DEVELOPMENT OF AN AC-POWERED ATMOSPHERIC-PRESSURE, FLOWING MICROPLASMA FOR GAS-PHASE NANOPARTICLE SYNTHESIS

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I-MIN HUANG

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Dissertation Advisor: Dr. R. MOHAN SANKARAN

Department of Chemical Engineering
CASE WESTERN RESERVE UNIVERSITY

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CASE WESTERN RESERVE UNIVERSITY
SCHOOL OF GRADUATE STUDIES

We hereby approve the thesis/dissertation of

I-MIN HUANG

Candidate for the degree of

Master of Science

Committee Chair

DR. R. MOHAN SANKARAN

Committee Member

DR. CHUNG-CHUIN LIU

DR. DANIEL J. LACKS

Date: 08/19/2014

*We also certify that written approval has been obtained for any proprietary material contained therein.
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Development of an AC-Powered Atmospheric-Pressure, Flowing Microplasma for Gas-Phase Nanoparticle Synthesis

I-MIN HUANG

Abstract

We present an alternating current (AC)-powered atmospheric-pressure microplasma for gas-phase synthesis of nanoparticles. The microplasma is formed inside a quartz tube with a powered copper ring electrode on the outside and a tungsten wire on the inside, in contact with the plasma. The electrical properties of the plasma including the voltage and current waveforms are characterized as a function of input power. The plasma length is found to increase with increasing power, reaching a maximum of 4.3 cm at a peak-to-peak voltage of 4 kV. As proof-of-concept, we demonstrate the synthesis of nickel nanoparticles from nickelocene vapor. The particles are monitored in real time by aerosol mobility measurements. Particle size distributions are obtained as a function of nickelocene vapor concentration and input power. Increasing the nickelocene concentration is found to increase the mean diameter and produce a broader range of particle sizes. Interestingly, at higher powers and longer plasma lengths, the particle diameter is found to decrease. Finally, we show that this design allows arrays of microplasmas to be formed with a
single power supply and mass flow controller, offering a potential route to scaling up nanoparticle synthesis.
1. Introduction

Plasma synthesis has recently emerged as an attractive approach for the preparation of nanoscale materials. In general, vapor precursors are dissociated by energetic species and particles are homogeneously nucleated in the gas phase. [1,2,3] The method is high purity, scalable, and non-equilibrium, allowing novel materials such as silicon, iron oxide, and diamond [1,4,5] to be produced far from their thermodynamic temperature and pressure stability. [6,7]

A drawback of plasma processes is that low pressures are typically required to facilitate gas breakdown and operate the plasma stably. [4,6,8,9] Low pressure operation requires vacuum equipment that can be complicated and expensive. For this reason, atmospheric-pressure plasmas have gained attention for their potential use in materials applications including nanoparticle synthesis. [2,3,10,11] To date, most of the studies with atmospheric-pressure plasmas for nanoparticle synthesis have been limited to direct current (DC) operation which is inefficient, introduces contaminants, and is difficult to scale up. Atmospheric-pressure plasmas are usually small scale, referred to as microplasmas, and scale up requires parallel operation in an array. [10] When DC power is used to operate the plasma, parallel operation is difficult since the power will be conducted through a single path of least resistance (i.e. one element of the array).
A potential alternative to operating atmospheric pressure plasmas in arrays is pulsed operation, for example by alternating current (AC). While AC plasmas have been extensively studied in various geometries and applications, to our knowledge no study exists of AC microplasmas for nanoparticle synthesis.

Here, we present a design of an AC atmospheric-pressure, flowing microplasma for the synthesis of nanoparticles by homogenous nucleation. Because the design is somewhat different than those previously reported, we first focus on characterization of the plasma source itself by imaging and electrical measurements. We then test the plasma for nanoparticle synthesis using a chemistry that has been previously studied with DC microplasma systems, the dissociation of the metal-organic precursor, nickelocene. [3,10,11] The formation of nickel (Ni) nanoparticles from nickelocene is studied by online aerosol mobility measurements. Preliminary results for the materials analysis of the Ni nanoparticles are also presented.

2. Experimental setup and methods

An alternating current (AC) powered microplasma reactor was designed based on the combination of a DC microplasma and a floating electrode DBD (dielectric barrier discharge) jet. [3,10,11,13,14] Briefly, a 6.35mm wide copper ring was attached to the outside of a quartz capillary tube with an outside diameter (O.D.) of
6 mm and an inner diameter (I.D.) of 1 mm, and operated as the high voltage electrode. A 2.54 cm tungsten wire with a diameter of 0.1 mm was grounded and inserted into the quartz tube. We note that the plasma could not be ignited without the ground electrode inside the quartz tube, in contact with the plasma. A detailed schematic of the AC microplasma reactor is illustrated in Figure 1.

Figure 1. Schematic of AC microplasma reactor. The microplasma which formed inside a quartz tube with a copper ring on the outside and a tungsten wire inside in contact with the microplasma as the powered and ground electrodes, respectively. The voltage and current waveforms were monitored by an oscilloscope with a high voltage probe and a Pearson probe, respectively.

The quartz tube was sealed with standard 6.35 mm Swagelok fittings to pressurize with gas flow. The gas flow rates were controlled by digital mass flow controllers
(MFC). In order to ignite the plasma, voltage was applied from a PVM500 AC power supply. In a typical experiment, the gas flow was introduced to flush and fill the quartz tube with the inert gas (argon), the power supply was then turned on, and the voltage was slowly increased until the plasma was ignited. Finally the voltage was set to obtain the desired voltage and current. The plasma would normally ignite at ~0.4 kV peak-to-peak. The voltage and current waveforms were measured by a digital oscilloscope (Tektronix 2430) which was connected to a high voltage probe to measure the voltage, and a Pearson probe was used to measure the current. Figure 2 shows a photo graph of the AC microplasma operating at a voltage at 4 kV and current 3.6 mA.

Figure 2. Photo of AC microplasma operating in Ar flow a voltage at 4 kV and current
3.6 mA.

As proof-of-concept, we studied the nucleation and growth of nickel (Ni) nanoparticles in the AC microplasma from the metal-organic precursor, biscyclopentadienyl nickel or nickelocene. Figure 3 schematically shows the experimental arrangement that was used to introduce nickelocene in the microplasma and synthesize and monitor Ni nanoparticles. Nickelocene is a solid powder at room temperature, but forms a vapor with an equilibrium vapor pressure of ~1.3 Pa at 293K. [3] In order to introduce nickelocene vapor at controlled concentrations in the AC microplasma, we loaded the powder in a stainless steel tube using a glove box, capped the ends with glass wool to prevent the powder from being blown out, and sealed the ends with valves preventing air and moisture from reacting with the powder. The sealed powder was then connected to an Ar gas line to sublime the vapor into the AC microplasma reactor. An additional flow of pure Ar gas was mixed with the nickelocene vapor to control the final concentration and total flow rate in the microplasma. The total gas flow rate was maintained constant at 100 standard cubic centimeters per minute (sccm) in all experiments. The concentration of nickelocene was specified as a volume concentration which was based on the volumetric flow rate ratio of nickelocene to the total gas flow. A DC
microplasma reactor was also operated under the same conditions providing side-by-side comparisons.

Figure 3. Schematic of experimental setup for the synthesis of Ni nanoparticles in an AC microplasma. The nickelocene was introduced in the microplasma by sublimation and the final vapor concentration was controlled using a digital mass flow controller system. The Ni nanoparticles were monitored on line by aerosol mobility measurements.

The nucleation and growth of Ni nanoparticles could be monitored on line with a scanning mobility particle sizing (SMPS) system. The scanning mobility particle sizing (SMPS) system consists of a differential mobility analyzer (DMA) (TSI, Inc., Model 3080) and a condensation particle counter (CPC) (TSI, Inc., Model 3776). Briefly, nanoparticles flow out of the microplasma as an aerosol. The aerosol is
charged with a known charge distribution by a sealed radioactive source (Kr$^{85}$). The charged aerosol then enters the DMA where the particles are separated based on their gas-phase electrical mobility. The size-classified particles are then directed into the CPC where butanol is condensed on their surface and the particles are detected by optical scattering. Overall, the system allows particle size distributions (PSDs) of aerosols between~2 to 100 nm to be obtained and measured.

Additional characterization of the nanoparticles was carried out by collecting the particles. The aerosol was directly deposited as a thin film by electrostatic precipitation (TSI, Inc., Model 3089). The thin films were then characterized by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS).

3. Results and discussion

The operation of the AC microplasma under different applied voltages and currents was investigated in this study. Figures 4 (a)-(d) show the appearance of the AC microplasma at different voltages. At low voltages (~1 kV), the plasma was localized to the position of the Cu electrode; this was consistent with ignition occurring at the powered electrode. Increasing the voltage was clearly found to increase the length or volume of the plasma from approximately 1.27 to 4.3 cm. The plasma appeared to expand from the Cu electrode in both directions, but
primarily towards the gas flow inlet where there was no tungsten wire. The tungsten wire was at ground, plasma expansion was confined in this direction.

Figure 4. Photos of AC microplasma operating in 100 sccm Ar at peak-to-peak voltages of (a) 1 kV, (b) 2 kV, (c) 3 kV, and (d) 4 kV. The plasma is observed to expand from 1.27 to 4.3 cm as the voltage is increased from 1 to 4 kV.

Voltage and current waveforms at these same operating conditions are shown in Figures 5 (a)-(d). In general, the voltage waveforms appeared to be sinusoidal and symmetric while the current waveforms were triangular. The triangular current waveform was consistent with previous reports for a similar AC powered microplasma where a floating electrode DBD jet was formed and may result from filamentary discharge formation during each pulse. [13,14] The voltage and current
waveforms were shifted, with the current lagging behind the voltage by approximately ~¼ cycle. In an AC circuit, a displacement current is produced which is what is observed here. We note that the current waveform was measured even in the case of no plasma (i.e. before ignition). In future studies, we will attempt to separate this displacement current from the discharge current which is of interest.
Figure 5. Voltage (black) and current (blue) waveforms of AC microplasma at peak-to-peak voltages of (a) 1 kV, (b) 2 kV, (c) 3 kV, and (d) 4 kV. The current waveform is shifted and is the displacement current produced by the AC circuit.
The dependence of AC microplasma operation on nanoparticle nucleation and growth was studied by monitoring Ni nanoparticles with the SMPS system. Figures 6 (a)-(c) show PSDs of Ni nanoparticles synthesized in the AC microplasma at different nickelocene vapor concentrations and applied voltages. The PSDs were obtained after steady-state was reached, which was approximately after 30 minutes, when the distributions did not appreciably change from scan to scan. For each vapor concentration, increasing the applied voltage was found to shift the PSDs to a smaller mean diameter with a lower particle concentration and narrower distribution. This was unexpected because increasing the applied voltage was observed to increase the plasma volume which should allow particles to grow larger through additional cracking of the precursor and supply of growth species.

As the nickelocene vapor concentration increased, the mean particle size and particle concentration increased, and the overall PSD broadened. This was consistent with an increase in growth species which leaded to enhanced particle growth and agglomeration. Interestingly, a vapor concentration of above ~20%, increasing the applied voltage showed relatively little effect on the PSDs. The CPC had an upper limit for detection the particle concentration may be even higher but could not be measured by our current instrument.
Figure 6. Aerosol mobility measurements of Ni nanoparticles synthesized from nickelocene vapor in the AC microplasma at volume concentrations of (a) 10%, (b) 20%, and (c) 30%. The peak-to-peak voltages were 1 kV (black), 2 kV (red), 3 kV (blue), and 4 kV (green).
These results were compared with a DC microplasma where the volume was more confined. Figures 7 (a)-(c) show PSDs measured from a DC microplasma at the exact same nickelocene vapor concentrations. The particle size and concentration were found to increase with precursor vapor concentration and decrease with power (discharge current), in agreement with the AC microplasma results. The latter result suggested that the decrease in particle size and concentration may be the result of gas heating at higher powers which leaded to vaporization of growth species or the particles themselves. [6,10,15]
Figure 7. Aerosol mobility measurements of Ni nanoparticles synthesized from nickelocene vapor in a DC microplasma at volume concentrations of (a) 10%, (b) 20%, and (c) 30%. The discharge currents were 3 mA (black) and 6 mA (red).
Ni nanoparticles synthesized at a volume concentration of 20% nickelocene and peak-to-peak voltage of 4 kV were deposited directly from the gas phase onto a Si substrate and analyzed by SEM and EDX. SEM and EDX were performed on a Nova NanoLab 200 FEG-SEM/FIB. Figure 8(a) shows a representative SEM images of the deposited material. The nanoparticles appeared to be severely agglomerated, creating a thick film. EDX was carried out at two regions, one where the film containing Ni nanoparticles was apparent (Figure 8(b)) and another where no nanoparticles were present and only the background substrate could be observed (Figure 8(c)). The EDX spectra showed lines corresponding to Ni only in the region where nanoparticles were probed, confirming the presence of Ni nanoparticles.
Figure 8. (a) SEM of Ni nanoparticles deposited directly from the gas phase as a film on a Si substrate. Region 1 and 2 indicated where EDX scan were acquired. (b) EDX of region 1 where nanoparticles are observed. (c) EDX of region 2 where no nanoparticles could be observed.
In order to demonstrate the possibility of scaling up this approach, an array of AC microplasma reactors were fabricated. The experimental arrangement consisting of four individual AC microplasmas powered by a single power supply and coupled to...
a single gas line as shown in Figure 9 (a). A digital MFC supplied a total of 400 sccm of
Ar which was split into 100 sccm for each microplasma element. As shown in Figure
9 (b), the array could be ignited and operated by the power supply at a voltage of 4
kV and current of 9.8 mA, similar to a single AC microplasma.

4. Summary and Conclusions

We have introduced an AC powered, atmospheric-pressure, flowing microplasma for gas-phase synthesis of nanoparticles. Compared to other atmospheric-pressure microplasmas typically operated by DC power, the AC microplasma system eliminates the use of some metal electrodes which can contaminate the process allowing arrays to be formed enabling scaled up operation.

This process is generic and should allow the synthesis of a wide-range of nanoparticle materials at atmospheric pressure which is currently a significant challenge for plasma-based synthesis. Future studies will focus on controlling the size, as well as the assessing and tuning the structure and properties of the materials.
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