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Novel low-intensity phase-selective laser-induced breakdown spectroscopy of TiO_2 nanoparticle aerosols during flame synthesis

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ABSTRACT

Novel low-intensity laser-induced breakdown spectroscopy (LIBS) is employed to conduct an *in situ* study on swirl flame synthesis of TiO_2 nanoparticles. Collected emissions agree well with Ti atomic spectra from the NIST database. In contrast to traditional application of LIBS on particles, the power used here is much lower (~35 mJ/pulse or 28 J/cm^2 at 532 nm); and no macroscopic spark is visually observed. Nevertheless, the low-intensity LIBS shows interesting selectivity—only exciting Ti atoms in particle phase, with no breakdown emission occurring for gas molecules (e.g. titanium tetraisopropoxide precursor, air). The emission intensity increases as the nanoparticles grow in the synthesis flow field, plateauing as the particles become larger than 6 nm, indicating the absorption efficiency to be size-dependent for small particles. The signals saturate at a fluence of ~16 J/cm^2. When the precursor concentration is larger than 150 ppm (corresponding to particle sizes of 6–8 nm), the emission intensity increases linearly with precursor concentration. The selectivity of the low-intensity LIBS for such application could be advantageous for tracking nanoparticle formation and for measuring particle volume fraction during gas-phase synthesis or other systems. The size-dependent absorption efficiency could be used to measure nanoparticle size *in situ*.

1. Introduction

Nano-sized TiO_2 particles have great potential in a wide range of photocatalytic and photovoltaic applications, including purification of air and water [1,2], selective catalytic reduction (SCR) of NO_X [3], chemical gas sensors [4,5], and dye-sensitized solar cells (DSSCs) [6–8]. Flame synthesis is well known to produce TiO_2 nanoparticles less than 10 nm at high production rates with controllable sizes [9–12]. The residence time from burner to substrate is usually as short as a few milliseconds, but allows for chemical conversion (homogeneous and heterogeneous) from precursor to TiO_2 monomers, coagulation and coalescence of TiO_2 nanoparticles, and deposition of particles driven by thermophoresis and diffusion [13,14]. The fast time scale, as well as steep temperature gradient, is well-suited for producing metastable phases, with the associated dynamics being far from equilibrium. As such, non-intrusive *in situ* studies are essential in understanding growth mechanisms. Graham and Homer [15] and Glumac et al. [16] employed elastic laser light scattering (ELS) to obtain information on nanoparticle size, since Rayleigh scattering intensity scales with the sixth power of particle diameter. Yang and Biswas [17] used ELS to study the characteristic times associated with sintering of TiO_2 agglomerates during flame synthesis. Liu et al. [18] conducted *in situ* Raman spectroscopy of TiO_2 nanoparticles during low-pressure flame synthesis, showing the crystallization of nanoparticles into the anatase phase. Maffi et al. [19] and Cignoli et al. [20] proposed that laser-induced incandescence (LII) can be used to study the size evolution of TiO_2 nanoparticles during flame synthesis.

In this work, relatively low-intensity (~35 mJ/pulse, weakly focused by a 500-mm focal length plano-convex lens) laser-induced breakdown spectroscopy (LIBS) is employed *in situ* to study flame synthesis of TiO_2 nanoparticles. LIBS is a type of atomic emission spectroscopy which uses a highly energetic laser pulse to ablate, atomize, and excite samples in a laser-induced plasma. It has been widely used to analyze a variety of samples including solids, liquids, gases, and biological materials with minimal sample pretreatment [21–24]. The plasma emission reveals the emission lines for each element detected in the plasma volume. LIBS has been shown to be quantitative [25] and can be spatially-resolved for measuring particles [26]. Although molecular information is largely eliminated with LIBS, recent work applying LIBS on nanoaerosols (~100 nm) has divulged information on elemental ratio [27]; and previous work in combustion has used elemental ratios to determine

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equivalence ratios in hydrocarbon–air mixtures [28], as well as elucidate vapor–particle interactions in flames [29]. LIBS has also been applied in flame synthesis to measure the stoichiometry of SiC_x nanoparticles [30].

The low-intensity LIBS technique presented in this work is different from classical high-intensity LIBS, for example in the works referenced above. With no macroscopic visible spark observed during the measurements, disturbances on the flow field seem negligible, and no delay in signal collection is needed. Given the reduced power, where the laser fluence is in-between the breakdown thresholds of gas and particle phases, high selectivity is observed between emissions from atoms within nanoparticles versus atoms from gas-phase molecules (e.g. TiO_2 monomers). Moreover, the emission intensity seems to increase with nanoparticle size, reaching a plateau at a certain size (~6 nm). We apply this new technique to the *in situ* study of flame synthesis of nanoparticles.

2. Experimental setup

The stagnation swirl flame setup for TiO_2 nanoparticle synthesis is shown in Fig. 1; additional details can be found in Refs. [11,14]. Briefly, the main parts of the setup include a stainless steel nozzle (burner) with 18 mm inner diameter, an internal swirler positioned 70 mm upstream of the nozzle outlet, and a water cooled substrate. Premixed gases of O_2, CH_4, and N_2, are fed into the burner, forming a stagnation swirl flame between the nozzle and substrate, with separation distance fixed at 19 mm. The swirl number is ~0.25, corresponding to the low-swirl flame regime [31,32]. The substrate temperature, monitored by a 1-mm bead K-type thermocouple embedded inside the substrate, is controlled to be 373 ± 10 K by regulating a flow rate of cooling water. For all experimental runs, the gas-flow rates are set at 2.4 L/min for CH_4, 26.4 L/min for N_2, and 7.0 L/min for O_2. The precursor (titanium tetraisopropoxide, TTIP, Aldrich, 97%), is radiantly heated in a bubbler at 353 ± 1 K with a temperature-controlled SCR. A portion of the N_2 flow serves as carrier gas. By weighing the precursor-containing bubbler before and after experiments, the precursor loading rate is determined to be 0.025 g/min for 1 L/min carrier gas. Combined with the total flow rate, the precursor concentration is 116 ppm when the carrier gas is 2 L/min. Thus, the precursor concentration is varied by adjusting the flow rate of the carrier gas. All gases are preheated to 368 ± 5 K to prevent TTIP condensation within the delivery line (which is also heated and temperature controlled) to the burner. The burner/substrate assembly is attached on a two-dimensional translation stage with axial (i.e. vertical) and radial adjustment, so that the flow field can be probed with the laser-beam and collection optics fixed. TEM grids mounted on a thermophoretic sampling probe collect as-synthesized TiO_2 nanoparticles. Transmission electron microscopy (TEM, JEOL 2010, 200 kV) and X-ray diffraction (Siemens diffractometer, ICDD database) are employed to characterize the samples.

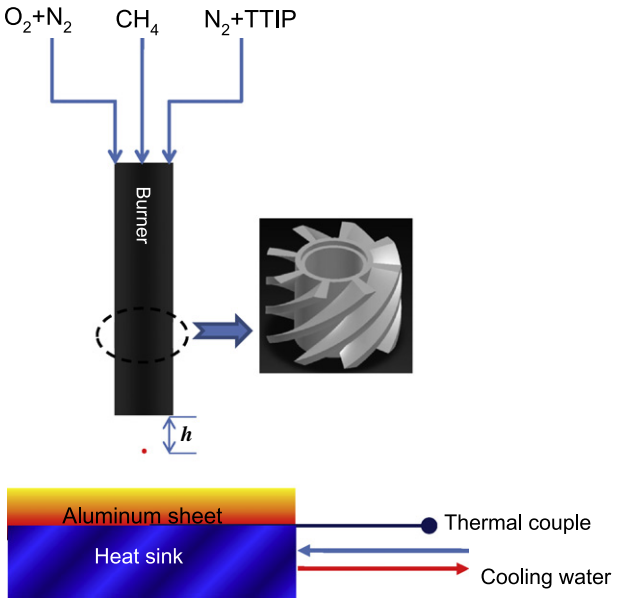

Fig. 1. Schematic of the stagnation swirl flame setup for TiO_2 nanoparticles synthesis.

The setup for the laser-based diagnostics is illustrated in Fig. 2. The second harmonic (532 nm) of an Nd:YAG laser operating at 10 Hz serves as excitation source. The beam is focused by a 500 mm focal-length plano-convex fused silica lens to a waist diameter of ~200 μm. As seen from Fig. 2, the collection optics consists of two 300 mm focal-length achromats, a holographic notch filter (Kaiser Optics, SuperNotch-Plus, 532 nm), an image rotator, and a depolarizer. Thus, the scattered light from a 200 μm diameter by 1 mm length measurement volume at the beam focus is collected at 90° into a 0.5 m spectrometer (Acton SpectraPro 2500i, f/6.5) with 2400 groove/mm holographic grating and 200 μm slit width. The wavelength resolution is ~0.1 nm. The detector is an ICCD camera (Princeton Instruments PIMAX 1300HQ-25-FO), gated to minimize the interference from flame emissions and other sources. The typical gate width is 20–200 ns, and the typical collection time is 20–400 s (200 shots to 4000 shots) for laser induced emissions. The typical power used in the low-intensity LIBS measurement is 35 mJ/pulse, corresponding to a local fluence of 28 J/cm^2 at the focal point.

Gas-phase temperatures are determined using spontaneous Raman spectroscopy (SRS). The vibrational band of N_2 (centered ~2330 cm^{-1} shift) is used to obtain the gas-phase temperature by least-squares fitting the shape of the Q-branch spectrum to a library of theoretical spectra [33,34]. The laser power is 50 mJ/pulse for the SRS measurement, with an accumulation time of 300 s. The uncertainty of the measurement is ±50 K.

3. Results and discussion

The temperature profile (with no precursor loading), as measured by SRS between the burner and substrate along the axis of symmetry, is displayed in Fig. 3. The abscissa is the distance from burner exit, marked as *h* in Fig. 1. Previous studies have shown that the synthesis process has small effect (<50 K) on flame temperature when the precursor concentration is low [12]. The measurements show that the temperature increases by more than 1000 K from 6 mm to 12 mm, roughly corresponding to the flame zone. The highest temperature is found to be 1846 K, close to the calculated adiabatic flame temperature of 1863 K, at a distance of 14 mm downstream from the burner exit. The temperature at distances further than 14 mm decreases slightly due to heat loss to the cool substrate.

Post-experiment analytical characterization of the synthesized nanoparticles is shown in Fig. 4. The precursor concentration is 116 ppm, calculated from a carrier gas flow rate of 2 L/min. XRD (ICDD database, PDF#97-015-4602) reveals that the particles are in the anatase phase. No significant rutile phase is detected. The TEM photograph in the upper right of Fig. 4 shows the morphology of some TiO_2 nanoparticles sampled during synthesis at ~2 mm above the substrate (corresponding to ~17 mm from the burner exit). The average particle diameter is ~6 nm. The low degree of aggregation indicates a short coalescence time, where coalescence occurs faster than collisions given the local high temperature. The TEM photograph in the lower right of Fig. 4 shows TiO_2 nanoparticles collected from the substrate post-experiment. The particles are uniformly 6–8 nm. Negligible growth in particle diameter is observed between the two TEM photos, implying that further coalescence is