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# Low temperature catalytic reactivity of nanodiamond in molecular hydrogen

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ABSTRACT

In this paper, the reaction dynamics of hydrogen termination of nanodiamond annealed at low temperature (500 °C) in molecular hydrogen atmosphere is reported. *In-situ* residual gas analysis of nanodiamond particles (4–5 nm) during annealing/hydrogenation indicates $C_3$-radical desorption which incites a free radical reaction through the reduction of molecular hydrogen to atomic hydrogen. Consequently, as released atomic hydrogen facilitates C–H adsorption on the surface of nanodiamond which was confirmed using infrared spectroscopy. This explains how nanodiamond particles can play a key role in hydrogen ($H_2$) dissociation and be terminated by the hydrogen (H) at relatively low temperature.



## 1. Introduction

Nanometer-size diamond particles, first synthesized in 1963 [1] exhibit remarkable potential in diverse areas of research owing to their unique physical, optical and surface chemical properties [2–4]. Properties such as intense luminescence without photobleaching, high surface area and adaptive chemical reactivity, and non-cytotoxicity make nanodiamond (ND) attractive in various biomedical applications such as drug delivery, imaging or biolabeling etc. [4–7]. However, for optimal and specific drug or biomolecule loading, interactions and stability on diamond surface are still challenging tasks due to surface inhomogeneity and contamination [8]. A major obstacle to diamond particles being used in bio-systems is particle aggregation [9,10]. This process is mostly driven by graphitic or amorphous carbon structures and various oxygen related surface groups on the NDs surface which originate from their production, purification and irradiation to induce color centers [8,11]. To date, numerous efforts have been made to minimize these issues such as applying ultrasound, thermal annealing and a number of wet chemical treatments [12–15]. In practice, however, all of these approaches have drawbacks. For example, wet chemical acid treatments result in residual contamination [8,13], high temperature thermal treatments lead to the formation of $sp^2$ or amorphous carbon [16] as well as the degradation of $sp^3$ surface properties [17]. It has therefore become necessary to functionalize NDs as a prerequisite to integration with bioactive moieties.

Surface hydrogenation of nanodiamond in the gas phase is widely accepted to yield the least surface contamination with maximum homogeneity, narrowest colloidal particle size distribution and highest zeta potential, negative electron affinity, and is facile bio-chemical linker for further modification [18–21]. In addition to bio-applications, hydrogen termination has also become an essential treatment for producing diamond seeds for the growth of thin films [22,23]. A facile and cost-effective hydrogenation process for NDs is therefore of great interest to the scientific community. The conventional way of hydrogenation is via activation of molecular hydrogen with microwaves or hot filament (temperature ~2000 °C) [24,25]. Previously, the authors have shown an alternative way of successful hydrogenation of NDs via low temperature (500 °C) annealing in molecular hydrogen atmosphere [19]. It was demonstrated that the technique is predominately effective on small grain size (<10 nm) particles while less efficient on those of larger sizes.

The aim of this study is to investigate this mechanism of hydrogen termination on ND, i.e. how bond dissociation of molecular hydrogen can occur at such low temperatures (500 °C). As the surface of small grain size diamond particles is an abundant

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source of amorphous or disordered $sp^2$ structured carbon, it was assumed that these could have some catalytic effect. This technique is therefore less efficient for diamond powder of larger particles sizes. Under low temperature annealing, fragments of $sp^2$ carbon could be desorbed as gas phase carbon radicals such as $C_2$, $C_3$ etc. These reactive carbon species could transform hydrogen molecules to atomic hydrogen through the radical reaction and promote the formation of C–H structure on the diamond surface. In this work, the residual gas analysis *in situ* of ultra-dispersed diamond (UDD) particles during annealing clarified the existence of $C_3$ and its reaction with hydrogen ($H_2$) was confirmed by characterizing C–H feature on UDD using Fourier Transform infrared spectroscopy (FTIR).

## 2. Experimental

### 2.1. Methods

Synthetic ultra-dispersed diamond (UDD) particles of grain size 4–5 nm were sourced from Plasma Chem GmbH, Germany. Surface hydrogenation was carried out by annealing in molecular hydrogen at 500 °C as previously described [19]. The as-prepared hydrogenated UDD were transferred in air to a UHV chamber for IR measurements. For all FTIR measurements, untreated and hydrogen-treated UDD of concentration 2 mg/60 μl were dispersed in deionized water and drop cast onto Si-substrates with 20 μl of solution. They were then dried in vacuum for 24 h. To obtain larger volumes of specimen, drop casting was repeated two/three times over the previous layer. Hydrogen treated and untreated samples were annealed using electrically controlled heating device under UHV at various temperatures ranging from 100 °C to 800 °C without added $H_2$. The sample holder was prepared using Tantalum foil and wire. The samples were placed in the UHV chamber directly in the path of the infrared beam of the FTIR measurable. All IR measurements were performed *in-situ* at room temperature after the samples have been subject to various temperatures annealing. FTIR measurements were conducted *in-situ* at chamber pressure ~$4 \times 10^{-8}$ Torr and the spectra were collected using a Bomem MB154 FTIR with MCT-liquid nitrogen cooled detector. The resolution was set to be 4 $cm^{-1}$, and 400 scans were used. To avoid IR background signal from the elevated temperatures, annealed samples were cooled down to room temperature for the measurement. Ambient humidity around the FTIR was ~38–40%.

For mass spectroscopic analysis of the products of nanodiamond annealing in vacuum, an AMETEK Dycor System 200 Residual Gas Analyzer (RGA), attached to the UHV chamber, was used and spectra were collected during sample heating. During the measurements the base pressure was approximately $4.0 \times 10^{-8}$ Torr. A bare sample holder with Si substrate was annealed up to 800 °C for 30 min in UHV and the corresponding mass spectrum was recorded, the obtained spectrum served as the background signal. In the annealing experiments, samples were heated for 30 min for each temperature step ranging from 100 °C to 800 °C. The mass spectrum was recorded every 10 min for a certain temperature.

## 3. Results and discussion

Fig. 1(a) shows the FTIR spectrum of hydrogenated UDD measured at room temperature in the range of 600 $cm^{-1}$ to 3500 $cm^{-1}$ under UHV. The C–H stretching band, ranging from 2800 $cm^{-1}$ to 3000 $cm^{-1}$ provides a confirmative fingerprint of hydrogenation on nanodiamond [25]. This work will focus on this feature, the detail of which is depicted in Fig. 1(b). In the C–H spectrum of ultra-dispersed diamond (at room temperature), two broad peaks centered at 2878 $cm^{-1}$and 2945 $cm^{-1}$ are observed. These peaks are attributed hydrogen bonded to the C (111) and C (100) surfaces on the diamond particles for expected hydrogenation. In a typical C–H spectrum of hydrogenated nanodiamond, for example ~5 nm size, these peaks are at 2870 $cm^{-1}$ and 2940 $cm^{-1}$ with sharp and distinct shape [25]. The slight mismatch of the peak positions in the spectra can be explained by the variation of diamond grain size. The broad shape of the peaks is the result of surface contamination with hydrocarbons, originating from the exposure to atmosphere before the hydrogenated UDD was placed in the UHV chamber.

To understand the origin of C–H peaks, i.e. whether H has been terminated to $sp^2$ or $sp^3$ core carbon site, the hydrogenated sample was annealed at various temperatures ranging from 100 °C to 800 °C in vacuum (~$4.0 \times 10^{-8}$ Torr) without added $H_2$. The corresponding spectra in Fig. 1(b) show that as the temperature increases, the C–H peaks gradually sharpen and then become completely distinguished at 800 °C. This result clearly indicates desorption of hydrocarbons or disordered carbons bounded loosely on the surface of UDD and reveals the C–H adsorption on the surface of core $sp^3$carbons. The two peaks at 2878 $cm^{-1}$ and 2945 $cm^{-1}$ are C (110):H mixed with C (111):H and C (100):H respectively. The absence of C (111):H is the effect of domain size, where the size of C (111)-1 × 1 facets created on the nanodiamond are too small to provide the characteristic CH stretching feature in C (111). The C (111):H should appear at ~2835 $cm^{-1}$, and the redshift of the C (111):H has been explained as the domain size effect as the coupling of surface finite two-dimensional array of dynamic dipoles that predicts the red-shift of this feature [25].

Fig. 2 shows the mass spectroscopic analysis of desorbed gases while the untreated UDD was annealed at 500 °C in UHV (Chamber base pressure ~ $4.0 \times 10^{-8}$ Torr). In the background analysis, some common gases such as $H_2$ (m/z = 2, 1), $CO/N_2$ (m/z = 28), $H_2O$ (m/z = 18, 17), $CO_2$ (m/z = 44), and perhaps $CH_4/O$ (m/z = 16) were observed. These gases are a common background in UHV systems. In addition the peaks at m/z = 32 and 40 are attributed to $O_2$ and Ar which are also common at relatively low vacuum (~$10^{-8}$ Torr) [26–28]. As mass spectrometry allows passing charged particles with defined q/m ratio (charge/mass), some of the doubly charged ions or so called cracked fragments of $^{28}CO/N_2$ and $^{40}Ar$ respectively are obvious. Some heavy hydrocarbon fragments, $C_3H_3$ (m/z = 39), $C_3H_4$ (m/z = 41), $C_3H_5$ (m/z = 42) and $C_3H_7$ (m/z = 43), are present with negligible intensity which could originate from unavoidable oil contamination in the vacuum system, although the chamber was baked out at 150 °C for 7 days continuously before the experiment was conducted [26].

The peak at relatively low intensity m/z = 12 is attributed to a carbon signal which may also result from pump oil contaminants. In addition, there are some shoulder peaks around the larger peaks such as $H_2O$, $CO/N_2$ which could be the fragments of other dominant gases dissociated by the spectrometer filament [26,27]. Compared to the background, in the spectrum of UDD annealed at 500 °C two distinct peaks are observed at m/z = 36 and 38, displayed in the inset of Fig. 2. It can be concluded that these peaks are attributed to $C_3$ radical, a reactive carbon species, and its hydrocarbon $C_3H_2$ [29]. This result indicates that as-received UDD particles contain disordered/$sp^2$ carbon groups on their surface which promote the desorption of carbon $C_3$ radical during annealing.

The process of $C_3$ desorption can be followed through the opposite of $C_3$ insertion in carbon material thin film growth as described elsewhere [30]. We propose that this reactive radical is responsible for the dissociation of $H_2$ by inducing free radical reaction during hydrogen treatment of UDD at relatively low temperatures.

We have proposed that the observed $C_3$ radical might play a key role in creating atomic hydrogen by inducing a free radical reaction