CO_2 reduction to syngas and carbon Nanofibres by plasma assisted *in-situ* decomposition of water

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S1: Material synthesis and Characterisation:

The NiO/Al_2O_3 catalyst was a commercial nickel catalyst with 33 wt% NiO supplied by Johnson Matthey. Identification of NiO/Al_2O_3, reduced Ni/Al_2O_3 and deposited carbon nano fibres (CNFs) was done by PANalytical X'pert pro X-ray diffractometer using Cu K_α (λ = 1.541 Å radiation, 30 mA, 40 kV). Temperature Programmed Reduction (TPR) of unreduced and reduced NiO/Al_2O_3 catalysts was carried out in a flow system (Quantachrome Autosorb-IQ automated gas sorption analyser) equipped with a thermal conductivity detector (TPR-TCD). Temperature programmed oxidation (TPO) of CNFs after HNO_3 treatment have done in a TGA instruments. The morphologies of CNFs deposited on the surface of inner electrode along with the colloidal nano/micro particles were examined by using an FEI model TECNAI G 220 S-Twin

TEM instrument. Raman spectra of as produced CNFs were recorded on a Bruker Senterra dispersive Raman microscope with laser excitation of wavelength of 532 nm.

S2: Experimental Section:

The DBD was generated in a cylindrical quartz tube with an inner diameter of 20 mm (Fig. 1). The quartz barrier had a wall thickness of around 1.5 mm with an inner diameter of 20 mm. Copper wire wrapped around the quartz tube for 150 mm length acted as the outer electrode. A stainless steel (SS-316) rod of 13 mm was used as the inner electrode resulting in a discharge gap was 3.5 mm and a corresponding discharge volume of 27.2 cm^3. A high voltage (Yaskawa Varispeed F7 AC inverter, AC voltage 0-40 kV and frequency 50-1000 Hz variable) alternating current in the range 14 to 24 kV at 100 Hz frequency was applied to ignite the discharge. The voltage (V) and charge (Q) waveforms were recorded with an oscilloscope (Tektronix, TDS 2014B) using a 1000:1 high voltage probe (Agilent 34136A HV). The charge Q was measured by measuring the voltage across the capacitor connected series to the ground electrode. The area of the Lissajous diagram characterizes the energy dissipated in the discharge during one period of the voltage. The average power (W) dissipated in the discharge was calculated by multiplying the area with the frequency. The residence time of the gas inside the reactor has been calculated by the following relation (1).

$$Residence\ time\ (Rs.Time) = \frac{Discharge\ volume\ (ml)}{Flow\ rate\ (^{ml}/_{\mathrm{sec}})} \qquad (1)$$

Where, discharge volume (V) = $\pi\ (r_2 - r_1)^2 \times l$

r_2 = radius of the quartz tube

r_1 = radius of SS electrode

l = discharge length

The flow rate of the gas was controlled with mass flow controllers (GFC-17, Aalborg-USA). CO_2 gas was introduced into the reactor through a Teflon tube and its concentration at the outlet was measured with a gas chromatograph (Shimadzu GC-2014) equipped with a TCD detector and a packed column. The conversion at each voltage was measured after 30 minutes. The concentration of hydrogen was confirmed with a hydrogen gas analyser (Siemens, calomat 6E), whereas a GC-MS (Thermofisher) was used to identify the products formed.

Figures:

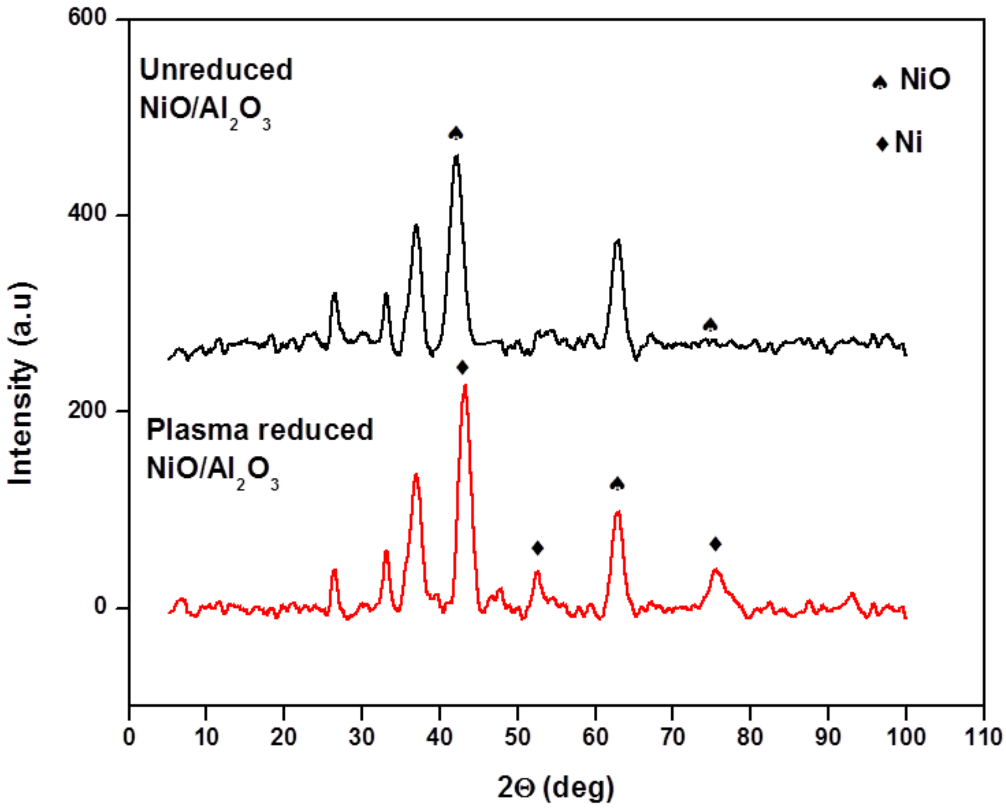

Fig. S1.XRD patterns of NiO/Al_2O_3 catalyst a) no treatment, b) after H_2 plasma-reduction

NiO species had been reduced to Ni. Ni peaks at 2θ = 44.1°, 52.2°and 76.2° (Richardson et al., 2004). The sharp Ni peaks indicate that the sample has a large crystallite size of (18-20 nm).

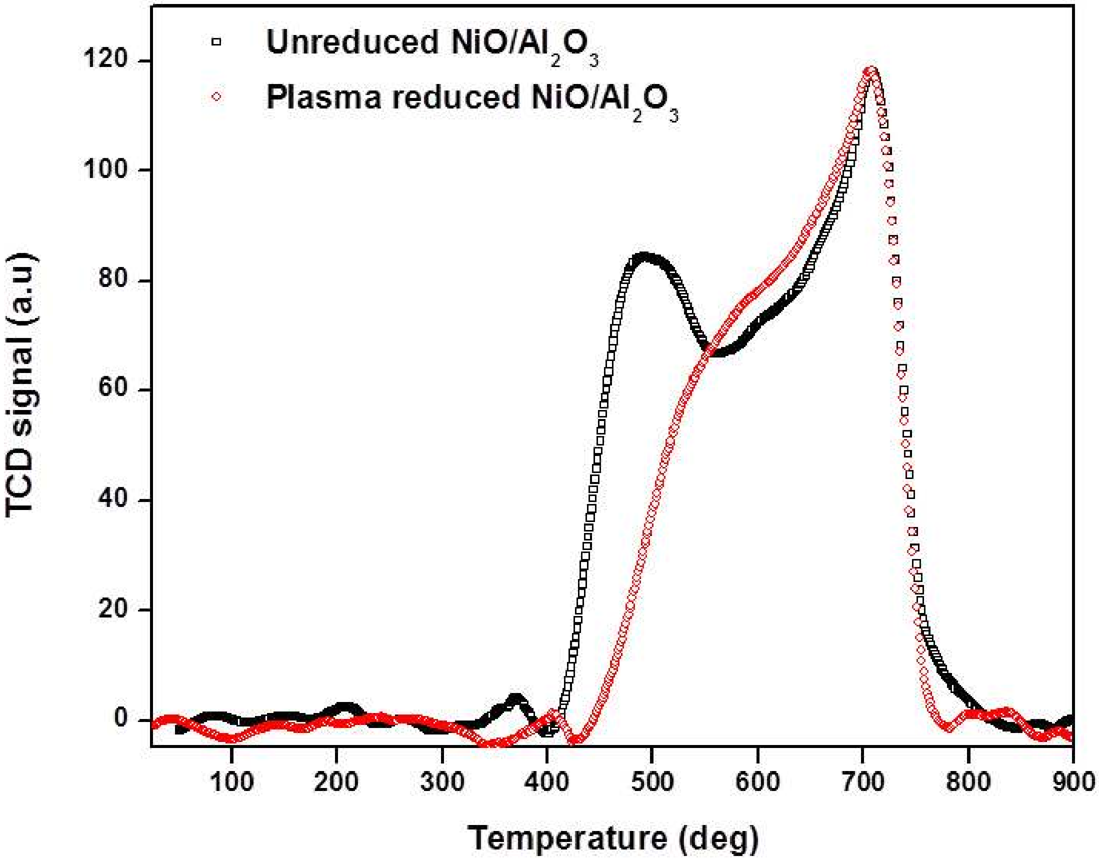

Fig. S2. TPR spectra of NiO/Al_2O_3catalyst (Black) , H_2 plasma-reduced NiO/Al_2O_3(Red).

Two reduction peaks are observed for unreduced NiO/Al_2O_3 centered at 450 and 750 °C, which correspond to the reduction of fixed NiO phase on the Al_2O_3 support and $NiAl_2O_4$ phase, respectively (Twigg and Richardson, 1993). The absence of a low temperature reduction peak in plasma reduced NiO/Al_2O_3 suggests that the Ni reduction degree is about roughly 20-30% during plasma treatment.

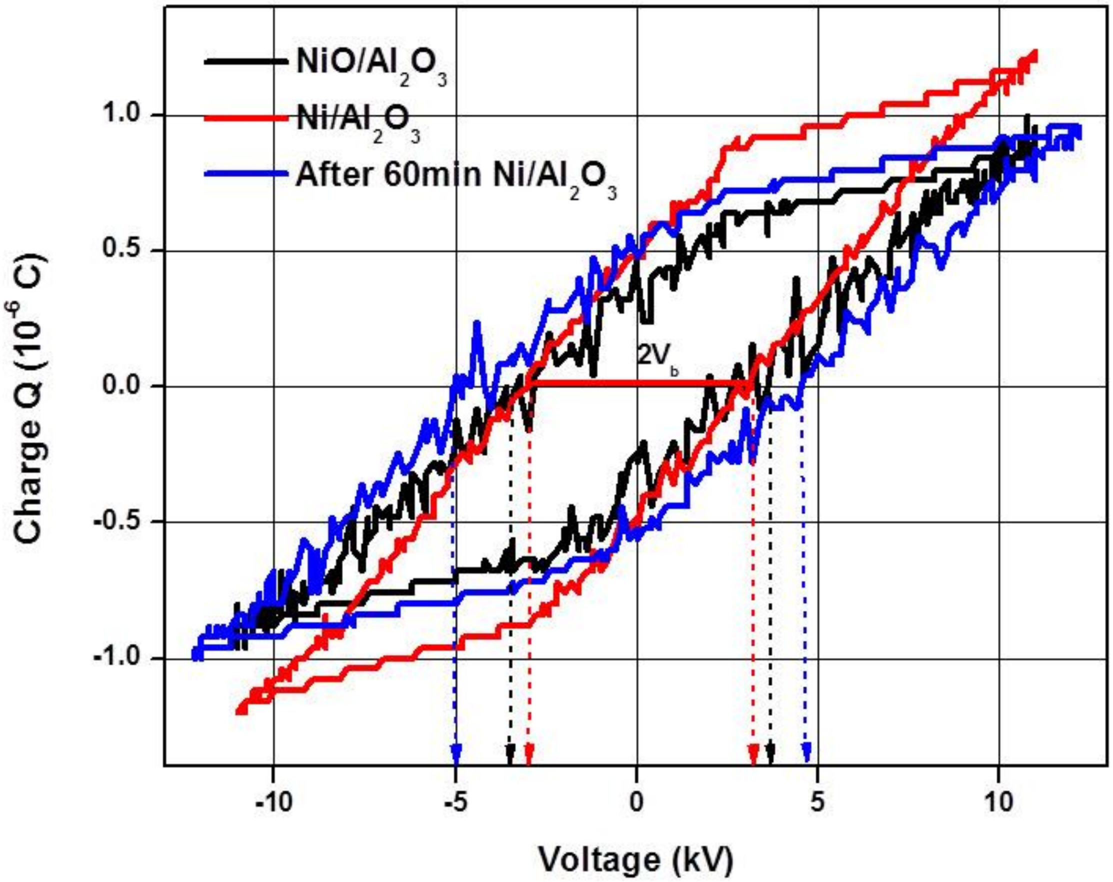

Fig. S3. V –Q Lissajous diagram at 3.5 mm discharge gap and 50 Hz frequency of CO_2 and H_2O splitting in NiO/Al_2O_3, Ni/Al_2O_3 and Ni/Al_2O_3 after 60 min post reaction at constant capacitance (2.2 μF) and at applied voltage fixed at 22kV. This indicates the formation of CNFs on surface of Ni catalyst may increase the breakdown voltage and decreases total capacitance of the dielectric reactor at long period of reaction.

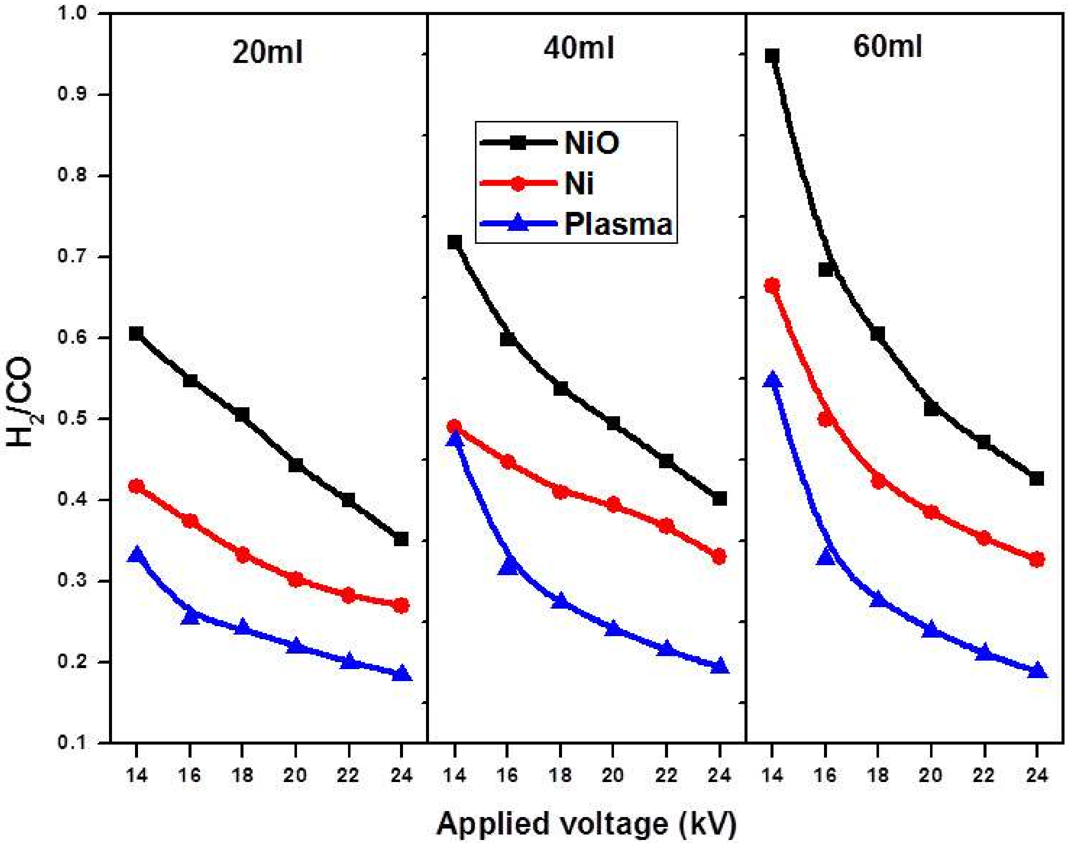

Fig. S4. Syngas ratio at different residence times under plasma, NiO and Ni catalysts.

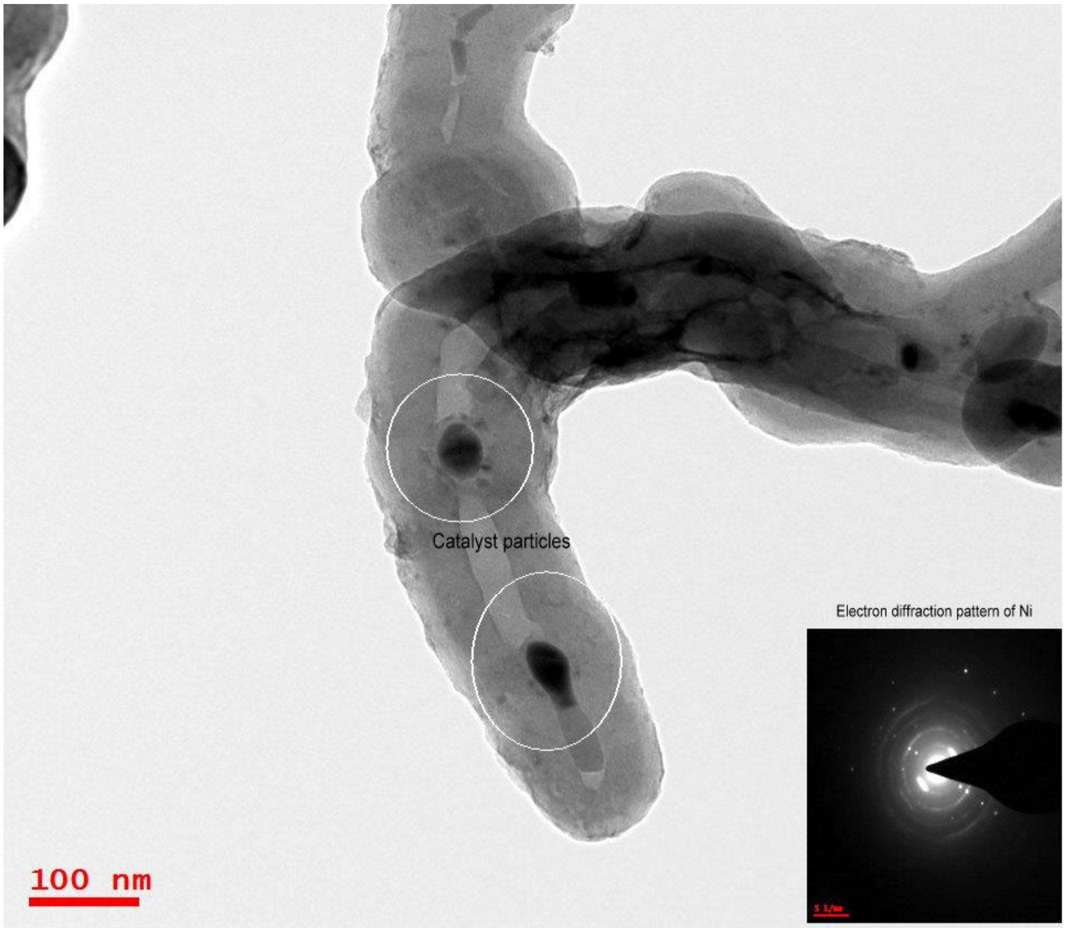

Fig. S5. The morphologies of CNFs deposited on the surface of inner electrode along with the diamond shaped colloidal nanoparticles (inset representing the diffraction pattern of Ni particles has trapped in CNFs). The diameter of bulk CNFs is about 110 nm and a hollow tube in the centre has a diameter ~ 60 nm.

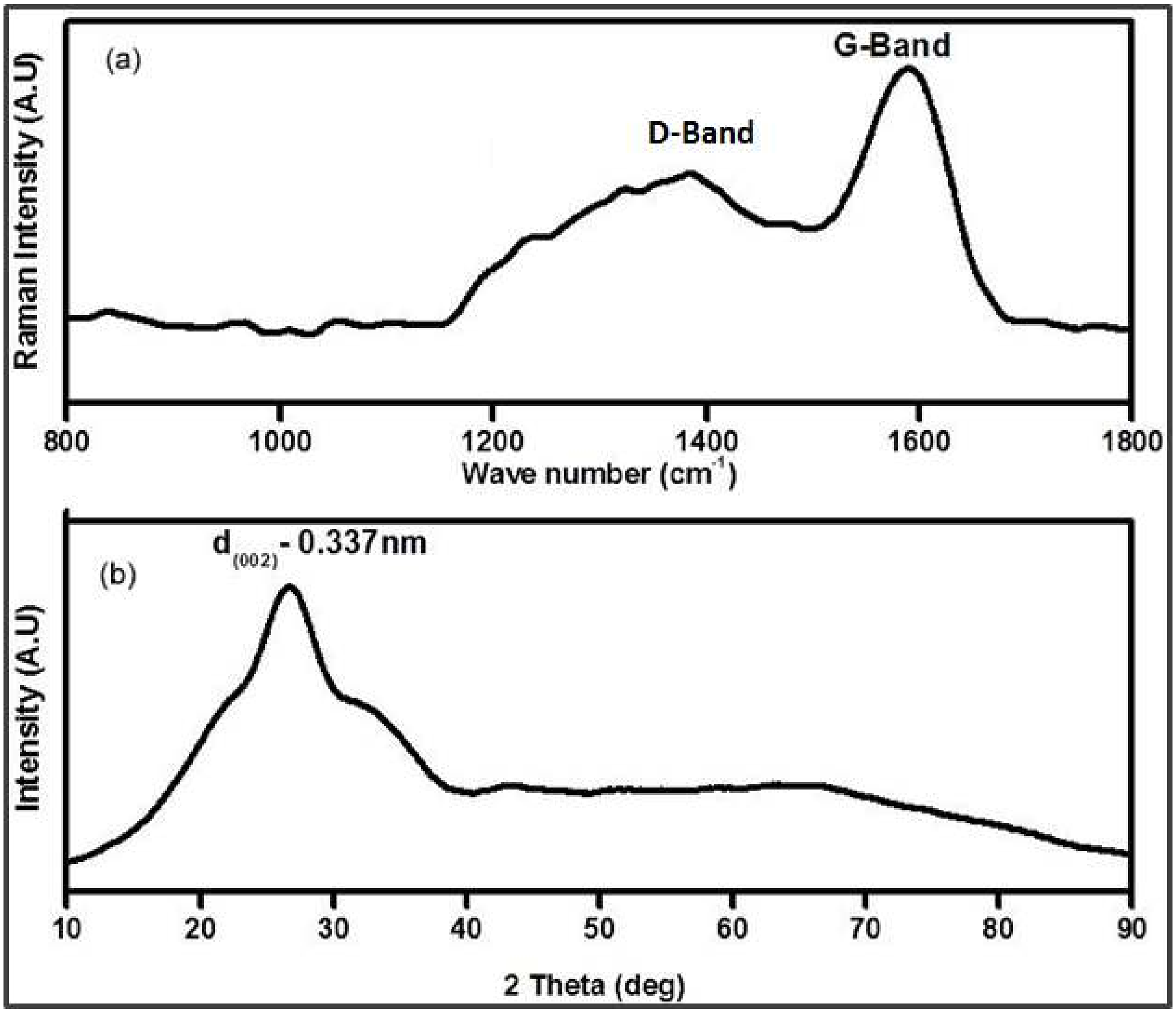

Fig. S6. (a) Raman and (b) XRD spectra of CNFs deposited on inner electrode

The Raman spectra (S6(a)) confirms the intense G-band at 1600 cm^{-1} due to in-plane displacement of carbon atoms in the hexagonal sheets and D-band centred at 1400 cm^{-1} is due to disordered arrangement. The interlayer spacing of graphite d_{002} plane from XRD (S6 (b)) is 3.3542 A˚, which is complemented by the TEM diffraction pattern (3.36 A˚ from S5). Therefore, the CNFs formed during the reaction are graphitic in nature.

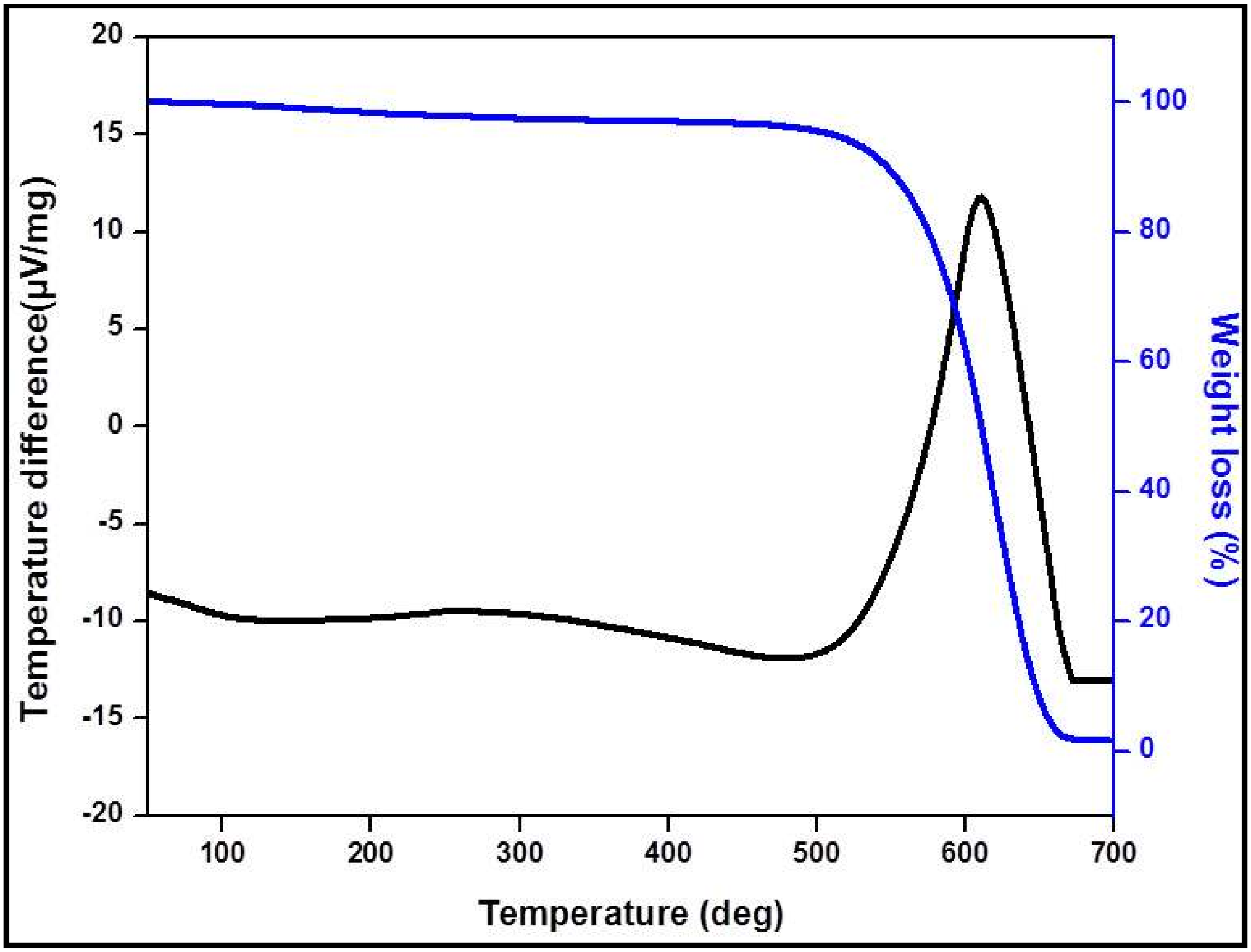

Fig. S7. Temperature programmed oxidation of CNFs after oxidation (HNO_3) treatment. It clearly confirms on-set oxidation only at temperature > 800K indicating the stability of CNFs and resulting carbon showed graphitic character (Chen et al., 2009).

References:

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