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Plasma-assisted purification of nanodiamonds and their application for direct writing of a high purity nanodiamond pattern

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ABSTRACT

In this paper, we demonstrate a new approach for purifying nanodiamonds using an atmospheric-pressure plasma jet. Oxygen gas is continuously dissociated in the plasma jet and generates reactive oxygen, which plays a key role in removing non-diamond carbon, including graphite and amorphous carbon. The purification process was evaluated by UV-Raman (325 nm) and X-ray photoelectron spectroscopy. This technique was applied to create a high purity nanodiamond pattern in the polymeric system of polyvinyl alcohol (PVA) and nanodiamonds using a localized plasma jet. Overall, the plasma-assisted purification of nanodiamonds enabled to the fabrication of patterns with low electrical conductivity and high thermal conductivity.

1. Introduction

Nanodiamond (ND) powder has been of great interest because of its extreme hardness, high Young's modulus, chemical stability, high thermal conductivity, high electrical resistivity, and biocompatibility [1]. These attributes enable the use of ND in a large number of potential applications such as biocompatible composites [1], drug delivery systems [2–4], stable catalyst supports [5], and chemically resistant chromatographic materials [6].

Commercially available ND has mainly been produced by detonation synthesis, but the detonation soot contains many impurities, including metallic compounds, graphite, and amorphous carbon. Therefore, it is essential to remove these species to obtain high purity ND for application. The most common approach is the wet chemical process [6–10]. A strong acid at an elevated temperature easily removes metallic compounds and non-diamond carbon, including graphite and amorphous carbon [7,8]. However, the process is dangerous and expensive because of the need for corrosion-resistant equipment and the cost of chemical waste disposal [11,12]. Recently, an air-oxidation process was developed as an environmentally friendly process for the production of high purity ND powder [11]. Although the air-oxidation process has been employed by some ND manufacturers, it still requires a long processing time of 5–48 h [11,13]. Ozone-enriched air oxidation has also been demonstrated in a previous study [6,12,14,15]. Although the technology for purification with ozone is broadly used in the industry, residual ozone is toxic and causes aggressive destruction of substances [11].

Compared with other techniques, the plasma-based technique may offer a unique advantage because non-equilibrium reactions can be induced at low temperatures and with high purity products [16,17]. Plasmas are characterized by a complex physiochemical environment that includes electrically excited atoms and molecules, charged species (e.g., ions and electrons), and hot gases. Recently, an atmospheric-pressure plasma jet was employed for the synthesis and patterning of nanomaterials. For example, electrons in the plasma initiate the electrochemical reaction and form nanoparticles [18,19], the atomic hydrogen generated by the plasma reduces the oxidation status of graphene oxide [20], and the localized plasma creates arbitrary patterns of metal nanoparticles in a polymeric film [21,22].

In a previous study, interactions such as ozone oxidation [6,12,15,23] and thermal oxidation [11] were used to purify non-diamond carbon, including graphite and amorphous carbon. Therefore, the generation of reactive oxygen by the plasma could enable effective purification of ND. However, the purification

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process requires selective oxidation of non-diamond carbon, since this is critically related to the yield of purified ND. Here we demonstrate a plasma-assisted ND purification process that allows for the selective removal of non-diamond carbon at atmospheric pressure and ambient conditions. The basic idea is that oxygen (O_2) plasma generates reactive oxygen and oxidizes non-diamond carbon. To demonstrate the role of reactive oxygen, we designed a control experiment using pure helium (He) plasma and compared the results with those obtained using the O_2 plasma. The ND purity was characterized by UV-Raman (325 nm) spectroscopy; a degree of purity comparable to that when using the wet chemical method was successfully achieved by the O_2 plasma treatment. In addition, we applied the ND purification technique to a direct writing process, to create an arbitrary pattern of pure ND.

2. Experimental methods

2.1. Materials

ND black powder (54.50% purity) and ND gray powder (98.30% purity)—produced by detonation synthesis—were supplied by NaBond Technologies Co. Ltd (Hong Kong). The properties and the composition of the ND samples are summarized in Table S1. A pellet die was custom built using a tungsten rod (W, $\phi = 4$ mm) and a titanium rod (Ti, $\phi = 10$ mm) purchased from Goodfellow. Polyvinyl alcohol (PVA, MW = 100000) and D-(-)-fructose were supplied by Sigma Aldrich. Finally, Vulcan XC-72 carbon black was donated by Cabot Corporation.

2.2. Methods

The atmospheric-pressure plasma jet was generated by single electrode. It consist of an inner electrode (tungsten rod, $\phi = 1.6$ mm), which is coupled to the power source, and the localized plasma was formed through a tip-nozzle of a glass tube. The carrier gas was coupled to the glass tube and controlled by a mass flow controller (MFC). The plasma-assisted ND purification was carried out with an O_2 plasma (5 sccm of O_2 and 500 sccm of He), which was compared with a pure He plasma (500 sccm). Before He plasma treatment, to minimize the effects of ambient oxygen, the apparatus was purged with He gas at 500 sccm for 1 h. The atmospheric-pressure plasma was driven by a low frequency (25 kHz) sinusoidal high-voltage source with 5 kV of an input voltage. For the experiments, an ND pellet was made by pressing ND black powder into a 4 mm pellet die, which was then fixed on a Si substrate using Kapton tape. Afterward, the plasma treatment was carried out with a plasma 1 mm in width and with a 3 mm gap between the substrate and the glass tip; these conditions were maintained during the experiments (See Fig. 1(a)). To make an ND/polymer composite film, 0.1 g (0.1 wt%) of ND black or carbon black was dispersed in DI water and 0.05 g (0.05 wt%) of D-(-)-fructose was added as a stabilizer for the ND nanoparticles. After 5 min of

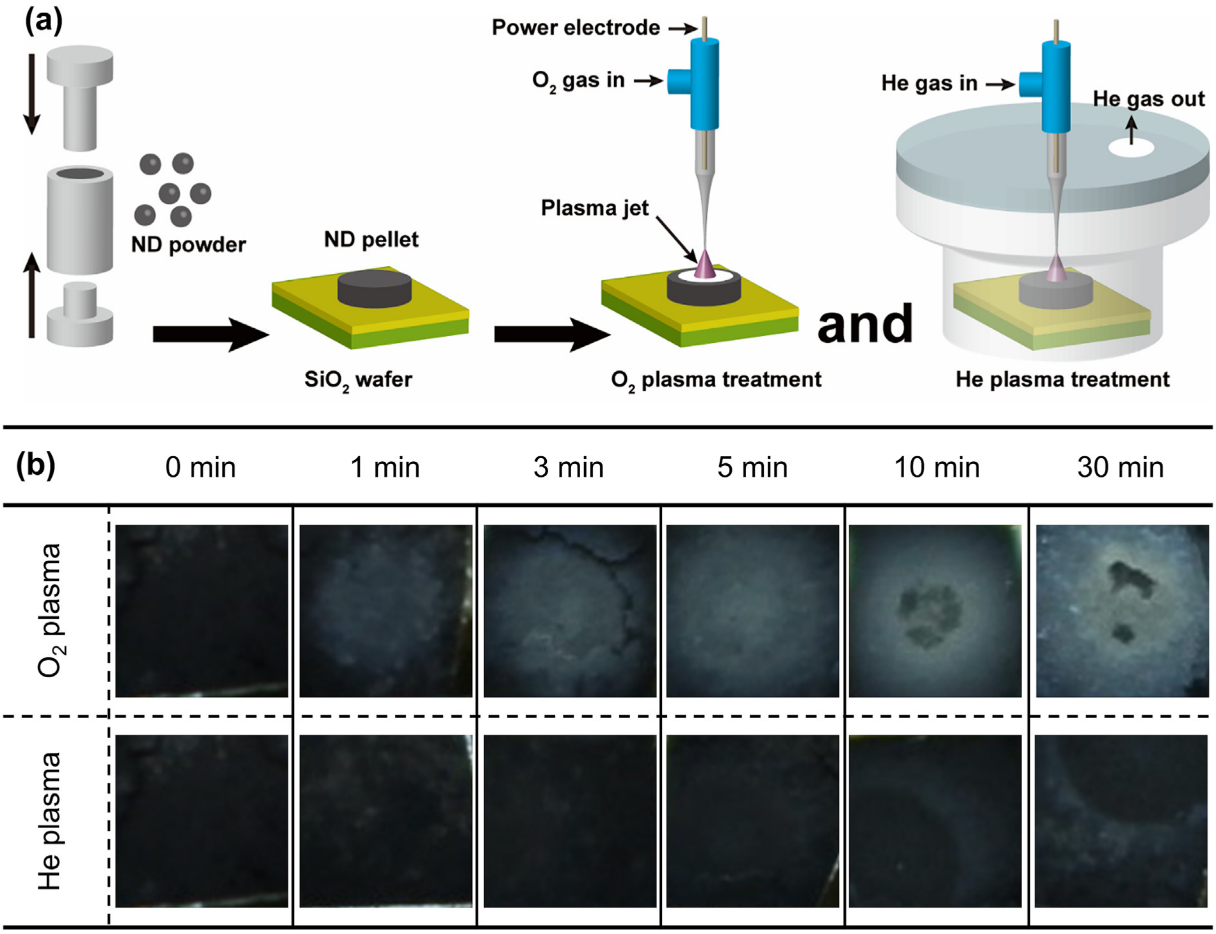

Fig. 1. (a) Schematic of plasma-assisted ND purification. ND black powder was pressed into a die and then the ND pellet was fixed on the SiO_2 substrate using Kapton tape. The plasma-assisted purification of nanodiamond by O_2 plasma and He plasma at various elapsed times. (b) Optical images of the purified ND pellet were obtained as a function of time based on plasma-assisted purification. (A colour version of this figure can be viewed online.)