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Study of automobile exhaust particles by spectromicroscopy

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Abstract In this paper, automobile exhaust particles of Gol and Santana 3000 were studied by spectromicroscopy. The STXM results show that the single particulate is sized at 500 nm, with the mass distribution reducing towards the center. The N 1s NEXAFS spectra of automobile exhaust particles have similar structure with those of nitrates, which can be deduced as the main chemical species of nitrogen in automobile exhaust particles. There are minor amounts of ammoniums and organic nitrogen compounds in automobile exhaust particles. A single Gol automobile exhaust particle was stack scanned in the energy range of 396–416 eV. By principal component analysis and cluster analysis, it can be deduced that there are main three chemical species of nitrogen. The particle surface consists of mainly nitrates, the inside consists of mainly ammonium and organic nitrogen compounds, and the middle layer is an intergradation consisting of mainly nitrates and organic nitrogen compounds.

Key words STXM, NEXAFS, Automobile exhaust particulate

1 Introduction

Motor emission is a complex mixture of hundreds of constituents in either gas or particle form. NO_x emissions from vehicles have a global warming impact; N_2O emission[1] is about 1% of the CO_2 emission from vehicles, and is estimated at 3.2 vol% – 23.5 vol% in emission fractions[2]. A motor exhaust particulate matter (PM) has a rough surface, which makes it easy for the PM to bind with toxins in the environment, hence increases hazards of particle inhalation. Such a particle is often an ultrafine particle, and an inhaled particle may penetrate deep into the lungs. Exposure to vehicle exhaust particles can cause acute irritation and neurophysiological, respiratory, and asthma-like symptoms and can exacerbate allergenic responses to known allergens[3,4], and children are more vulnerable to the exposure[5–7].

A single particle of vehicle exhaust particulate matter can be studied by SEM and TEM [8,9], synchrotron radiation[10] and mass spectrometry[11,12]. The high spatial resolution images of SEM and TEM, however, cannot provide any information on distributions of different chemical species; whereas the mass spectrometry results are just of bulk analysis. On a scanning transmission X-ray microscopy (STXM) of a third generation synchrotron radiation facility, one can do much better in this field of research. Combing high chemical sensitivity and spatial resolution, STXM can be used to examine a single particle of vehicle exhaust PM, with its near edge X-ray absorption fine structure (NEXAFS) of high energy resolution, and its X-ray absorption image with a spatial resolution of 30–50 nm. As a powerful tool for structure and function studies in submicron scale, STXM has been used widely in environment and material sciences[13–16]. Braun *et al*.[17] found that particulate matters from biomass burning and diesel exhaust differed distinctively from each other in X-ray spectra and carbon specific signatures, which can be employed for source apportionment. They distinguished carbon in the soot particles from

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hydrocarbons of residual lubricating oil using STXM and NEXAFS[18], and studied carbon species in airborne PM with C (1s) NEXAFS spectroscopy[19]. Liquids, extracts, solid core and surface functional groups could be quantified.

In this article, chemical species of nitrogen and submicron structure of automobile exhaust particles are studied by STXM.

2 Experimental

2.1 Sample preparation

Automobile exhaust particulates of Santana 3000 and Gol of Shanghai Volkswagen Corp., Ltd., were collected at experiment facilities in Shanghai Institute of Internal-combustion Engines. The cars were fueled by 93# gasoline and operated at full speed of 5500 $r \cdot min^{-1}$ on the platform. The exhaust went through a condenser and moisture separator before being led into an airproof chamber via a copper pipe. The automobile exhaust particles $PM_{2.5}$ were collected on a 200 mm × 250 mm fiberglass film with a large flux air sampler (CYQ 26). The reference materials were ammonium sulphate and sodium nitrate.

The automobile exhaust particles were deposited on a 20 nm thick carbon film with copper grids The distributed particles were cameraed under optics microscopy, and the dispersed particles were marked for STXM and NEXAFS experiments. The particles of about 1 μm in size were suitable for nitrogen absorption edge STXM experiment.

2.2 STXM and NEXAFS experiments

STXM experiments were performed on the soft X-ray spectromicroscopy beamline of Shanghai Synchrotron Radiation Facility (Fig.1), a third generation light source with 3.5 GeV 300 mA electron beam bunches in emittance of 3.9 nmrad. The X-ray is extracted from the elliptically polarized undulator (EPU), monochromized by the SX700 monochramator, and focused on sample by the zone plate. The transmitted X-rays are detected by quick proportional detector. The incident X-ray energy is adjustable from 250 eV to 2000 eV, and the flux from 10^6 to 10^9 phs/s. The energy resolution ($E/\Delta E$) is better than 2500@ 1840 eV and 10000@401eV, and the spatial resolution is less than 30 nm. The chamber was evacuated to less than 1.33×10^{-4} Pa. The sample stage consists of $x/y/z$ stack of coarse positioners, x/y fine positioners using piezos, and a rotation stage for computed tomography (CT). The piezo-actuated stage used for high resolution scans has a travel range of 100 μm with scanning resolution of 1 nm and repeatability of 5 nm. The rotation angle is read out with an encoder, and the angular resolution is better than 0.01°. The automobile exhaust particulates samples were analyzed with reference materials of ammonium sulphate and sodium nitrate. The NEXAFS spectra of N K-edge were recorded with 0.1 eV energy steps in dwell time of 1 s. In stack scan experiments, single atuomobile exhaust particle was scanned with dwell time of 2 ms and energy steps of 0.12 eV.

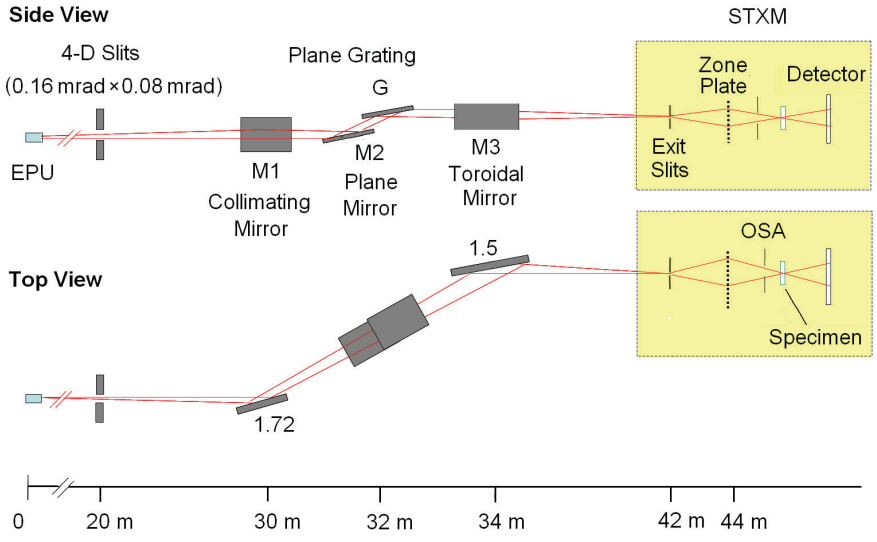

Fig.1 Layout of the SSRF soft X-ray spectromicroscopy beamline from side and top view.

3 Results and Discussions

Automobile exhaust particles $PM_{2.5}$ were deposited on silicon nitride wafers in thickness of 100 nm, adjusted to the focus plane, and scanned by 410 eV X-ray with 50-nm steps in an area of 10 μm×10 μm. Fig. 2A shows the discrete particles in rotundity in a size of 500 nm, with uneven mass distribution. With a higher areal density, the particle brim absorbed 20% of the X-ray, while the middle, of less areal density, absorbed 10% of the X-ray. In addition, some particulates agglomerated in catenaries of about 2 μm in size. For reducing the background interference, the particles were adhered to a 20 nm thick carbon film holder on copper meshes, and were scanned by STXM in 30-nm steps. Fig. 2B shows many small particles aggregated into a big particle. Due to non-uniform mass distribution of individual particulates, X-ray absorption differs dramatically between different parts of the particulates aggregation, from 10% to 50%. Fig. 2C shows the Gol particulate with a decreasing mass distribution towards the center, absorption of X-ray for the middle and the brim parts are 50% and 70% respectively.

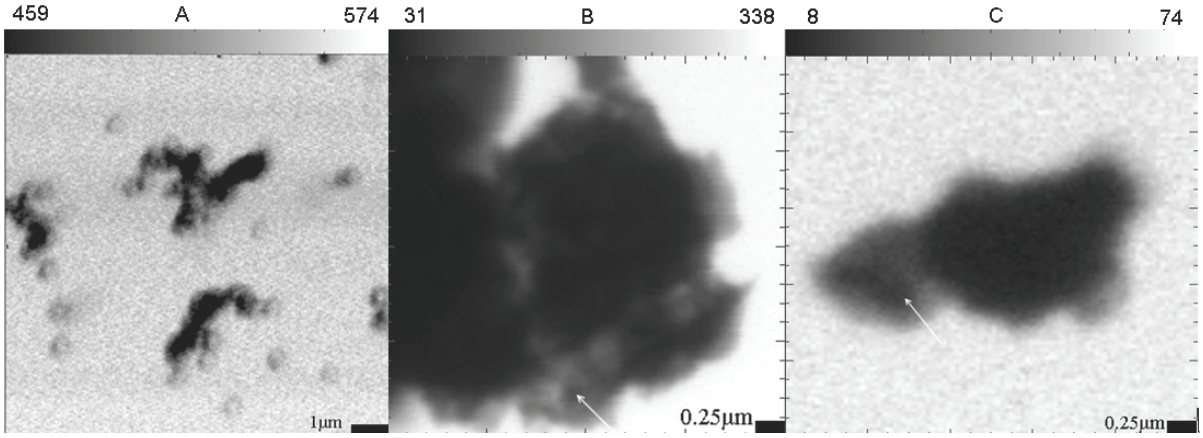

Fig.2 STXM images of automobile exhaust particles from Santana 3000 (A and B) and Gol (C) at 410 eV. A: 10 μm×10 μm, 50-nm steps B: 3 μm×3 μm, 30-nm steps C: 3 μm×3 μm, 30-nm steps

The single particles marked with arrows in Figs. 2B and 2C were chosen for nitrogen K-edge NEXAFS analysis. The spectra were recorded with step 0.1 eV and dwell time of 1 s. The results of automobile exhaust particles and reference materials of $NaNO_3$ and $(NH_4)_2SO_4$ are shown in Fig.3, with the KNO_3, NH_4NO_3, $(NH4)_3PO_4$ and 3-(Pyrrol-1-ylmethyl) pyridine spectra reported in Ref.[20]. Fig. 4 shows the analysis results of $NaNO_3$ and $(NH_4)_2SO_4$ by Ifeffit software. All N 1 s NEXAFS spectra share similar features: distinct transitions from inner shell to molecule orbit of 1 s→ π^* in 398–403 eV, distinct transitions of 1s→σ^* in 403–408 eV, and minor transitions of 1s→σ above 408 eV. The $NaNO_3$ spectrum shows significant π^* resonances at 401.7 eV, while the $(NH_4)_2SO_4$ spectrum shows broader σ^* resonances at 406 eV (twice as wide as $NaNO_3$) and the σ resonances of $(NH_4)_2SO_4$ is 1.5 times wider than that of $NaNO_3$.

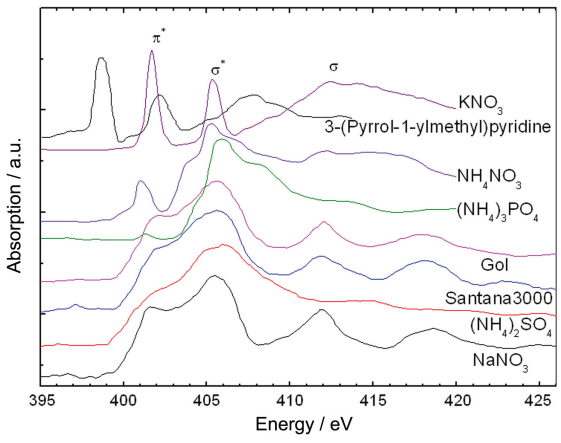

Fig.3 Nitrogen 1s NEXAFS spectra of automobile exhaust particles of Santana 3000 and Gol, and reference materials of $NaNO_3$, $(NH_4)_2SO_4$, $(NH_4)_3PO_4$[20], NH_4NO_3 [20], KNO_3[20] and 3-(Pyrrol-1- ylmethyl) pyridine [20].

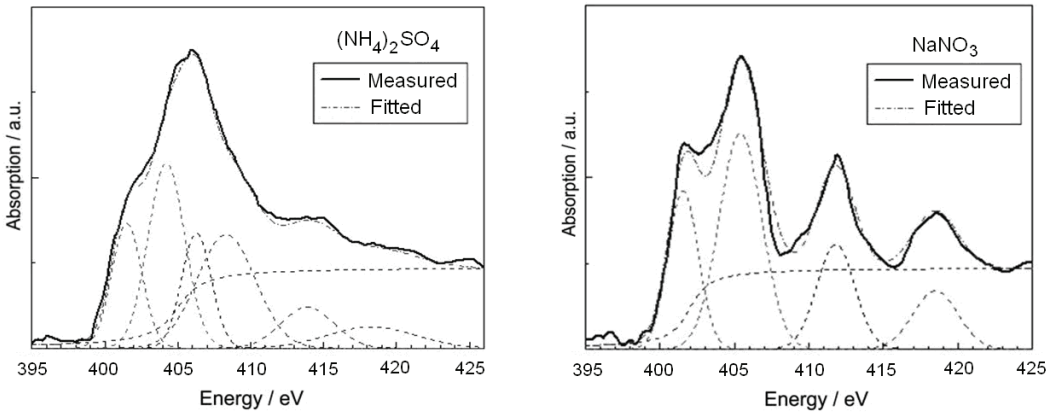

Fig. 4 Nitrogen 1s NEXAFS spectra of (a) $(NH_4)_2SO_4$ and (b) $NaNO_3$, fitted with Ifeffit software.

The nitrate NEXAFS spectrum in 400–410 eV differs obviously from that of ammonium. The σ^* resonances of ammonium are broader, with a shoulder structure. The σ resonances of ammonium are broader, too. In 412–421.8 eV, the spectra of automobile exhaust particles and nitrate show obvious σ resonances. However, in 413.5–421.8 eV, the spectra of ammonium show minor σ resonances. The σ^* resonances of automobile exhaust particles do not show distinct shoulder structure. The π^* resonance spectra of this experiment have similar structure with the spectra measured by Török *et al.*[21] who scanned $(NH_4)_2SO_4$ and $NaNO_3$ on Si wafer by TXRF-NEXAFS. In 397–399.7 eV the π^* resonance spectra of automobile exhaust particles are small, indicating that they contain nitrogen organic compounds and nitrogen oxides. Similar absorptions by nitrogen organic compounds and NO_x were found by Leinwebe *et al.*[20] and Jeong *et al.*[22].

Semi-quantitative evaluation of contributions of different nitrogen chemical species was performed using linear combination of the standard spectra of $(NH_4)_2SO_4$ and $NaNO_3$. The results show that the contributions of nitrate and ammonium to N 1s NEXAFS spectra of GoI are 71% and 27%, respectively, and 70% and 28%, respectively, for Santana 3000. In investigating aerosol particles of Budapest, Török *et al.*[21] found that the contributions of nitrate and ammonium to N 1 s NEXAFS spectra were 70% and 30%, respectively. Therefore, nitrates are main chemical species of nitrogen in city aerosol particles, as shown in Fig.3, the N 1s NEXAFS spectra of automobile exhaust particles have similar structure with those of nitrates. There are minor amounts of ammoniums and organic nitrogen compounds in automobile exhaust particles, but more reference organic compounds should be investigated because of the diversification and complexity of organic substances.

Chemical species of a GoI single particle was shown as a typical example in upper right of Fig.5. It was stack scanned in the range of 2 μm×2 μm, with 50-nm steps and 2-ms dwell time, in energy range of 396–416 eV with 0.12-eV steps. The stack data was analyzed by principal component analysis (PCA) and cluster analysis (CA), with the results showed in Table 1 and Figs.5 and 6. It is deduced that there are four principal components from the eigenvalues. And there are four clusters: 1) the background, 2) the surface of automobile exhaust particle, 3) the middle layer of particle, and 4) the center of particle. The inside of automobile exhaust particle differs from the outside in the following aspects: the particle surface has sharper

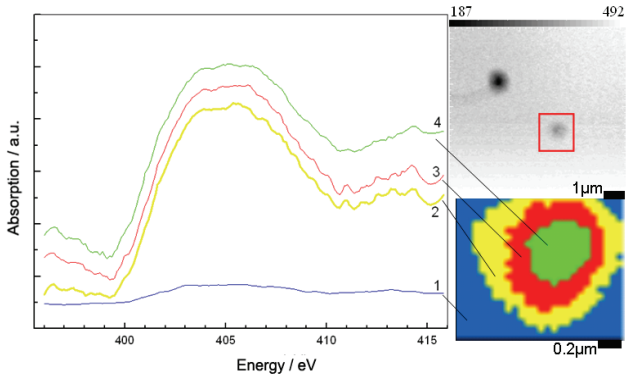

Fig.5 NEXAFS spectra of a GoI automobile exhaust particle (upper right) and the distribution (lower right) of its four components, as a result of principal component analysis and cluster analysis.

peaks at 401.7 eV and 405.7 eV, corresponding to the nitrate components; however, the inside has wider σ* resonances at 406 eV corresponding to the ammonium component, and absorption at 396.5 eV corresponding to the component of organic nitrogen compounds. The NEXAFS spectra of middle layer have the similar structure with the inside layer in 407– 415 eV, whereas similar structure with the surface layer is observed in 396–407 eV. The middle layer is the intergradations and mainly consists of nitrates and organic nitrogen compounds.

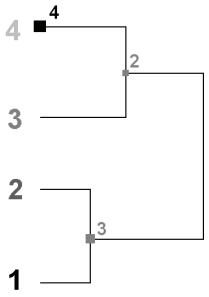

Fig.6 Dendrogram of Gol automobile exhaust particles by cluster analysis.

Table 1 Eigenvalue of principal component and the contribution of pixels in cluster.

Component index	Eigenvalue	Cluster index	Pixels in cluster / %
1	3511.9	1	36.5
2	15.9	2	29.7
3	6.3	3	21.5
4	3.1	4	12.2

4 Conclusions

The results of STXM show that single automobile exhaust particulate is sized at 500 nm, with uneven mass distribution. The N 1s NEXAFS spectra of automobile exhaust particles show similar structure characters with those of nitrates, which can be deduced as the main chemical species of nitrogen in automobile exhaust particles. There are minor ammoniums and organic nitrogen compounds in automobile exhaust particles. A single Gol automobile exhaust particle was stack scanned in the energy range of 396–416 eV. By principal component analysis and cluster analysis, it can be deduced that there are main three chemical species of nitrogen. The particle surface consists of mainly nitrates, the inside consists of mainly ammonium and organic nitrogen compounds, and the middle layer is an intergradation consisting of mainly nitrates and organic nitrogen compounds. This spectromicroscopy technique reveals structural and chemical differences in automobiles exhaust particles. The results will be of help for researches on reducing nitrogen oxides and design catalyzers. More nitrous reference materials shall be studied for identifying multiform chemical species of nitrogen.

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