Rapid communication

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In situ, real-time detection of soot particles coated with NaCl using 193 nm light

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ABSTRACT We report in situ, real-time detection of soot particles coated with NaCl using excimer laser fragmentation fluorescence spectroscopy (ELFFS). Carbon atom fluorescence at 248 nm and the Na D-line at 589 nm are used as signatures of soot and NaCl, respectively. Soot particles are encapsulated with a NaCl layer in a well-controlled inverted flame burner. NaCl particles are injected into the methane-air co-flow flame to coat the soot particles. ArF laser irradiation of the coated particles in an air stream at 1.14 J/cm^2 produces fluorescence from Na, C, and CH. At 0.69 J/cm^2, which is slightly above the fluorescence threshold, but not enough for considerable fragmentation of the particles, Na D-line persists with little carbon and no CH observed. These results suggest that the photolytic fragmentation-fluorescence using 193 nm excitation can be effectively used for in situ, real-time chemical analysis of core-shell nanoparticles.

1   Introduction

Core-shell heterostructures, including coated nanoparticles, have received much attention recently for their use as catalysts, high density recording media, nanoenergetic materials, and biomarkers [1, 2]. Heterogeneous particles have received interest in the atmospheric science and environmental health fields because of their potential influence on global climate change and adverse health effects. For example, when black carbon particles in the atmosphere are coated with an inorganic species such as NaCl, the sunlight absorbed by the particles drastically increases due to a lensing or focusing effect [3]. Nanoparticles also have the potential to cause adverse health effects because they can penetrate deeply into lung tissue and may act as a carrier of toxic material coated on the particle surface [4].

The core-shell particles are created by a multitude of techniques including wet chemistry, laser ablation, and in high temperature flames. Among these methods, flame synthesis is readily scaled for industrial applications and is most suitable for generating nanoparticle/gas suspensions. In laboratory experiments, Dufaux and Axelbaum [5] synthesized nanoscale particles in a sodium coflow flame. Titanium particles are coated with a NaCl layer, which prevents oxidation after their formation. Supersaturation of NaCl can be easily achieved at normal flame conditions, so encapsulation using gas phase NaCl can be controlled by varying flame conditions such as the flame temperature. In addition, the NaCl shell minimizes agglomeration and oxida-

tion of the core particled. Zachariah and co-workers [6] used a similar flame configuration to encapsulate silicon and germanium particles with NaCl. They found that spherical particles encapsulated with NaCl were generated at high temperatures, and the mean particle diameter increases with the flame temperature.

Quantitative chemical analyses of core-shell particles are often performed with electron microscopy or X-ray diffraction, which require intrusive particle collection techniques and are time consuming. Therefore, it is desirable to develop a fast, in situ, real-time analytical method for these particles. In addition, such technique may also open a way to study health effects of coated aerosol particles whose toxicity may be affected by the different species on the particle surface [7].

Potential in situ, real-time detection techniques that rely on laser-based chemical analysis include surface ionization mass spectrometry and excimer laser fragmentation fluorescence spectroscopy (ELFFS). ELFFS has been used to characterize combustion-generated species [8–11] and particles [12–16]. This technique employs pulsed UV laser light to fragment non-fluorescent molecules or particles into fluorescing species, whose emission is used to deduce information concerning the chemical composition and concentration. ELFFS differs from other laser-based aerosol monitoring methods, including laser-induced incandescence (LII) or laser-induced breakdown spectroscopy (LIBS), in that the particles are irradiated by UV laser light at moder-

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ate intensities (10^7–10^9 W/cm^2) and no long lifetime broadband emission associated with particle heating or optical breakdown is observed [12].

In this study we present recent results of the development of an in situ, real-time chemical analysis method for core-shell nanoparticles using 193 nm laser light, where the coated particles are partially disintegrated and the core and shell materials are detected separately at different laser conditions.

2   Experiment

Figure 1 shows the experimental apparatus of the inverted flame burner and the optical measurement system. A methane jet at 1.35 standard liters per minute (slpm) from a 1.9 cm diameter nozzle is surrounded by coflow air at 13 slpm in a 5 cm diameter, 48 cm long quartz tube, creating an inverted flame. The detailed burner configurations were reported previously [16–18]. Air at 6.85 slpm is supplied to a 3-jet nebulizer (BGI, CN-24), where approximately 2 μm droplets are generated from 0.5 M NaCl in deionized water. The droplets pass through a diffusion dryer (TSI, 3062) that removes water from the particle-laden flow, and solid NaCl particles in air stream are injected into the fuel line of the burner. The salt vaporizes in the partially pre-

mixed flame and produces a bright yellow color. After the quartz tube, the post-flame gas-particle mixture travels through a 5 cm diameter, 140 cm long stainless steel tube and is extracted at 4.9 slpm by an ejector pump (Fox, 611210) operated by 20 slpm air. The diluted mixture passes through a diffusion dryer and a gas denuder to eliminate combustion water and unburned gas phase hydrocarbons, respectively. The particle-laden flow exiting the denuder enters a BGI cyclone (KTL GK 2.05) at 7.6 slpm, where the particles larger than 1.2 μm are removed; 0.3 slpm of this flow is introduced to the laser interrogation region. A scanning mobility particle sizer (SMPS, TSI 3071A/3025A) measures the particle size distribution [17–20].

A Lambda Physik ArF excimer laser (LPX 210i) generates 20 ns pulses of 193 nm light at 4 Hz. A 3.8 cm diameter, 25 cm focal length, UV-grade fused silica CVI lens mildly focuses the laser beam. The laser energy is measured with a Gentec joulemeter (ED500+). The particles are introduced to the interrogation region from a 1 cm diameter nozzle and irradiated in the open air. We collect the fluorescence at a right angle with a 5 cm diameter biconvex collection lens that delivers the light to a GCA/McPherson 0.3 m scanning monochromator with a Hamama-

tsu R928 photomultiplier tube (PMT). The slit width of the monochromator is 0.4 mm, resulting in a 1.1 nm spectral bandwidth, and the monochromator is scanned at a rate corresponding to 2.4 shots/nm. The peak value of the emission during a time window approximately 200 ns around the laser pulse is recorded on a LeCroy LT342 digital oscilloscope for each single shot without any time-gating. A 5 shot Savitsky–Golay rolling average is used to smooth the spectral data [21, 22].

3   Results and discussion

Figure 2 shows the single shot emission spectra from the background air and the soot particles coated with NaCl irradiated at 1.14 J/cm^2. The spectrum of soot particles without NaCl is also presented; these particles are prepared by replacing the NaCl solution in the nebulizer with deionized water, keeping all other operating conditions fixed. The SMPS measurements show that the soot particles have a log-normal size distribution with a mean diameter of 48 nm, a number concentration of 6.7×10^5 cm^{-3}, a volume concentration of 1.0×10^{11} nm^3/cm^3, and a geometric standard deviation of 1.4. The coated particles have corresponding values of 67 nm, 1.6×10^6 cm^{-3}, 3.7×10^{11} nm^3/cm^3, and 1.5. In the flame, the injected NaCl particles are thermally dissociated as we observe bright yellow light emitted from the Na D-line. When soot particles are formed, the supersaturated gas phase NaCl molecules condense on the soot surface (the saturation temperature of NaCl is 1680 K) and form the core-shell particles, as demonstrated by earlier work [5, 6].

The background air spectrum shows the Shumann–Runge O_2 band from 220 to 350 nm. The peaks at 386 and 579 nm are the 2nd and 3rd order reflection of the laser light from the diffraction grating of the monochromator. The spectrum of irradiated soot particles also shows the O_2 band since the particles are suspended in air. The soot spectrum has two additional lines at 248 and 431 nm that are fluorescence from carbon atoms and CH, respectively [13]. The carbon atom fluorescence at 248 nm ($^1P_1^0 \rightarrow$ $^1S_0$) is efficiently detected using 193 nm light since the electronic transition of
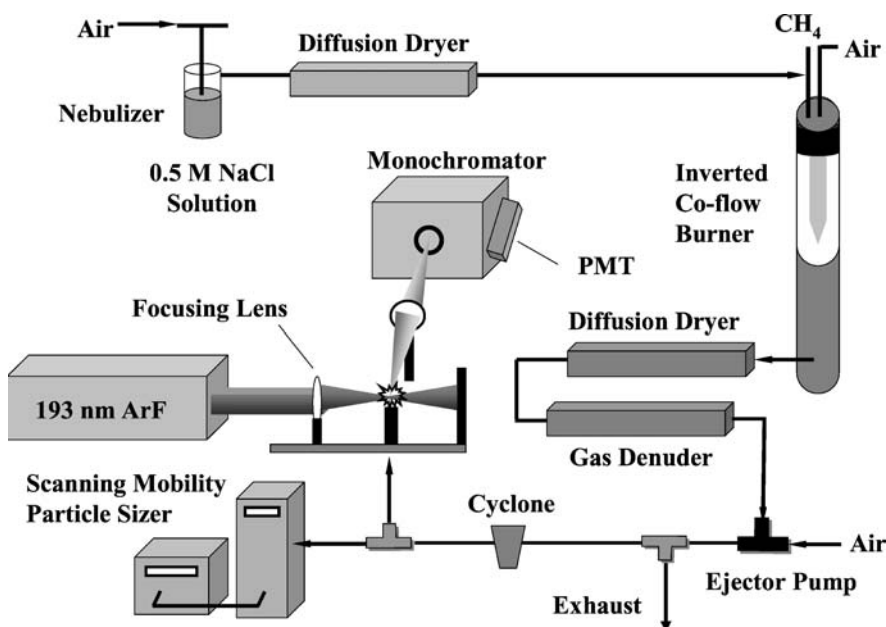

FIGURE 1   Experimental apparatus for producing soot particles coated with NaCl and the optical measurement system

gas phase carbon atoms overlaps with the laser output ($^1P_1{}^0 \leftarrow {}^1D_2$) [10]. The CH transition ($A\,^2\Delta \rightarrow X\,^2\Pi$) is also observed from the soot, indicating that partially premixed flame from the burner-nebulizer system produces particles with some organic fraction. In contrast, soot particles from a non-premixed flame in most other conditions of our burner did not have a significant organic fraction [23]. The C_2 Swan band at 468 nm, not present here, was observed from diesel soot along with C and CH lines in our laboratory [13]. That study showed that the detection limit for 248 nm carbon signal using ELFFS is approximately 0.2 ppb and the typical peak values of CH is 6 to 45% of the carbon signal. The CH signal observed in this study falls into this range.

The spectrum of the soot particles with NaCl has a peak at 589 nm as well as C and CH lines. The electronic transitions of Na form a doublet at 589.0 and 589.6 nm ($3\,^2P_{3/2}$, $3\,^2P_{1/2} \rightarrow 3\,S_{1/2}$ or D-line) [24, 25], but we could not resolve the doublet since the spectral resolution of our system is approximately 1.1 nm. Nunez and Omenetto [15] observed the spectrally resolved Na doublet from NaCl and other Na-containing particles using ELFFS and reported that the detection limit of Na emission is approximately 1 pg/cm^3 or 0.4 ppb for a 100 shot average.

The gas phase atomic and molecular fluorescence results from photo-induced disintegration of the irradiated particles. The 193 nm photons disintegrate a fraction of each particle into gas phase species that subsequently undergo electronic transitions. Note that laser heating of the particles by 193 nm laser irradiation is negligible as there is no blackbody-type broadband emission in the spectra (Fig. 2). The lack of thermal radiation is consistent with polystyrene and gold nanoparticles irradiated by 193 nm light at 10^7–10^9 W/cm^2 in our laboratory [12, 19, 26]. Above 10^9 W/cm^2 ($\sim$ 20 J/cm^2), optical breakdown occurred and intense white light was generated from the resulting plasma [12]. Photo-fragmentation at low laser fluences partially disintegrates the irradiated surface of the particles by direct photochemical bond breaking, which leaves the rest of the irradiated particle at nearly constant temperature. When we employed
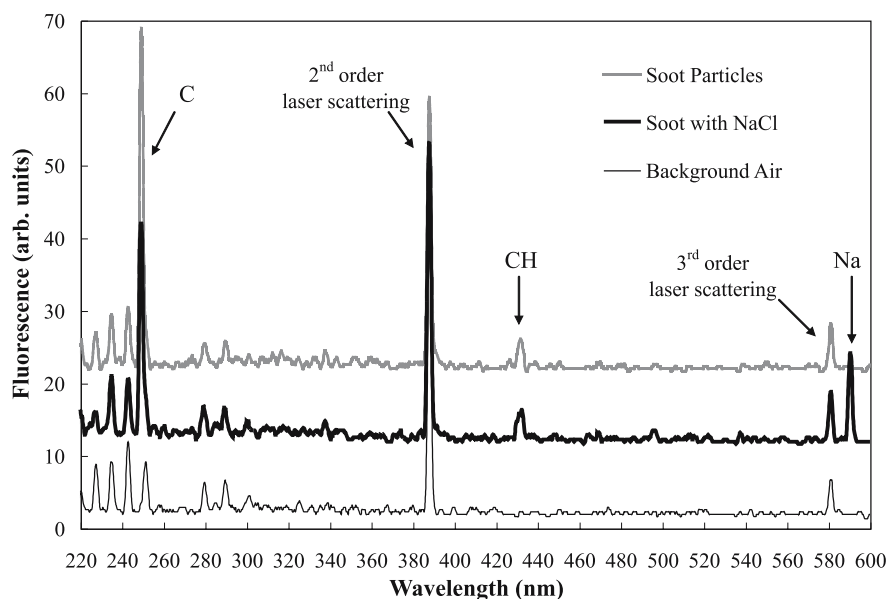
FIGURE 2 Spectra of single shot emission measurements at 1.14 J/cm^2 and 4 Hz. The fluorescence of the soot particles and soot particle with NaCl are shifted for clarity. The emission lines at 248 and 589 nm are carbon atoms and Na D-line, respectively. The Shumann–Runge O_2 band from 220 to 350 nm is clearly observed in all cases, and 431 nm line is CH fragmented from soot
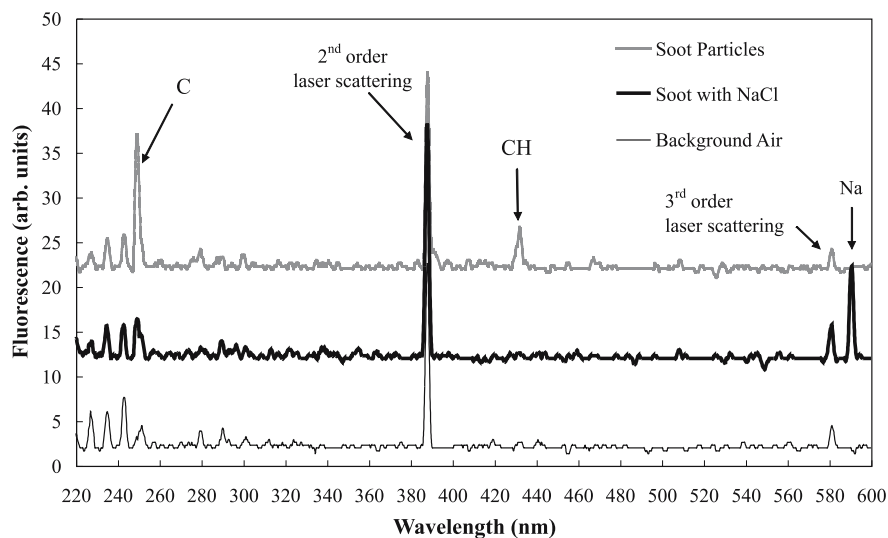
FIGURE 3 Spectra of single shot emission measurements at 0.69 J/cm^2 and 4 Hz. The fluorescence of soot particles and soot particle with NaCl are shifted for clarity. Note that Na D-line is observed from soot particles coated with NaCl while C and CH lines are reduced at this condition

532 nm light at similar fluences, we did observe long lifetime broadband incandescence from the same particles. Garrison and Srinivasan [27] also reported that 193 nm photons decompose the poly(methylmethacrylate) surface layer-by-layer above 0.01 J/cm^2 with high quantum yield of direct photochemical bond breaking.

Figure 3 presents another set of spectra for the soot, soot and NaCl, and clean air at a laser fluence of 0.69 J/cm^2. This laser fluence is chosen because it is above the lower limit of the flu-

ence to produce detectable fluorescence, yet not enough to disintegrate a significant fraction of the particles. In previous studies, we observed C and Na fluorescence from soot and NaCl particles in our system at the fluences as low as 0.46 and 0.3 J/cm^2, respectively. Even below these fluences, we observed that the laser irradiation significantly modifies the size distributions of soot [17], NaCl [20], and other particles [19, 26].

The soot spectrum, in Fig. 3, is very similar with the previous case at 1.14 J/cm^2; C and CH signals as well

as O_2 emission are observed, but the peak values are lower due to the lower laser light intensity. In the spectrum of the soot particles with NaCl, the Na D-line is present, similar to that at $1.14\,J/cm^2$. However, the carbon emission at 248 nm is only slightly greater than the background O_2 fluorescence peak at 250 nm. The ratio of C to Na signals decreases from 2.3 to 0.5 for the laser fluences from 1.14 to $0.69\,J/cm^2$. The significant decrease in the carbon signal from soot, while Na emission is clearly present, indicates that the soot particles are coated with a NaCl layer. If the salt did not encapsulate the soot particles, and the soot and NaCl particles were present separately in the laser probe volume, the carbon signal would be clearly seen, similar to what is observed in the soot particle spectrum.

To use this technique as a quantitative method, it is necessary to estimate the fraction of each particle fragmented by UV illumination. The exact value is unknown, but we use a scaling parameter, called the photon-to-atom ratio (PAR), which is a ratio of the number of photons absorbed in a particle to the number of atoms in the particle. We developed this non-dimensional number to assess the degree of disintegration of homogeneous nanoparticles [17, 19, 20], and found that a similarity is observed with particles of different materials and sizes when PAR is used instead of fluence: carbon atom fluorescence signals from soot and polystyrene particles increase linearly with PAR up to 1.5 and saturate above a PAR = 3.0, where every particle fully disintegrates [12, 28]. Determining PAR for the core-shell particles produced in this study is difficult, since their optical properties differ from homogeneous particles, and the thickness of the shell material is unknown. If we assume that the particles are simply soot with a diameter of 67 nm, the PARs are 1.3 and 0.8 for 1.14 and $0.69\,J/cm^2$, respec-

tively. This rough estimate suggests that there are not enough photons to significantly disintegrate the soot particles encapsulated with a NaCl layer, and the lack of carbon signal at the lower PAR $(0.69\,J/cm^2)$ is likely because only the shell material is fragmented. A future study will measure particles of different thicknesses of NaCl to quantitatively determine species concentrations and evaluate the effects on the particle fragmentation and the resulting spectroscopic signals.

The implementation of ELFFS as a quantitative detection scheme for core-shell nanoparticles needs more rigorous investigation. However, the results suggest that in situ real-time chemical analysis of coated particles can be achieved on the order of a minute using the photochemical characteristic of 193 nm light, which is certainly promising.

4   Conclusions

We developed an in situ, real-time detection scheme for core-shell nanoparticles using 193 nm pulsed laser light. We use carbon atom fluorescence at 248 nm and Na fluorescence at 589 nm for signatures of soot and NaCl, respectively. At $1.14\,J/cm^2$, C, CH, and Na emissions are observed from soot particles and soot particles with NaCl. When the laser fluence is reduced to $0.69\,J/cm^2$, C and CH emissions from the soot particles with NaCl decrease dramatically, indicating that soot particles are encapsulated with NaCl. At the lower fluence, the shell material is detected preferentially. This method could be useful in studying heterogeneous atmospheric particles and their environmental impacts.

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