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Morphology and chemical characteristics of micro- and Nano-particles in the haze in Beijing studied by XPS and TEM/EDX

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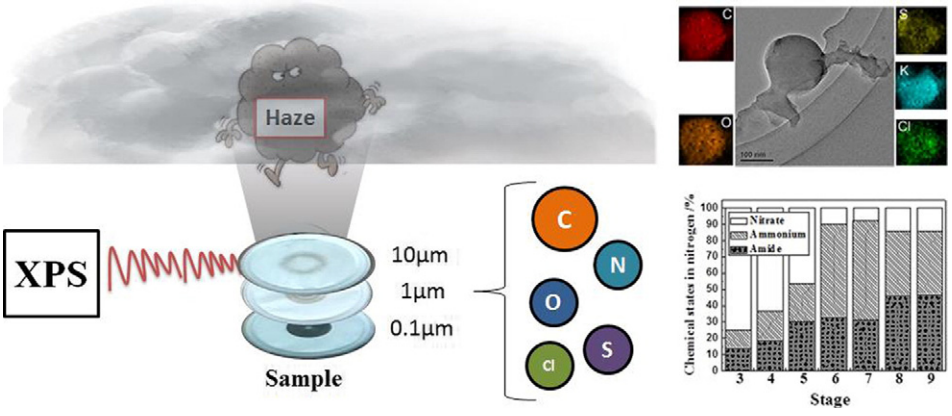
HIGHLIGHTS

- The element composition of particles from 100 nm to 10 μm in haze was discussed
- The chemical state was dominated by the particle size
- The surface of PM was acidity
- XPS was shown a useful tool in the aerosol research

GRAPHICAL ABSTRACT



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ABSTRACT

X-ray Photoelectron Spectroscopy (XPS) is a useful surface sensitive tool to explore the particulate matter with different particle sizes. In this work, we report the analysis of elemental species in particulate matter with size ranging from 100 nm to 10 μm during the autumn haze of 2014 in Beijing. The size dependence of element composition and chemical state distribution on the particle surface was investigated. It was found that the number of investigated element species decreased from 8 (at stage 2) to 4 (at stage 10) with the decrease of particle sizes down to 100 nm, which is in accordance with the result from Transmission electron microscopy (TEM/EDX) observations. Three chemical states of nitrogen, the amide group (399.9 eV), the ammonium group (401.6 eV), and the nitrate group (407.2 eV), were confirmed according to the different binding energies. Nitrate was the main composition on the coarse particles, while the percentage of amide and ammonium at stage 3 (13.9% and 10.8% respectively) increased on the fine particles at stage 9 (46.8% and 38.8% respectively). The relative ratio of sulfate and ammonium (calculated 1:1) in the fine particles suggests that there is no enough NH_4^+ to neutralize

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chemical state
TEM

the sulfuric acid and the surface of the PM is acidic. The result is useful to investigate the generation processes and the sources of collected particles.

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1. Introduction

Urban haze is generally related with high levels of airborne particulate matters (PM) emitted by kinds of anthropogenic sources as well as gas-to-particle conversion (Lelieveld et al. 2015; Menon et al. 2002; Gao et al. 2015; Tsai et al. 2007). It has attracted worldwide concerns in the past few years because of its significant effects on public health, light absorption and global climate. Different kinds of organic and inorganic components are adsorbed on PM surfaces (Quinn et al. 2015; Kirillova et al. 2010). The constituents of the surfaces can potentially affect hygroscopic properties and surface behaviors of particulate matters (Wang et al.,2015; Wu et al.,2015; Canagaratna et al.,2007; Massey et al.,2012). And at the same time, there is a trend that PM sizes have a great impact on such affection. Many papers have reported the chemical characteristics of PM species in different places with different methods of analysis (He et al.,2015; Li et al.,2015; Aiken et al.,2007; Suzuki 2006; Midander et al. 2012).

Elemental composition is one of the most important aspects for PM characters. Many studies employing off-line methods and real-time analysis methods were devoted to interpret the relationship between constitution changes at different environments. Generally, in the off-line methods, inorganic components in PM were analyzed by ion chromatography(IC) (Aneja et al. 2006) and inductively coupled plasma mass spectroscopy (ICP-MS) (Gao et al. 2015). For organic components, GC/MS is usually a useful tool to obtain the information about PAHs (He et al. 2006), FTIR and NMR (Duartea et al. 2007) were applied to assess the functional groups of the organic matters from atmospheric aerosol. However, in those bulk analyses, the sample needs to be processed before tested (should be dissolved in water or organic solvents) (Tao et al. 2014). Then, these methods require big amounts of PM samples and could not provide the timely change situations for the aerosol.

Nowadays, there are real-time instruments which having a high time resolution to analyze the PM, such as aerosol mass spectrometry (AMS) and particle-into-liquid sampler (PILS). (Orsini et al. 2003; Gao et al., 2008) Although they provide the particle information with high time resolution, their fast detection method also has some disadvantages. AMS can give the composition information of the single particle while can not give the morphology distribution and composition information at the same time; it can provide the bulk information while not the surface situation.

The surface of the aerosol particle is the most important reaction location for atmospheric chemistry and is different with the bulk composition, yet few papers pay attention to it. When the traditional filter-based sampling technique is combined with X-ray photoelectron spectroscopy (XPS) analysis, the size dependence of the element species on the surface and the unique information about the chemical state distribution in the haze can be studied in our experiment. We aim to promote the use of this sophisticated analytical tool to gain new insights into the surface of PM from atmospheric aerosols research.

The local electronic structure of active surfaces of samples is very different from the bulk. This is because the growth process of PM is accompanied with substance absorption. Therefore the PM surface will inevitably experience many chemical and physical processes.

This method has several significant advantages: it is accurate (sensitive for the sample surface because of the short effective detection depth), quick (without pretreatment) and easy to perform (very small sample amount). As a result, not only the element species but also the chemical state of elements as well as the relative amount of different chemical states were given (Cheng et al. 2013; Atzei et al. 2014; Qi et al. 2006). The concentration of elements was determined with an accuracy of up to 0.1 atm%. We believe that the information on the original surface state in the fine particulate matters would be valuable for understanding their physical/chemical characteristics, their sources, their behaviors and formation mechanisms.

2. Methods

2.1. Sample collection

Aerosol samples were collected for 48 h simultaneously on the building rooftop of National Center for Nanoscience and Technology using a 13-stage impactor sampler starting from 10 a.m. on October 18 lasting to 10 a.m. on October 20, 2014, which was a heavy haze period. The sample collection site is far from industrial area. The micro-orifice uniform deposit impactor Nano-MOUDI (model 125B, MSP Co.) was equipped with Teflon filters with a diameter of 47 mm. No XPS signals of the pollutants such as N and S were detected from the blank filter. The sampling flow rate for the Nano-MOUDI was 10 L/min, and the parameters of each stage were shown in Table 1. After sampling, the filter was covered by tin foil and put into a refrigerator kept at about 255 K. There is no other drug in the refrigerator.

The traditional filter sampling method was used in this paper, hence there should be some loss of semi-volatile materials during the sampling. Since we put the emphasis on the elemental species change and the chemical state distribution of sulfur and nitrogen, the lost of semi volatiles, mainly organic matters, will have little effect on our results.

2.2. Instrument

The information on composition of elements was studied by XPS in the Thermo Fisher Scientific ESCALAB 250 Xi spectrometer with the monochromatic Al Ka X-rays source (1486.6 eV). All peaks were referenced to the C1s binding energy for adventitious carbon at 284.8 eV. Quantification was performed using a Shirly background. Transmission electron microscopy (TEM) observations and energy dispersive X-ray spectroscopy were carried out using a FEI F20 instrument under 200 kV. The quality and error for the instrument was monitored based on the test result on standard bulk samples Au, Ag and Cu, and the standard deviation for them are 0.007, 0.005 and 0.004 respectively.

3. Result and discussion

3.1. PM mass concentration distribution

The filters were weighted on a Mettler Toledo XS105 Dual Range balance to an accuracy of 0.01 mg before and after sample collection. The

Table 1
Aerodynamic particle diameters of the aerosols deposited on each entry of the impactor.

stage	Aerodynamic particle diameter /μm
1	> 10
2	10–5.6
3	5.6–3.2
4	3.2–1.8
5	1.8–1.0
6	1.0–0.56
7	0.56–0.32
8	0.32–0.148
9	0.18–0.1
10	0.1–0.056

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