Electronic Supporting Information (ESI†)

Efficient electrocatalytic oxygen reduction over metal free - nitrogen doped carbon nanocapsules

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Experimental details

Synthesis of $Gd_2O_2CO_3$ and Gd_2O_3 filled carbon and nitrogen doped carbon nanocapsules

Gadolinium (III) diethylene triaminepentaacetate (99%) was purchased from Aldrich. For a typical synthesis of core-shell nanocapsules was carried out using Swagelok union cells, 0.5 g of precursor was filled into the cell at room temperature under atmospheric conditions. The cell was closed tightly and then placed at the center of the muffle furnace. The temperature was raised at a heating rate of 20 ˚C per minute up to a required temperature (700 ˚C), where it was held for 3 h. The reaction took place under the autogenic pressure of the precursor. The closed cell was gradually cooled to room temperature and opened with the release of a little pressure. The yield of products obtained at 700 and 900 ˚C are found to be 50 and 35 wt%, respectively. The yield was with respect to the weight of precursor. 100 mg of oxide filled carbon was stirred in 5 mL of concentrated HCl for 12 h to remove the oxide core. The carbon nanostructures were recovered by centrifuging the contents at 6000 rpm for 10 min. The black compound was washed thoroughly with copious water and ethanol and stored under vacuum.

The phase purity of the products was examined by X-ray diffraction (XRD) using a Rigaku RINTUltimaIII powder XRD using Cu *K*α radiation at 40 kV and 40 mV. Transmission electron microscopy (TEM) images of the nanostructures were obtained by a JEOL JEM1011 microscope operated at an acceleration voltage of 100 kV and a JEOL-2010 high resolution TEM (HRTEM) instrument with an accelerating voltage of 200 kV. Samples for TEM and HRTEM were prepared by ultrasonically dispersing the products into absolute ethanol, placing a drop of this suspension onto a copper grid coated with an amorphous carbon film, and then drying under

air. The size distribution of nanoparticles was determined by measuring diameters of 100 nanoparticles randomly selected on the TEM images. The X-ray photoelectron spectroscopy (XPS) measurements were carried out using JEOL JPS-900 in ultrahigh vacuum, axis hemisphere monochromatized Mg Kα cathode source at 75–150 W using a low energy electron flood gun for charge neutralization. Survey and high resolution individual metal emissions were taken at a medium resolution, with pass energy of 50 eV and a step of 1 V. Binding-energy values were calibrated by using C 1s from a carbonvalue taken as 284.6 eV.

Electrochemical Tests:

A single glass compartment, three-electrode cell was employed for the electrochemical studies. Pt wire and silver/silver chloride (Ag/AgCl) saturated KCl were used as counter and reference electrodes, respectively. A 0.28 cm^2 area glassy carbon (GC) served as the working electrode. The electrochemical studies were carried out using PARSTAT 2273 (Princeton Applied Research) at room temperature. LCV was performed in a potential range of 0 to –1.0 V at 10 mV s^{-1}. NCNC (3 mg) was dispersed in water (250 μL) for 20 min in an ultrasonicator. The dispersed NCNC (40 μL) was placed on pre cleaned GC and dried in an oven at 80 ˚C for 2 min. 5% Nafion (10 μL) was dropped on GC and dried at room temperature. The solvent was evaporated, and the Nafion acted as a binder to hold the sample to the electrode. The electrolyte was degassed with nitrogen before the electrochemical measurements. The oxygen reduction activities were measured by hydrodynamic voltammetry using a rotating-disc-electrode in an oxygen-saturated 0.1 M KOH at room temperature. For comparison, Pt/C (E-TEK) 10 wt% was used.

Characterization of $Gd_2O_2CO_3$ and Gd_2O_3 filled carbon nanostructures

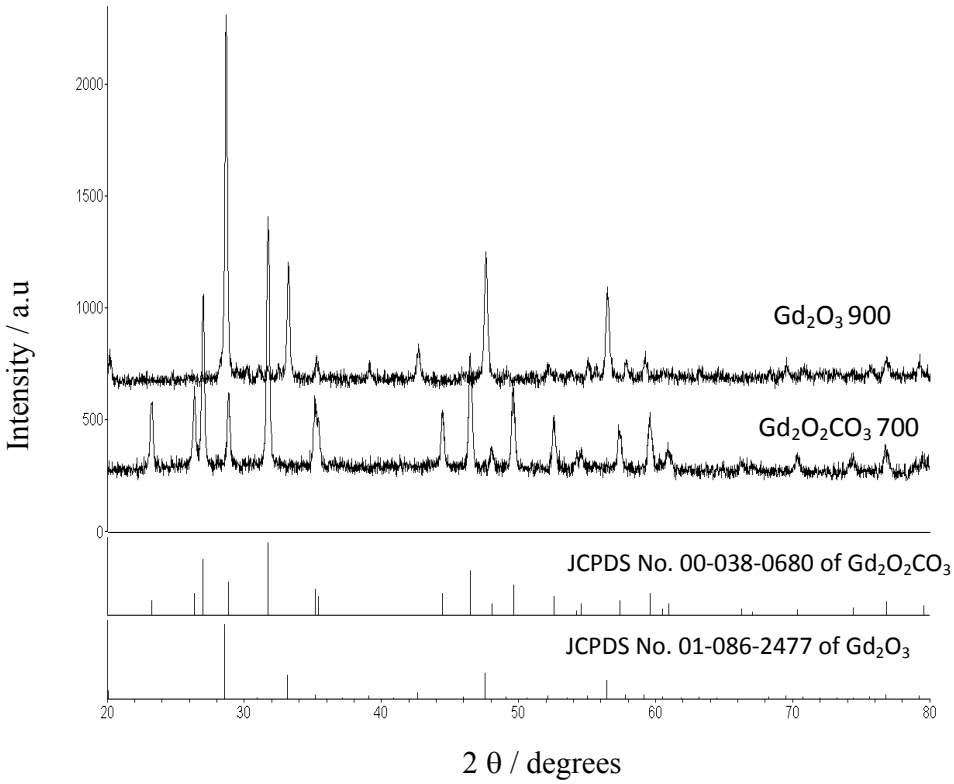

Fig. S1. XRD patterns for products obtained at 700 and 900 ˚C and standard JCPDS patterns are given as vertical lines in the bottom of XRD patterns.

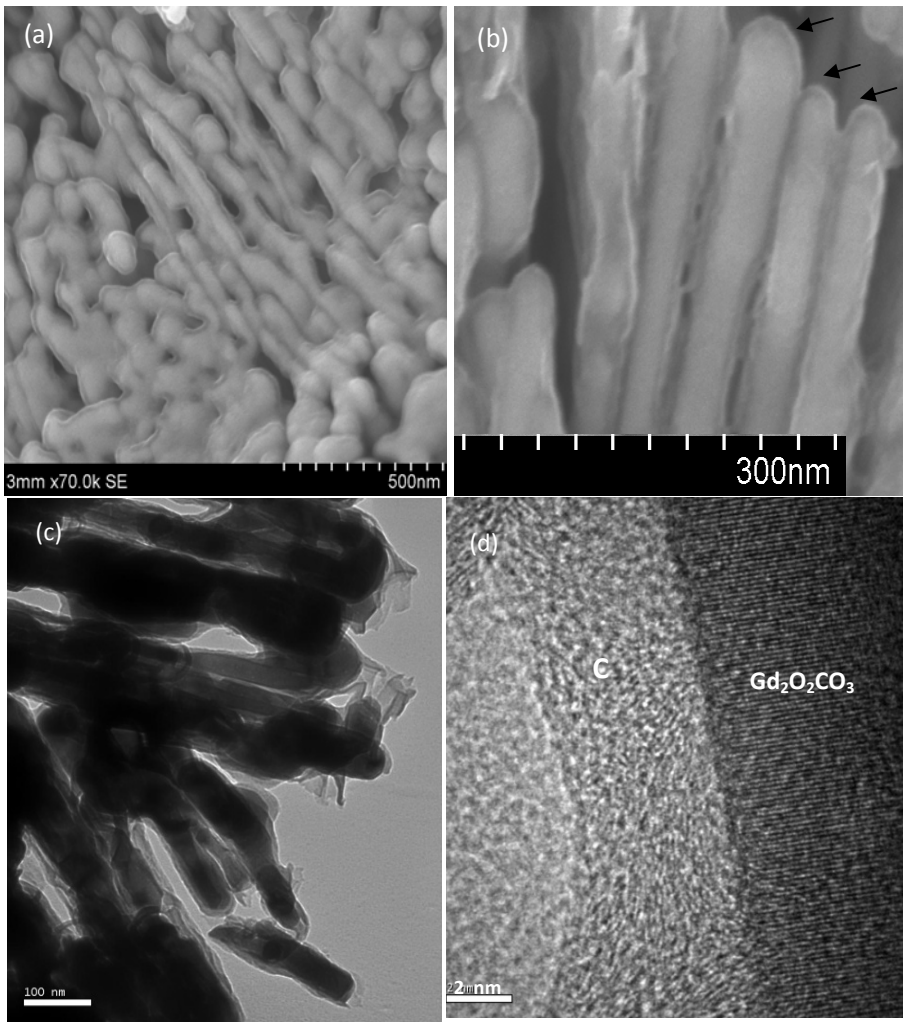

Fig. S2. SEM images of product obtained at (a) 700 and (b) 900 ˚C and (c, d) TEM images product obtained at 700 ˚C. HRTEM image shows clearly the turbostatic carbon shell with crystalline core as evidenced by the lattice fringes. The arrows show uniform carbon coating.

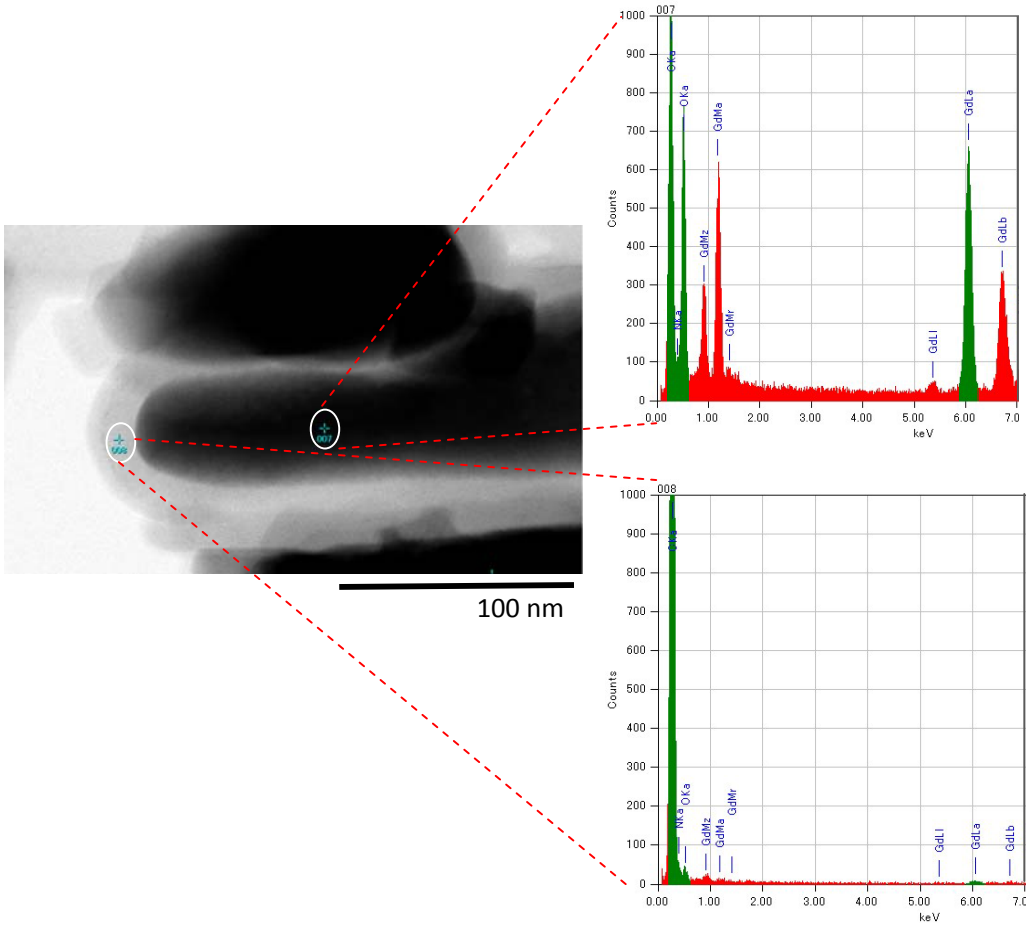

Fig. S3. EDX spot analysis coupled with TEM. The image shows clearly the distinctive bright field contrast difference between the filled material and the shell. The corresponding EDX spectra are given for filled material and shell. The spot analysis clearly shows the filled material is Gd oxide and shell is nitrogen doped carbon.

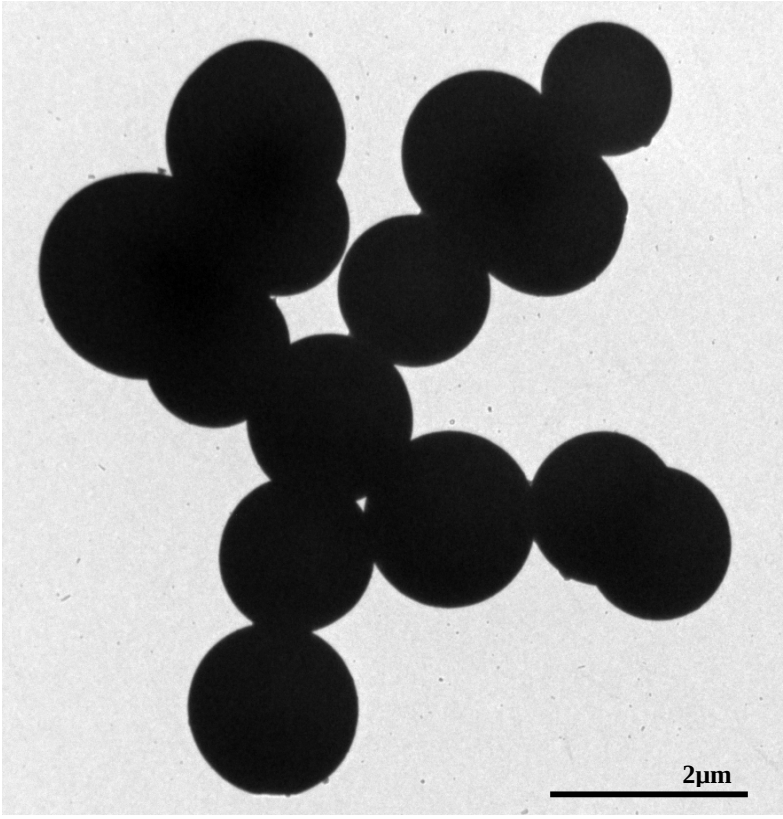

Fig. S4. TEM image of product obtained at 700 ˚C using diethylene triaminepentaacetate as a precursor.

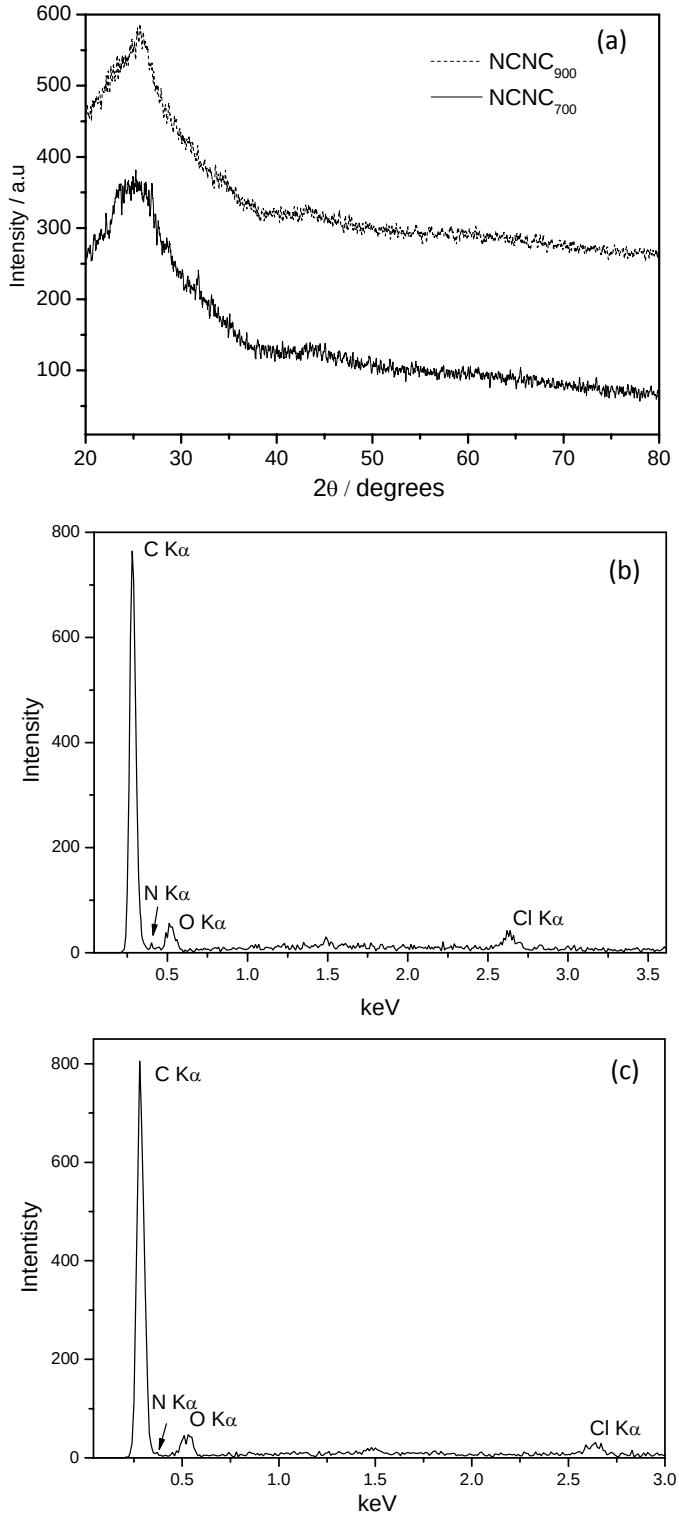

Fig. S5 . (a) XRD patterns NCNCs and EDAX spectra of (b) $NCNC_{700}$ and (c) $NCNC_{900}$ show only carbon, nitrogen and oxygen. The absence Gd peak is a clear evidence of the complete removal $Gd_2O_2CO_3$ or Gd_2O_3 .

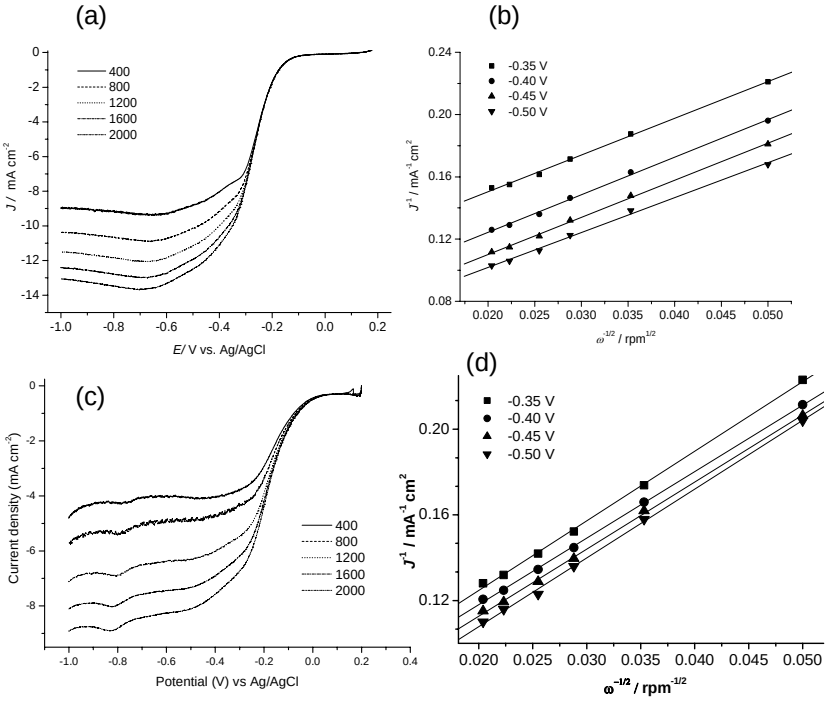

Fig. S6. (a, b) RDE voltammograms recorded for a $NCNC_{900}$ and corresponding Koutecky–Levich plots (J^{-1} vs. $\omega^{-1/2}$) at different electrode potentials and (c,d) RDE voltammograms recorded for a Pt/C and corresponding Koutecky–Levich plots (J^{-1} vs. $\omega^{-1/2}$) at different electrode potentials, recorded in aqueous 0.1 M KOH saturated with oxygen at different rotation rates.

Table S1. The physical and electrochemical properties of nitrogen doped carbon nanocapsules

Catalyst	Surface area $m^2 g^{-1}$	N content (Wt %)	N/C ratio	Nitrogen distribution (at %)					Number of electron transfer, n	Kinetic Current Density, J_k mA cm^{-2}
				N_1	N_2	N_3	N_4	N_5		
$NCNC_{700}$	38.0	7.1	0.088	27.6	61.8	8.4	2.2	-	3.96	20.1
$NCNC_{900}$	87.6	3.2	0.037	19.8	63.3	7.2	5.3	4.4	2.45	17.6
Pt/C	-	-	-	-	-	-	-	-	3.92	16.8