication. Then, the solution (20 μL) was drop-casted on the GC electrode surface (0.2475 cm^2) and air-dried with an infrared lamp. CV, i-t chronoamperometric measurement, and RRDE voltammetry were all performed using a CHI 760D electrochemical analyzer and a MSR electrode rotator at a rotation rate of 1500 rpm. RRDE voltammograms for Nanocapsule/GC electrode in 0.1M KOH solution saturated with O_2. Linear sweep voltammetry (LSV) was performed with a scan rate of 0.005 V/s, whereas the Pt ring electrode was polarized at 0.5 V to oxidize the HO_2^- intermediates collected from the modified GC disk electrode. The transferred electron number (n) per oxygen molecule in the ORR process was calculated using the equation $n = 4I_D / (I_D+I_R/N)$, where I_D is the Faradic disk current, I_R is the Faradic ring current, and N = 0.37 (collection efficiency reported by the manufacturer).

Theoretical method and model: Density functional theory calculations were performed with DMol3 package. Double-numeric quality basis set with polarization functions (DNP) was used for all the atoms. The generalized gradient approximation (GGA) with the spin unrestricted Perdew, Burke, and Ernzerhof (PBE) functional was used. A thermal smearing of 0.005 Hartree (Ha) and a real-space cutoff of 3.7 Å were adopted. The geometry convergence tolerance for energy change, max force, and max displacement were 0.00001 hartree, 0.002 hartree/Å, and 0.005Å, respectively. Complete LST (linear synchronous transit)/QST (quadratic synchronous transit) methods were used to find the transition states of elementary steps. The model used is shown in Fig. S6. Only a non-periodic small model was considered due to limited computational conditions. All the edge nitrogen atoms are terminated with hydrogen atoms. As a whole, the cluster contains 30 carbon atoms, 49 nitrogen atoms and 27 hydrogen atoms. The atomic structures are fully relaxed in all calculations. The side view of the optimized structure clearly showed the structure is not planar, which means the structure most likely to grow into capsular structure with the number of atoms increasing theoretically.

The ORR processes were simulated beginning with the adsorbed intermediate molecule OOH on the model. At the beginning, OOH species is placed at the all possible adsorption sites, e.g. top sites of N and C atoms; bridge sites of N-C bonds; centers of the hexagonal ring and the cavity of surface.

Supporting figures and tables:

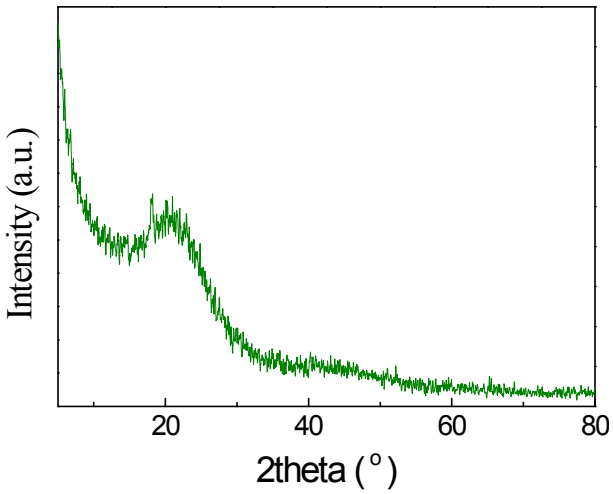

Fig. S1 Powder XRD pattern of the as-synthesized CNHNC.

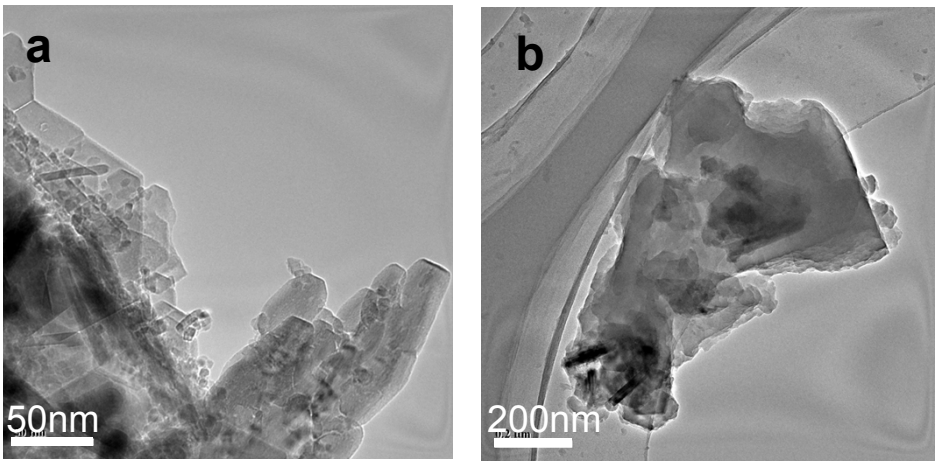

Fig. S2 TEM images of the samples with heating rate of (a) 10 °C/min and (b)5 °C/min.

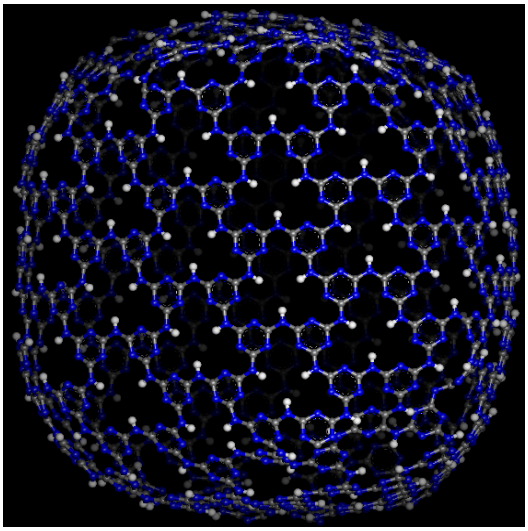

Fig. S3 The sketch map of the CNHNC carried out using Materials Studio. The grey, blue, and white balls represent C, N and H atoms, respectively.

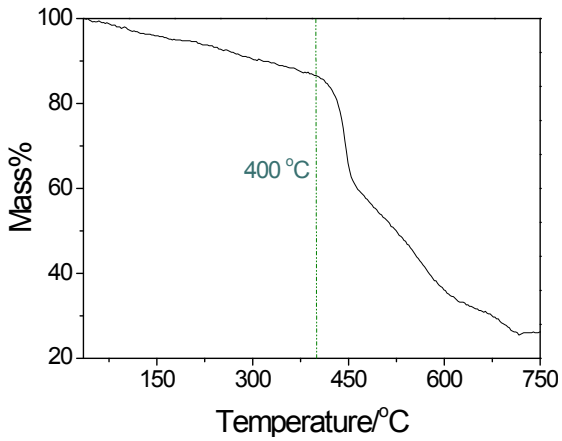

Fig. S4 TG curve of the as-synthesized CNHNC in nitrogen atmosphere.

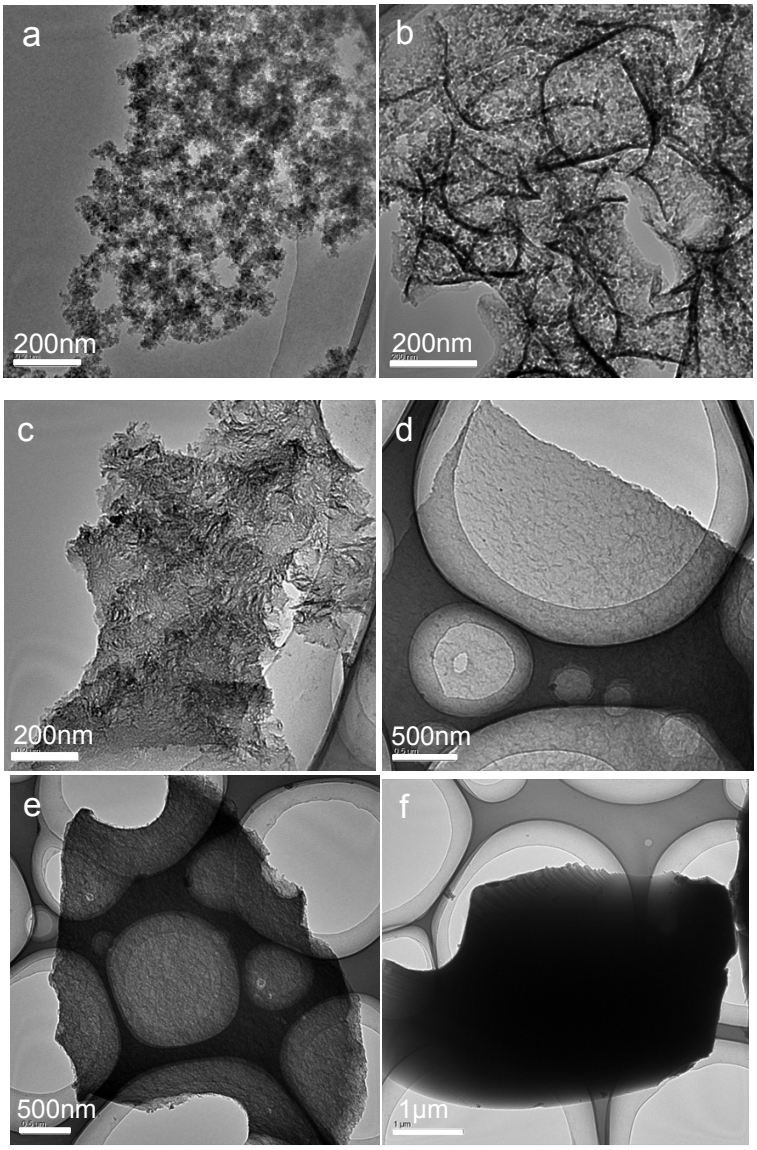

Fig. S5 TEM images of the CNHNC in different evolution stages: (a) as-synthesized; (b) 300°C; (c) 400 °C; (d) 500 °C; (e) 600 °C; (f) 700 °C.

Thermal gravimetric analysis (TG) was conducted under nitrogen atmosphere to understand the thermal stability of the nanocages, the TG curve (Fig. S3) exhibits that the nanocages show high stability below 400 °C. Furthermore, what interesting is that the as-synthesized nanocages could fuse and transform into two-dimensional nanosheets after annealed. The morphology of the CNHNC evolves with the annealing temperature rising, and TEM images of different evolution stages are shown in Fig. S4. The as-synthesized nanocages may further condense and form many wrinkles at the fresh joints under 300 °C, the wrinkles become smooth and even disappear while the temperature increases, and assemble into beautiful two-dimensional nanosheets at 500 °C. If the temperature is too high, the nanosheets will evolve into much thicker sheets.

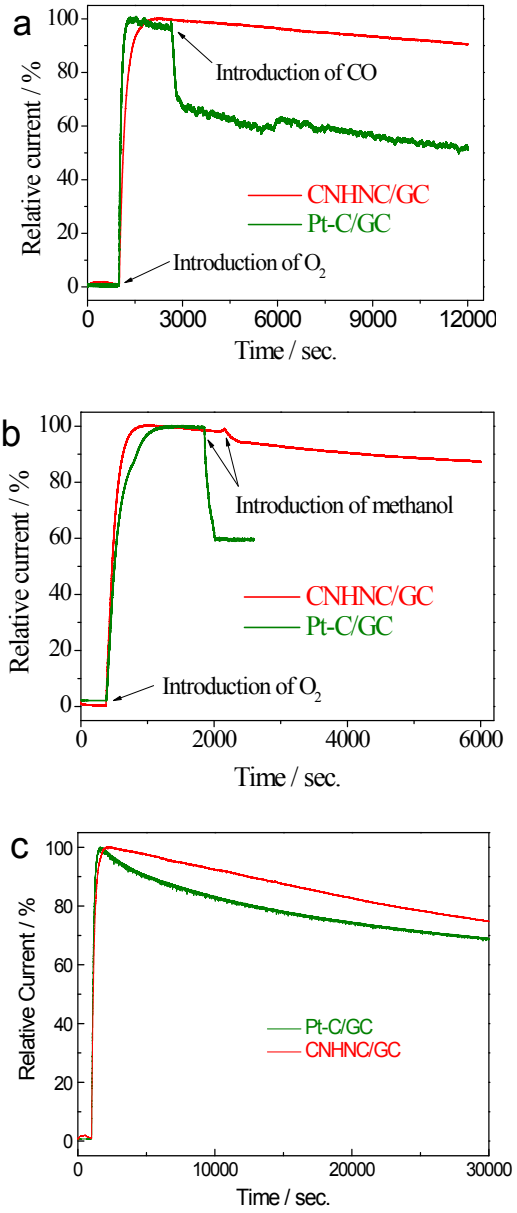

Fig. S6 The i-t responses to the introduction of 10% CO (a) and 3M methanol (b) in O_2-saturated 0.1M KOH at -0.45 and -0.20 V, respectively. (c) The i-t chronoamperometric responses of CNHNC/GC and Pt-C/GC electrodes in O_2-saturated 0.1M KOH at -0.45 and -0.20 V, respectively.

Furthermore, the nanocages exhibit an exceptional resistance to CO poisoning, with a constant activity upon the introduction of CO into the reaction system. On the contrary, the Pt-C catalyst is quite easily deactivated by CO (Fig. S5a). O_2 reduction on the nanocages was not influenced by methanol, similar to the previous reported metal-free catalysts, and a 40% decrease in current appears at the Pt-C/GC electrode upon the addition of methanol (Fig. S5b). Durability tests display that the nanocages show slightly better performance than Pt-C catalysts. After 30000 s of reaction, the two catalysts lose the current with 26% and 31%, respectively (Fig. S5c).

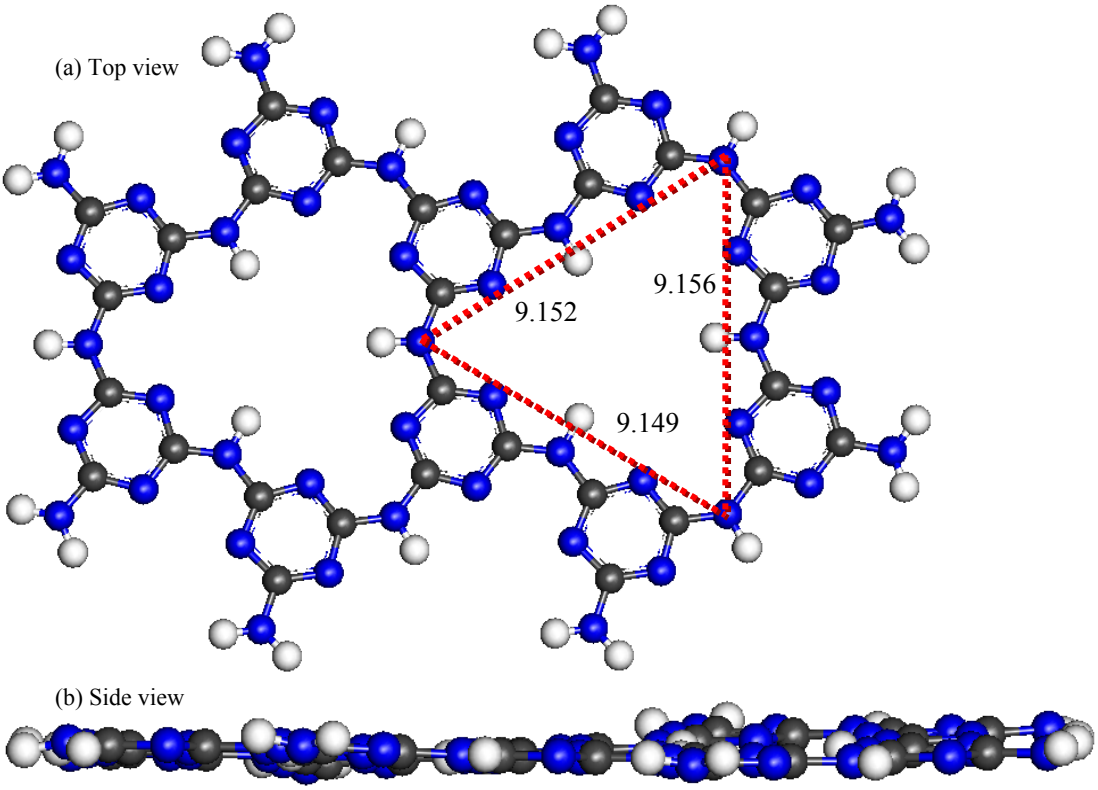

Fig. S7 An atomic model used for simulation. The grey balls represent C atoms, while the blue and white ones present N and H atoms, respectively. The red dotted lines are used to indicate the triangle-shaped cavity, the three numbers are the three side lengths of the triangle. The cavity is triangle-shaped with the three "side lengths" of 9.152, 9.149 and 9.156 Å, respectively.

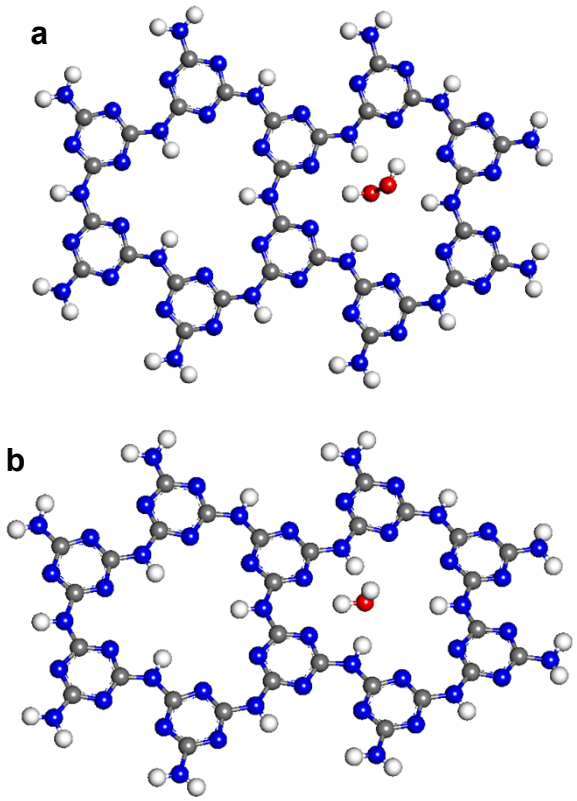

Fig. S8 The top view of H_2O_2 (a) and H_2O (b) species adsorbed in the cavity. The grey, blue, red and white balls represent C, N, O and H atoms, respectively.