UBIQUITOUS COMBUSTION-GENERATED CARBONACEOUS ULTRAFINE PARTICLES ($PM_{0.1}$) (CUFPs) IN THE ATMOSPHERE: POLLUTANTS SANS FRONTIÈRES

P.A.Sermon*, J-C.Eloi and M.P.Worsley (*paul.sermon@brunel.ac.uk)

Nano and Biomimetic Materials Laboratory, Wolfson Centre, Brunel University, Uxbridge, Middx., UB8 3PH, UK

Introduction

Nanoparticles (NPs) are found in the atmosphere, in water and in exhaust gases. Carbon blacks are used for toners, etc. 62% of primary nanoparticles ($PM_{0.1}$) in the atmosphere of the UK in 1998 were emitted by road traffic. Some have looked at their composition and others compared those found indoors and outdoors. Engineered NPs are drivers of environmental particle effects. Carbonaceous soot particles arising from the incomplete combustion of hydrocarbons remain undesirable for health, environmental and combustion energy efficiency reasons arise from diesel engines, furnaces or fires. Rosalind Franklin used XRD to analyse graphitizing and non-graphitizing carbons as they were heated.

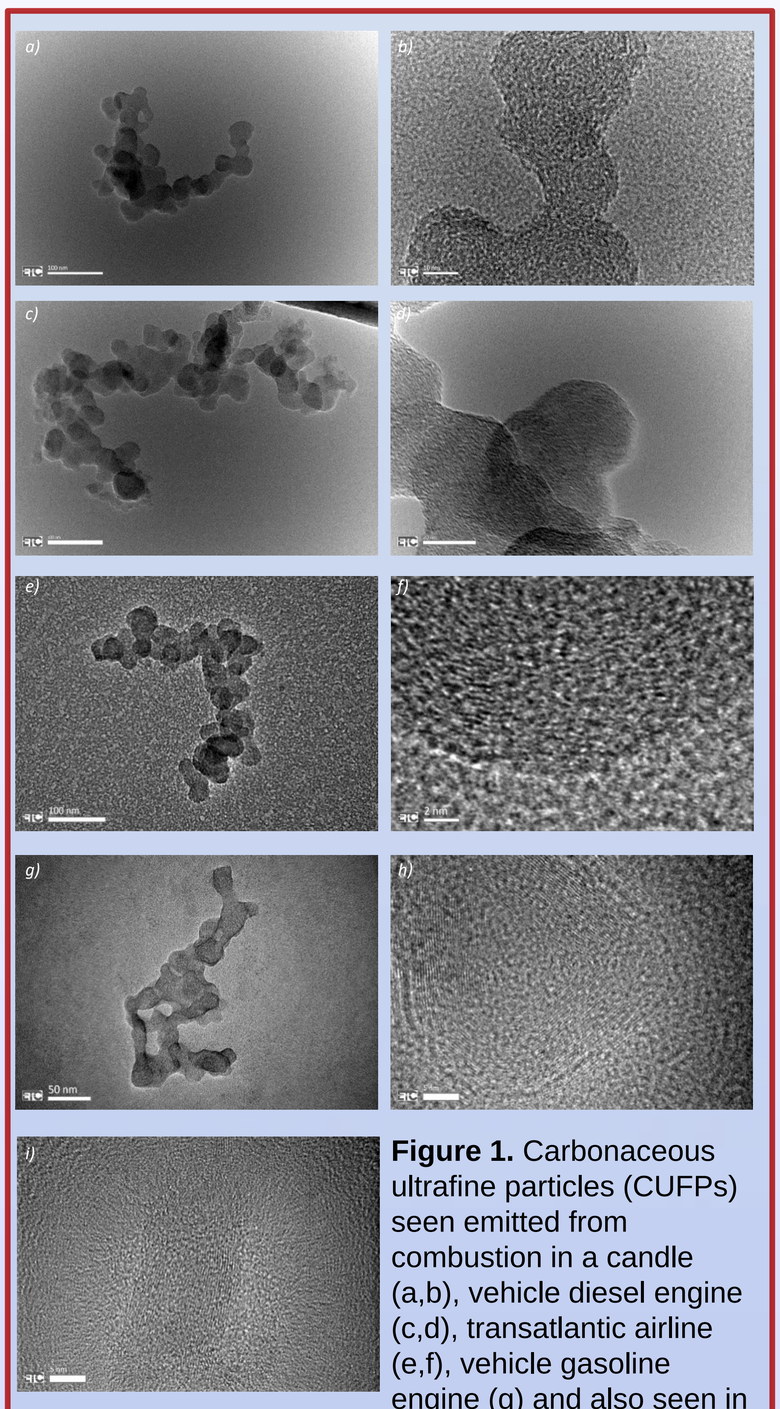


Figure 1. Carbonaceous ultrafine particles (CUFPs) seen emitted from combustion in a candle (a,b), vehicle diesel engine (c,d), transatlantic airline (e,f), vehicle gasoline engine (g) and also seen in the atmospheres in the london tube (h,i).

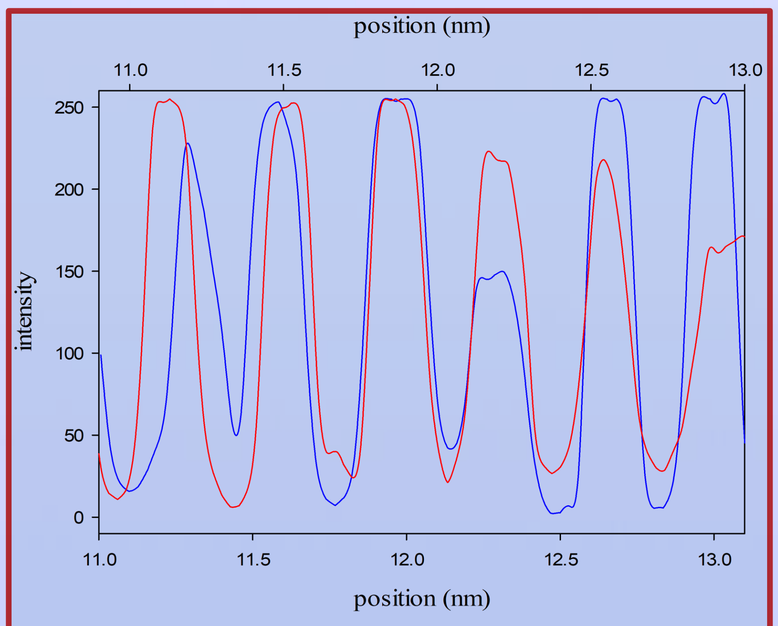


Figure 4. Average interlayer spacings seen in nano-spheres-triangles (red; see Figure 3h) and nanotubes (blue; see Figure 3i) for the atmosphere in Zurich were 0.345nm.

Transmission electron microscopy (TEM) was used to study soot particles. It sees very small (2-10nm) liquid-like precursor nanoparticles (NPs) and chain-like aggregates. HRTEM, DFTEM and XRD have found multi-ring polyaromatic hydrocarbons (PAHs) in precursor soot NPs and hexagonal geometries of PAHs preserved in the basal planes of soot crystallites. TEM has long been a primary tool in assessing

i. the size (d_p) of emitted liquid-like primary spherules or nanoparticles and
ii. soot chain-like aggregates

In (i) d_p rose from 18 to 36nm as the height above the burner (Z) rose to a maximum, but no spherule NP structure was noted. D'Alessio suggested that the spherule NPs were aliphatic in nature, especially as they are transparent in the visible.

In (ii) aggregation of primary particles increased with Z and analysis of the number of spherules in an aggregate (N) was related to the maximum aggregate length (L) through the fractal dimension D_f: $N=k_L.(L/d_p)^{D}f$ or $(N=k_f.(R_g/d_p)^{D}_f$. TEM analysis revealed $1.82<D_f<1.9$ for soot aggregates using logN plots against $\log(L/d_p)$. Indeed as Z increased from 2mm to 11mm TEM saw a switch from single NPs to aggregates (as time increased). TEM evidence exists for carbonaceous soot particles in terms of d_p, R and D_f, but what about their structures; are shell combustion particles formed?

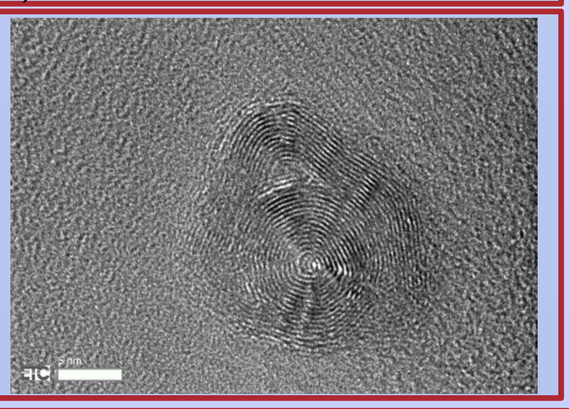
Wagner suggested that 'there is something between molecular PAHs and soot'…noting that 'we usually look at things we can catch easily' by the experimental methods currently available. XRD and TEM are relevant to the analysis of large and submicroscopic soot samples. In HRTEM one might see (002) diffraction and concentric circumferential graphitic layers in spherules around a more amorphous core. In carbons it was thought that a concentric crystallite model of carbon black microstructure might be relevant. In diesel soots c/2=0.383nm, but parameters such as circularity, elongation, length, orientation and fractional coverage are also accessible through HRTEM. Interestingly, a partially graphitized carbon black with 0.34nm 002 spacing has been suggested as a HRTEM test object. Certainly the lattice plane spacing in the (002) direction of graphite as 0.352nm; TEM was used to analyse chain-like aggregates in soots and lattice fringes for carbon pseudo-spherical onions, nanoballoons, iocosahedral, hexagonal and decahedral concentric-graphitic nanostructures (some of which may have been prebiotic nucleation sites); soots showed signs in TEM of graphitization on heating to 3273K or in arc soots. When nanotubes are seen, there was 0.34nm between the graphitic basal planes in nanotubes.

One of the present authors reported [1] on unusual carbon-based nanofibers/chains among diesel-emitted particles that can migrate indoors [2] eliciting a respiratory response in humans [3]. The pulmonary and trancheobronchial retention of particles [4] rose to 50-70% and 20-40% as the particle size decreased from 100mm to 10nm, which could lead to transfers to the blood stream and then other organs. The % daily mortalility in the Chinese city of Shenyang was related to the particle size number of airborne $PM_{0.25}$-PM_{10} particulates [5]; cardiovascular mortality rose as the particle size decreased (but the respiratory mortality did not).

Experimental

Hence combustion-derived carbonaceous ultrafine particles (CUFPs) were collected [1] and were then analysed by HRTEM on holey carbon grids using a Jeol 2100 FEG-TEM.

Fig.3h→



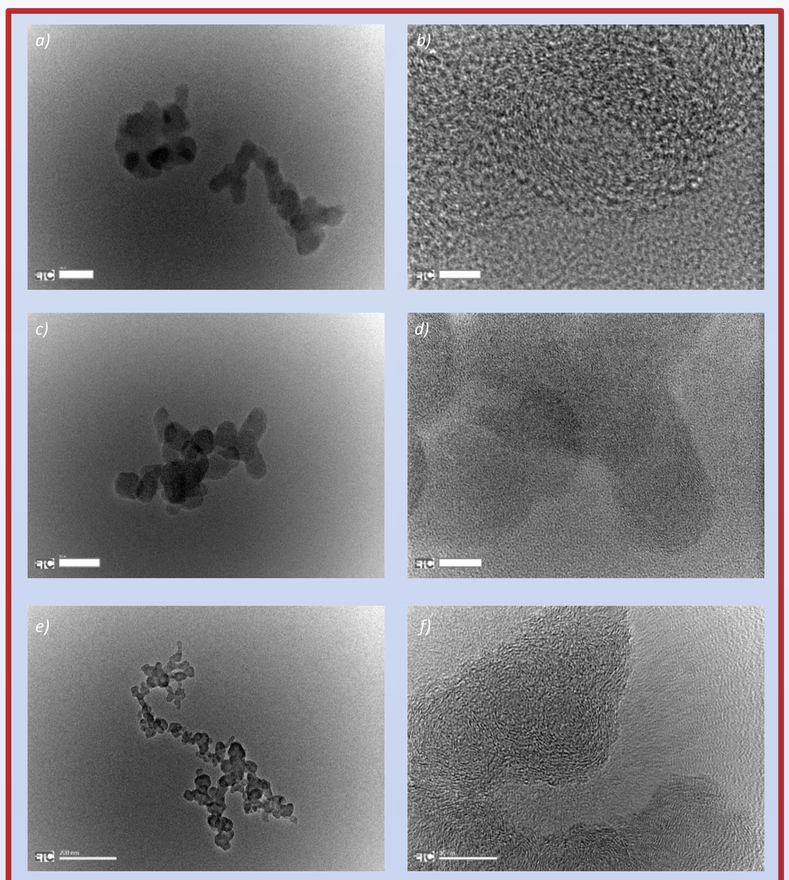


Figure 2. Carbonaceous ultrafine particles (CUFPs) seen emitted from combustion sources found in the atmosphere at London Heathrow (a,b), Uxbridge, West London (c,d) and at Buckingham Palace in central London (e,f).

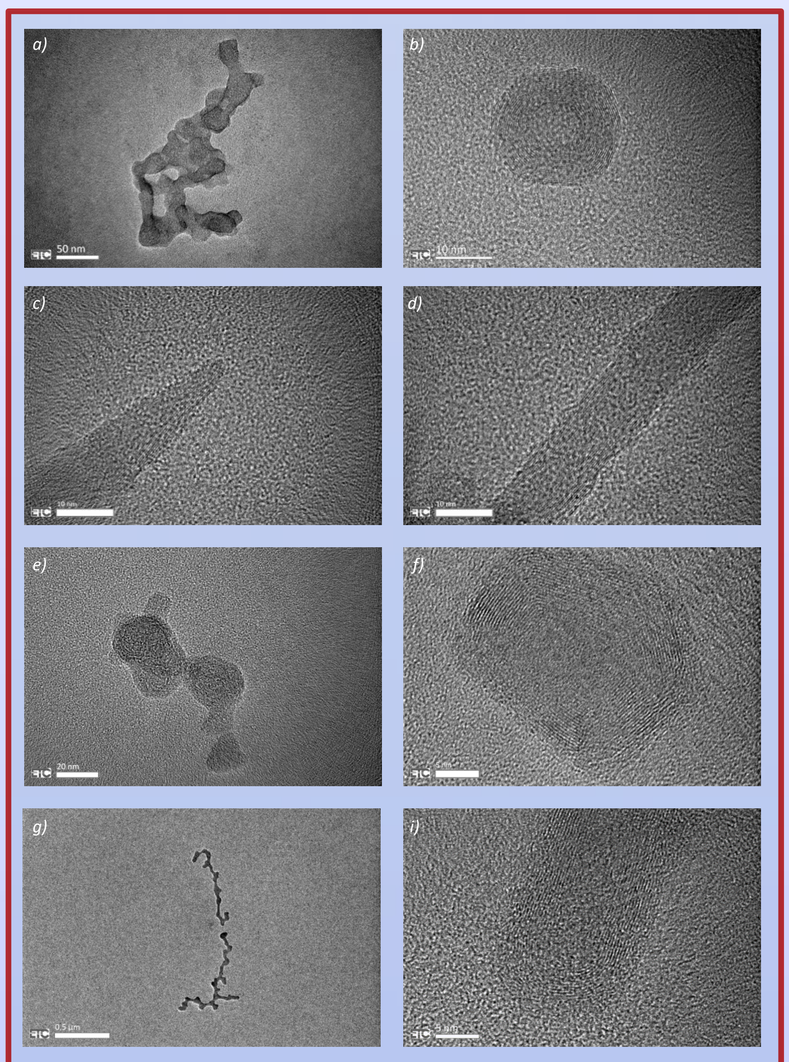


Figure 3. Carbonaceous ultrafine particles (CUFPs) seen emitted from combustion sources found in the atmosphere at Little Italy, New York (a-d), Rothaus, Langstrasse, Zurich (e-h) and Buchau, Austria (i). Fig.3h is to the left in this poster.

Results, Discussion and Conclusions

As previously, HRTEM has been used here to analyse lattice fringes of such combustion-generated soots [6]. CUFP nanostructures seen here by HRTEM in Figures 1-3 include:

i. chain-aggregates (see Fig.1a,c,e and g, Fig.2a,c and e and Fig.3a, f and i) [7]
ii. Spheres (see Fig.1b,d and f and Fig.2a, d and f), onions (see Fig.3g) and filled onions [8]
iii. hollow (twinned) spheres (see Fig.3b), carbon shells and hollow onions seen on annealing at say 2523K [9]
iv. angular (see Fig.1h and 3g) [8] and
v. tubes (Fig.1i, 3c, d and h) [1,10]

that are similar to those seen previously. The analysis in Figure 4 shows that the average interlayer spacing seen in nano-spheres-triangles (Fig.3g) and nanotubes (Fig.3h) for the atmosphere in Zurich were 0.345nm. Such a value is similar to that seen [1] (0.34nm) between the graphitic basal planes in nanotubes. The observation of co-existence of spherical and angular nanostructures [11] in Fig.3h with interlayer spacings of 0.345nm in Fig.4 is interesting because of the expected transition from the latter to the former, where the conversion of soot precursor particles to mature soot aggregates in flames is closely related to carbonization [12]. Figs.1-3 suggest CUFPs are not merely a diesel, airport, European or urban issues.

It is clear that TEM is one method of analysing individual NPs and UFPs from the atmosphere after sampling with little or no preparation, but possibly there needs to be spatial and temporal resolution to sampling; maybe it now has to be complemented by EELS-Raman-TPO-RGA. It may also be that one should deduce [13] biologically-relevant surface areas of CUFPs and their fractal aggregates [14], where NP toxicology suggests adverse effects may occur through the lungs, digestive tract or skin.

Shortly we will report on the effect of vehicle engine fuel and EGR on emitted soot particles and the interaction of such CUFPs on algae and vegetation in the context of green routes to urban pollution control.

Acknowledgements. The authors acknowledge the help of W.Sermon and T.Sermon in some measurements.

References. [1] Evelyn, Mannick and Sermon *Nano Lett*. **3** (2003) 63; [2] Zhu, Hinds, Krudysz, Kuhn, Froines and Sioutas *Aero.Sci.* **36** (2005) 303; [3] Bonvallot et al, *Amer.J.Resp.Cell Molec.Biol.* **25** (2001) 516; [4] Stuart *Environ.Health persp.* **16** (1976) 41; [5] Meng, Ma, Chen, Zhou, Chen and Kan *Environ.Health Persp.* **121** (2013) 1174; [6] Wal *Comb.Sci.Technol.* **126** (1997) 333; Koylu, Faeth, Farias and Carvalho *Comb.Flame* **100** (1995) 621; Wong *Carbon* **26** (1988) 723; [7] Zwanger and Banhart *Philo.Mag*. **72B** (1995) 149; Wal, Tomasek, Street, Hull and Thompson *Appl.Spectros*. **58** (2004) 230; Cabioc'h, Thune and Jaouen *Phys.Rev.* **65B** (2002) 132103; Ugarte *Chem.Phys.Lett*. **207** (1993) 473; [8] Bacsa, de Heer, Ugarte and Chatelain *Chem.Phys.Lett.* **211** (1993) 346; Zhang, O'Brien, Heath, Liu, Curl, Kroto and *J.Phys.Chem.* **90** (1986); [9] Lambert, Ajayan and Bernier *Syn.Metals* **70** (1995) 1475; [10] Ugarte *Carbon* **33** (1995) 989; [11] Dobbins, Govatzidakis, Lu, Schwartzman and Fletcher *Comb.Sci.Technol.* **121** (1996) 103; [12] Maynard in discussion on p.2749 on Donaldson, Stone, Gilmour, Brown and MacNee *Philo.Trans.Roy.Soc.Lon*. **358A** (2000) 2741;[13] Koylu, Xing and Rosner *Langmuir* **11** (1995) 4848