Activation of aerial oxygen to superoxide radical by carbon nanotubes in indoor spider web trapped aerosol

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Domestic spider webs trap partly burnt combustion contaminants in indoor floating aerosols. These are shown to possess defective carbon nanotube particulates containing very stable carbon centred free radical. When inhaled the carbon radical readily activates aerial oxygen to superoxide radical, thus demonstrating the possibility of spontaneous intracellular generation of reactive oxygen species in intact cells.

Keywords: Aerosol, multiwalled carbon nanotube, reactive oxygen species, spin frustrated carbon nanotube, superoxide radical.

A major part of the personal exposure occurs in enclosed environment as people spend approximately 90% of their time indoors. Indoor air pollution is assessed from the available chemicals and dust settled in a confined place1. This includes combustion sources such as solid fuels, biomass, oil, gas, kerosene, coal needed for energy; tobacco, candle, faulty electric gadgets, incense and products from diverse human activities. Countries in the southern hemisphere extensively use room ventilators (fans) to combat heat and sultry weather. Within weeks, the blades of these ventilators turn black with the deposition of combustion particulates. The ingredients present in domestic airborne aerosols play a significant role in producing toxicological effects. Being sufficiently small and insoluble, these get adequate time to penetrate the deepest areas of the lungs triggering asthma attacks and aggravate suffering. Respirable particulate matter cause lung inflammation by inflammasome activation known to be triggered by reactive oxygen species (ROS)2. Nano-sized carbon black aggravates neurodegenerative diseases3. Hypotheses to identify the responsible particles have focused on shape and size, content like silica, asbestos or heavy metals, bio-aerosols and black carbon related particles. Spider webs were used to trace heavy metals associated with motor vehicle emissions4,5.

We used domestic indoor spider webs (Figure 1) to capture airborne combustion products confined in the indoor space. These spider webs varying from one day to two weeks old were collected from inside of houses within the residential area in the campus of Indian Insti-

tute of Technology Kanpur (IITK; 80.20’E and 26.26’N) during June–December 2007. The contaminated spider web with airborne particulates was subjected to analysis in raw form and also after chemical treatments to clean the particulates and acid soluble metal ion contaminants from the web silk. With the probes SEM (scanning electron microscopy) and EDAX were recorded with FEI Quanta 200 Hv and Tecnai 20 G2 200 kV. STWIN was used for TEM (transmission electron microscopy) analysis and XRD (X-ray powder diffraction) and the AFM (atomic force microscopy) were carried out with Pico scan Model (Molecular imaging, US) in air under ambient conditions at room temperature. Silicon nitride tip (micromesh) was used and the size of the cantilever tip (radius of curvature) was less than 10 nm. The spring (force) constant of cantilever was 1 N/m. The images were taken in noncontact mode and the EPR (electron paramagnetic resonance) measurements were recorded at room temperature using a Bruker EMX spectrometer with microwave frequency 9.8 GHz, modulation amplitude 10 G, modulation frequency 100 kHz and microwave power 0.21 mW. Electronic spectra were recorded using a PE-Lambda-35 UV–Vis spectrometer and Raman spectra using WITEC model Raman spectrometer.

Figure 1 shows the domestic spider with its web and Figure 2 a shows its EDAX analysis with detectable presence of C, N, O, Mg, Al, Si, Cl, Na, K, Ca, Pb and Fe. The collected web materials were washed with alcohol to remove greasy matter, air dried and the residue was treated with 6 M HCl at 108°C for 16 h to hydrolyse the silk. The soluble part was centrifuged off and the remaining residue was washed with water to ensure leaching out

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of traces of organic components and any residual soluble metal contaminants. The insoluble black residue was centrifuged, washed several times with water and air dried. The EDAX of the cleaned particulates showed the presence of only carbon, silicon and oxygen as shown in Figure 2.b.
The black residue showed the presence of only carbon, oxygen and silicon by EDAX (not shown) with the elimination of other trace elements found in untreated EDAX (Figure 2a). Corresponding SEM image revealed the presence of carbon nanotubes (Figure 3a). Its AFM (Figure 3b) supports the presence of carbon nanotubes accompanied by some silica lumps.

The TEM image of the purified residue showed the presence of multiwall carbon nanotube (MWCNT) with relaxed diameter 20–50 nm range with several turns and junctions (Figure 4a). Further, its high resolution transmission electron microscopy (HRTEM) image showed uneven obstruction present in the channels (Figure 4b and c). Figure 4d showed at the outer surface of the MWCNT several defects (pointed out by black arrows) and the interlayer spacing in the MWCNT, ~3.4 Å has been marked which corresponds to the 002 distance of graphitic carbon. Defects like turns and kinks may cause bonding frustration in graphene’s carbon leaving trapped carbon centred radicals in defective MWCNT. Such radical species are readily identified by EPR spectroscopy. The raw web particles showed room temperature EPR spectrum (Figure 3c) comprising one broad and one narrow signal. On washing with dilute hydrochloric acid in the cold, the raw web loses most of the metals present, particularly iron. This gently acid-washed residue or the final residue (after hydrochloric acid treatment under pressure to hydrolyse and to remove the silk proteins) showed identical EPR spectrum retaining the narrow resonance with $g = 2.002$ (Figure 3d). This evidently supports the fact that we are dealing with a stable EPR active species. It is interesting that this EPR active species is retained in the raw spider web even after harsh acid purification treatments suggesting its stability under the graphene matrix. This can happen when carbon nanotubes (CNTs) are associated with defects and turns and kinks. These CNTs may be termed as spin frustrated carbon nanotube (SFCNT).

Interestingly, these SFCNT show spectacular properties on exposure to aerial oxygen. SFCNT slowly activate oxygen present in air to produce superoxide radical, which is a potent reactive oxygen species (ROS). We confirm this reaction by nitro blue tetrazolium test (Figure 5a). Raman spectrum of these SFCNT (Figure 5b) showed the presence of sp$^2$ carbon along with sp$^3$, suggesting the presence of defects in graphene structure. The inhalation of these nanosized SFCNT particles which are floating inside the room may be effortless in breathing.
Recently, graphitic carbon was shown to catalyse aerial oxidation and this may correlate the role of nanosized carbon black affecting neurotransmitter levels and pro-inflammatory expressions. In case of graphitic carbon, its nonavailability in nanosize form indoors prevents its inhalation. This is not valid for SFCNT as they readily float in the air, according to our present observation. This study showed that indoor spider webs within days collect matter by trapping considerable amount of floating particulates inside a room which are potent materials for uptake by effortless human breathing. The catalytic action of SFCNT in generating superoxide radical strongly suggests that these may trigger direct inflammatory type activation. Thus, these abiotic SFCNT may imitate impulsive pseudo phagocytosis.

Degradation of SFCNT is difficult and its size may not allow ready precipitation causing its gradual accumulation in indoor aerosols which on exceeding a threshold may lead to catastrophic consequences.

Impact of the 2004 earthquake on the limestone caves in North and Middle Andaman Islands

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We evaluated the effects of the great earthquake of December 2004 on 43 inland caves in the Andaman and Nicobar Islands. Data was collected before and after the earthquake. The number and size of fallen rocks within the caves were taken as a measure of physical damage to the caves. Rockfall was greater in caves located above ground ($Z = 3.543$, $P = 0.000$) and in larger caves ($\chi^2 = 18.545$, $df = 3$, $P = 0.000$), indicating significantly higher damage to these caves. The impact of damage to the microclimate and ecosystem inside the caves is also discussed.

Keywords: Andaman and Nicobar Islands, habitat alteration, limestone caves, rockfall, tsunami.

The Arakan Yoma arc through Myanmar, Andaman and Nicobar Islands to Sumatra and beyond is a seismically active zone. Geologically, the Andaman island arc can be separated into two concentric arcs: the outer arc is sedimentary and includes the main chain of islands, whereas the inner arc which includes Barren and Narcondam Islands is volcanic. The rocks occurring in these islands are mainly marine deposits from Cretaceous to Recent.

Caves can form only in lithified rocks, i.e. the rocks formed by aggregation of particulate matter and their location is controlled by the original sediment character and diagenetic history, i.e. changes that result from the sedimentary processes during the transformation of the sediments into rock.

The Andaman and Nicobar Islands, located between $6^\circ45^\prime$N–$13^\circ41^\prime$N and $92^\circ12^\prime$E–$93^\circ57^\prime$E, have several caves and cave complexes. Most caves in the Andaman and Nicobar Islands fall into two broad categories: (a) those formed by underground drainage and erosion in Limestone Formations, the channels thus formed have been later cut into by sub-aerial erosion and exposed, and (b) those formed in sea cliffs by marine erosion of rocks.

Of the several caves in the Andaman and Nicobar Islands, Sankaran located and mapped 384 caves, of which 61.5% (236) were inland (located within the forest) and the rest coastal (located on the shore). Among the 236 inland caves, 86% were underground, of which 1% was located at the origin of a stream. Fourteen percent of

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