# Fast production of organosilicon nanoparticles by plasma-induced decomposition of hexamethyldisiloxane liquid

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A technique for the fast production of organosilicon nanoparticles by sustaining plasmas in hexamethyldisiloxane (HMDSO) is presented. The discharge is obtained by applying pulse microsecond electric fields between pin-to-pin electrodes immersed in HMDSO. The plasma as well as the nanoparticles are characterized.

## 1. Introduction

To address a number of challenges related to the "emerging" field of nanotechnology, it is important to develop knowledge, tools and expertise for the synthesis and functionalization of nanomaterials that may take the form of isolated nanoparticles, nanowires or aggregates of nanostructures. In this context, as an alternative to conventional chemical approaches, we have explored the potential of plasmas produced in liquid precursors for fast nanoparticle synthesis. From a fundamental point of view, we wish to establish links between the physicochemical properties of the plasma produced in the liquid and the dynamic plasma-liquid-nanoparticle interactions. From a technological point of view, we aim to impart new chemical functionalities to the plasma-generated nanoparticles depending on the application. Synthesis of nanoparticles using electrical discharges sustained in liquids was first reported in 2001 [1]. Since then, two major techniques were developed and explored. The first one is based on the erosion of electrodes immersed into the liquid [2], while the second relies on plasma-liquid interactions [3]. In the latter case, arc regimes should be avoided to suppress electrodes erosion. These techniques were demonstrated for the synthesis of different carbon nanostructures (e.g. nano-horns, nano-onions, nano-flowers, nano-clusters, etc.) and other metallic particles supported by carbon matrix [4].

Here, we have extended this technique to the synthesis of organosilicon nanoparticles by sustaining plasmas in hexamethyldisiloxane (HMDSO) using microsecond electric fields in a pin-to-pin configuration. This precursor was selected because it is often used for plasma deposition of hydrophobic SiOCH and hydrophilic SiOx coatings on various substrates and for plasma synthesis of nano-powders by gas-phase chemical reactions [5,6]. Moreover the dielectric nature of HMDSO reduces experimental complications.

## 2. Experimental setup

The experimental setup is schematically depicted in Fig. 1. A pin-to-pin electrode configuration is used. Electrodes are tungsten wires with radius of 0.5 mm and are mechanically polished to have an apex radius of curvature of ~100 μm. Both electrodes are immersed in the liquid HMDSO precursor with volume of 10 mL.
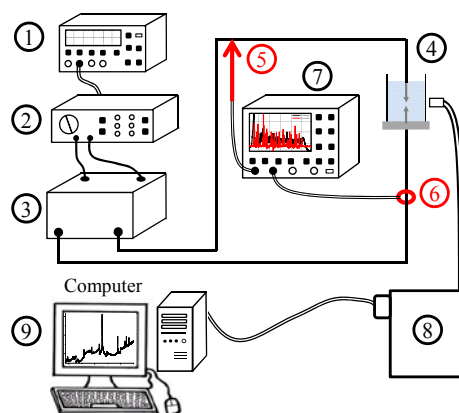


Fig. 1. Schematics of the experimental setup.

The inter-electrodes distance was set at ~100 μm and the experiments were performed at three applied high voltage (HV) namely 5, 10 and 15 kV. Concerning the HV, there are three units denoted 1, 2 and 3 in Figure 1. Unit 1 is an arbitrary function generator (AFG) (Tektronix, 3021B) that defines the operating frequency, the pulse shape (sine, pulse, etc.) and the pre-amplified amplitude. Unit 2 (Crest

Audio model 8001) is the amplifier that can amplify up to ~180 V. Unit 3 is high voltage transformer (600VA, 60 V/9 kV, Montoux) that was conceived to be used at frequencies between 1 and 20 kHz. In order to control the number of discharges during one oscillation period, we used the HV power supply in pulse mode. The frequency was fixed at 1.0 kHz (period is 1 ms) with 30% duty cycle. The treatment time was fixed to ten minutes.

## 3.Results and discussion
### 3.1. Electrical measurements

The plasma sustained in HMDSO was characterized by electrical measurements (voltage and current) using HV (Tektronix, P6015A, USA Model, 1000x 3.0pF, 1000MΩ, item 5 on Fig. 1) and current (LILCO limited, UK, Model 13w5000, item 6 on Fig. 1) probes. A typical current-voltage characteristics is shown in Fig. 2.
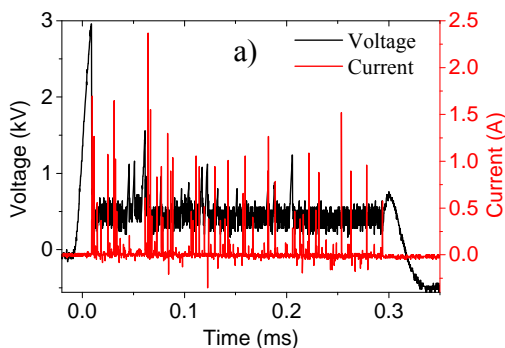


Fig. 2. Current-voltage characteristic of the discharge produced in liquid HMDSO at 5 kV.
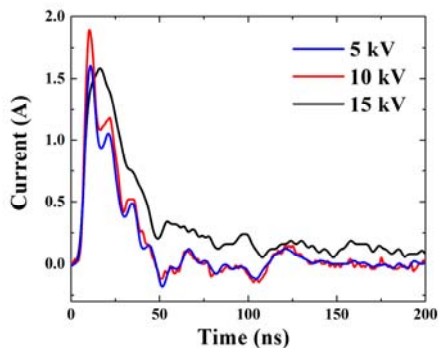


Fig. 3. Discharge current as a function of time at 5, 10 and 15 kV applied voltages.

I-V measurements showed that the discharge (partial discharge) was running in spark mode. We observed about 50, 70 and 110 micro-discharges (i.e. current peaks) during one oscillation period of the 1 kHz electrical stimulation in the case of 5, 10 and 15 kV applied voltages, respectively. The current

behavior shown in Fig. 3 revealed that the duration of each micro-discharge was ~50 ns in all cases. Deposited charge and dissipated energy per micro-discharge were estimated by the time-integration of the current and voltage times current plots. As expected, we found that the deposited charge per micro-discharge increased with the amplitude of the applied voltage, going from 25 to 70 nC as the voltage rose from 5 to 15 kV. A similar behavior was observed for the dissipated energy per micro-discharge, with values of 10.4, 15.6 and 24.0 µJ for 5, 10 and 15 kV voltages, respectively.

### 3.2. Optical emission measurements

Time-averaged Optical Emission Spectroscopy (OES) was performed using a PI-Acton spectrometer equipped with a 300 mm focal length monochromator and a Pixis 256E charged-coupled device (CCD) camera. Emission spectra were taken between 200 and 900nm with a 1200 lines/mm grating. The entrance slit of the spectrometer was set to 10µm, yielding a spectral resolution (full width at half maximum) of about 0.4 nm at $\lambda = 777$ nm. All recorded spectra were corrected for the spectral response of the optical fibre, monochromator, and detector.
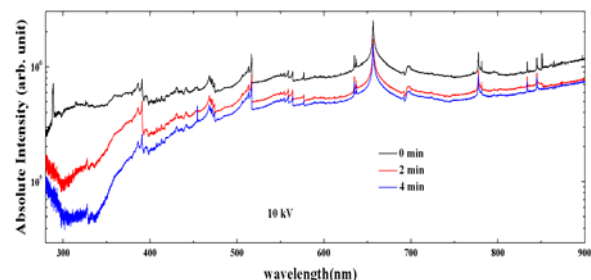


Fig. 4. OES spectra of the discharge produced in liquid HMDSO as a function of duration time at 10 kV.

As shown in Fig. 4, OES revealed the apparition of strong $C_2$ (Swan system) bands along with Si I line at 390 nm, H I line at 656.3 nm and O I line at 777 nm. Si I line at 288 nm was also seen; this line disappeared at later times due to the formation of nanoparticles, which induced significant change in the color of the liquid and ultimately blocked UV emission. W I line was also seen at 638.28 nm due to the erosion of the electrode material.

Stark broadening of the $H_\alpha$ (656.3 nm) emission line was used to determine the electron density of the HMDSO plasma. In our conditions, Fig. 5 indicates that the line shape can only be fitted using two Lorentzian profiles, with FWHM of {2.2; 13.7 nm} for 5 kV, {1.4; 13.5 nm} for 10 kV and {0.9;

14 nm} for 15 kV of applied voltages. Such broadening results in electron densities of {$3\times10^{17}$; $6\times10^{18}$ cm$^{-3}$} for 5 kV, {$1.5\times10^{17}$; $6\times10^{18}$ cm$^{-3}$} for 10 kV and {$7.4\times10^{16}$; $6\times10^{18}$ cm$^{-3}$} for 15 kV. Similar two Lorentzian behaviours of the H$_\alpha$ line were reported in previous studies of plasmas produced in liquids [7] and suggest the presence of two plasma modes, a low- and high-density mode. In our experimental conditions, the electron density in the low-density mode decreased with increasing applied voltage while the electron density in the high-density mode remains constant.
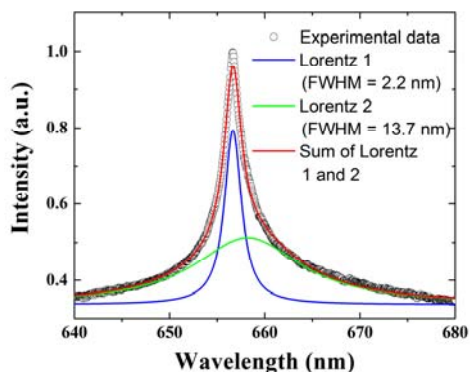


Fig. 5. Fitting of H$_\alpha$ line by two Lorentzian profiles with FWHM of 2.2 and 13.7 nm at 5 kV.
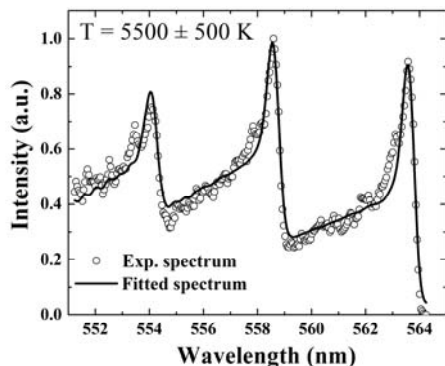


Fig. 6. Experimental and synthetic spectra of C$_2$ swan molecular band system that give a rotational temperature of 5500 ± 500 K at 10 kV excitation.

A rotational temperature was determined based on the emission from the C$_2$ Swan observed in Fig. 4. This was realized by comparing measured emission spectra with those from a synthetic spectra using the rotational temperature as the adjustable parameter. Calculations were performed using the method developed by Cardoso *et al.* [8] in the range of 552 to 564 nm. A typical example is shown in Fig. 6 for 10 kV excitation. The estimated temperature is in the range of 5500 ± 500 K and was fairly constant for all applied voltages investigated in this work. Such high

values of the rotational temperature (5000 to 10000 K) were also observed in previous studies of similar kind of discharges produced in liquids [2].

### 3.3. Characterization of nanoparticles

The liquid progressively changed color during the processing. It became black, which suggests the presence of decomposed carbon-based nanostructures. In addition, in the case of 15 kV excitation, the production rate was so high that only after 2 minutes of discharge treatment, the plasma emission could no longer be recorded. As discussed above, the presence of W I line in the OES spectra suggests significant erosion of electrode material. However, we expect this erosion to be minimal as no important change in the morphology of the electrode surface was observed after repetitive plasma treatments. We thus expect that the majority of the particles produced in liquid HMDSO to result from the precursor decomposition.
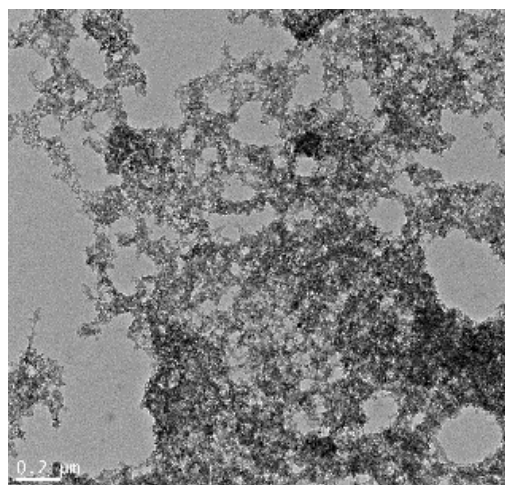


Fig. 7. TEM image of the synthesized nanoparticles in HMDSO liquid. The applied voltage was 15 kV.

High-Resolution Transmission Electron Microscopy (HR-TEM) was used to examine the structure and morphology of the nanoparticles produced after plasma production in HMDSO. As shown in Fig. 7 from the large scale TEM image (scale of 200 nm), the size of the nanoparticles was in the 5-10 nm range.

The normalized Energy-dispersive X-ray (EDX) spectrum presented in Fig. 8 (black line) and obtained from the large scale TEM image displayed in Fig. 7 shows that the nanoparticles formed in HMDSO liquid plasmas are essentially composed of silicon, oxygen, and carbon. However, small scale HR-TEM images (scale of 5 nm) also revealed the presence of W particles. Such image is presented in

Fig. 9a and the corresponding EDX spectrum is shown in Fig. 8 (red line). Enlarge view of Fig 9a, shown in the insets, indicates the presence crystalline and amorphous nano-particles. The interatomic distance deduced from such image was 2.5 Å. Electron diffraction patterns presented in Fig. 9b revealed that the diffracted particles have interatomic distances of 2.5, 1.5 and 1.3 Å. This corresponds to the (110), (200) and (211) planes of tungsten, respectively. This suggests that the crystalline particles are essentially of W.
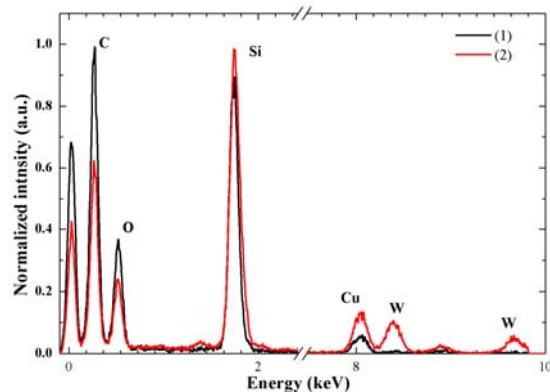


Fig. 8. Normalized energy-dispersive X-ray spectroscopy (EDX) spectrum; black line for nanoparticles shown in Fig. 7 and red line for nanoparticles shown in Fig 9(a).

The analysis described above indicates that over the range of experimental conditions examined in this study, plasma-electrode interactions cannot be ignored. This result is consistent with the expected HMDSO decomposition following discharge ignition, with only minimal erosion of the tungsten electrode. It is worth mentioning that the carbon peak in EDX spectra cannot solely be attributed to silicon-oxycarbide nanoparticles but also to the TEM grid. Cu peak is also due to the TEM grid.
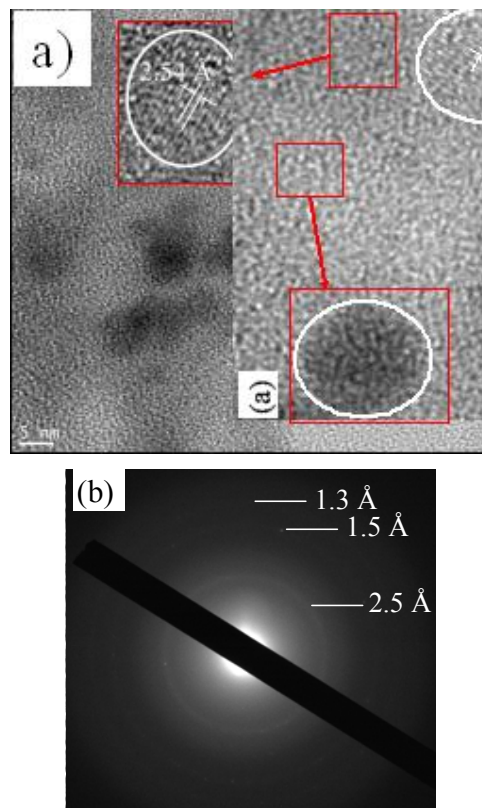
Fig. 9. a) HR-TEM image and b) electron diffraction pattern of nanoparticles synthesized in HMDSO liquid.

## 5. References
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