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Vaporization of bulk metals into single-digit nanoparticles by non-thermal plasma filaments in atmospheric pressure dielectric barrier discharges

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ABSTRACT

A compact, inexpensive and simple dielectric barrier discharge (DBD) design is presented with related electro-thermal properties for the production of metal nanoparticles.

Nanoparticle formation and growth mechanisms are depicted from size distributions and chemical analyses of particles collected just after the 70 kHz DBD in nitrogen. At first, it is confirmed that the initial local vapor flux is produced from the spots of interaction between plasma filaments and different metal electrodes (Au, Ag, and Cu). Amorphous and crystalline pure metal primary nanoparticles with diameters below 5 nm are then produced by physical nucleation in expanding vapors jets. Finally, some small agglomerates with diameters still below 5 nm are also formed by ballistic agglomeration of a fraction of these primary particles. This happens at the end of the vapor jet expansion, as well as after the production during the transit between subsequent filaments in the DBD. The first local agglomeration step can be limited at reduced energy per filament by lowering the initial vapor flux in smaller gaps, while the second growth step depends on the transit time in the DBD. Hence, such "low" energy plasma filaments (up to a few tens of μJ) lower the initial vapor flux to control the agglomeration. DBD were thus successfully tested for the production of tailored nanoparticles with tunable size, controlled morphology of spherical agglomerates and the same composition as the metal electrode.

The production per unit energy (mol J^{-1}) is related to both plasma and material properties. Besides, neglecting vapor and nanoparticles losses, the mass production rate (g s^{-1}) depends on the input power related to the product of the energy controlling the production per filament times the number of filaments per second, for any given material.

This non-thermal plasma process presents great potentialities for nano-technologies since it is performed at atmospheric pressure and can be used to reach size-dependent properties of nano-materials, without any gaseous precursor or solvent.

1. Introduction

Size-dependent properties are reported for particles smaller than 50 nm (Kodas & Hampden-Smith, 1999; Schmid, 2010). Hence, the ideal nano-material production process should control the size, the composition and the structure of primary nanoparticles as well as the coagulation enlarging the size distribution.

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Nano-particles suspended in gases are formed by evaporation of liquid droplets or by condensation of vapors. In both cases, homogeneous nucleation occurs when the saturation concentration is overcome (saturation vapor pressure in gases and solute concentration for crystallization in liquids). Nucleation here refers to the bottom-up gas phase process producing nanoparticles from condensable vapors.

In reactive nucleation processes, condensable species are produced by chemical reactions between gaseous precursors and excited species from flames, plasmas or lasers. High production rates are reached but purity of the so-produced nanoparticles still is a critical limit that deserves to be addressed (e.g. in Pratsinis (2008) for flames, in Vollath & Szabó (2006) and in Kortschagen's chapter from Samukawa et al. (2012) for low pressure plasmas, as well as for ambient pressure processes by plasmas in Belmonte et al. (2011), and in Massines et al. (2012), or by lasers in Sublemontier et al. (2011)).

To reach pure nanoparticle production, physical nucleation by cooling hot vapors evaporated from solid materials has been first developed for low pressure coating process. Solid vaporization is also performed at ambient pressure to produce particles with the same composition than the solid target. Continuous thermal arc or short successive and focused energy deposits on the material by lasers and sparks (first reported by Altgeld et al., 1980) are used. The interaction surface is referred to spot with related power densities above 10^{10} W m^{-2} and energy densities up to 10^{6} J m^{-2} above the threshold fluency of 10^{3} J m^{-2} for metal vaporization (e.g. for lasers in Gamaly, 2011 and Dewalle et al., 2011). Then, high nucleation rates lead to concentrations of primary nanoparticles above 10^{10} cm^{-3}, favorable to fast coagulation. The so-produced aerosol presents mean diameters up to a few hundred nm (Kodas & Hampden-Smith, 1999; Horvath & Gangl, 2003; Byeon et al., 2008; Buesser et al., 2009; Bau et al., 2010). Agglomeration has been limited in sparks by dilution (Feng et al., 2013), by quenching in pin-to-hole configurations (Han et al., 2012), and by unipolar charging (Park et al., 2014). Sparks in liquids also leads to a fraction of unagglomerated nanoparticles embedded in carbon (Hamdan et al., 2013). Besides, less energetic non-thermal plasma filaments (0.1–10 mJ prevented sparks and 10–100 μJ streamers) still lead to final size distributions with count mean diameters from 10 to 100 nm, arising from coagulation of primary nanoparticles (Borra, 2008; Borra et al., 2009, 2011).

The paper describes another method to produce even smaller primary metal particles from 1 to 5 nm and to control the agglomeration with final diameters still below 5 nm. To do so, less energetic plasma filaments (from 1 to tens of μJ) are used to reduce the initial vapor flux. To compensate this low local vapor production per filament, filaments are repeated more than 10^{6} s^{-1} for ms transit times in lab-scale DBD at 70 kHz.

In such streamer-like discharge filaments, the transition to thermal spark must be avoided by limiting the reduced electric field (E/N with N the gas density) and the related current. In that respect, DBD have been developed using an AC voltage with at least one dielectric material (barrier) between the electrodes. The electric field in the gap depends on the applied voltage and on charges first migrating in the gap and then deposited on dielectric surface during the development of filaments (Gibalov & Pietsch, 2000; Eliasson & Kogelschatz, 1991). Surface polarization first amplifies the electric field to trigger economic plasmas filament development and then hinders the transition from non-thermal streamer to thermal spark. In air and nitrogen at atmospheric pressure, thin and transient discharge filaments, also called micro-discharges in most of the DBD litterature (Eliasson & Kogelschatz, 1991), develop with diameters of ~10–100 μm and durations of ~20–500 ns. Here, the expression “discharge filament” includes all phases from Townsend pre-breakdown avalanches to streamer development towards the cathode, surface discharges and quenching.

A simple DBD design is presented with electro-thermal properties for the production of nanoparticles from the surface of solids. Nanoparticle formation and growth mechanisms are discussed from Selected Area Electron Diffraction (SAED) and Transmission Electron Microscopy (TEM) analysis.

Finally, production per unit energy (mol J^{-1}), the final particle size and the mass production rate (g s^{-1}) of nanoparticles are related to plasma parameters, to properties of materials for gold, silver and copper as well as to transit times in the plasma.

2. General set-up and aerosol measurements

The experimental set-up is presented in Fig. 1. Plasma reactors are fed with N_2 at STP. Transit times in the gap lie from 1 to 20 ms in lab-scale DBD.

Reactive nucleation may arise from gaseous impurities converted into condensable species by reactive non-thermal plasmas. It can be suppressed using filtered dry inert or non-reactive gases. Then whatever 99.99–99.999% purities used, similar aerosol measurements are performed and detected aerosol can only be produced by physical nucleation of vapors emitted from spots of plasma filaments.

2.1. Electro-thermal characterization of DBD

Figure 2 shows the plane-to-plane DBD reactor design that has been used with millimeter gaps. This lab-scaleDBD is made of metal electrodes (Ag, Au or Cu with diameters of 4, 8 and 8 mm respectively), facing the dielectric material (Al_2O_3) polarized at 70 kHz by a 2×3 cm² electrode. This asymetric planar DBD has been used for electrical characterization. Indeed, the accurate electrical characterization of current pulses related to properties of discharge filaments requires an electrode area smaller than 1 cm^2 to prevent from too numerous pulses occurring at the same time on larger electrodes (Jidenko & Borra, 2006). Different gap lengths from 1 to 3.65 mm were fed with 1 to 10 lpm N_2 to keep the gas velocity constant at 0.5 m s^{-1}, for all the results presented here.