Supporting Information
Microfluidic size selective growth of palladium nano-particles on carbon nano-onions

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Synthesis of CNOs

The CNOs were prepared by cracking methane over stainless steel catalyst essentially as per our published procedure.[3] However, in order to improve the homogeneity of the catalyst, instead of directly immersing the stainless steel into distilled water; water vapour was directly introduced to treat the SS316L stainless steel mesh. Air was fed into a simple water vapour generator at 2000 sccm and bubbled through water in a thermostatically controlled bath at 90°C. Once saturated, the air was then directed into the side valve of a tube furnace held at 900°C, through a length of thermally insulated pipe to prevent the vapour from condensing. The airflow and constant feed of saturated air created an even distribution of water vapour throughout the furnace, in which the catalyst was held for 3 hrs.

The methane cracking facility and procedure are also similar to that in our previous report,[3] except for the space velocity and reaction temperature. The space velocity was now scaled up from 30 to 1000 mL $g^{-1}cat.min^{-1}$ and the reaction temperature was increased to 900 °C. The methane conversion efficiency was increased from 80% to 90%. Scanning Electron Microscopy (SEM, A Zeiss 1555 VPSEM), Transmission Electron Microscopy (TEM, A Jeol 3000F FEGTEM), and X-Ray Powder Diffraction (XRD, A Siemens D-5000 Powder XRD) were used to characterize the carbon product. The as-synthesized carbon was highly graphitic (a strong principal 002 peak at $2\theta = 26°$ was observed in the XRD pattern). TEM revealed the expected carbon onion structure encapsulating the catalyst particle, which were removed by a modification of an earlier procedure,[3] using a combination of nitric acid washing and air oxidation. We found that air oxidation engendered a lot of surface defects on CNOs, and we now use a combination of nitric acid washing and magnetic separation. This purification procedure involves the following steps: 1.5 g of as-synthesized carbon is well mixed with 300 ml 60 wt% HNO_3, and held under reflux conditions at 90°C, over a 40 hr period. The liquid phase oxidation reaction was stopped at intermittent stages to assess any change in purity and mass loss at different exposure times. The carbon-acid mixture was diluted with 4 parts of distilled water to cool it down and render it safer for handling. Once diluted and cooled, the mixture was then centrifuged at 4000 rpm for 10 min to then decant the acid. The remaining carbon was then rinsed thoroughly in distilled water and centrifuged again for 10 min to then decant the water, with this step being repeated several times until the carbon was completely neutralised. Magnetic separation was used at intermittent stages of the liquid phase oxidation process to improve the purity, attrition, and graphitic structure of the carbon. It is a non-destructive method that is easily scalable, and very well suited to purifying carbon from the methane cracking process since all the Ni, Co, and Fe catalysts are highly ferromagnetic. Ethanol was selected to suspend the carbon particles since it has a lower surface tension than water, and helped to improve the wettability of the highly hydrophobic carbon sample. The first step of the magnetic separation process involved dispersing the carbon sample in ethanol inside a beaker at a ratio of 100 mg: 150 ml, followed by sonication for 10 min. Once well dispersed, a neodymium bar magnet was then lowered into the beaker to attract the impure carbon onto its surfaces. The impure carbon was then rinsed off into a separate beaker, and the magnet separation step repeated until no carbon was attached to its sides. After separation, the purified carbon was centrifuged, dried, and collected; whilst the impure carbon was reintroduced to the liquid phase nitric acid oxidation process, and the entire magnetic separation process repeated until all the carbon was purified. We have found that our previous method of employing nitric acid washing together with air oxidation could only yield CNOs of 92.0 wt% purity, whereas over 99.0 wt% pure CNOs were obtained by using the nitric acid washing and magnetic attractive separation.

Functionalization of CNOs

1 mg of CNOs was mixed with excess *p*-phosphonic acid calix[8]arene (10 mg) with 10 mL MilliQ water, and the mixture was ultrasonicated for 10 min using a sonic lance speed 4 (Sonifier 150, Branson, CT, USA), affording a black colloidal suspension. The solution was then centrifuged at a speed of 4000 rpm for 5 min to remove undispersed particles. The supernatant was collected and used in further reactions.

Plasma Etching of CNOs

Low vacuum plasma etcher, Plasma Prep$_5$ was used to etch CNOs for the total duration of 6 minutes, as three exposures of 2 minutes each. 1 mg of plasma cleaned CNOs was dispersed in 10 mL MilliQ water, and the mixture ultrasonicated for 10min using a sonic lance speed 4 (as above) affording a black colloidal suspension. The undispersed particles were removed from the solution by centrifugation at a speed of 4000 rpm for 5 min. The supernatant was collected and used in further reactions.

Vortex Fluidic Device (VFD)

VFD is a form of process intensification with continuous flow capabilities, and is effective in producing particles of uniform size distribution. It has a rapidly rotating 10 mm glass tube inclined at 45^o, Fig. 1. Shearing in the film arises from the interplay between centrifugal and gravitational forces, the thin film being parabolic in shape, although at high speed this approximates to having a thin film along the tube. An important feature of the thin film is that it is maintained for a fixed volume of liquid within the tube (confined mode), which overcomes the need for using large volumes of liquids for shearing processes associated with conventional continuous film flow microfluidic platforms.

Dispersion of Pd nanoparticles on CNOs using VFD

1 µl of palladium solution, as 0.1 mol/L 35% H_2PdCl_4 in aqua regia was dropped into 5 ml of CNOs solution. The mixture was sonicated for 3 minutes then left to stand overnight. The excess Pd(II) complex was removed by centrifugation at room temperature at 4000 rpm

for 30 min. The resultant supernatant was withdrawn using a pipette, and then the sediment was re-dispersed in DI water, and centrifuged for a total of three times.

A solution of CNOs-Pd was placed into VFD for 60 seconds at room temperature, rotating at 2000, 5000 and 7500 rpm, under an atmosphere of hydrogen gas. The resulting solutions were centrifuged as above, and the process repeated three times to make sure there was no residual palladium(II) in the sample.

Table S1 : Diameter of Pd NP attached to CNOs (based on 50 particles counted)

Speed of VFD	**Average size of PdNP(nm)**	**standard deviation**
2000	6.98	0.97
5000	4.35	0.40
7500	2.33	0.45
batch	12.76	6.38
partial pressure hydrogen (bar)	**Average size of PdNP(nm)**	**standard deviation**
0.01	24	6
0.25	13	2
0.75	4.5	0.4

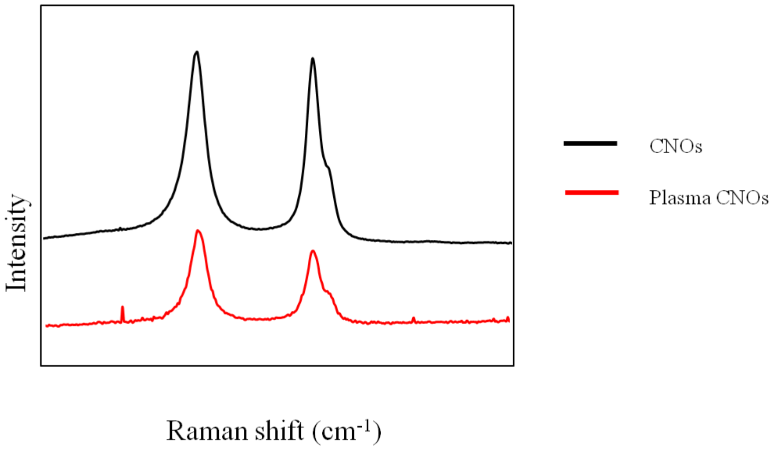

Figure S1 Raman spectra for CNOs and plasma treated CNOs.

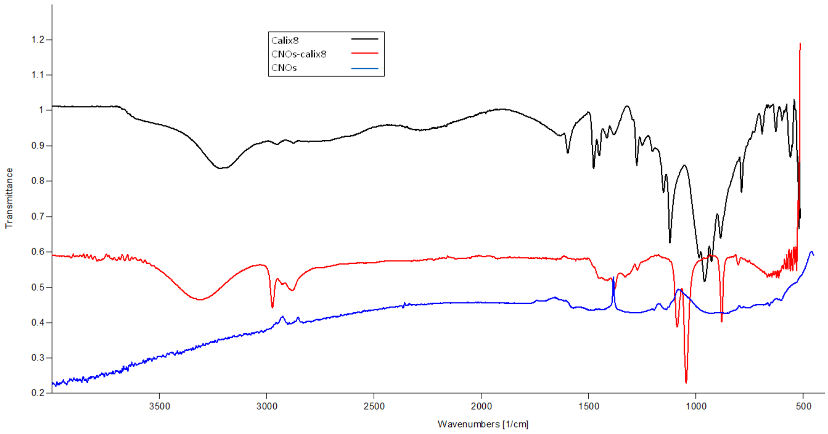

Figure S2: FTIR spectra of Calix8, CNOs-C8 and CNOs

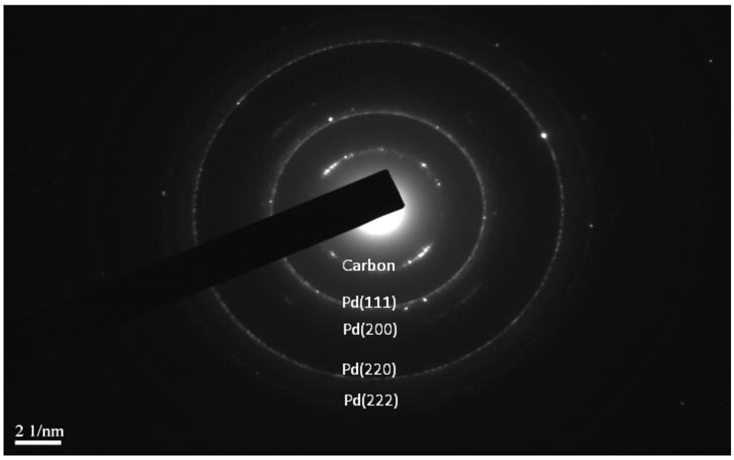

Figure S3: SAED of CNOs-*p*-phosphonic acid calix[8]arene-Pd composite.

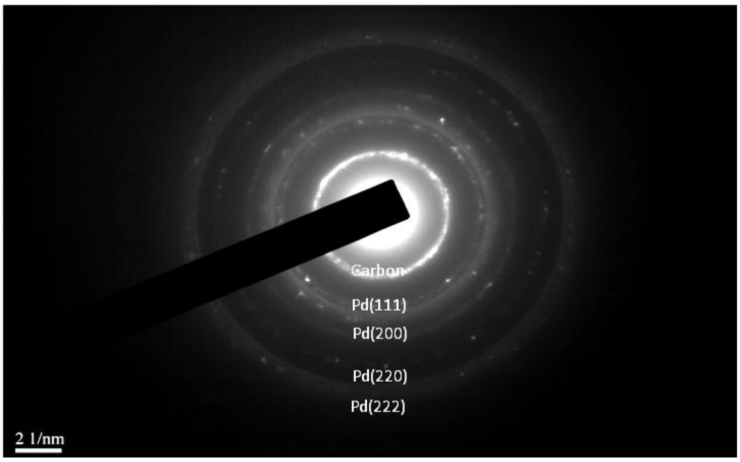

Figure S4: SAED of plasma etched CNOs-Pd composite.

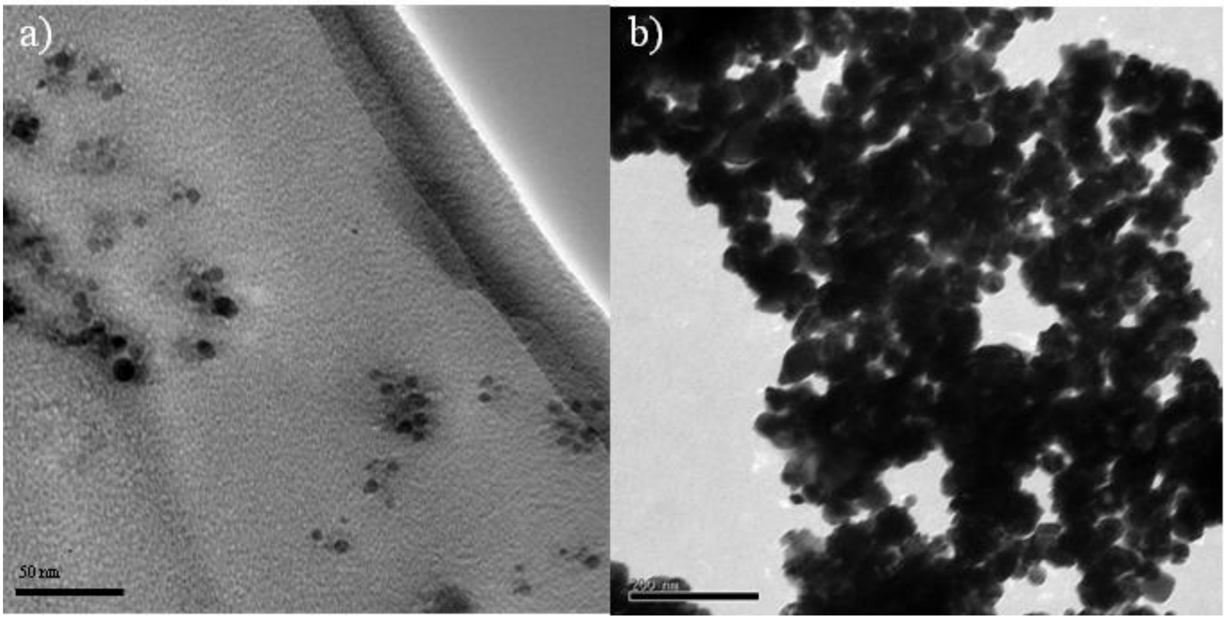

Figure S5 : Palladium nanoparticles produced in the absence of CNOs in the VFD with the tube rotating at 5000 rpm for 1 minute under an atmosphere of hydrogen in the presence (a) and absence of the calixarene (b). For (a) 1 μL of palladium solution was mixed with 10 mg of *p*-phosphonic acid calix(8)arene and milli-Q water was added to make up 1 mL, with the resulting solution centrifuged to separate the particles from excess Pd(II). For (b) the same procedure was used except that the solution only contained Pd(II) in milli-Q water.