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Chemical modification of diamond surface with various carboxylic acids by radical reaction in liquid phase

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Abstract

Chemical modification of diamond surface with carboxylic acid was attempted by the radical reaction of radical initiator under mild conditions. The peak intensity assigned to the aromatic C–H bond decreased by increasing the number of the benzene ring in carboxylic acid. The number of the carboxylic acid introduced on diamond surface decreased by increasing the number of the benzene ring in carboxylic acid. One of the reasons for this decrement should be the steric hindrance. The zeta potential was not affected by the treatment with the aromatic carboxylic acids. The diamond powders treated with carboxylic acids, which are fluorescent materials, were irradiated with UV light. However, all the samples did not fluoresce because the number of the carboxylic acid introduced on diamond surface is small.
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Keywords: Diamond properties and applications; Diamond surface; Radical reaction; Surface modification

1. Introduction

Diamond is a promising industrial material because of its properties, such as hardness, large band gap, transparency over a wide wavelength region, high thermal conductivity (most of these functions are physical properties). Much research has been performed regarding the application of diamond in various industrial fields [1].

All organic materials contain carbon atoms in their molecular structures. It is known that most organic functional groups have various functions, such as ion exchange, molecular recognition, DNA immobilization, formation of covalent bonding and so on (most of these functions are chemical properties).

Therefore, if the diamond surface is controllably modified with organic functional groups, we can make a new organic–inorganic functional material, which possesses the physical functions of diamond and the chemical functions of the organic functional group.

So far, several studies have focused on the chemical modification of diamond surface [2–12]. However, most of the experiments in these studies were performed in the vapor phase. Moreover, very few papers have reported the organic chemical reaction on a diamond surface [5,6], and our group has been the only one to elucidate the organic chemical reactivity on diamond [13–16].

Most of the research works related to the diamond surface has been performed from a physical standpoint (the theory and the technique of surface physics [17,18]). Highly expensive equipment (high vacuum apparatuses, highly sensitive spectroscopy, and high purity materials, etc.) has been used in these studies. However, these highly expensive experimental apparatuses are not practical in industrial applications. In contrast, most of the experiments of chemical reactions do not require the use of such expensive equipment. Therefore, a chemical reaction process is more suitable for industrial applications. Moreover, the technology of chemical engineering can be used in the application of chemical reactions to chemically modify a diamond surface.

We have already reported the chemical modification of the diamond surface with aliphatic carboxylic acids [19]. In this study, we report the chemical reactivity between the aromatic carboxylic acid and a diamond surface.

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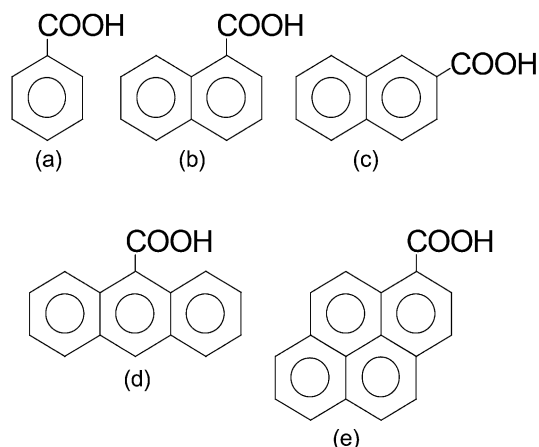*E-mail address:* tsubota@kmt-iri.go.jp (T. Tsubota).

Fig. 1. Chemical structures of the carboxylic acid used in this study (a) benzoic acid; (b) 1-naphthoic acid; (c) 2-naphthoic acid; (d) 9-anthracene carboxylic acid; (e) 1-pyrene-carboxylic acid.

2. Experimental

Commercial diamond powder (Tomei diamond MD500; average diameter 500 nm) was used as the diamond substrate in this study. First, the diamond powder was washed using mixed mineral acids (HF + HNO_3, HNO_3 + H_2SO_4), and then was heated in H_2 gas. These treatment conditions have been reported elsewhere [13–16].

The apparatus for the chemical reaction process has been described elsewhere [15]. Hydrogenated diamond powder (0.1 g), lauroyl peroxide (0.05 g), and aromatic carboxylic acid (benzoic acid (Fig. 1a), 1-naphthoic acid (Fig. 1b), 2-naphthoic acid (Fig. 1c), 9-anthrace-necarboxylic acid (Fig. 1d), 1-pyrenecarboxylic acid (Fig. 1e) are suspended in toluene (5 ml). Argon gas was bubbled into the suspensions while these were heated at 75 °C for 2 h in order to activate the radical initiator. After this chemical reaction process, the diamond powders were washed a few times with organic solvent, such as chloroform and so on, and then dried in a vacuum dryer. The dried diamond powders were re-washed a few times with chloroform or another solvent for ensuring the complete removal of residuer.
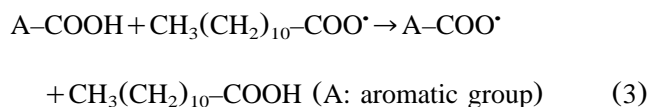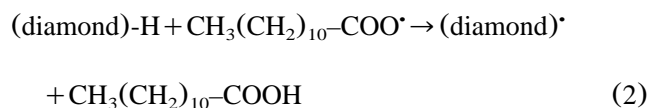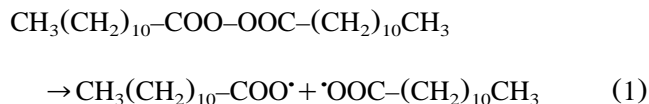
The surface of the diamond powder was characterized by means of diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy (JASCO FT/IR-700). A field emission type scanning electron microscope (FE-SEM) (HITACHI S-4000) was used to observe the microstructure of the diamond particles. BET measurement (QUANTACHROME AUTOSORB-1) was performed in order to evaluate the specific surface area of the diamond powder.

3. Results and discussion

The diamond particles used in this study had multi-faceted surfaces, and the specific surface area of the diamond powder was 9.94 m^2 g^{-1} as has been reported elsewhere [15].

The IR spectra for the diamond powders treated with various aromatic carboxylic acids are shown in Fig. 2. So far, we have already reported that the organic radical species derived from diacyl peroxide can abstract the hydrogen atom on diamond surface [15] and that aliphatic carboxylic acids can be introduced on diamond surface [19]. From the results of these studies, we can presume that the chemical reaction in this study is as follows,

$$CH_3(CH_2)_{10}–COO–OOC–(CH_2)_{10}CH_3$$

$$\rightarrow CH_3(CH_2)_{10}–COO^{\bullet} + {}^{\bullet}OOC–(CH_2)_{10}CH_3 \quad (1)$$

$$(diamond)\text{-}H + CH_3(CH_2)_{10}–COO^{\bullet} \rightarrow (diamond)^{\bullet}$$

$$+ CH_3(CH_2)_{10}–COOH \quad (2)$$

$$A–COOH + CH_3(CH_2)_{10}–COO^{\bullet} \rightarrow A–COO^{\bullet}$$

$$+ CH_3(CH_2)_{10}–COOH \text{ (A: aromatic group)} \quad (3)$$

$$(diamond) + A–COO^{\bullet} \rightarrow (diamond)\text{-}OOC–A \quad (4)$$

We have reported that the radical species derived from benzoyl peroxide has a stronger ability of the hydrogen abstraction on the diamond surface than that derived from lauroyl peroxide [20]. However, when benzoyl peroxide is used as the radical initiator, we cannot identify the origin of the aromatic C–H bond on
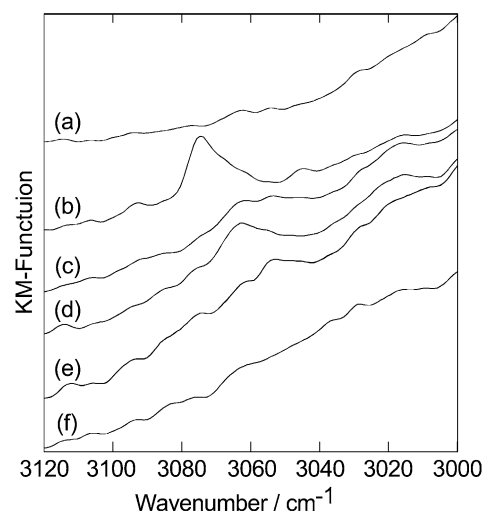

Fig. 2. IR spectra for the diamond powders treated with aromatic carboxylic acids (a), treated with only lauroyl peroxide; (b), treated with benzoic acid; (c), treated with 1-naphthoic acid; (d), treated with 2-naphthoic acid; (e), treated with 9-anthracenecarboxylic acid; (f), treated with 1-pyrenecarboxylic acid.
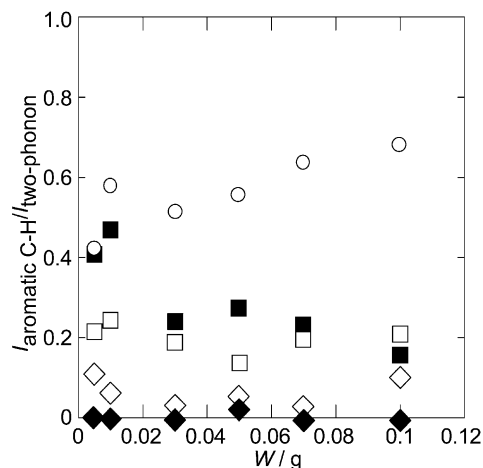
Fig. 3. Dependences of the ($I_{\text{aromatic C–H}}/I_{\text{two-phonon}}$) value on the amount of the added aromatic carboxylic acid ○, treated with benzoic acid; □, treated with 1-naphthoic acid; ■, treated with 2-naphthoic acid; ◇, treated with 9-anthracenecarboxylic acid; ◆, treated with 1-pyrenecarboxylic acid.

Fig. 4. Dependences of the ($I_{\text{aromatic C–H}}/I_{\text{two-phonon}}$) value on the reaction time ○, treated with benzoic acid; □, treated with 1-naphthoic acid; ■, treated with 2-naphthoic acid; ◇, treated with 9-anthracenecarboxylic acid; ◆, treated with 1-pyrenecarboxylic acid.

diamond surface. Therefore, we used lauroyl peroxide as the radical initiator for this study. After the chemical reaction process, no peaks assigned to the aromatic C–H bond appeared in the IR spectrum for the diamond powder treated with only lauroyl peroxide. However, the peaks assigned to the aromatic C–H bond appeared at more than 3000 cm^{-1} in all the IR spectra treated with aromatic acid, as shown in Fig. 2.

It is known that the peak intensity at 2160 cm^{-1}, which is assigned to two-phonon adsorption, can be applied as an initial standard for the relative quantification of the diamond surface condition [15]. Dependences of the ($I_{\text{aromatic C–H}}/I_{\text{two-phonon}}$) value on the amount of the added aromatic carboxylic acid are shown in Fig. 3. The intensity of the peaks assigned to the aromatic C–H bond decreased with increasing the number of the benzene ring in the carboxylic acid used in the reaction process. As for all the diamond powders treated with aromatic acids, the addition of more than 0.01 g is useless for the increase in the ($I_{\text{aromatic C–H}}/I_{\text{two-phonon}}$) value. Dependences of the ($I_{\text{aromatic C–H}}/I_{\text{two-phonon}}$) value on the reaction time are shown in Fig. 4. The intensity of the peaks assigned to the aromatic C–H bond
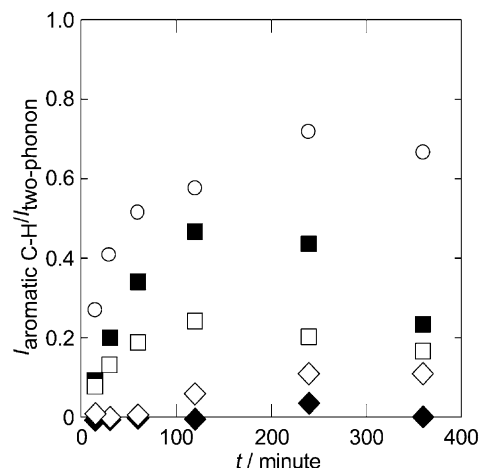
decreased with increasing the number of the aromatic ring in the carboxylic acid used in the reaction process. The ($I_{\text{aromatic C–H}}/I_{\text{two-phonon}}$) value increased with increasing reaction time up to approximately 120 min, and then slightly decreased. The reason for the decrement of the ($I_{\text{aromatic C–H}}/I_{\text{two-phonon}}$) value over 120 min is unclear. However, it was clear that the long reaction time is useless for the increase in the amount of the carboxylic acid introduced on diamond surface.

The ($I_{\text{aromatic C–H}}/I_{\text{two-phonon}}$) values are listed in Table 1. The number of the aromatic C–H bond in carboxylic acids depends on the kind of carboxylic acid. Therefore, if the peak intensity per one C–H bond is equal, the relative amount of the functional group introduced on diamond surface is estimated by the (X/N) value (X: $I_{\text{aromatic C–H}}/I_{\text{two-phonon}}$, N: the number of the aromatic C–H bond in carboxylic acid). The relative (X/N) value of the diamond powder treated with 1-naphthoic acid is 0.30. However, that of the diamond powder treated with 2-naphthoic acid is 0.58. If the chemical reaction proceeded as shown in Eqs. (1)–(4), the steric hindrance of 1-naphthoic acid is larger than that of 2-naphthoic acid against diamond surface. Moreover, the steric hindrance of 9-anthracenecarboxylic acid is larger than that

Table 1
The peak intensities at more than 3000 cm^{-1} for the diamonds treated with carboxylic acid

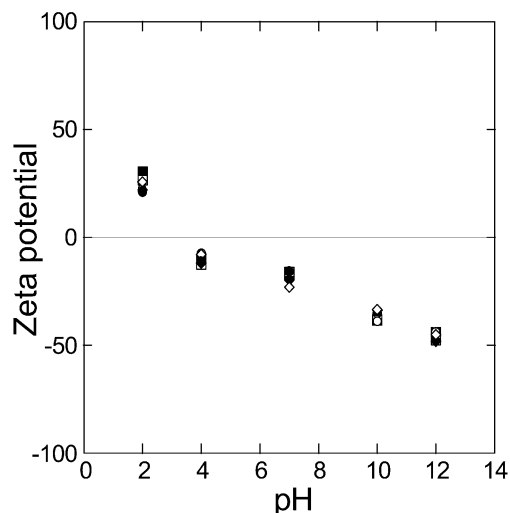|	X: ($I_{\text{C–H}}/I_{\text{two-phonon}}$)	N: the number of the C–H bond	X/N	Relative value
benzoic acid	0.58	5	0.12	1
1-naphthoic acid	0.24	7	0.035	0.30
2-naphthoic acid	0.47	7	0.067	0.58
9-anthracenecarboxylic acid	0.061	9	0.0068	0.058
1-pyrenecarboxylic acid	0.0037	9	0.00041	0.0036

Fig. 5. Dependences of the values of zeta potential in water for the diamond powders treated with carboxylic acid on pH ●, hydrogenated diamond; ○, treated with benzoic acid; □, treated with 1-naphthoic acid; ■, treated with 2-naphthoic acid; ◇, treated with 9-anthracenecarboxylic acid; ◆, treated with 1-pyrenecarboxylic acid.

of 1-naphthoic acid against diamond surface. Therefore, the order of the relative (X/N) value should be explained by the steric hindrance, as for 1-naphthoic acid, 2-naphthoic acid, and 9-anthracenecarboxylic acid. The steric hindrance of 1-pyrenecarboxylic acid should not be so much larger than that of 9-anthracenecarboxylic acid against diamond surface. The relative (X/N) value of the diamond powder treated with 1-pyrenecarboxylic acid is greatly smaller than that of the diamond powder treated with 9-anthracenecarboxylic acid. The steric hindrance may not be the only reason for the difference of the relative (X/N) value, as for 9-anthracenecarboxylic acid and 1-pyrenecarboxylic acid.

Dependences of the values of zeta potential in water for the diamond powders treated with carboxylic acid on pH are shown in Fig. 5. The value of zeta potential was independent of the kind of the used carboxylic acid. Moreover, the value of zeta potential of hydrogenated diamond powder, which is the starting material of this study, was similar to those of all the treated diamond powders.

It is known that 1-naphthoic acid, 2-naphthoic acid, 9-anthracenecarboxylic acid, and 1-pyrenecarboxylic acid are fluorescent materials. The diamond powders treated with these fluorescent materials were irradiated with UV light (approx. 350 nm). However, all these treated diamond powders did not fluoresce. So far, we have reported that benzoyl peroxide is more effective for the hydrogen abstraction reaction of diamond surface than lauroyl peroxide [20]. We can presume that the amount of the carboxylic acid introduced on diamond surface treated with benzoyl peroxide is larger than that

treated with benzoyl peroxide. Therefore, the diamond powders treated with these fluorescent materials and benzoyl peroxide were also irradiated with UV light (approx. 350 nm). However, all these treated diamond powders did not fluoresce. The reason for no fluorescence must be that the numbers of the carboxylic acid introduced on diamond surface were small.

4. Conclusions

Diamond surface was reacted with aromatic carboxylic acid using lauroyl peroxide under mild condition. The peak intensity assigned to the aromatic C–H bond decreased with increasing the number of the benzene ring in carboxylic acid. The evaluated amount of the carboxylic acid on diamond surface was decreased with increasing the number of the benzene ring in carboxylic acid. One of the reasons for this decrement should be the steric hindrance of carboxylic acid. The values of zeta potential in water for these diamond powders unchanged after the treatment with the aromatic carboxylic acids. The diamond treated with 1-naphthoic acid, 2-naphthoic acid, 9-anthracenecarboxylic acid, or 1-pyrenecarboxylic acid, which are fluorescent materials, were irradiated with UV light. However, all these diamonds did not fluoresce. The reason of no fluorescence should be that the number of the carboxylic acid introduced on diamond surface is small.

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