Supporting Information

Morphological and Crystallinity Differences in Nitrogen-Doped Carbon Nanotubes Grown by Chemical Vapour Deposition Decomposition of Melamine over Coal Fly Ash.

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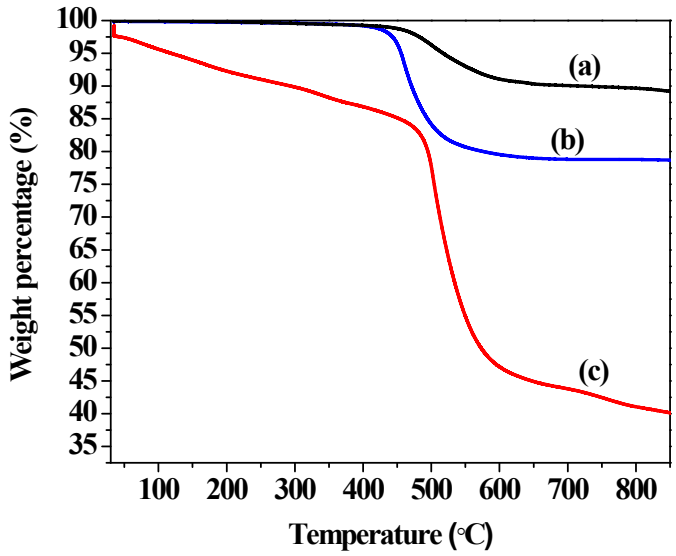
(S1)



S1. TGA thermogram of carbonaceous materials synthesized at (a) 800 °C (b) 850 °C and 900 °C.

The samples synthesized at different temperatures were heated from 30 to 900 °C in oxygen, the resulting temperature profiles were plotted in Fig S1 whereby it was observed that 60 % of the sample synthesized at 900 °C combusted whereas 11 and 22 % of the samples synthesized at 800 and 850 °C respectively, were combusted.

(S2)

M_1= initial mass of melamine

M_2= mass of carbonaceous material formed

M_3= mass of melamine unused

$$\%Yield = \frac{M_1 - (M_2 + M_3)}{M_1} \times 100\%$$

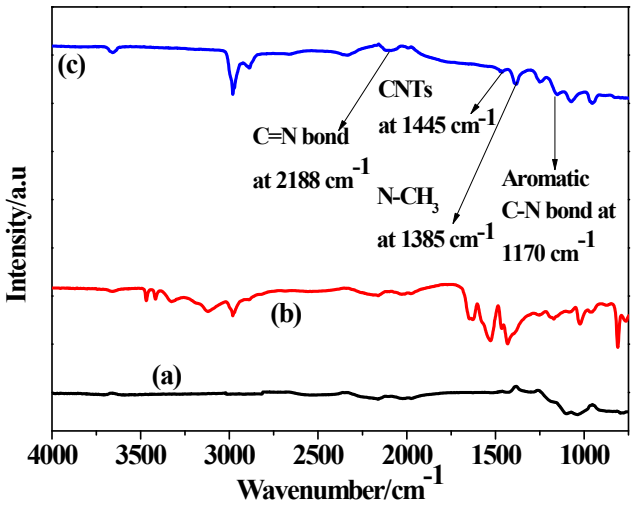
S2. Percentage yields of carbonaceous material synthesized from CFA and $Fe@CaCO_3$

Synthesis temperature (°C)	800	850	900
% Yield (CFA NCNTs)	24	31	44
% Yield ($Fe@CaCO_3$ NCNTs)	28	33	51

The percentage yields of NCNTs grown from $Fe@CaCO_3$ was found to be slightly higher than those grown from CFA. The amount of the active metal in both catalysts was approximately equal, this explained the almost equal product yields.

(S3)

The FTIR absorption spectrum obtained for raw CFA (Fig S3 (a)) revealed no significant peaks between 1500 and 4000 cm^{-1}. On the other hand, the FTIR spectrum of melamine (Fig S3 (b)) revealed four low intensity absorption peaks in the 3000-3500 cm^{-1} region (stretching and vibrational modes associated with the N-H bonds), stronger absorption peaks in the 1200-1700 cm^{-1} region (characteristic of the aromatic melamine skeleton, composed of sp^2 and sp^3 C-N bonds) and absorption peaks in the finger print region at 600 cm^{-1} (attributed to the C-N bond in primary amines).[1]

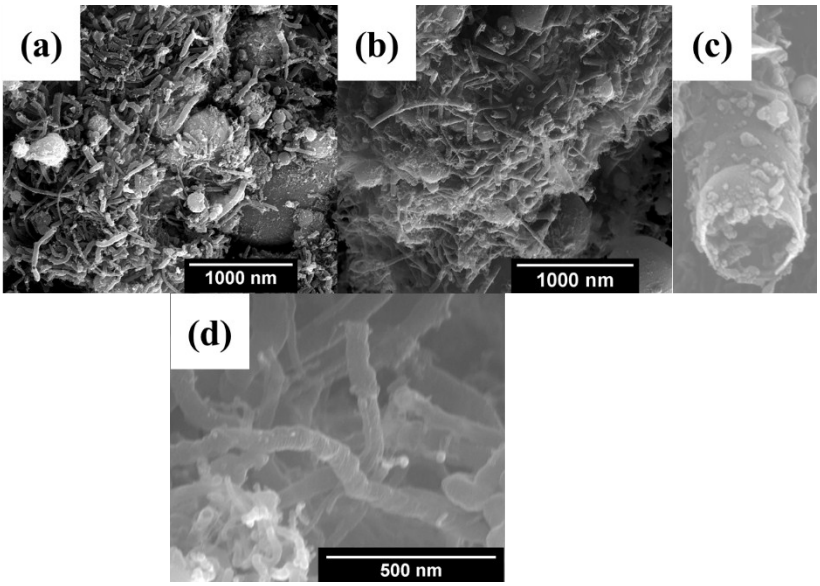


S3. FTIR spectra of: (a) Fly ash, (b) Melamine and (c) CNTs synthesized at 900 °C.

The absorption spectra of all the CNTs were observed to be similar and hence one example was chosen for the purpose of this discussion. Significantly, the FTIR spectrum of the as-synthesized CNTs (Fig S3 (c)) differed from that of undecomposed melamine. Adsorption modes that were present on the melamine absorption spectrum in the 3000-3500 cm^{-1} region were not present on the spectrum of the CNTs, except for a weak band at 3600 cm^{-1} which was attributed to adsorbed water molecules. This suggested that all the amide bonds N-H bonds present in melamine were destroyed during its decomposition on the CFA catalyst. A few more absorption bands in the 1000-1800 cm^{-1} region were present in the FTIR spectrum of the CNTs. The most significant peaks observed in this region were those of the CNTs (1445 cm^{-1}), C-N bond (1170 cm^{-1}), N-CH_3 (1385 cm^{-1}) and C=N (2188 cm^{-1}), from which it was deduced that melamine had been decomposed into NCNTs.[2] Some of these were also observed by Zhao *et al*. when comparing the FTIR spectra of melamine and turbostratic

carbon nitride which was prepared from melamine. Zhao *et al*. attributed the extra absorption peaks to the condensation of the melamine triazine skeletal structure.[3]

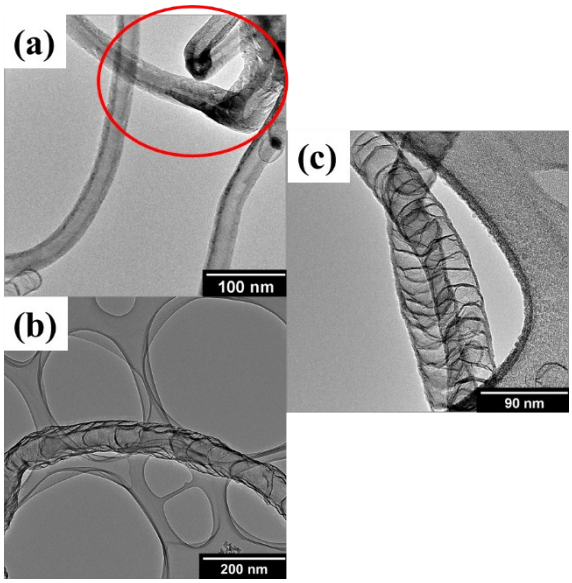
S4



S4. SEM images of NCNTs synthesized at (a) 800 °C, (b-c) 850 °C and (d) 900 °C.

The NCNTs synthesized at 800 °C had smooth surfaces as shown on S4 (a). The NCNTs synthesized at 850 °C, as shown in S4 (b-c), were observed to be circular and hollow with compartments separating each hollow and circular segment (S4 (c)). The NCNTs synthesized ta 900 °C (S4 (d)) also had irregular walls. However, these were not as pronounced as those observed in the case of those that were synthesized at 850 °C.

(S5)

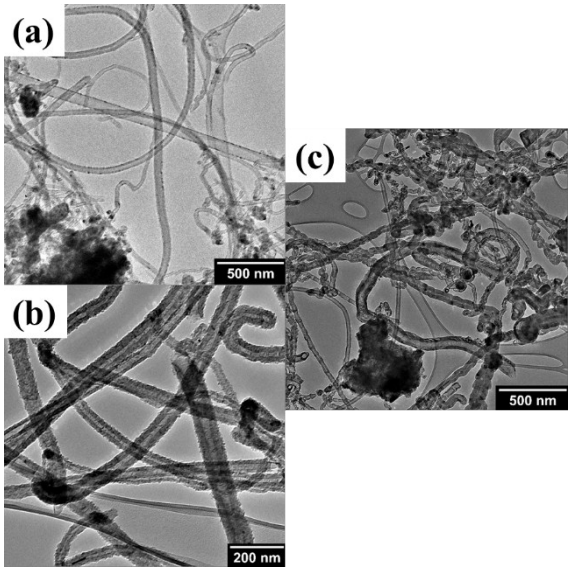


S5. TEM images showing the morphology of some of the tube variants synthesized at: (a) 800 °C, (b) 850 °C and (c) 900 °C.

There were some morphological variations that were observed in the TEM images of the NCNTs synthesized using CFA. For instance the NCNTs synthesized at 800 °C had morphological defects, such that grooves within the multiwalled carbon

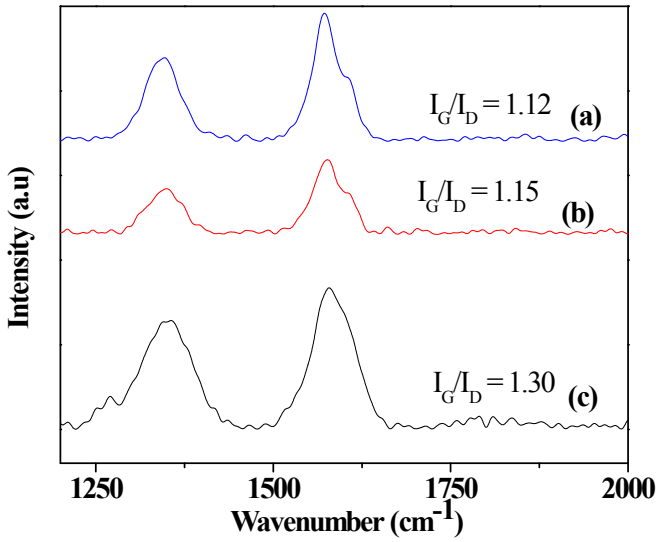
nanotubes were apparently beginning to develop (S5 (a)). In the case of the NCNTs synthesized at 850 °C (S5 (b)), a minority of the NCNTs had a morphology, where less circular grooves were observed and the walls were not as developed as those observed for the majority of the tubes. As was the case with the other NCNTs, morphological variations were also observed for a small fraction of NCNTs synthesized at 900 °C (S5 (c)).

(S6)



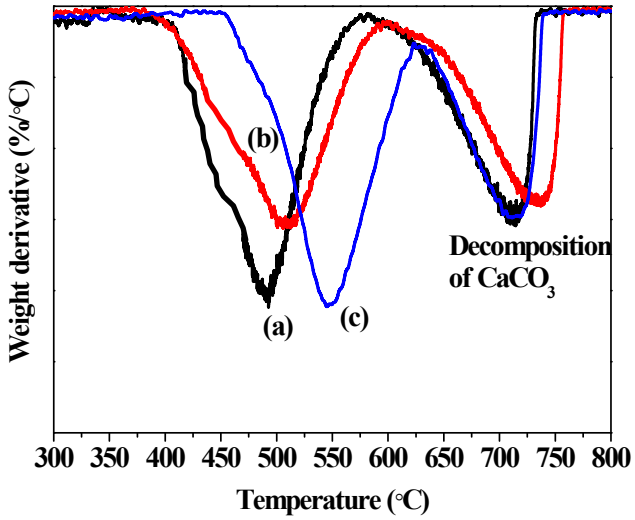
S6. TEM images of NCNTs grown from Fe@$CaCO_3$ at (a) 800 °C, (b) 850 °C and (c) 900 °C.

(S7)



S7. Laser Raman spectra for NCNTs synthesized on Fe@$CaCO_3$ at: (a) 800 °C, (b) 850 °C and (c) 900 °C.

(S8)



S8. TGA derivative profiles for NCNTs synthesized on Fe@$CaCO_3$ at: (a) 800 °C, (b) 850 °C and (c) 900 °C.

References

1 M. K. Marchewka and a. Pietraszko, *J. Phys. Chem. Solids*, 2003, **64**, 2169–2181.

2 A. Misra, P. K. Tyagi, M. K. Singh and D. S. Misra, *Diam. Relat. Mater.*, 2006, **15**, 385–388.

3 Y. C. Zhao, D. L. Yu, H. W. Zhou and Y. J. Tian, *J. Mater. Sci.*, 2005, **40**, 2645–2647.