

Chemical modification of diamond powder using photolysis of perfluoroazooctane

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Photolysis of perfluoroazooctane with diamond powders led to chemical modification of the surface with the introduction of perfluorooctyl ester and ether functional groups, the presence of which was confirmed by means of FT-IR, XPS and ^{19}F NMR measurements.

Diamond is a material which has been widely investigated because of its various unique properties such as electrical, thermal and mechanical properties.¹ Chemical modifications of diamond surfaces have been expected to lead to improvement of its behavior.²⁻⁴ There have been recent studies on the introduction of organic functional groups such as benzoyloxy,⁵ cyano⁶ and alkyl substituents⁷ on the surfaces of diamond films and powders terminated with hydrogen or oxygen by using photo- and thermochemical methods.

On the other hand, perfluoroalkyl-containing organic compounds have attracted much attention in the fields of medicinal chemistry and materials science because of their unique properties derived from the presence of fluorine atoms, namely biological activities and water/oil repellent properties.⁸ Previously we reported that photolysis of perfluoroazooctane (**1**) gave perfluorooctyl radicals effectively in solutions under mild conditions for perfluoroalkylation of organic compounds.⁹ Introduction of substituents containing fluorine atoms would result in improvement of the behavior of diamond surfaces, *e.g.* enhanced lubricity and stability under extreme conditions.¹⁰ To date, fluorination of diamond surfaces has been studied by use of F_2 gas,¹¹ CF_4 plasma¹² and X-ray irradiation.¹³ These methods have problems involving handling of the reactions and make it necessary to use special vessels. In this paper, we report on a useful method for chemical modification of diamond powders with perfluoroalkyl substituents by using photolysis of **1** under mild conditions.

A typical experiment is described as follows. Azo compound **1** (3.7 mg) in perfluorohexane (4 ml), prepared according to the literature,¹⁴ was irradiated with a low-pressure mercury lamp for 8 h at room temperature in the presence of diamond powder (10 mg) purchased from Tomei diamond industry Co., Ltd. (MD500, 500 nm) and under an argon atmosphere with stirring. After removal of the perfluorohexane solution from the reaction mixture, the residual powders were washed with perfluorohexane and hexane. The washed powders were analyzed with microscopic FT-IR, X-ray photoelectron and solid-state ^{19}F NMR spectrometers.

Fig. 1a, b shows the FT-IR spectra of the diamond powders before and after irradiation of **1**. The sample after the photoreaction exhibits a new peak at 1196 cm^{-1} assigned to C–F stretching bands and a red shift of the carbonyl stretching vibration from 1792 to 1751 cm^{-1} . It is known that the surface of untreated diamond powder has carbonyl groups such as carboxylic acids and cyclic ketones.^{15,16} These results suggest that the perfluorooctyl radical generated by photolysis of **1** abstracted hydrogen from the carboxylic acid group, and then the reaction of another C_8F_{17} radical with the carboxylic radical gave perfluorooctyl ester groups attached on the surface of diamond powders (Scheme 1).

In order to confirm the formation of the perfluorooctyl ester functionality on the diamond surface, the fluorinated material

was treated under hydrolysis conditions in aq. NaOH. The FT-IR spectrum of the hydrolyzed material showed that the ester group reverted to a carboxylic acid with a peak due to the carbonyl group of the untreated diamond powder as shown in Fig. 1c. However, the C–F stretching bands remained around 1200 cm^{-1} and peaks at 2930 and 2856 cm^{-1} were observed in the region of C–H stretching bands after hydrolysis. These results reveal that perfluorooctylation and hydrogenation of cyclic ketones on the surface of the diamond powders occurred to form perfluorooctyl ether groups which could remain

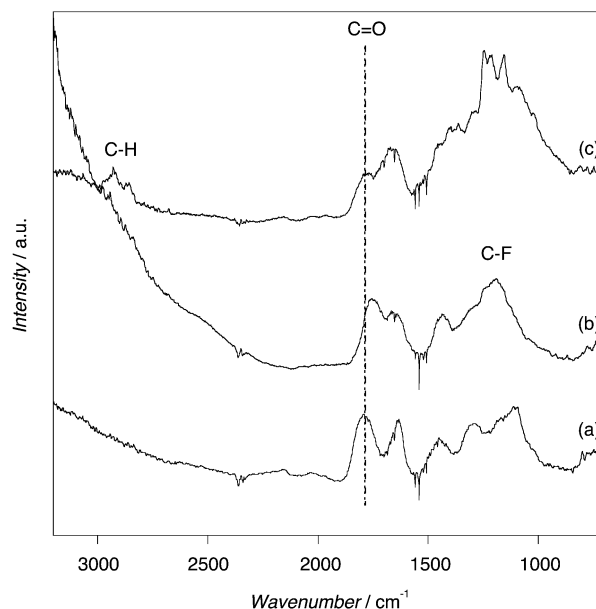
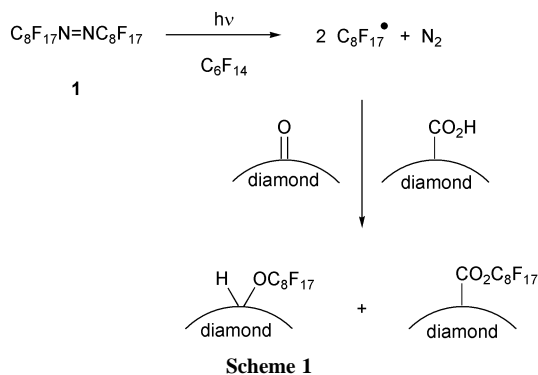


Fig. 1 FT-IR spectra of (a) untreated diamond powders, (b) diamond powders after perfluoroalkylation treatment and (c) hydrolyzed fluorinated powders.



unaltered under hydrolysis conditions, accompanied by esterification of the diamond powders as shown in Scheme 1.

As shown in Fig. 2, XPS spectra of the diamond powders were measured before and after perfluorooctylation, showing that a new peak at 694.4 eV of fluorine 1s was observed after irradiation. In the carbon 1s region, a strong peak at 293.1 eV is found with higher binding energies ascribed to carbon atoms bound to fluorine atoms compared with the untreated diamond powders. Additionally, binding energies of 534.6 and 538.0 eV of oxygen 1s were also observed due to C=O and C–O, respectively.

Moreover, the presence of the fluorinated surfaces on diamond powders was characterized by solid-state ^{19}F NMR for further confirmation. The spectrum shown in Fig. 3 exhibited signals at $\delta -79.2$ ppm ($-\text{OCF}_2-$) and $\delta -119.2$ ppm ($-\text{CF}_2-$). The lack of signals due to $-\text{NCF}_2-$ moieties shows that introduction of perfluorooctyl groups on diamond surfaces occurred, not physical adsorption of **1**.

Photolysis of azo compound **1** with diamond powder led to chemical modification of the surface forming perfluorooctyl ester and ether functional groups. The introduction of the perfluoroalkyl substituents was confirmed by FT-IR, XPS and ^{19}F NMR measurements. Application of this method to diamond and related materials thin films as a lubricant is under investigation.

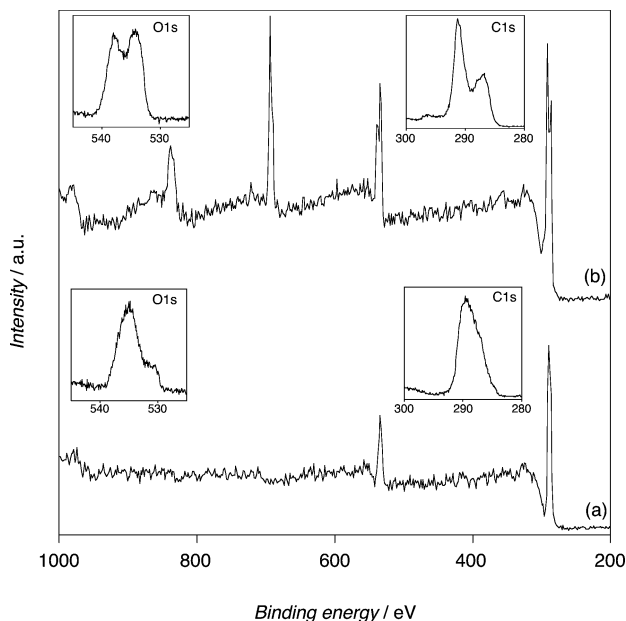


Fig. 2 XPS spectra of diamond powders (a) before and (b) after irradiation with perfluoroazooctane (**1**). The inset shows the carbon 1s and oxygen 1s spectra of the untreated and fluorinated diamond powders.

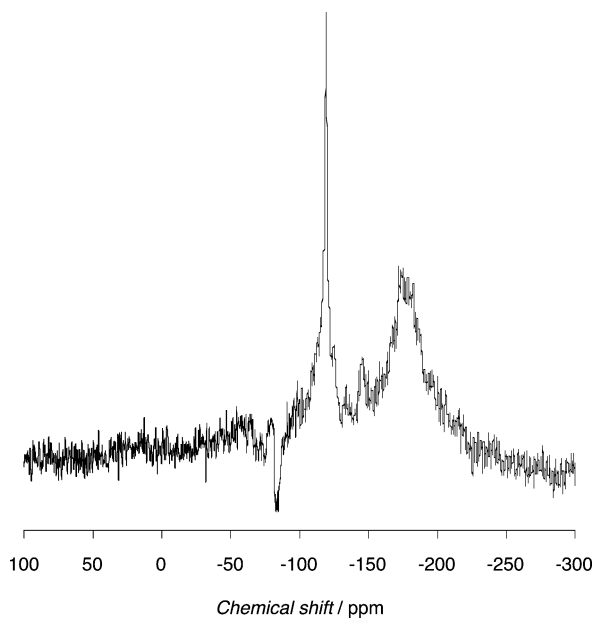


Fig. 3 ^{19}F NMR spectrum of fluorinated diamond powders.

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