Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Metal Free, End-opened, Selective Nitrogen-Doped Vertically Aligned Carbon Nanotubes by Single Step By *in-situ* Low Energy Plasma Process

Ganjigunte. R. S. Iyer, and Paul. D. Maguire

Supplemental documents to support the manuscript

(a) Growth and optimisation of vertically aligned carbon nanotubes

To optimise the diameter and length of the MWCNTs catalyst thin films of Fe was deposited on Si substrate for different thicknesses (5, 20, 40 nm). The Fe coated samples were pre-heated to 750 $^{\circ}$C for 5 minutes followed by the growth of MWCNTs using microwave plasma process, in a mixture of methane and nitrogen (20:40). Fig. S1(a, b, c) shows the SEM images of the nanotubes grown at different catalyst thicknesses and insets, the metal catalyst islands after the pre-treatment respectively. Fig. 1(d) represents the interdependence of the catalyst film thickness and diameter of the nanotubes. As observed for various catalyst thicknesses the diameter of the nanotubes eventually depends on the particle size which is related to the catalyst film thickness, illustrating the interdependence between them. As the diffused carbon precipitates from the saturated catalyst surface the metal particle grow along the tube at the top leading to tip growth. For smaller catalyst film thickness, broken down into smaller sized particles, leads to the formation of a single nanotube well separated from each other. In the films of larger thickness (40 nm), the particles formed being large, leads to greater adhesion and the interaction of the particles with the substrates requires higher force and longer time for the nanotube formation. Also, the diffusion of carbon into the larger catalyst particles requires longer time than that of smaller catalyst island. The smaller sized metal particles from thin films enhance the nanotube growth rate as they can be easily detached from the substrate compared to the thick films. Hence for a fixed growth time, the length of the nanotubes decreases with the increase of catalyst thickness. In this investigation we subjected Vertically aligned multi walled CNTs for further plasma treatments for metal catalyst removal and n-doping as described in detail in the manuscript.

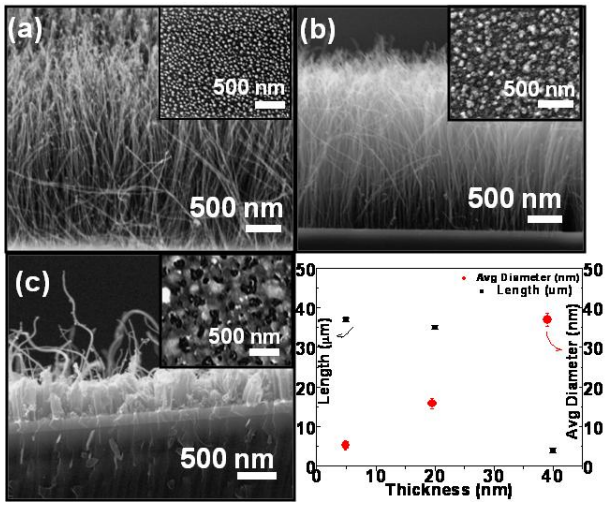

Fig. S1:(a),(b),(c) nanotubes synthesized from iron catalyst of thicknesses 5, 20 and 40 nm and insets are the corresponding nano islands post treatment. (d) Plot of interdependencies of the nanotube diameter and length to the catalyst thickness.

b) Wettability of UT (untreated) and nitrogen ECR plasma treated CNTs (N-MWCNTs)

In order to measure the surface wettability of untreated (UT) and nitrogen ECR plasma treated (N-MWCNTs) we employed static contact angle goniometry (CAM 2000, KSV instruments Ltd., Finland) using De-ionized water by manual Hamilton 1 ml adjustable precision syringe with proprietary easy to use "One Touch Dispenser" mechanism. Fig. S2 illustrates the contact angle measurements for the UT, which shows the super hydrophobic nature of the CNTs. Fig S2(a) depicts the image of water droplet on UT MWCNT surface (procured by the CCD camera), while Fig. S2(b) shows the surface profile developed to determine the contact angle and it was found that water angle on MWCNT surface was ~150^{o}. The measurements for the N-MWCNTs were not possible due to the quick wetting (spreading) of the water droplet on the CNT surface.

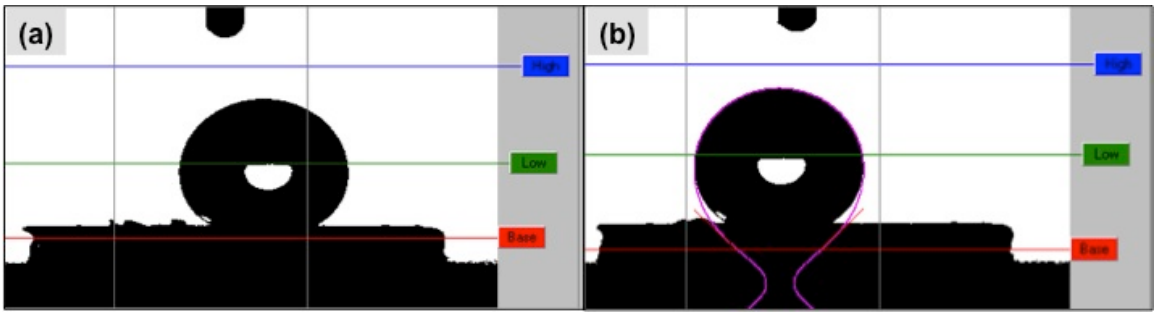

Fig S2. Contact profile for the UT (a) before the contact angle measurement (b) contact angle profile as developed for the measurement.