Sulfur-functionalized Diamond Powder Surface for Attachment of Gold and Biomolecules

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A useful method of modifying the surface of diamond powders with sulfur-containing functionalities was developed by the use of the photolysis of elemental sulfur. The sulfur-modified diamond powder exhibited a surface-attachment behavior to gold nanoparticles through the sulfur-containing linkage. In brief, the exposure of the modified diamond powders to gold colloids resulted in gold nanoparticles being attached to the diamond powders. The introduction of sulfur-containing functional groups and gold nanoparticles on the diamond surfaces was confirmed by means of XPS, DRIFT and mass spectroscopy analyses. Subsequently, the probe DNA attached onto the gold-modified diamond powder showed a DNA hybridization behavior by the treatment with a fluorescence-labeled target DNA oligonucleotide.

Key words: diamond powder, chemical modification, sulfur, gold, biomolecules

1. INTRODUCTION

Diamond has attracted much attention for use in a wide range of applications because of its unique electronic, optical and mechanical properties [1]. In particular, diamond powder is widely utilized as an abrasive and promote nucleus formation in the fabrication of diamond films by chemical vapor deposition (CVD) [2]. The surface modification of diamond powder is expected to lead to the improvement of its performance, making it possible to introduce novel functionalities onto the surfaces. Recent studies have reported the introduction of organic functional groups onto the surface of diamond powder using photo- and thermochemical methods [3-7].

Organic compounds containing thio- and thiol groups are biologically active substances [8] and show a good affinity with gold resulting in the formation of a self-assembled monolayer. Because of the properties of sulfur atoms, the organosulfur chemistry in functionalized surfaces has been widely investigated in the field of self-assembled monolayers, which are employed effectively as model systems to determine the structural and chemical properties of organic interfaces and thin films [9]. Recently, the formation of a diamondoid monolayer on gold film was reported using self-assembly of thiol-modified diamondoid surfaces [10], however, the preparation of thio-modified diamondoid required multi-step reactions.

Previously we reported that radical reactions assisted by irradiation with UV light led to an effective process for the chemical modification of carbon materials with various functionalities [11-13]. Commercially available elemental sulfur is easily photolyzed to give corresponding thio-radicals [14]. We report on a convenient method of modifying the surface of hydrogen-terminated diamond powder with sulfur-containing substituents by the photolysis of elemental sulfur and their attachment behavior to gold and

biomolecules.

2. EXPERIMENTAL

Elemental sulfur was purchased from Wako Pure Chemical Industries, Ltd. Carbon disulfide and hexane were obtained from Kanto Chemical Co., Inc. Hydrogen-terminated diamond powder was prepared by the hydrogenation of commercially available diamond powder, obtained from Tomei Diamond Co., Ltd. (MD500, particle size 500 nm), in accordance with the literature [15]. A gold colloid was also prepared in accordance with the literature [16]. The thiol-modified DNA (S1: HS-C₆H₁₂-T15-GC TTA TCG AGC TTT CG) and oligonucleotides (Cy1: 5'-Cy5 CG AAA GCT CGA TAA GC-3' and Cy2: 5'-Cy5 CG ATT GCT CCT TAA GC-3') labeled with Cy5 fluorescence tags were obtained by Tsukuba Oligo-service, Japan.

Elemental sulfur (30 mg) in carbon disulfide (4 ml) was irradiated using a 20 W low-pressure mercury lamp (Eikosha EL-A20) through a UV-cut filter (< 200 nm) at room temperature in the presence of hydrogen-terminated diamond powder (30 mg) and in an argon atmosphere while stirring. After the reaction mixture was washed ultrasonically with three 2 ml portions of carbon disulfide and hexane then filtered centrifugally to remove the unreacted starting materials, the samples were analyzed by DRIFT, XPS, mass spectroscopy and Raman spectroscopy.

The attachment of gold nanoparticles onto the surface of sulfur-modified diamond powder was carried out by exposing the powder to 0.3 mM gold colloid (5 ml) overnight while stirring. After washing ultrasonically with three 2 ml portions of distilled water and filtering centrifugally to remove the unreacted gold colloid, the samples were analyzed by XPS.

Subsequently, the gold-modified diamond powder was treated with a thiol-modified single-strand probe DNA (S1: 0.13 μ M, 1 ml) by stirring for 7 h at room

temperature. After removing the aqueous solution by filtering centrifugally, the diamond powder was washed with water. The following exposure of target (Cy1) and mismatch (Cy2) nucleotides (50 μ M, 1 ml) with stirring overnight at room temperature to the probe DNA-treated diamond powder was performed with stirring overnight at room temperature. The samples were analyzed by fluorescence microscopy.

DRIFT spectra were recorded using a JASCO FT/IR-680 Plus spectrometer with a DRIFT attachment (JASCO DR-81). For data evaluation, the Kubelka-Munk (KM) transformation was applied to the DRIFT spectra. XPS was carried out by a PHI ESCA model 5800 spectrometer using monochromated aluminum K α radiation with a pass energy of 23.5 eV. Raman spectra were measured with a JASCO NRS-2100 laser Raman spectrometer using the 514.5 nm line of an argon ion laser with 100 mW power, and no baseline correction was made. The chemically modified powder was analyzed by a mass spectrometer (JEOL JMS-AMSUN200) using the direct insertion method. An Olympus BX51M was applied for the optical and fluorescence microscope analysis.

3. RESULTS AND DISCUSSION

3.1 Sulfur-modified diamond powder

The XPS spectra of the diamond powder were measured before and after the treatment with elemental sulfur upon irradiation (Fig. 1a, b). Two new peaks at 165.6 and 228.8 eV of sulfur 2p and 2s, respectively, were observed after irradiation together with a carbon peak at 285.0 eV. In the carbon 1s region, the peak became broad due to the mixture of C-C bonds and C-S bonds with a higher binding energy than that of the hydrogenated diamond powder (Fig. 1c). The deconvoluted of C1s spectrum of the sulfur-modified diamond powder has a main peak at 285.0 eV ascribed to the C-C bond together with peaks at 285.8 and 286.2 eV due to two types of C-S bonds. As shown in Fig. 1d, the deconvoluted S2p spectrum of the modified diamond powder also exhibited two types of S2p bonds.

Figure 2 shows the DRIFT spectra of hydrogenated diamond powder and diamond powder treated with elemental sulfur after irradiation. The sample after photoreaction has new peaks in the region of 1000–1300 cm^{-1} , attributed to a C=S stretching band and CH_2 -S bending vibration, and a decrease in the C-H stretching vibration of 2931 and 2834 cm^{-1} derived from the hydrogenated diamond powder. The results of DRIFT and XPS measurements suggest that the surface photoreaction of hydrogen-terminated diamond powder took place to give sulfur-modified diamond powder with -SH and C=S moieties. The ratio of C-SH and C=S moieties is 1.0 : 1.4 and 1.0 : 1.2 estimated by XPS C1s and S2p analyses, respectively.

A plausible reaction mechanism as shown in Scheme 1, is discussed. Polysulfide radicals generated by the ring cleavage of elemental sulfur upon irradiation abstracted hydrogen atoms from the hydrogenated diamond powder to produce polysulfides terminated with both thiol and sulfur radicals, and then the sulfur radicals reacted with the remaining carbon radicals on the diamond surface. The polysulfide bonds ($-\text{S}_n-$) were easily cleaved to form thiol substituents on the surface

Fig. 1. XPS spectra of (a) hydrogenated diamond powder, (b) diamond powder after irradiation with elemental sulfur, (c) C1s spectrum and (d) S2p spectrum of sulfur-modified diamond powder. The inset shows C1s spectra.

via the formation of a thio radical $\text{C-S}^\cdot$. In the presence of a methyl group on the diamond surface, hydrogen abstraction and subsequent S-S bond cleavage took place simultaneously to give thiocarbonyl groups via the formation of $-\text{CH}_2\text{S}^\cdot$ radicals on the surface. This reaction mechanism is supported by a mass spectrum of components generated by heating sulfurized diamond powder to 300 $^\circ\text{C}$, which exhibited two peaks at m/z 32

Fig. 2. DRIFT spectra of (a) hydrogenated diamond powder and (b) diamond powder after treatment by sulfur modification.

Scheme 1. Chemical modification on the surface of diamond powder with sulfur moieties.

and 44, ascribed to -S and -C=S groups, respectively (Fig. 3a). Moreover, the mechanism is consistent with the relative bond energies of S-S and C-S bonds of 61-64 and 74 kcal/mol [17], respectively, meaning that the S-S bonds become weak upon photoirradiation.

The Raman spectra of hydrogenated diamond powder and diamond powder after treatment by irradiation with elemental sulfur were measured as shown in Fig. 3b, c.

Fig. 3. (a) Mass spectrum of sulfur-modified diamond powders after heating to 300 °C. Raman spectra of (b) hydrogenated diamond powder and (c) diamond powder functionalized with sulfur-containing substituents.

The treated diamond powder exhibited a characteristic diamond peak at 1331 cm^{-1} similar to that of hydrogenated diamond films at 1333 cm^{-1} . This indicates that the chemical modification of the diamond powder by the photoreaction did not affect its diamond bulk structure. It is known that the fluorescence of samples is the main limitation of Raman scattering experiments due to the generation of a luminescence background. Osticioli et al. reported that the Raman spectra of sulfur compounds show background modulations originating from sulfur atoms [18].

3.2 Gold-modified diamond powder

The attachment of gold nanoparticles to sulfur-functionalized diamond powder was investigated by exposing a gold colloid to modified diamond powder. As shown in Fig. 4, an XPS spectrum of sulfur-functionalized diamond powder after treatment with the gold colloid exhibits a new peak of Au4f at 84.9 eV together with a C1s peak at 285.0 eV and an S2p peak at 164.7 eV. This indicates that gold nanoparticles were

Fig. 4. XPS spectra of sulfur-modified diamond powder after treatment with gold nanoparticles.

attached to the surface of the diamond powder through thiol and thiocarbonyl linkages by self-assembly.

Since gold nanoparticles attached to the surface of the sulfur-modified diamond powder through sulfur-containing linkages as described above, a further investigation was made regarding the exposure of the attachment of a thiol-modified probe DNA to the gold-modified diamond powder and the following exposure of target and mismatch DNA with fluorescence tags. As shown in Fig. 5, the fluorescence emission was observed only in the case of the treatment of the target DNA (Cy1), while no emission in the case of the mismatch DNA (Cy2). These results indicate that the gold-modified diamond powder was attached to the probe DNA by self-assembly and will be applicable to a detection agent of biomolecules. The advantage of Au nanoparticle interlink for DNA attachment is shorter steps from diamond powder to DNA attachment, compared with an ordinary method that needs 4 steps from H-diamond [19].

Fig. 5. (a) Optical and (b) fluorescence images of the probe DNA-modified diamond powder after the treatment with a target DNA (Cy1), and (c) optical and (d) fluorescence images with a mismatch DNA (Cy2).

4. CONCLUSIONS

The photoreaction of hydrogenated diamond powder in the presence of elemental sulfur is useful for the chemical modification of diamond powder with thiol and thiocarbonyl functional groups using a radical-based process. The modified diamond powder can be attached to a gold nanoparticle surface through sulfur-moiety linkages. Furthermore, the attachment of a

thiol-modified probe DNA to the gold-modified diamond powder led to the discrimination of target and mismatch DNA with fluorescence tags. The fluorescence emission was observed only in the case of the treatment of target DNA. The gold-modified diamond powder was found to be applicable to a detection agent of biomolecules by confirming fluorescence analysis.

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