A ~~Study~~study on the ~~Key Factors Determining~~influence of inorganic ions, organic carbon, and microstructure on the ~~Hygroscopic~~hygroscopic property of ~~Black Carbon~~soot

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Abstract. ~~Black carbon (BC)~~Soot is a crucial component of aerosols in the atmosphere. Understanding the hygroscopicity of ~~BC~~soot particles is important for studying their role as cloud condensation nuclei (CCN~~) and ice nuclei (IN~~), as well as their chemical behavior and atmospheric lifetime. However, there is still a lack of comprehensive understanding regarding the factors that determine the hygroscopic properties of ~~fresh BC~~soot. In this work, the hygroscopic behavior of ~~BC~~soot particles generated from different types of fuel combustion and aged with SO_2 for varying durations ~~were~~was measured by a vapor sorption ~~analyzer while various~~analyser. Various characterizations of ~~BC~~soot were conducted to understand the key factors that influence the hygroscopic properties of ~~BC~~soot. It was found that ~~the presence of~~ water-soluble substances in ~~BC facilitates~~soot facilitate the completion of monolayer water adsorption at low relative humidity~~, while also increasing~~ and increase the number of water adsorption layers at high relative humidity. On the other hand, ~~BC~~soot prepared ~~by~~from fuels burning ~~organic fuels, which~~ typically lacks water-soluble inorganic ions~~, primarily exhibits~~ and their hygroscopicity ~~characteristics~~ is primarily influenced by organic carbon (OC) and microstructure. Furthermore, the hygroscopicity of ~~BC~~soot can be enhanced by the formation of sulfate ~~ions~~ due to heterogeneous oxidation of SO_2. ~~This~~These finding sheds light on the critical factors that affect ~~BC~~soot hygroscopicity during water adsorption and allows for estimating the interaction between water molecules and ~~BC~~soot particles in a humid atmosphere.

Keywords: ~~black carbon~~soot, hygroscopicity, multilayer adsorption, water-soluble ions, organic carbon, microstructure, heterogeneous reaction

Introduction

~~Black carbon (BC)~~Soot particles are produced by incomplete combustion processes of carbon-containing materials ~~(Nie et al., 2020; Wei et al., 2020). The current global emission of BC has been estimated to be 3-8 TgC yr^{-1}~~(Petzold et al., 2013). The current global emission of soot has been estimated to be 3-8 TgC per year (Forster et al., 2007). ~~BC~~Soot aerosol can influence climate by directly absorbing solar radiation and affecting cloud formation and surface albedo through deposition on snow and ice (Liao et al., 2015; Peng et al., 2016), which results in the contribution of ~~BC to global warming second only to that of CO_2 (Jacobson, 2001). In addition, BC~~soot to anthropogenic radiative forcing second only to that of CO_2 (Bond et al., 2013; Cappa et al., 2012; Liu et al., 2017). In addition, soot particles can significantly enhance the atmospheric oxidation capacity (He et al., 2022) and contribute to the formation of secondary aerosols by providing active surface for the heterogeneous reactions of gaseous pollutants like NO_2, SO_2, and volatile organic compounds (VOCs) (Tritscher et al., 2011; Han et al., 2017; Zhang et al., 2022b; Liu et al., 2023). Moreover, ~~BC~~soot particles also pose a health risk by causing and enhancing respiratory, cardiovascular, and allergic diseases (Janssen et al., 2011; Lin et al., 2011). Due to its significant effect on global climate change, regional air quality and human health, the physicochemical properties of ~~BC~~soot have attracted much attention in recent decades.

Hygroscopicity is one of the most important physicochemical properties of ~~BC~~soot, which largely determines the cloud condensation nuclei (CCN~~) and ice nucleation (IN~~) activity as well as the consequent radiation forcing (Semeniuk et al., 2007; Ramanathan and Carmichael, 2008; Friedman et al., 2011). On the other hand, the hygroscopicity of atmospheric particles is important for their chemical behavior because water molecules were found to significantly affect the heterogeneous transformation of gaseous pollutants on ~~BC~~soot surfaces (Zhao et al., 2017; He and He, 2020; Zhang et al., 2022b). The hygroscopic behavior of ~~BC~~soot has been widely studied. It was found that ~~fresh BC~~soot prepared in laboratory or commercial ~~BC~~soot appears to be hydrophobic as there is no noticeable uptake of water at unsaturated humidity. For instance, the commercial ~~BC~~soot and spark discharge ~~BC~~soot particles shrunk with increasing RH during the growth factor measurements by hygroscopicity tandem differential mobility analysers (H-TDMA) (Weingartner et al., 1997; Henning et al., 2010). This was explained with a restructuring of the agglomerated particles. Due to the inverse Kelvin effect, water condenses in small angle cavities of ~~BC~~soot particles, which leads to capillary forces on the branches of the aggregates and cause them to collapse. Different from the commercial ~~BC~~soot and spark discharge ~~BC~~soot, diesel ~~BC~~soot, aircraft ~~BC~~soot and biomass smoke particle showed obvious particle size growth with increasing RH (Popovicheva et al., 2008; Carrico et al., 2010). This indicates that the chemical composition of ~~BC~~soot is an important factor affecting its hygroscopicity. Our previous study suggested that combustion conditions could affect morphology and microstructure of ~~BC~~soot, which has significant effect on the hygroscopicity (Han et al., 2012).

~~BC~~Soot aerosols experience internal mixing with ~~non-BC~~other compounds (inorganic, organic, or inorganic/organic mixtures) as aging after their emission (Shiraiwa et al., 2007; Matsui et al., 2013). Field observations have demonstrated that the presence of BC-coating materials greatly influences both the hygroscopic properties and the CCN properties (or the wet removal) (Ohata et al., 2016; Li et al., 2018; Hu et al., 2021). Several laboratory studies have also simulated the hygroscopic changes of ~~BC~~soot particles during atmospheric transport and aging. ~~BC~~Soot particles generated from incomplete combustion of propane were exposed to the oxidation products of the OH-toluene reaction, resulting in an organic coating that increased the hygroscopicity of the particles (Qiu et al., 2012). Moreover, the aging process of propane flame ~~BC~~soot through NO_2 oxidation of SO_2 was found to produce inorganic hydrophilic coating materials and significantly enhance the CCN activity of ~~BC~~soot particles (Zhang et al., 2022a).

The hygroscopicity of ~~BC~~soot can vary significantly depending on its source and aging processes, which has implications for regional air quality and climate. However, previous studies have often focused on specific factors influencing the hygroscopicity of a particular type of ~~BC~~soot, lacking a comprehensive understanding of the key factors determining the hygroscopic properties of ~~fresh BC~~soot. In this study, we conducted measurements to determine the hygroscopicity of ~~BC~~soot produced from different fuels and aged with SO_2 for different time. In addition, the chemical composition and microstructure of ~~BC~~soot were characterized for each ~~BC~~soot sample. The main objectives of this study were to compare the hygroscopicity of ~~BC~~soot from different sources and analyze the effect of OC, water-soluble ions and microstructure on the multilayer adsorption of ~~BC~~soot surface water. Moreover, the impact of heterogeneous aging reactions on the multilayer adsorption of water on the surface of ~~BC~~soot particles was also explored. This study contributes to a deeper understanding of the hygroscopicity and atmospheric impacts of ~~BC~~soot particles in the atmosphere.

2.Experimental section

2.1 ~~Black carbon Production.~~ Soot samples.

Prepared ~~BC~~soot particles were obtained by burning n-hexane, decane ~~and~~or toluene (AR, Sinopharm Chemical Reagent Lo., Ltd) in a co-flow system as described in our previous studies (Han et al., 2012; Zhao et al., 2017)~~. Diesel black carbon (DBC~~. Briefly, the co-flow burner consisted of a diffusion flame maintained in a flow of synthetic air. Soot was collected on a quartz disc (7 cm in diameter) over diffusion flame and then stored in a brown bottle (Agilent). Diesel soot (DS) was collected from the diesel particle filter (DPF) of a China VI heavy-duty diesel engine (ISUZU from China). A diesel engine bench test was run under the conditions of World Harmonized Transient Cycle (WHTC). China VI fuels were used in the study, meeting the GB T32859-2016 standard. Printex U ~~black carbon (UBC~~powder (U-soot) from Degussa (CAS No.: 1333-86-4) was used as a model ~~BC~~soot. These types of ~~BC~~soots are usually used in laboratory simulation as representative of ~~BC~~soot in the atmosphere (Liu et al., 2010; Han et al., 2012; Zhang et al., 2022b).

The aging experiments were performed in a quartz flow tube reactor. ~~UBC~~Prior to the reaction, 0.05 g U-soot powder was placed into ~~a~~the quartz flow tube reactor. The experiments were maintained at ~~298 K~~25 °C. Zero air was used as the carrier gas~~, and the~~ with a total flow ~~tube~~ rate ~~introduced in the flow tube reactor was~~about 700 ml min^{-1}. The SO_2 concentration was 5 ppm. The relative humidity (RH) ~~was adjusted by varying the ratio~~ of ~~dry zero air to wet zero air at~~ aging reaction was 50 % ~~and measured by a~~ RH ~~sensor (~~(recorded with Vaisala HMP110). To simulate solar irradiation, a high uniformity integrated xenon lamp (PLS-FX300HU, Beijing Perfectlight Technology Co., Ltd.) of 270 mW cm^{-2} was used as the light source. Its visible spectrum ranges from 330 to 850 nm.

2.2 Characterization of ~~black carbon~~soot

A transmission electron microscope (H-7500, Hitachi) was used to investigate the morphologies of soot particles. DS sample was ultrasonically dispersed in ethanol while other soot samples were ultrasonically dispersed in ultrapure water (18.2 MΩ cm). Then, a droplet of suspension was deposited onto a Cu microgrid. An acceleration voltage of 200 kV was used for measurements. The diameter of particles was analyzed by ImageJ 1.41 software.

Raman spectra of ~~BC~~soots were obtained with a Renishaw inVia Raman microscope system using a 532 nm excitation wavelength. The exposure time for each scan was ~~60s~~60 s. Data were acquired and analyzed using Renishaw WiRE 5.4 software.

The content of OC was measured using a thermal-optical transmittance OC/EC analyzer (Sunset laboratory Inc., Forest Grove, OR) with modified NIOSH 5040 protocol and produced four OC fractions (OC1, OC2, OC3, and OC4 at 150, 250, 450, and 550 °C respectively), OP (~~pyrolysed~~pyrolyzed organic) fraction (a pyrolyzed carbonaceous component determined when transmitted laser returned to its original intensity after the sample was exposed to oxygen), and three EC fractions (EC1, EC2, and EC3 at 550, 700, and 800 °C, respectively). OC is defined as OC1+OC2+OC3+OC4+OP and EC is defined as EC1+EC2+EC3-OP (Chow et al., 1993; Li et al., 2016).

The ~~species~~chemical compositions of OC in ~~BC~~soots were~~ analyzed and~~ identified via gas chromatography coupled with mass spectrometry (GC–MS, Agilent 6890–5973). 5 mg ~~BC~~soot was first ultrasonically extracted for 10 min using 10 ml of dichloromethane (CH_2Cl_2), which was filtered through a quartz sand filter. The obtained supernatant liquid was subsequently concentrated using the N_2 blowing method for final analysis. The gas chromatograph was equipped with a DB-5MS 30 m × 0.25 mm × 0.25 mm capillary column and the mass spectrometer employed a quadrupole mass filter with a ~~70eV~~70 eV electron impact ionizer. The temperature of the programmed temperature vaporizer was held at 270 °C. The initial oven temperature was set at 40 °C for 2 min, then increased step-by-step to 150 °C (by 5 °C min^{-1}) for 5 min, 280 °C (by 10 °C min^{-1}) for 10 min, and 320 °C (by 10 °C min^{-1}) for 5 min.

For ion chromatography (IC) measurement, about 5 mg of ~~BC~~soot particles were extracted by ultrasonication with 10 mL ultrapure water (~~specific resistance ≥ ~~18.2 MΩ cm) for 10 min. Then, the extract was filtered through a 0.22 mm PTFE membrane filter. The obtained solution was analyzed using a Wayee IC-6200 ion chromatography system equipped with a SI-524E anionic analytical column. An eluent of 10 mM KOH was used at a flow rate of 1.0 mL min^{-1}.

2.3 Hygroscopic properties of ~~black carbon~~soot

The hygroscopic properties of ~~BC~~soots were investigated using a vapor sorption analyzer (VSA, Q5000 SA, TA Instruments), which has been applied to study hygroscopicity of atmospherically relevant particles in previous work (Chen et al., 2019; Gu et al., 2017). VSA utilizes a highly sensitive balance to measure the mass change of a sample as a function of RH at a given temperature. The instrument has a measurement range of 0−100 mg with a sensitivity of 0.01 μg, allowing for precise analysis. The temperature could be controlled in the range of 5−85 °C with an accuracy of 0.1 °C, and RH could be regulated in the range of 0−98 % with an absolute accuracy of 1 %. To ensure the accuracy of RH measurements, we routinely measured deliquescence relative humidities (DRHs) of NaCl, $(NH_4)_2SO_4$, and KCl, and the difference between measured and theoretical DRHs did not exceed 1 %, confirming the reliability and accuracy of the instrument.

Hygroscopicity of ~~BC~~soot was investigated at ~~298K~~25 °C. Figure 1 displays the change of RH and normalized sample mass with experimental time in a typical experiment. ~~UBC~~U-soot was dried at < 1 % RH and the sample mass under dry conditions was typically 1−5 mg. After that, RH ~~was~~ increased ~~to 90 % start at 10 %~~ step by step~~, and at~~ from 10 % to 90 %, with an increase of 20 % per step. At each ~~step, RH was increased by 20 %; at each RH~~point, the ~~sample~~adsorption of water on samples was considered to reach an equilibrium when its mass change was < 0.05 % within 60 min~~, and then RH was changed to the next value.~~ .

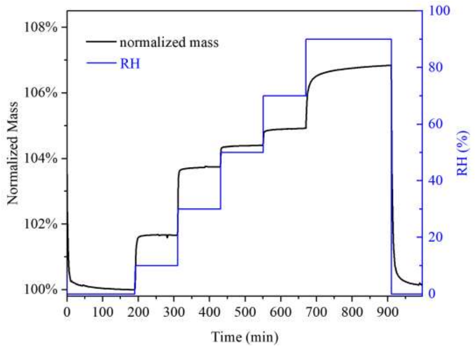


Figure 1. RH (blue curve, right y axis) and normalized sample mass (black curve, left y axis) as a function of experimental time during one experiment in which hygroscopic properties of ~~UBC~~U-soot were examined at ~~298K~~25 °C.

3.Result and discussion

3.1The morphology and vapor adsorption isotherms of various ~~black carbon~~soot

Figure 2 shows TEM images of soot samples. All soot samples exhibit a long chain like aggregate shape composed of typical spherical particles, which is consistent with previous studies (Han et al., 2012; Liu et al., 2010).

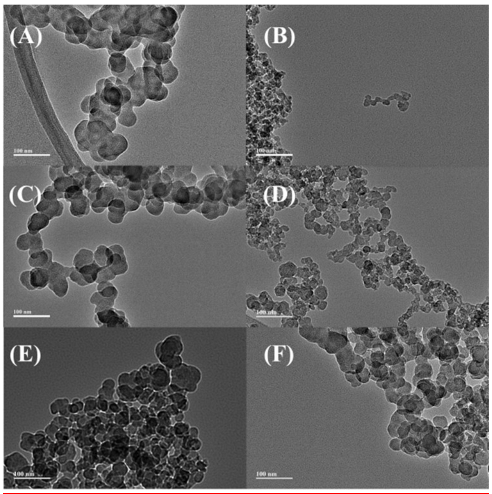


Figure 2. TEM images of n-hexane flame soot (A), decane flame soot (B), toluene flame soot (C), diesel soot (D), U-soot aggregates (E) before and (F) after aged with 5 ppm of SO_2 for 10 h.

Figure 3 shows the diameter distribution of soot particles. Particles exhibit a relatively uniform particle size distribution. Notably, the proportion of spherical particles with large diameter (> 35 nm) of aged U-soot was slightly greater than that of fresh U-soot. Nevertheless, the average particle diameter ($\bar{d}_p$) of U-soot and SO_2 aged U-soot are 39.55 nm and 41.60 nm, respectively, suggesting weak effect of SO_2 heterogeneous reaction on the size distribution of U-soot particles.

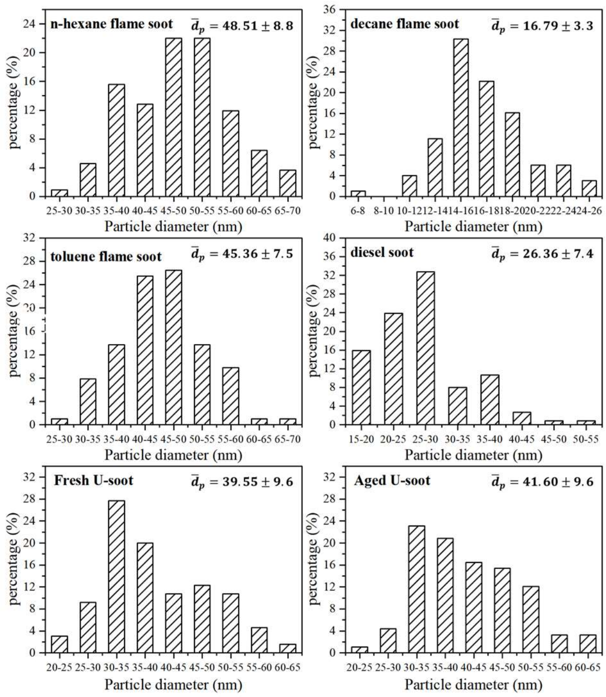
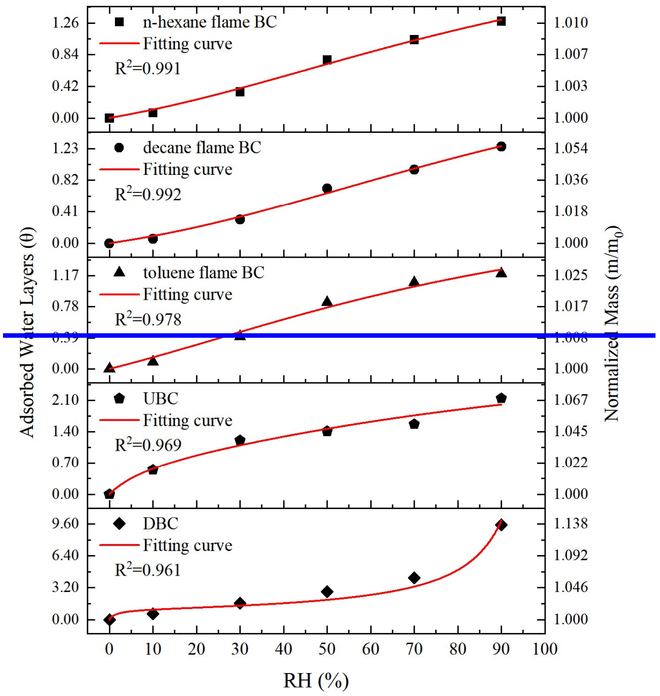


Figure 3. Diameter distribution of n-hexane flame soot, decane flame soot, toluene flame soot and diesel soot and U-soot particles before and after aged with 5 ppm of SO_2 for 10 h.

Figure 4 shows the normalized sample mass (normalized to that at < 1 % RH, m/m_0) as a function of RH for five ~~kinds~~types of ~~BC~~soot. Three types of prepared ~~BCs~~soots (n-hexane ~~BC~~flame soot, decane ~~BC~~flame soot and toluene ~~BC~~flame soot) exhibited lower water adsorption per unit mass sample under each RH condition compared to ~~DBC~~DS and ~~UBC~~U-soot particles. Specifically, at 90 % RH, ~~DBC~~DS showed the highest water adsorption ~~of~~among all ~~BC types~~soot samples, with a m/m_0 value of 1.138, followed by ~~UBC~~U-soot with a value of 1.067. Moreover, among the three prepared ~~BCs~~soots, decane flame ~~BC~~soot exhibited the highest hygroscopicity~~, as indicated by its~~ with a normalized sample mass of 1.054 at 90 % RH.~~-~~



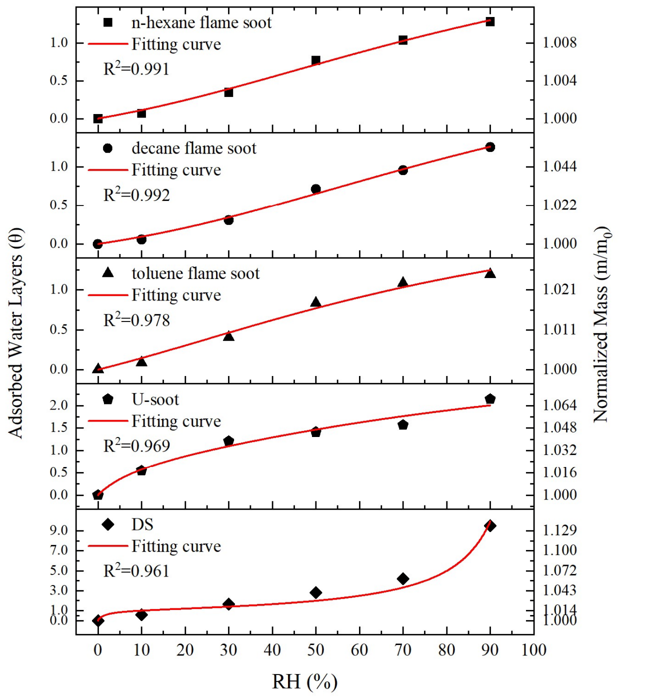


Figure ~~2~~4. Water adsorption isotherms of ~~BCs~~soots, fitting curves (lines) with BET equation and the measured sample mass change (normalized to that at < 1 % RH, i.e., m/m_0) of ~~BCs~~soots as a function of RH (up to 90 % RH).

In order to further analyze the adsorption characteristics of water on ~~BC~~soot, the isotherms of ~~BC~~soot were fitted with the Brunauer-Emmett-Teller (BET) equation. As shown in Fig. ~~2~~4, the isotherms of prepared ~~BC~~soot and ~~UBC~~U-soot could be well fitted with three-parameters BET equation with the assumption of limited adsorbed water layers as following Eq. (1~~)~~) (Brunauer et al., 1938; Goodman et al., 2001; Ma et al., 2010; Tang et al., 2016):

$$V = \frac{V_m c \frac{P}{P_0}}{1-\frac{P}{P_0}} \times \frac{1-(n+1)\left(\frac{P}{P_0}\right)^n + n\left(\frac{P}{P_0}\right)^{n+1}}{1+(c-1)\frac{P}{P_0} - c\left(\frac{P}{P_0}\right)^{n+1}} \quad (1)$$

~~where~~Where, V is the volume of gas adsorbed at equilibrium pressure P, V_m is the volume of gas necessary to cover the surface of the adsorbent with a complete monolayer, ~~P is the equilibrium pressure of the adsorbing gas, and~~ P_0 is the saturation vapor pressure of the adsorbing gas at that temperature. n is an adjustable parameter given as the maximum number of layers of the adsorbing gas and is related to the pore size and properties of adsorbent. As a result, multilayer formation of adsorbing gas is limited to n layers at large values of P/P_0. The parameter c is the temperature-dependent constant related to the enthalpies of adsorption of the first and higher layers through Eq. (2) (Brunauer et al., 1938):

$$c = \exp\left(\frac{\Delta H_2^0 - \Delta H_1^0}{RT}\right) \quad (2)$$

~~where~~Where, ΔH_1^0 is the standard enthalpy of adsorption of the first layer, and ΔH_2^0 is the standard enthalpy of adsorption on subsequent layers and is taken as the standard enthalpy of condensation, R is the gas constant, and T is the temperature in Kelvin.

For ~~DBC~~DS, a notable increase in sample mass was observed between 70 % and 90 % RH. This can be attributed to a significant rise in the number of adsorbed water layers within this specific RH range~~. This hygroscopic characteristic of DBC particles~~, which leads to ~~an~~the inability to describe the adsorption isotherm ~~that cannot be adequately described by~~using the three-parameter BET equation~~, which assumes a limited number of adsorbed water layers~~. However, the two-parameter BET equation (Eq. (3)), assuming an unlimited number of adsorbed water layers, provides a better fit for the observed adsorption behavior of ~~DBC~~DS particles (Brunauer et al., 1938):

$$\sout{v = \frac{v_m c p}{(p_0-p)\{1+(c-1)(p/p_0)\}}} \; V = \frac{V_m c P}{(P_0-P)\{1+(c-1)(P/P_0)\}}$$

(3)

The fitted parameters, as shown in Table 1, provide valuable insights into the water adsorption behavior of different ~~BC~~soot. The threshold relative humidity for one monolayer (MRH) for the fresh prepared ~~BCs~~soots is approximately 70 ~~%.~~% RH. However, both ~~UBC~~U-soot and ~~DBC~~DS exhibit significantly lower MRH values (~~MRH_{DBC}~~=MRH_{DS} = 15 ~~%, MRH_{UBC}~~=% RH, $MRH_{U\text{-}soot}$ = 25.5 ~~%)~~% RH) compared to fresh prepared ~~BC~~soot. This suggests that ~~UBC~~U-soot and ~~DBC~~DS have a higher affinity for water uptake at lower RH levels ~~compared to~~than fresh ~~BC~~soot. At 90 % RH, prepared ~~BC~~soot and ~~UBC~~U-soot particles were found to have approximately 1.2 and 2.1 layers of surface water adsorbed, respectively. Interestingly, ~~DBC~~DS showed ~~a significantly higher number of surface water layers with~~ around 9.5 layers adsorbed at 90 % RH~~. This indicates that DBC has~~, indicating a strong propensity for water adsorption ~~and can accommodate a larger amount of adsorbed water compared to the other BC types.~~.

The water-soluble ions like SO_4^{2-} and NO_3^- in ~~BC~~soot samples were analyzed by IC, and the corresponding results are presented in Table 2. It was observed that the content of NO_3^- in all ~~BC~~soot samples, except for ~~DBC~~DS, was approximately 0.2 µg mg^{-1}. However, ~~DBC~~DS exhibited a higher NO_3^- content of 1.44 µg mg^{-1}, which could be due to the aging of high concentration NOx coexisting in the exhaust pipe. Regarding SO_4^{2-}, the fresh prepared ~~BCs~~soots did not show any detectable levels of SO_4^{2-}. In contrast, both ~~UBC~~U-soot and ~~DBC~~DS displayed notable amounts of SO_4^{2-}, with ~~UBC~~U-soot having a content of 2.54 µg mg^{-1} and ~~DBC~~DS having the highest content of 11.46 µg mg^{-1}, respectively. These results indicate that water-soluble inorganic ions (e.g., nitrates and sulfates) are dominant factor ~~to enhance~~for enhancing the hygroscopicity of ~~BC~~soot, which is consistent with previous studies (Carrico et al., 2010; Popovicheva et al., 2010)~~, highlighting the dominance of water-soluble inorganic ions in influencing the hygroscopic properties of BC.~~.

Table 1. Adsorption parameters for water uptake on ~~BC~~soot.

~~Black carbon~~Soot	BET area (m^2 g^{-1})	MRH (%)	*n*	*c*	R^2
n-hexane flame ~~BC~~soot	26.27	68.0	2.84	1.01	0.991
~~decane~~toluene flame ~~BC~~soot	70.97~~147.36~~	67.2~~72~~	2.~~92~~47	~~0.83~~1.37	0.~~992~~978
~~toluene~~decane flame ~~BC~~soot	147.36~~70.97~~	72.0~~67.2~~	2.~~47~~92	~~1.37~~0.83	0.~~978~~992

~~DBC~~DS	47.93	15.0	---	66.95	0.961
~~UBC~~U-soot	97.24	25.5	3.34	9.57	0.969
~~UBC~~U-soot aged 2h	~~10.67~~99.80	24.4	3.42	10.67	0.973
~~UBC~~UBCU-soot aged 6h	~~9.82~~101.46	25.0	3.59	9.82	0.956
~~UBC~~U-soot aged 10h	~~8.52~~98.96	26.2	3.82	8.58	0.944

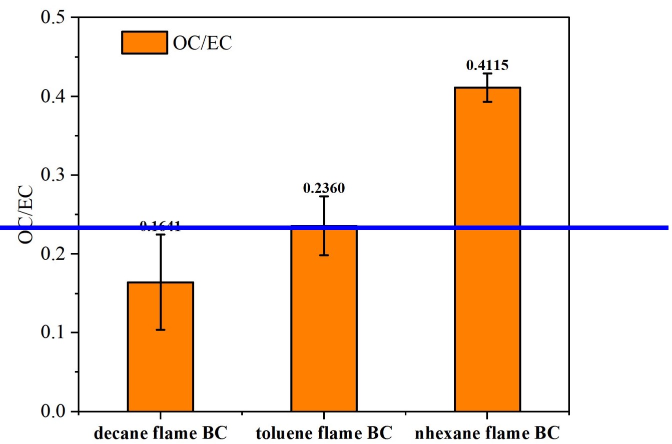
Table 2. Mass concentration of SO_4^{2-} and NO_3^- ~~on BCs measured by IC~~and the ratio of OC/EC of soots.

~~Black carbon~~Soot	Mass concentration of SO_4^{2-} (μg mg^{-1})	Mass concentration of NO_3^- (μg mg^{-1})	OC/EC
n-hexane flame ~~BC~~soot	0.00	0.19	0.41±0.02
~~decane~~toluene flame ~~BC~~soot	0.00	0.18	0.~~22~~24±0.04
~~toluene~~decane flame ~~BC~~soot	0.00	0.22	0.~~18~~16±0.06
~~DBC~~DS	11.46	1.44	0.14±0.02
~~UBC~~U-soot	2.55	0.24	0.12±0.03
~~UBC~~U-soot aged 2h	4.83	0.20	---
~~UBC~~U-soot aged 6h	7.14	0.19	---
~~UBC~~U-soot aged 10h	9.61	0.20	---

3.2 The factors controlling the hygroscopic properties of prepared ~~black carbon~~soot

Compared with ~~DBC~~DS and ~~UBC~~U-soot, prepared ~~BCs~~soots are more hydrophobic (Fig. ~~2~~4) due to ~~less~~containing fewer water-soluble inorganic ~~ion contained~~ions (Table 2). However, there are still significant differences in the hygroscopic behavior of ~~BCs~~soots prepared from different fuels. In order to analyze the differences in the hygroscopicity of different prepared ~~BC~~soot, the relative content and species of OC and microstructure of ~~BC~~soot were characterized. ~~Fig. 3 shows the ratio of OC/EC of BC~~

~~samples.~~ It was found that the n-hexane flame ~~BC~~soot has the highest OC/EC ratio, followed by toluene flame ~~BC~~soot, and decane flame ~~BC~~soot has the lowest OC/EC ratio~~.~~ (Table 2). It should be noted that the ratio of OC/EC is negatively correlated with their hygroscopicity, indicating that organic carbon is not conducive to the adsorption of water on the surface of ~~BC~~soot. The impact of OC on the hygroscopicity of ~~BC~~soot is still a subject of debate. Some field observations results have indicated that particles with high OC/EC ratio were preferentially removed by precipitation and the condensation of photochemically generated secondary organic carbon on ~~BC~~soot particles could cause enhancement of hygroscopicity (Dasch and Cadle, 1989; Li et al., 2018). However, HTDMA measurements have shown that neither hygroscopicity nor droplet activation of the fresh propane ~~BC~~soot particles depend on the OC content (Henning et al., 2012). Therefore, it is necessary to analyze the specific OC species present in prepared ~~BC~~soot particles to gain a better understanding of their role in hygroscopicity.



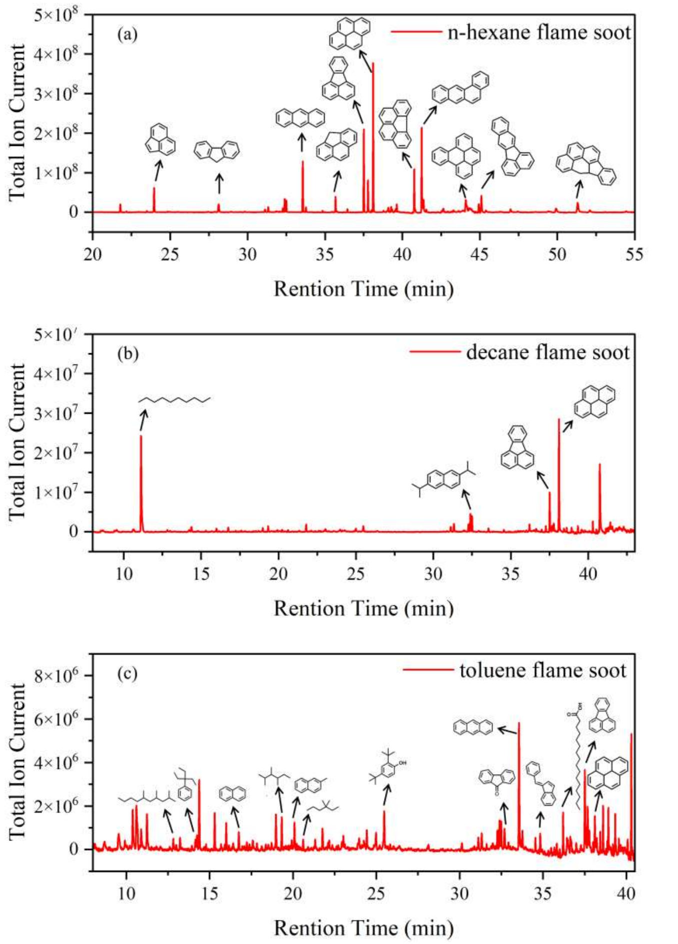
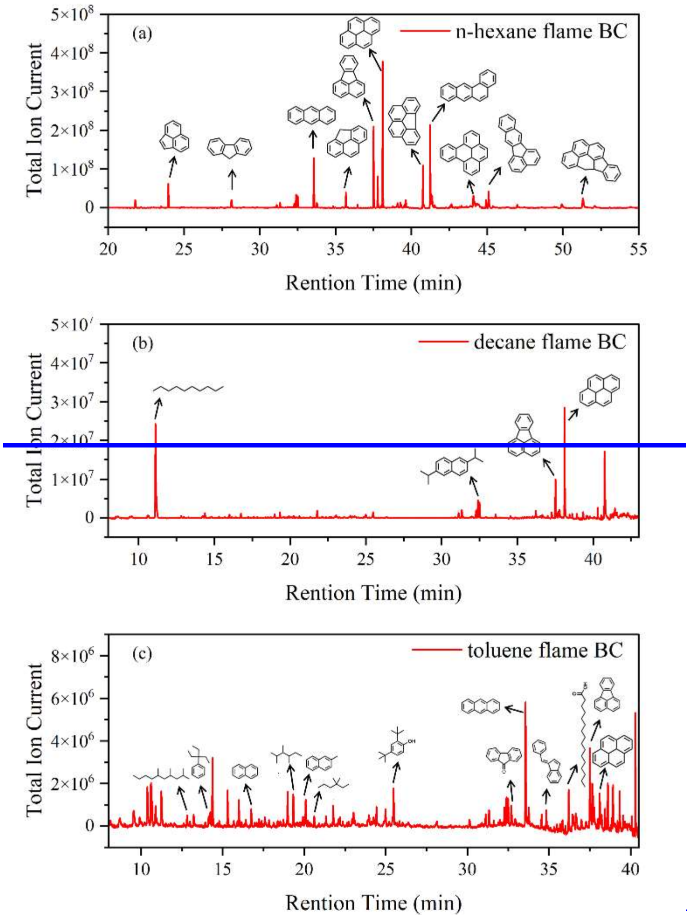
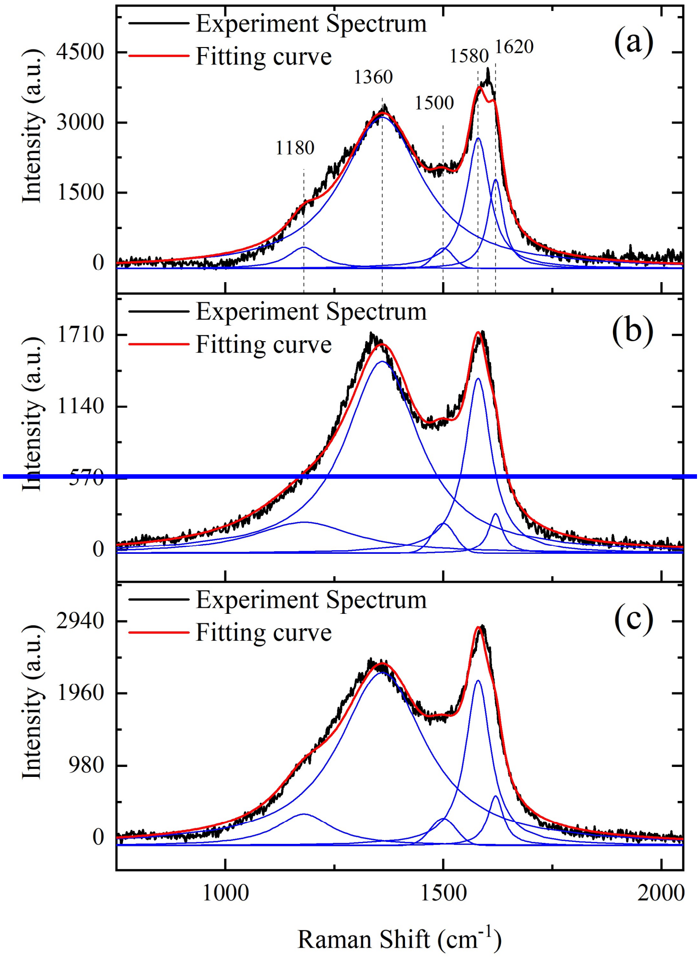


Figure 3. the ratio of 5OC/EC of prepared BC measured by a thermal-optical transmittance



~~Figure 4~~. Total ion chromatogram extracts of prepared ~~BCs~~soots. (a) n-hexane flame ~~BC~~soot. (b) decane flame ~~BC~~soot. (c) toluene flame ~~BC~~soot.

In order to obtain the composition of OC in different ~~BC~~soot, the samples were extracted by CH_2Cl_2 and the extract was analyzed by GC-MS. ~~Fig. 4~~Figure 5 shows the GC-MS analysis of OC extracted from different prepared ~~BC~~soot. The major components are polyaromatic hydrocarbons (PAHs) like Anthracene, Fluoranthene and Pyrene in all ~~BC~~soot samples. It is well known that PAHs are usually formed simultaneously with ~~BC~~soot during ~~prepared~~combustion. In n-hexane flame ~~BC~~soot, PAHs are the main OC while other components are scarce, which is consistent with the results of Han et al~~.~~ (Han et al., 2012). For decane and toluene flame ~~BC~~soot, long-chain alkanes such as decane or 2,3,4-trimethyl-hexane are present in the OC fraction. The characteristic features and peculiarities of the adsorption of water vapor on ~~BC~~soot are primarily caused by the tendency of polar water molecules to form hydrogen bonds (Vartapetyan and Voloshchuk, 1995). However, PAHs are weakly polar organic compounds. Thus, the ability of π-electrons in the PAH aromatic ring to form weak hydrogen bonds with water molecules or the interactions with water molecules are either almost absent or are negligible (Lobunez, 1960). The oxygen-containing functional groups of organic compounds are substantial centers for the formation of hydrogen bonds with water molecules. In toluene flame ~~BC~~soot, certain OC compounds (2,4-Di-tert-butylphenol, palmitic acid and 9-fluorenone) possess oxygen-containing functional groups like hydroxyl groups, carboxyl groups and quinone. However, these OC compounds also contain substantial hydrophobic parts (aromatic ring and hydrocarbon part). ~~The~~ Despite a small amount, the contribution of these hydrophobic ~~part of a molecule, which is quite small,~~functional groups to the hygroscopicity ~~is~~could be dominant (Kireeva et al., 2010). For long-chain alkanes found in decane and toluene flame ~~BC, composed solely of carbon and hydrogen atoms~~soot, they are typically considered hydrophobic. In general, OC constituents detected in these prepared ~~BC~~soot samples could impede water adsorption on ~~BC~~soot surfaces. Hence, the presence of these OC compounds leads to hydrophobic characteristics and diminishes the water adsorption capacity of prepared ~~BC.~~ soot.



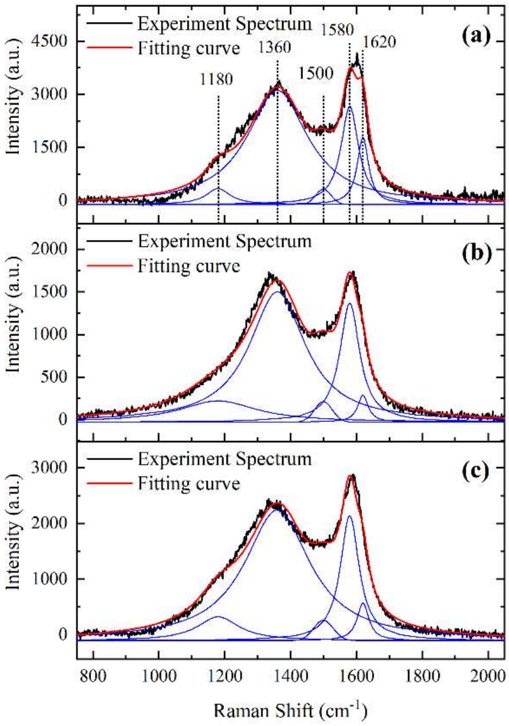


Figure ~~5~~6. Raman spectra of (a) n-hexane, (b) decane and (c) toluene flame ~~BC~~soot.

In order to study the relationship between the microstructure and vapor adsorption capacity of ~~BC~~soot, Raman analysis on ~~BC~~soot samples were conducted. Figure ~~5~~6 shows the first-order Raman spectra of three prepared ~~BCs~~soots with good curve-fitting results (R^2~~≥~~ ≥ 0.982), which display well known bands of ~~BC~~soot near 1580 (G band) and 1360 cm^{-1} (D band). The G band is a typical characteristic of crystalline graphite, while the D band is only observed for disordered graphite. A detailed analysis of the first-order Raman spectra was performed using the five-band fitting procedure proposed by Sadezky (Sadezky et al., 2005). Four Lorentzian-shaped bands (D1, D2, D4, and G, centered at about 1360, 1620, 1180, and 1580 cm^{-1}, respectively) and one Gaussian-shaped band (D3, centered at around 1500 cm^{-1}) were used in the curve-fitting process (Sadezky et al., 2005; Ivleva et al., 2007; Liu et al., 2010). The D1 band arises from the A_{1g} symmetry mode of the disordered graphitic lattice located at the graphene layer edges. The D2 band is attributed to the E_{2g} symmetry stretching mode of the disordered graphitic lattice located at surface graphene layers. The D3 band originates from the amorphous carbon fraction of ~~BC~~soot. The D4 band is related to the A_{1g} symmetry mode of the disordered graphitic lattice or C−C and C=C stretching vibrations of polyene-like structures, polyenes and ionic impurities also contribute to the D4 band (Sze et al., 2001; Sadezky et al., 2005). The G band is assigned to the ideal graphitic lattice with E_{2g} symmetry vibration mode. The integral intensity ratio (I_D/I_G) of D and G bands ~~could reflect the~~

~~comparative content of disordered carbon at graphene layer edges and surface graphene layers, and the~~was found to be related to the graphite crystallite size L_a (as determined by X-ray) (Knight and White, 1989; Schwan et al., 1996):

$$\frac{44}{L_a} = \left(\frac{I_D}{I_G}\right) \qquad (4)$$

The intensities of D and G bands have been widely determined using the sum of D1 and D4 bands and the sum of D2 and G bands~~. Table 3 shows that the I_D/I_G of three prepared BCs have positive correlation with their hygroscopicity. These results imply that disordered graphitic lattice (D1), graphitic lattice, polyenes, or ionic impurities (D4) could be favorable for the adsorption of water on BC.~~ (Knauer et al., 2009). Table 3 shows similar changing trends between the I_{D4}/I_G of the three prepared soot samples and their hygroscopicity, while the L_a of the three prepared soot samples exhibits a negative correlation. These results imply that disordered graphitic lattice, polyenes, or ionic impurities (D4) could potentially serve as adsorption sites for water molecules. Moreover, graphite crystallite with smaller size could have higher adsorption capacity of water in soot.

Table 3. Parameters I_{D1}/I_G, ~~I_{D2}/I_G,~~ I_{D4}/I_G ~~and~~, I_D/I_G and L_a of n-hexane, decane and toluene flame ~~BC~~soot.

Fuels	I_{D1}/I_G	I_{D4}/I_G	~~I_{D2}~~I_D/I_G	~~I_D/I_G~~L_a(Å)
n-hexane	~~3.82~~2.59 ± 0.13	0.~~49~~33 ± 0.~~02~~01	2.87 ± 0.~~48±0.06~~13	~~2.87~~15.34 ± 0.~~13~~69
toluene	~~3.38~~2.87 ± 0.~~05~~03	0.~~50~~42 ± 0.~~11~~09	3.23 ± 0.~~17±0.08~~09	~~3.23~~13.62 ± 0.~~09~~38
decane	~~3.17~~2.69 ± 0.~~30~~08	0.~~85~~75 ± 0.01	3.49 ± 0.~~17±0.08~~15	~~3.49~~12.63 ± 0.~~15~~53

3.3 The effect of aging process on the hygroscopicity of ~~black carbon~~soot.

Based on the hygroscopicity measurements of ~~UBC~~U-soot and ~~DBC~~DS (Fig. ~~2~~4 and ~~3,~~ Table 2), it is evident that the ~~presence of~~coating water-soluble inorganic ions (e.g., sulfates and nitrates) can enhance the hygroscopicity of ~~BC~~soot particles. Field observations have shown that the mass fractions of ammonium, sulfate, and nitrate increase with the aging of fresh biomass burning particles (Pratt et al., 2011). To investigate the impact of sulfate formation during the aging process on ~~BC~~soot hygroscopicity, we aged ~~UBC~~U-soot with SO_2 for different durations and measured their hygroscopic properties accordingly. The results revealed an increase in sulfate ions on ~~UBC~~U-soot with longer aging times (Table 2) while the MRH of ~~UBC~~U-soot remains relatively unchanged with SO_2 aging (Table 1).

However, at 90 % RH, the adsorbed water layers on ~~UBC increases with increasing aging times (Fig. 6).~~ U-soot increases with increasing aging times (Fig. 7). It should be noted that there is a good linear relationship (R^2 = 0.9997) between sulfate formed from SO_2 aging and adsorbed water mass at 90 % RH, where a corresponding water absorption mass increase by 1.82µg for every 1µg of SO_4^{2-} produced on the surface of U-soot.

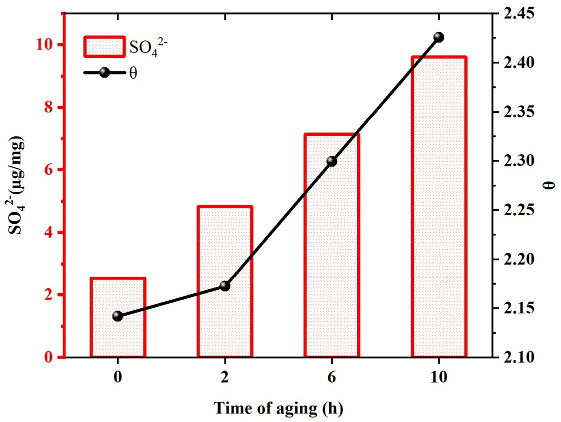


Figure ~~6~~7. Amounts of sulfates on ~~UBC~~U-soot and the adsorbed water layers (θ) at 90 % RH of ~~UBC~~U-soot as a function of the time of aging.

Our previous ~~studies have also indicated~~study has found that the heterogeneous reaction between SO_2 and ~~BC~~soot leads to the formation of sulfuric acid coating on ~~the surface of BC~~soot (Zhang et al., 2022b). In this study, the sulfate detected on ~~UBC~~U-soot could also exist in the form of sulfuric acid. However, IC results demonstrated that the amount of newly generated sulfate on ~~UBC~~U-soot after ~~12~~10 hours of aging was only 0.706 % of its original mass (Table 2). This small amount is insufficient to cause a significant difference in mass growth at low relative humidity ~~which~~such as cause little change in MRH. However, Kireeva et al. showed that the water adsorption isotherm of graphitized thermal soot coated with a small quantity of sulfuric acid showed a significant increase in the mass growth factor ~~slope of the coated soot~~ at relative humidity levels above 90 % (Kireeva et al., 2010). Zhang et al. found that coating with sulfuric acid could increase the mass growth factor of ~~BC~~soot to above 1.2 at 80 % RH relative to fresh particles (Zhang et al., 2008). Our results also demonstrated that a noticeable augmentation in the amount of water adsorbed on SO_2 aged ~~BC at high relative humidity levels.~~soot at 90 % RH, which is positively correlated with the amount of sulfate generated. Based on these findings, it can be concluded that varying amounts of sulfuric acid produced through heterogeneous oxidation on the surface of ~~BC~~

~~lead~~soot leads to noticeable differences in the amount of adsorbed water at high relative humidity~~ levels~~. These findings are consistent with previous studies ~~demonstrating~~ that coating with sulfuric acid ~~increases~~can increase the hygroscopicity and ice nucleation activation of ~~BC~~soot (Demott et al., 1999; Möhler et al., 2005; Wyslouzil et al., 1994).

4.Conclusion

In this study, we employed a vapor sorption analyzer to investigate the hygroscopicity of ~~BC~~soot particles from different sources and at different stages of aging with sulfur dioxide. Multiple characterizations of ~~BC~~soot particles were also performed. ~~DBC~~DS and ~~UBC~~U-soot contained water-soluble ions, such as sulfates and nitrates, which enabled them to undergo monolayer adsorption at lower relative humidity and increase the number of water absorption layers at higher relative humidity. In contrast, fresh prepared ~~BC~~soot particles, which have negligible amounts of water-soluble ions, were more hydrophobic. Their hygroscopicity mainly depended on the organic carbon content and microstructure. ~~A lower~~Lower content of hydrophobic OC and ~~a~~ more disordered graphitic lattice, ~~graphitic lattice,~~ polyenes, or ionic impurities made prepared ~~BC~~soot particles more prone to water adsorption. The aging of ~~UBC~~U-soot particles with SO_2 resulted in the formation of water-soluble sulfate ions, which promotes an increase in the hygroscopicity of ~~BC~~soot particles. This study analyzed the key factors determining the hygroscopic property of ~~BC, including water-soluble ions, organic carbon content, and microstructure. And provides a basis for improving~~soot, which can improve our understanding of the hygroscopic behavior of ~~sulfate-mixed BC in the atmosphere, which could~~fresh soot and help to evaluate changes in hygroscopicity during the heterogeneous reactions of ~~BC~~soot particles with pollutant gases in future studies.

Data availability

The experimental data are available upon request to the first or corresponding authors

Author Contributions

QM contributed to the conception of the study, ZS and LC designed and conducted this experiment, YL helped to prepare samples. QM, PZ, TC, BC, MT and HH helped perform the analysis with constructive discussions. ZS and QM wrote the paper with input from all coauthors. All authors contributed to the final paper.

Competing interests

The authors declare that they have no conflict of interest.

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