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Atmospheric pressure synthesis of diamondoids by plasmas generated inside a microfluidic reactor

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ABSTRACT

Diamond molecules, so-called "diamondoids", have shown a high potential for various nanotechnology applications, however the elaboration—especially of larger diamondoids—by organic chemical synthesis is complicated or even impossible. Plasma synthesis represents another possible approach, but the detailed diamondoid growth mechanisms in pulsed laser or electric discharges are still not understood.

This study investigates the effect of plasma gas chemistry on the synthesis of diamantane from adamantane and possible reaction intermediates, using dielectric barrier discharge (DBD) microplasmas generated inside continuous flow quartz microreactors.

The DBDs were realized in argon–hydrogen–methane mixtures, and adamantane was used as a nucleus for the diamondoid growth. Gas chromatography–mass spectrometry (GC–MS) was used for sample analysis, and optical emission spectroscopy was employed for probing the electric discharges.

From the GC–MS measurements, the synthesis of diamantane could be confirmed, the yield of diamantane increasing with the amount of hydrogen. In contrast, the addition of methane did not have any marked effect on the synthesis.

The results suggest that hydrogen plays a similar role for the growth of diamondoids as in the synthesis of diamond by chemical vapor deposition, i.e. abstraction of hydrogen terminations from the diamondoid surface.

1. Introduction

Nanodiamonds, with typical sizes ranging from 2 to 20 nm, have become the topic of intensive research because of their advantageous properties that make them useful for a wide range of applications [1]. In particular, diamond nanoparticles are non-cytotoxic, which makes them ideal for biolabeling [2] and as scaffolds for new drugs [3]. Moreover, nanodiamonds have shown promise for spintronic applications, namely quantum information and technology [4]. The most commonly used method to synthesize nanodiamonds is by detonation synthesis [5], however, this approach leads to non-uniform size distributions and non-well defined terminations such as graphitic shells, making it necessary to purify and oxidize the obtained nanodiamonds after synthesis [6].

On the other hand, diamond molecules—or diamondoids—could be considered as prototypical nanodiamonds. Diamondoids consist of sp^3-hybridized carbons that form rigid cage structures, the smallest being adamantane (Ada, $C_{10}H_{16}$). Theoretically, larger diamondoids can be formed by fusing a certain number n of adamantane units, which leads to clusters possessing structures that can be matched to the diamond lattice [7]. In contrast to nanodiamonds, diamondoids possess well-defined structures and surface terminations consisting of hydrogen. Diamondoids have been found to possess properties that make them suitable for many different applications, e.g., pharmaceutics and medicine [8,9], and because of their negative electron affinity [10], they are anticipated to be applicable as new optoelectronic materials [11]. Moreover, the bandgap of diamondoids can be changed by modifying their size or by attaching functional groups [12], or even by encapsulating other molecules inside their cages [13], which makes them suitable as possible building blocks for functional nanostructures [14] and molecular electronics [15].

While the existence of diamondoids with $4 < n \leq 11$ was demonstrated [16,17], with the exception of the 1st and 2nd members—adamantane ($n = 1$) and diamantane ($n = 2$)—the availability of diamondoids with $n > 2$ remains very limited. To date, the only higher diamondoids realized by organic synthesis are triamantane [18] and anti-tetramantane [19]. The main cause is that with increasing cage number, the amount of potential reaction steps and intermediates mounts exponentially [20]. Another reason is the lack of adequate precursors. Because of this, other possibilities for the synthesis of diamondoids have been investigated.

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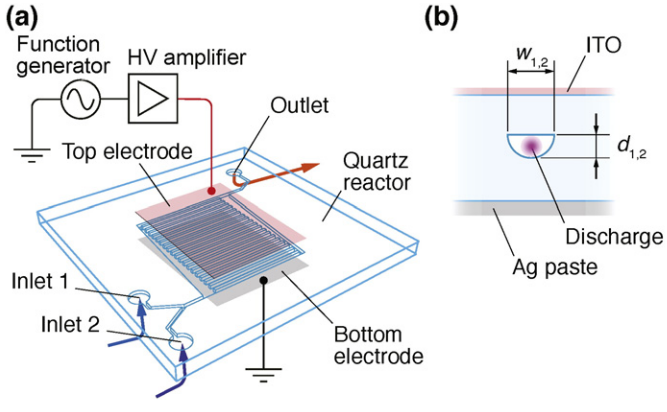

Fig. 1. Simplified schematics of experimental setup and cross-section of plasma microreactor. (a) Three-dimensional view of quartz microreactor containing 20 microchannels. Inlets 1 and 2 were used for the different types of source gases. (b) Cross-section of a single microreactor channel with indium-tin oxide (ITO) and silver (Ag) electric contacts on the top and bottom, respectively. The channel widths and depths of the reactors were different for the single (d_1, w_1) and multi-channel (d_2, w_2) reactors.

For example, larger diamondoids were synthesized from smaller ones by sealed tube pyrolysis, under conditions similar to natural oil cracking, however, the reaction yields were only of the order of ppm [21]. On the other hand, electric discharges generated in supercritical xenon enabled the fabrication of nanodiamonds [22] and diamondoids [23]. Diamondoids were also fabricated by pulsed laser ablation plasmas in supercritical fluids, namely xenon [24] and CO_2 [25]. Using high-pressure continuous flow microreactors [26,27], it was demonstrated that the diamondoid yields compared to those of conventional batch macroreactors can be increased, but carrying out high-pressure microplasma synthesis is relatively demanding. Because of this, we investigated alternative processing methods that could be realized at lower pressures.

There have already been a few studies on continuous flow synthesis of nanostructures at low and atmospheric pressures. For example, the rapid continuous gas phase growth of semiconductor nanowires has been demonstrated [28], and the growth speed and morphology were shown to be influenced by the flow rate and precursor size. In addition, continuous flow microplasma reactors operated at atmospheric pressure have been used for the synthesis of metallic nanoparticles [29,30] and nanodiamond [31].

In our previous research [32], we developed an atmospheric pressure continuous flow process using dielectric barrier discharge (DBD) plasma microreactors fabricated out of borosilicate glass. The main purpose of that work was to examine whether diamondoids could be produced by microplasmas at atmospheric pressure. For this, the smallest diamondoid (adamantane) was used as a nucleus, and the synthesis was realized by microplasmas generated in gases typically employed for chemical vapor deposition (CVD) diamond growth [33], namely argon, hydrogen, and methane. Another goal of that first study was to investigate the reaction mechanisms that might lead to diamondoid formation. For this, we analyzed reaction intermediates, specifically those that are likely to emerge during diamondoid growth. In particular, we investigated those substances that could arise when considering that diamondoids are formed by the abstraction of hydrogen, followed by the addition of methyl groups [27].

The present study is a continuation and extension of our previous work [32], with a focus on the influence of higher hydrogen concentrations on the diamondoid synthesis by DBDs generated at atmospheric pressure inside quartz microfluidic chip reactors.

The paper is organized as follows: in Section 2, we describe the experimental approach adopted for the synthesis of diamondoids, and the results and their discussion are presented in Section 3.

Table 1
Experimental conditions adopted for the diamondoid synthesis. The adamantane concentration ρ was estimated from its vapor pressure [34]. For a temperature of 323 K, the adamantane vapor pressure is about 0.11 kPa, which corresponds to an adamantane content in the gas of about 0.1%.

		Values (Single channel)				Values (Multi-channel)				
Gas composition (%)	Argon	59	60	89	90	59	60	89	90	60
	Methane	1	0	1	0	1	0	1	0	0
	Hydrogen	40	40	10	10	40	40	10	10	40
Total flow rate Q_{tot} (sccm)		6				10				1
Residence time t_{res} (ms)		8				75				754
Average temperature T (K)		323				323				323
Adamantane concentration ρ (g m^{-3})		5.6				5.6				5.6
Pressure P (kPa)		100				100				100
Applied voltage V_{appl} (kV$_{p-p}$)		8.10–9.50				5.25–6.55				6.30–6.75
Applied frequency f (kHz)		10				10				10
Plasma generation time t (min)		200				120				667

2. Experimental approach

The experimental setup employed for the experiments has already been described in detail elsewhere [32]. For the sake of completeness, Fig. 1(a) and (b) shows a simplified schematic of the modified custom-made microplasma reactor that was employed for the present study. Except for the new quartz fluidic microreactors and the gas compositions, the experimental setup—heating circuit, electric and optical emission spectroscopy measurements—was identical to the one used previously [32].

We used both single and multi-channel quartz microreactors, whose sizes were 30 × 30 mm^2, with a total thickness of 1.5 mm (Covalent Materials Corp.). The fluidic channels (width $w_1 = 500 \pm 50$, depth $d_1 = 100 \pm 10$ for the single channel reactors; width $w_2 = 400 \pm 50$, depth $d_2 = 200 \pm 20$ for the multi-channel reactors) were engraved by pulsed laser ablation, before fusing the two parts of the reactors by thermal bonding. In the case of the single channel reactors, the length of the top high-voltage (HV) electrode was 20 ± 1 mm, while for the multi-channel reactors, it was $10^{+1.0}_{-0}$ mm (the super- and subscripts indicating the tolerances[1]). The top HV electrode was fabricated from a transparent indium tin oxide film (ITO), which enabled visual observation of the microchannels and the plasma. Silver paste (Aremco-Bond™ 525) was used for the bottom, grounded electrode, and for the contacts on the ITO top electrode. For the experiments, the quartz microchip reactors were fixed inside a compression holder (Covalent Materials Corp.) that contained the gas inlets and outlets.

Table 1 lists the detailed experimental conditions. Prior to each synthesis experiment and before flowing the reactant gases into the cell, the system was evacuated using a rotary pump. Small amounts (8–10 mg) of adamantane powder (Ada, $C_{10}H_{16}$, purity >99.0%, Tokyo Chemical Industry Co., Ltd.) were placed inside a miniature stainless steel sample cylinder (internal volume 10 cm^3). The sample cylinder, the tubings of the inlets and the microreactor were all heated to an average temperature of 323 K, to increase the amount of adamantane in the gas phase. The adamantane concentration was estimated from the sublimation pressure p_{Ada} of adamantane, which is given by $\ln(p_{Ada}/\mathrm{kPa}) = 50.9129 - 8494.5 \cdot (T/\mathrm{K})^{-1} - 4.6395 \cdot \ln(T/\mathrm{K})$, which is valid for $T = 254$ K to 543 K [34]. The concentration of adamantane in the gas phase, ρ, was evaluated assuming that the feed gas-adamantane mixture is a perfect gas, and for $T = 323$ K, $\rho \sim 5.6$ g m^{-3}.

The adamantane was then introduced into the microreactor by mixing it with the source gases and by flowing it through the reactor, the flow rates being controlled by mass flow controllers. The gases used for the synthesis were argon (Ar, purity >99.999%), hydrogen

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[1] Positive tolerance of 1.0 mm, negative tolerance of 0 mm.