



Chemical modification of diamond surface with $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) using benzoyl peroxide

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ABSTRACT

The chemical reactivity of a hydrogenated diamond surface with $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) when using benzoyl peroxide was investigated in this study. After the reaction processes the shapes of the IR spectra changed. It was confirmed from the XPS measurements that halogen atoms existed on the samples after the reaction process. The position of the IR peak at $ca. 700\text{ cm}^{-1}$ depended on the kind of halogen in $X-(C_6H_4)-COOH$. Moreover, the peak position depended on the kind of constitutional isomer, that is, ortho-, meta-, or para-. It was confirmed from the experimental results of this study that halogen-containing organic functional groups can be introduced onto a diamond surface.

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1. Introduction

In the past, some research has been carried out related to chemical reactions of the diamond surface. The chemical reactivity of the diamond surface with gaseous materials has recently been investigated to elucidate the growth reaction of CVD diamond. Ando et al. have investigated the adsorption of various elements onto the a diamond surface [1,2]. Most recent studies related to chemical reactions on the diamond surface have been aimed at functionalization of the diamond surface. In these studies, chemical reactions in the liquid phase have often been used for the surface reaction. Nakamura et al. and Strother et al. have reported surface reforming of diamond using a photochemical reaction [3–5]. Matrab et al., Marutani et al., and Li et al. have reported functionalization of a diamond surface by using atom transfer radical polymerization (ATRP) [6–8]. Kruger et al., Lee et al., and Lafosse et al. used nano-sized diamond particles as the substrate for chemical modification [9–12]. Ikeda et al., Saito et al. and Miller et al. have reported the results of studies on the chemical reaction of a diamond surface via a Cl-terminated surface [13–15]. Azambre et al. have investigated the reactivity of a diamond surface with NO_2 [16]. Pertrick et al. have investigated potassium adsorption on hydrogen- and oxygen-terminated diamond (100) surfaces [17]. Goeting et al. have reported surface reforming of a diamond electrode [18]. Visbal et al. have reported treatment of a diamond surface with chloroform [19]. We have been studying the chemical reactions of diamond surfaces with organic radicals [20–27], and have reported that benzoyl peroxide is effective for carrying out chemical reactions of a hydrogenated diamond surface [27]. In the present study, we investigated the chemical reactions of a hydrogenated diamond surface with $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$),

using benzoyl peroxide to introduce a wide variety of organic functional groups onto a diamond surface.

2. Experimental

Commercial diamond powder (average particle diameter: 500 nm) was used as the diamond substrate for this study. The diamond powder was washed with mixed acid ($HF + HNO_3$) at room temperature for 4 h and then rinsed with distilled water. After drying, the diamond powder was washed with mixed acid ($H_2SO_4 + HNO_3$) at $80\text{ }^\circ\text{C}$ for 4 h and then rinsed with distilled water. The diamond powder treated with acids was heated at $900\text{ }^\circ\text{C}$ for 5 g in an H_2 flow for the synthesis of hydrogenated surface diamond powder. The hydrogenated surface diamond powder (0.1 g), BPO (benzoyl peroxide) (0.05 g), and $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) (0.05 g) were stirred in benzene (5 ml) by Ar bubbling, and the flask containing the solvent was then heated in an oil bath at $75\text{ }^\circ\text{C}$ for 2 h. The chemical structures of $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) are shown in Fig. 1. The detailed experimental conditions for the chemical reaction process have been reported previously [27]. After the chemical reaction process, the diamond powder was washed with benzene and then dried in a vacuum chamber. After this vacuum process, the diamond powder was washed with benzene and then dried in a vacuum chamber. After the vacuum drying process, the diamond surface conditions were measured by FT-IR. XPS measurements were also carried out to confirm the existence of N atoms on the diamond surface. The details of the measurement method have been previously reported [27].

3. Results and discussion

The IR spectra for the diamond powders reacted with $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) (ortho position) and benzoic peroxide are shown in Fig. 2. We have previously reported that the radical species derived

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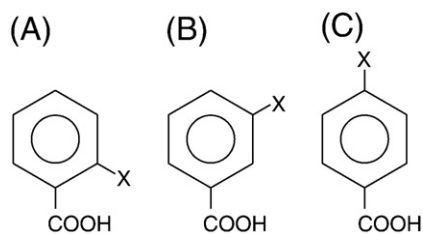


Fig. 1. The chemical structure of $X-(C_6H_4)-COOH$. (A), ortho-; (B), meta-; (C), para-; $X = F, Cl, Br, I$.

from benzoyl peroxide can abstract the hydrogen atoms on the diamond surface [27]. The presumed chemical structure of the organic functional groups introduced onto the diamond surface after the reaction process is (diamond)-OOC-(C_6H_5). In this study, we added both benzoyl peroxide and $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) (ortho position) to the reaction system. Our results show that the intensities of the peaks derived from the aliphatic C-H bond at less than 3000 cm^{-1} , which can be assigned to the C-H bond on the hydrogenated diamond surface, decreased after the reaction process. We can therefore conclude that $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) (ortho position) does not obstruct the hydrogen abstraction reaction of the radical species derived from benzoyl peroxide. The shapes of the IR spectra of samples treated with $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) (ortho position) were similar to those of the IR spectra of diamond powder treated with benzoyl peroxide. However, the position of the peak at $ca. 700\text{ cm}^{-1}$ depended on the kind of halogen atom in $X-(C_6H_4)-COOH$. In general, the peak positions of the C-X bond ($X = F, Cl, Br, I$) are $1400\text{--}1000\text{ cm}^{-1}$ ($X = F$), $800\text{--}600\text{ cm}^{-1}$ ($X = Cl$), $600\text{--}500\text{ cm}^{-1}$ ($X = Br$), and around 500 cm^{-1} ($X = I$). Although the order of the peak position of the samples treated with $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) is the same as that of the C-X bond ($X = F, Cl, Br, I$), the peak positions of the samples are rather different from that of the C-X bond. Therefore, the peak at $ca. 700\text{ cm}^{-1}$ should be assigned to not the C-X bond but the C-H bond in $X-(C_6H_4)-COOH$.

We have previously reported that a portion of the organic compound containing the COOH group, such as $CH_3(CH_2)_n-COOH$ ($n = 0\text{--}16$) or aromatic carboxylic acid, can react with the diamond surface when using a diacyl peroxide, such as benzoyl peroxide or

lauroyl peroxide [24,27]. We can therefore presume that $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) (ortho position) reacted with the diamond surface in the chemical reaction process in this study. When $CH_3(CH_2)_n-COOH$ ($n = 0\text{--}16$) reacts with a hydrogenated diamond surface, the presumed chemical structure of the organic functional group introduced on diamond surface is (diamond)-OOC-(CH_2) $_n$ CH $_3$. Therefore, in the present case we can presume that the chemical structure of each introduced organic functional group is (diamond)-OOC-(C_6H_4)-X, which is similar to that of (diamond)-OOC-(C_6H_5). It is therefore reasonable to assume that the IR spectra of the samples treated with (diamond)-OOC-(C_6H_4)-X would be similar to those of the sample treated with benzoyl peroxide. The existence of a halogen atom in the structure is likely the reason for this difference in the peak position of the out-of plane C-H bend of aromatic the C-H bond at $ca. 700\text{ cm}^{-1}$.

When $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) (meta-position) or $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) (para-position) was added in the reaction process instead of $X-(C_6H_4)-COOH$ ($X = F, Cl, Br, I$) (ortho position), the intensity of the C-H peaks at less than 3000 cm^{-1} decreased and the shape of the IR spectra for the samples became similar to that for the sample treated with benzoyl peroxide after the reaction process. Therefore, all the isomers (ortho-, meta-, and para-) could react with the diamond surface during the reaction process in this study.

In order to analyze the elements on the sample surface after the reaction process, XPS measurements were performed. The XPS spectra of the samples are shown in Fig. 3. As seen in the figure,

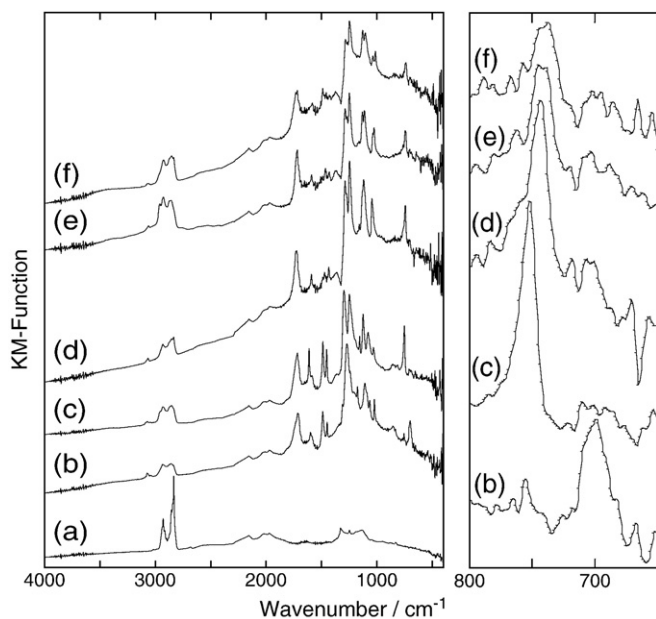


Fig. 2. IR spectra for the diamond powders reacted with 0.05 g of $X-(C_6H_4)-COOH$ in benzene at 75 °C (a), hydrogenated diamond; (b), treated with benzoyl peroxide; (c), $X = F$; (d), $X = Cl$; (e), $X = Br$; (f), $X = I$.

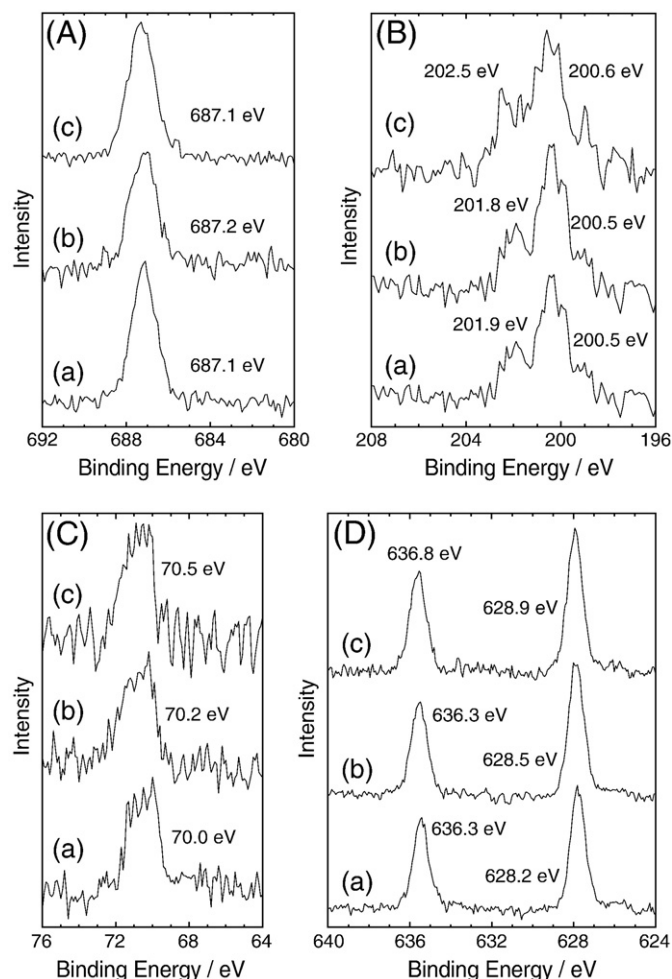


Fig. 3. XPS spectra for the diamond powders reacted with 0.05 g of $X-(C_6H_4)-COOH$ in benzene at 75 °C. (A), $X = F$; (B), $X = Cl$; (C), $X = Br$; (D), $X = I$. (a), ortho-; (b), meta-; (c),

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