Luminescence characteristics of individual Beijing haze aerosol particles

Li Wang[a,b], Zhangpeng Bai[a,b], Yiqun Pi[a,b], Yadi Zhai[a,b], Yinqi Zhang[a,b], Zhengguang Yan[a,b,*], Yuan Ji[a,b,**], Xiaodong Han[a,b,***]

[a] Institute of Microstructure and Property of Advanced Materials, Beijing University of Technology, Beijing, 100124, China
[b] Beijing Key Laboratory of Microstructure and Properties of Solids, Beijing University of Technology, Beijing, 100124, China

GRAPHICAL ABSTRACT
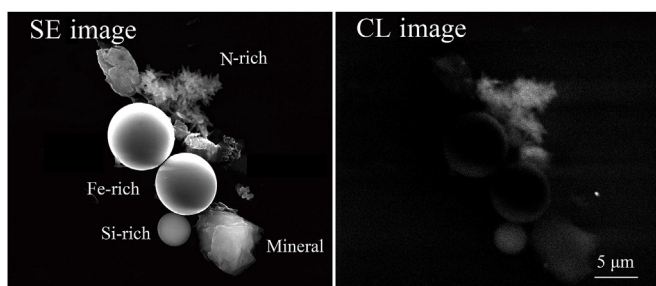
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ABSTRACT

The rapid development of industrialization and urbanization has led to haze in Beijing that has garnered world attention. For the first time, we studied the luminescence properties of individual haze aerosol particles by using a scanning electron microscope (SEM) coupled with a cathodoluminescence (CL) spectrometer. CL analysis has rarely been reported for haze particles, however, we found that many haze particles showed varied luminescence characteristics. Many types of mineral dusts showed strong CL emission in the visible light wavelengths. Nitrogen-rich secondary particles had a strong CL emission in the UV wavelengths. Anthropogenic particles such as fly ash and Fe-rich, Ti-rich, and carbonaceous materials had much weaker CL responses. The mixture of mineral dusts and other species showed lower CL intensity and widened CL spectra, which continuously covered the UV-VIS-IR portion of the spectrum and which contrasted with the CL emissions of original mineral dusts and pure secondary salts. The sensitivity of CL spectra with respect to tiny changes in components, impurity, and valences enabled the CL spectroscopy to provide a unique perspective with which to analyze highly complicated mixtures of haze particles.

1. Introduction

Atmospheric aerosols in haze pollution episodes have been widely investigated by field measurements, microanalysis, and modeling for their serious impacts on the climate, environment, and human health (Shi et al., 2003; Bytnerowicz et al., 2007; Feng and Penner, 2007; Viana et al., 2008; Li et al., 2014; Poechl and Shiraiwa, 2015). Typical haze particulate may be identified as $PM_{2.5}$ or PM_{10}, i.e. having an aerodynamic diameter less than 2.5 μm or less than 10 μm, respectively (McKenna et al., 2008). Haze aerosol species include primary coarse

particles such as mineral dusts and sea salts along with organic particles, anthropogenic carbon (soot), fly ash, biomass burning particulate, and transition- or heavy-metal-containing particles) (Li and Shao, 2013) as well as secondary particles (sulfate, nitrate, ammonium, carbonate, and sodium salts). The secondary particles are generated in a heterogeneous reaction process on the surface of alkaline mineral dusts and metallic particles in the presence of acidic gases (NO_2, SO_2, CO, and CO_2) and organic volatiles through chemical reactions (Laskin et al., 2005; Zhu et al., 2011; Estillore et al., 2016; Gard et al., 1998).

Electron microscopy can simultaneously provide information about the morphology, chemistry, crystallization, and luminescence of individual haze particles (Reimer, 1998; Goldstein et al., 2003; Rong et al., 2006; Furuta et al., 2005; Hu et al., 2016; Pósfai et al., 2003), which could be of primary interest for understanding their microstructure, evolution history, and impact on the environment. A transmission electron microscope (TEM) has a very high resolution of less than 0.1 nm. The TEM with selected area electron diffraction (SAED) and equipped with an energy dispersive X-ray spectrometer (EDS) is suitable to analyze nanometer-sized, but not micrometer-sized, haze particles. A scanning electron microscope (SEM) has a high resolution of less than ~1 nm. The SEM-EDS is suitable for analyzing mineral dust, which is 30–80% of the mass in all PM_{10} and $PM_{2.5}$ and which ranges from 10 nm to several micrometers in size. Furthermore, the SEM's combined cathodoluminescence (CL) (Chad and Phillip, 2007) and electron backscatter diffraction (EBSD) ability (Schwartz et al., 2009) has considerably extended its analytical capabilities, although it has rarely been used for haze particles until now.

Many types of minerals have distinguished luminescence properties. Cathodoluminescence (CL) represents light emissions from the ultraviolet (UV) to the infrared (IR) region of the spectrum when particles are exposed to an electron beam. The position, intensity, width, and shape of CL spectra change with particle size, composition, crystal structure, defect, impurity, and doping levels (Chad and Phillip, 2007; Horvarth, 1993). In addition, luminescence emission is sensitive to material composition and the structure of the host lattice, especially tiny changes on components, impurity, dopants, and valence, compared with the EDS (Marfunin, 1979), as the origin of the luminescence is from conduction to valence transitions and phonon modes. The characteristic X-ray results from core-level transitions, which are largely unaffected by bonding as the core orbitals do not take part. Therefore, CL spectra may provide a unique perspective with which to analyze the composition and multiple phases in a highly complicated mixture of haze particles, i.e., to characterize fine-grained luminescent minerals with similar topography, chemistry, or crystallization. However, the interpretation of CL spectra is more difficult than that of the characteristic X-ray spectrum (Pagel et al., 2000; MacRae and Miller, 2003). A combination of CL and X-ray spectra will increase the reliability of phase identification for luminescent minerals, although until now, there are few studies of the CL on haze particles.

In this paper, we report on our studies of the first luminescence responses of mixed haze particles by the SEM equipped with CL and EDS spectrometers. Gathering comprehensive information on their morphology, luminescence, and composition will enable an understanding of the species and luminescence properties of individual haze particles as well as their mixing states.

2. Experiments

Since 2013, we have collected over 800 samples of aerosol particles in severe haze episodes in a fixed sampling site at the Beijing University of Technology (39.87°N, 116.48°E). The site is surrounded by heavy traffic, subway construction, and residential areas. The air quality index (AQI) varied from 60 on a good day to 475. This information is recorded at the following site: http://www.cma.gov.cn/. We analyzed these particles using the SEM-CL-EDS system. The concentrations of major pollutants from monthly reports of Beijing Municipal

Environmental Protection Bureau were shown in Figure S1, Supplementary Information (SI).

Haze aerosols were collected using a medium flow particle collector (TH150-CIII, Tianhong Corp., China), in which a single-layer cutter was used to collect either PM_{10} or $PM_{2.5}$. A sampling period of 1 h at a flow rate of 100 L/min was pre-optimized for minimal particle-to-particle contact. Most particles were collected on a TEM Cu grid coated by an amorphous carbon (C-coated Cu grid) which was first set onto a quartz fiber filter (Whatman, UK) and then onto the cutter.

We used different substrates for the EDS-CL measurements of the haze particle samples based on the following considerations. The C-coated Cu grid (see Cases #2 and #3) showed Cu and carbon peaks in EDS spectra. Using a Si chip as a substrate worked in favor of detecting carbonaceous matter and carbonates (see Case #1), but interfered with Si-containing haze particles such as silicate, silica, quartz, and fly ash. A SiO_2-Au-Si substrate, i.e., a Si chip on which a 50 nm Au layer and a 5 nm SiO_2 layer were deposited, enhanced CL emission intensity due to the surface plasmon polariton effect (Wang et al., 2016; Han et al., 2014) (see Table S3) but showed a small Au peak. It also enhanced Si and O peaks in the EDS spectra. Both the Si-chip and SiO_2-Au-Si chip would have strong CL emissions in visible light. An alloy steel substrate (see Case #4) provided a non-luminescent background but showed alloy steel elements of Cr, Fe, and Ni in the EDS spectra. All substrates were imperfect, but each provided information for CL and EDS analysis.

A field emission environment scanning electron microscope (ESEM) (FEI Quanta 600F) with CL (Gatan Mono3$^+$) and EDS (Oxford X-Max 80 mm^2) spectrometers was used. Operating conditions included primary electron energy of 15–30 keV, e-beam current of $10^{-8} \sim 10^{-10}$ A. EDS data were collected for 40–60 s live time and the elemental composition was obtained after a standard matrix correction. The CL spectrometer had a precision of 0.5 nm with a fine grating of 1200 1/mm and a highly sensitive cooled-PMT detector at 800–1500 V for CL imaging and spectral collection. A field emission SEM (JEOL 6500F) with an EDS-EBSD system (EDAX) was used for phase identification. EBSD data were collected by a Hikari CCD detector and analyzed by an OIM Data Collection software version 5.31.

Typically, the EDS provides semi-quantitative or qualitative data of element composition. For phase analysis based on EDS data we employ some considerations and assumptions. First, the element constituents of the substrate or sample could only be considered if they existed in the haze particles. Second, haze particles were usually assumed to contain only ambient stable species such as metal cations, oxyanions, and simple anions. Third, the charge equilibration based on the relative concentration ratio of element contents was considered when assigning a possible phase (Bai et al., 2018). Based on the EDS data, we summarized the composition of about 180 haze particles collected at the same time with the haze particles discussed in the text and SI as ternary plots. The ternary plots showing the contents of major mineral elements (Mg + Al + Ca or Mg + Al + Si + Ca), S + N, and Fe are given as SI, Figure S2.

3. Results and discussion

The detailed analysis by ESEM-CL-EDS on haze aerosol particles in Cases #1–4 is given in Figs. 1–6 and Supplementary Tables S1-S2. The particles analyzed were heterogeneously-mixed particles (Case #1), carbonate-rich particles (Case #2), particles analyzed by comprehensive ESEM-CL-EDS-EBSD techniques (Case #3), and particles collected on a rainy day (Case #4). Some additional information is given in SI, Table S3.

3.1. Case #1

Case #1 consisted of a highly heterogeneous mixture of haze particles, which varied in morphology, components, and CL emission (Figure 1 and SI Table S1, Table S2). Particles were put on a Si