Formation of Secondary Organic Aerosol on Pre-existing Soot Particles from OH Initiated Oxidation of Toluene

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Supporting Information

Additional Experimental Information

The main experimental components include a soot generation and size-selecting system, an environmental chamber, an injection device for gaseous species, an integrated aerosol analytical system, including two DMAs, an APM, a CPC, a Nephelometer, and a cavity ring-down spectrometer (CRDS) to measure the particle size, mass, hygroscopicity, and optical properties (Fig. S1).

Environmental Chamber. All experiments were performed in a 1.2 m^3 collapsible environmental chamber (Teflon® PFA), equipped with 18 black light lamps (F30T8/350BL, Sylvania) and surrounded by reflective aluminum sheets to maximize light intensity in the chamber. Between experiments, the chamber was cleaned and flushed overnight with purified air (Aadco 737-11, Aadco), and irradiated by black light lamps to remove any residues (see supplementary information for details). At the beginning of each experiment, the chamber was filled with ~750 l purified air. Typical background conditions of the clean chamber included that the particles number concentration was less than 0.01 cm^{-3}, NO$_x$ and O$_3$ concentrations were lower than 1 ppb, and the total hydrocarbons were less than 2 ppb.

Soot particles were generated from a modified Santoro-type laminar burner from incomplete combustion of propane. Particles were sampled through a pinhole on the sidewall of a chimney and diluted with dried, particle free nitrogen gas. A portion of the diluted sample was dried to < 5% RH via a Nafion drier (PD-070-18T-12SS, Perma Pure), charged by a bipolar ^{210}Po charger, and size-classified by DMA0 (3081, TSI). The monodisperse aerosol sample was neutralized by a second bipolar ^{210}Po charger and passed through two denuders containing Spectrum XB-17 and HS-600 (General Carbon). The purified soot sample was then introduced into the chamber, with a flow rate of 1.0 lpm for ~1.5 hr to allow the number concentration of soot particles to reach ~1000 cm^{-3}. H_2O_2 from an aqueous solution (16 wt %, 50 μL) was flushed into the chamber with 260 l purified air. Subsequently, an amount (1–10 ml) of the purified air saturated with toluene vapor at room temperature was carried into the chamber by 40 l of purified air. The nominal concentration of H_2O_2 in the chamber was 5 ppm to yield a steady OH concentration.[1] The initial toluene concentration was varied from 30 to 250 ppb for each experiment. A mixing fan was turned on for 30 s to thoroughly mix the soot particles and gaseous species, and the black light lamps were turned on to initiate H_2O_2 photolysis and the SOA formation process. The concentration of toluene was monitored by a proton transfer reaction mass spectrometer (PTR-MS, Ionicon). Typically, 5% toluene was consumed in each experiment. During the experiment, the RH and temperature in the chamber were about 8% and 303 ± 1 K, respectively.

Blank experiments were performed under several experimental conditions for one hour, including soot with black light, soot with toluene and black light, and soot with H_2O_2 and black light. No measureable change in the particle size or mass was observed in those experiments.

Transmission electron microscope (TEM) samples were taken by sampling from the

chamber at 1.0 lpm for 10 min through a low-pressure cascade impactor (PIXE), where aerosols were collected on 200 mesh Copper TEM grids with formvar/carbon film (Model 01800, Ted Pella). TEM images were examined using a JEM 2010 transmission electron microscope operated at 100 kV accelerating voltage.

Measurements of Particle Size and Mass[2-5]

Aerosols were sampled from the chamber into the aerosol system at 1.0 lpm. The size distribution and number concentration of soot particles in the chamber during the experiment were monitored with SMPS. The relative uncertainty in *Gfd* and number concentration measurements was less than 2% and 3%, respectively. Aerosol nucleation was efficiently suppressed because of the injector of soot particles and was only occasionally observed in the chamber. In the latter case, the size distribution of newly-formed particles was distinct from that of soot particles and did not interfere with the soot aging experiments. Particle mass was determined using DMA-APM-CPC. Calibration curve was obtained to correct any offsets by using spherical Polystyrene Latex (PSL) particles (Duke Scientific) with known sizes (46, 81, 97, 151 and 240 nm) and material density (1.05 g cm^{-3}).[3] The relative uncertainty in *Gfm* measurements was less than 3%. There was a small difference (~5 min) in the reaction time, when particle size and mass measurements were performed. As a result, the data of particle mass growth was fitted versus the reaction time to interpolate the *Gfm* value corresponding to that when the *Gfd* value was measured.

Coated soot particles were processed further by heating experiments (coated-heated soot).[4-5] It was found that the fresh soot generated by our burner contained less than 5 wt % volatile components. The mass of coated-heated soot was close to that of fresh soot (within 2%), suggesting that all the organic coatings were removed after the heating.

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Measurements of Aerosol Optical Properties. The optical system consisted of a commercial integrating Nephelometer (Model 3563, TSI) and a CRDS connected in series.[6-7] Particles were sampled at 6.0 lpm from the chamber into the optical system. The b_{sca} at 532 nm was calculated from a power law fit to the scattering coefficients at the three nephelometer wavelengths (450, 550 and 700 nm).[6] The b_{ext} was measured by the CRDS with a Q-switched pulsed laser (QG-532-500, CrystaLaser) producing light pulse at 532 nm, a stainless steel cell with aerosol inlet in the middle and outlet and two ends, and two high-reflectivity dielectric mirrors (Los Gatos Research) mounted on both ends of the cell.[6] A small dry nitrogen flow was constantly purging the mirrors to prevent aerosol contamination. Calibration and correction were performed for the optical system based on well-established procedures described in details elsewhere.[6] The random error in scattering and absorption coefficients was less than 1%.

Measurements of the Density and Hygroscopicity of Toluene-OH Oxidation Products. To measure of the density and hygroscopicity of the toluene-OH oxidation products, the clean chamber was injected with 300 ppb of toluene and 5 ppm of H_2O_2 to efficiently promote nucleation and growth of SOA. Black lights were then turned on to allow oxidation reaction to take place. Particles were allowed to nucleate and grow until they reached a desirable size distribution, monitored by SMPS. The poly-disperse aerosols had a long-normal size distribution with a peak maximum at ~60 nm. The lights were turned off when measurements of particle properties were conducted.

The particle mass m was determined for particles with mobility diameter D_p between 70–80 nm. The effective density, ρ_{org}, was calculated using Eq. (1), and there was little difference in ρ_{org} for different sizes. A ρ_{org} value of (1.34 ± 0.04) g cm^{-3} was determined by averaging the

density data for different sizes. Hygroscopicity growth was determined for particles with the mobility diameters of 50, 80 and 100 nm by HTDMA.

Calculation of the Volume Equivalent Hygroscopicity Growth Factor of Coated Soot

The volume equivalent hygroscopic growth factor $HGfd_{ve}$ is defined as the ratio between volume equivalent diameters D_{ve} of coated-wetted and coated soot particles.[8] It is assumed that the mass of condensed water is linearly proportional to that of organic coatings with a factor of k_w. As a result, when coated soot particles with a mass of m_p and a organic mass fraction of f_m_{org} are exposed to 90% RH, the resulting coated-wetted particles have a mass $m_{p,w}$ as:

$$m_{p,w} = (1 + k_w \cdot f\_m_{org})m_p \qquad (S2)$$

The organic mass fraction $f\_m_{org,w}$ in the coated-wetted soot is,

$$f\_m_{org,w} = \frac{f\_m_{org}}{1 + k_w \cdot f\_m_{org}} \qquad (S3)$$

Assuming a volumetric additivity for components in coated-wetted soot, its material density $\rho_{m,w}$ can be estimated as:

$$\frac{1}{\rho_{m,w}} = \frac{f\_m_{org,w}}{\rho_{org}} + \frac{k_w \cdot f\_m_{org,w}}{\rho_{water}} + \frac{1 - (1 + k_w)f\_m_{org,w}}{\rho_{soot}} \qquad (S4)$$

The volume equivalent diameter $D_{ve,w}$ for the coated-wetted soot particle is:

$$D_{ve,w} = \sqrt[3]{\frac{6m_{p,w}}{\pi \rho_{m,w}}} \qquad (S5)$$

The $HGfd_{ve}$ can then be calculated as $D_{ve.w}/D_{ve}$, where $D_{ve.w}$ and D_{ve} are the volume equivalent diameters of coated-wetted and coated soot particles, respectively.

Table S1. Properties of Fresh Soot Particles

| D_p, nm[a]	m_p, 10^{-16} g[b]	D_{ve}, nm[c]	N_{pp}[d]
82.4	1.47	54.1	20
101	2.34	63.2	32
155	7.77	94.3	105

[a] Mobility size determined by SMPS;

[b] Particle mass determined by DMA-APM-CPC;

[c] Particle volume equivalent diameter calculated by assuming the soot material density as 1.77 g cm^{-3};

[d] The number of spherical primary particles in one soot particle, assuming that the primary particle has a density of 1.77 g cm^{-3} and a diameter of 20 nm.
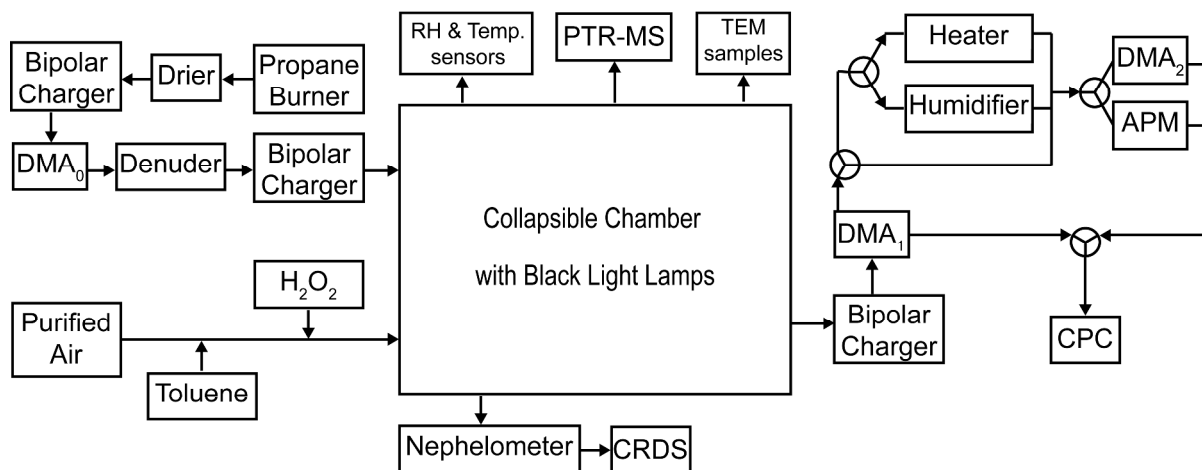
Figure S1. Schematics of the environmental chamber and instrument setup.
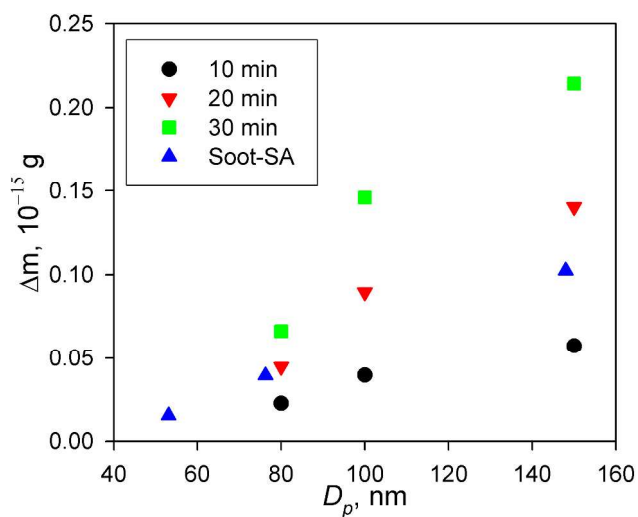
Figure S2. Absolute mass (Δm) of the organic coating of toluene-OH oxidation products as a function of the initial soot particle mobility size D_p, at three different reaction time: 10 min (black circles), 20 min (red down-triangles), and 30 min (green squares). The absolute mass of sulfuric acid coatings (Soot-SA, blue up-triangles) is adapted from Ref 2. Note that soot particles with larger initial mobility size always show larger increase in absolute mass of the coating.

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