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Clicking cyclophane to boron doped diamond surfaces

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"Click chemistry" was used to covalently attach acetylene-bearing cyclophane to azide-terminated BDD surfaces. The azide termination was obtained through an esterification reaction between 4-azidobenzoic acid and the terminal hydroxyl groups of oxidized BDD surfaces. The resulting surfaces were characterized using X-ray photoelectron spectroscopy (XPS), water contact angle and electrochemical measurements. As a result, alkyne-functionalized cyclophane can undergo click chemistry to conveniently attach these units onto a preformed azide-functionalized BDD surface.

cyclophane, boron doped diamond, click chemistry, esterification, azide

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The concept of click chemistry was introduced in 2002 by Sharpless [1]. It is based on the copper (I) catalyzed triazole formation through the classic Huisgen 1,3-dipolar cycloaddition between azides and alkynes [1,2]. It represents a chemically simple conjugation approach fulfilling many of the crucial requirements for mild surface immobilization [3,4]. Recently, these "click" reactions on polymer and solid surfaces have been reviewed [5,6], and due to its high selectivity, high yields and mild reaction conditions, numerous strategies to exploit this reaction to are now attractive to surface scientists [7,8]. Azides and alkynes are highly energetic functional groups with particularly narrow distributions of reactivity. Thanks to their weak acid-base properties, they are nearly inert toward biological molecules and the reaction conditions found inside living cells. Furthermore, azide and alkyne groups are easy to introduce into organic compounds by both nucleophilic and electrophilic reactions. One may therefore envision their incorporation into biological molecules by organic synthesis and chemical conjugation. Recently, this "click" methodology has been extended to feature interlocked structures (e.g. rotaxanes and catenanes) [9–16]. This methodology offers higher yields and better resulting structure compared to traditional methods.

In the search for new strategies to derivatize BDD surfaces, we extend this "click" methodology to a new alkyne-functionalized cyclophane conveniently "clicked" onto an azide-functionalized boron doped diamond surface, as shown in Figure 1. The synthesis of the alkyne-functionalized cyclophane was described in the literature [11]. Azide termination was obtained by esterification reaction of surface hydroxyl groups of the oxidized BDD with 4-azidobenzoic acid at room temperature, as shown in Figure 2. The advantage of using 4-azidobenzoic acid, a commercially available molecule, for the introduction of an azide group on the BDD surface is the fact that this molecule can be easily coupled to any –OH, –NH_2 or –SH terminated surface.

1 Experimental

1.1 Materials

All cleaning reagents were clean-room grade. All chemicals were reagent grade or higher and were used as received unless otherwise specified. Milli-Q water was used for all experiments. *N*, *N*-Dicyclohexylcarbodiimide (DCC), 4-Dimethylaminopyridine (DMAP), CuI, Anhydrous tetrahydrofuran (THF), Anhydrous dimethylformamide (DMF) and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) were purchased

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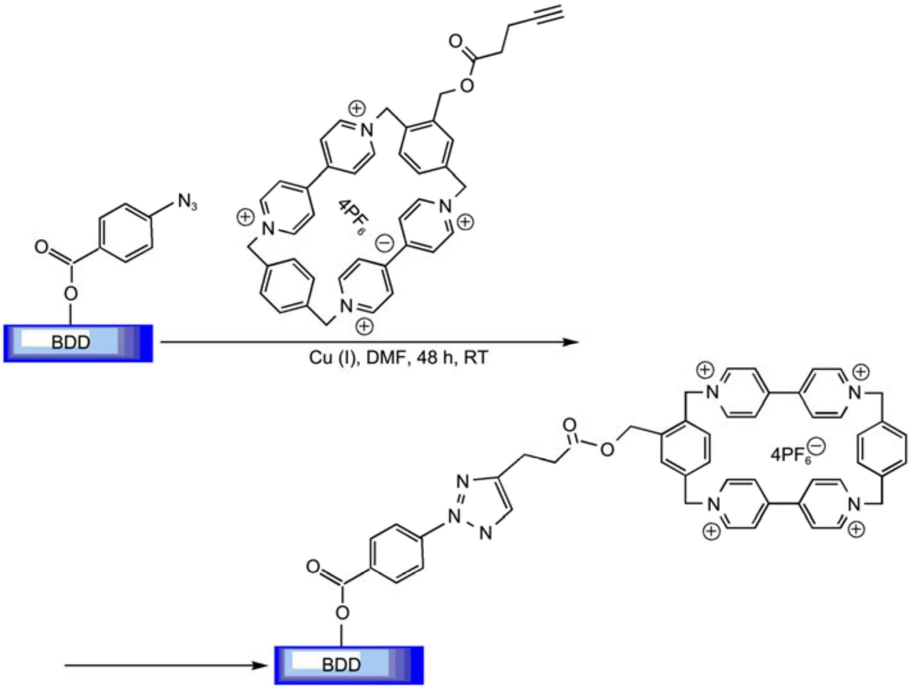

Figure 1 Scheme of clicking ethynyl cyclophane to azide-terminated diamond surface.

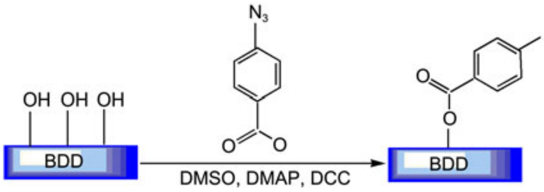

Figure 2 Esterification reaction scheme on diamond surface.

from Aldrich (Lyon, France). 4-Azidobenzoic acid was obtained from TCI Europe (Brussels, Belgium).

1.2 BDD sample preparation

Polycrystalline diamond layers were synthesized on a high purity p-type silicon wafer using microwave plasma-enhanced chemical vapor deposition (PECVD) technique in a conventional reactor [17]. The growth conditions used were as follows: substrate temperature 700–900°C, total gas flow of a mixture of 0.7% methane in hydrogen 100 sccm; total pressure in the reactor 20 Torr (30 mbar); microwave power 700 W. The dopant source was boron oxide set in a Pt crucible placed on the substrate holder near the silicon substrate.

1.3 Photochemical oxidation

A low pressure mercury arc lamp (UVO cleaner, Jelight, USA) was used to photochemically oxidize BDD samples for 55 mins as reported previously [18].

1.4 Esterification

4-Azidobenzoic acid (2 mmol), DCC (2.2 mmol) and 45 mg of DMAP were dissolved in 20 mL dry THF. The oxidized BDD was immersed in the solution and left at room temperature for 24 h under a nitrogen atmosphere. The sample was removed from the solution, washed with THF, dichloromethane, ethanol and finally with water, and then dried under a nitrogen stream.

1.5 “Clicking” cyclophane on azide-terminated BDD surface

The azide-terminated BDD surface was immersed in a solution of alkyne-functionalized cyclophane (0.04 mmol) in DMF (10 mL) at room temperature. Then CuI (0.004 mmol) was added. The solution was kept for 48 h in the dark in a glove box and the solvent was carefully removed under high vacuum. DMF was added to remove unreacted starting materials. The resulting surfaces were washed with THF and dried under a stream of nitrogen.

1.6 Surface characterization

Water contact angles were measured using deionized water. A DropMaster 500 (Kyowa Interface Science, Saitama, Japan) was used for measuring the contact angles. X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCALAB 220 XL spectrometer from vacuum Generators. All electrochemical experiments were performed using an Autolab potentiostat 30 (Eco Chemie, Utrecht, and the Netherlands). The sample was mounted in a polytetrafluoroethylene (PTFE) holder with a copper contact. Electrochemical experiments were performed using a classical three-electrode device in a solution of acetonitrile (0.1 mol/L

Bu4NPF6) with a platinum wire was used as counter electrode and BDD as working electrode.

2 Results and discussion

2.1 Water contact angle measurements

Water contact angle measurements were used to examine the macroscopic evolution in the wetting properties of the boron-doped diamond electrode before and after functionalization (Table 1).

The as-prepared BDD is hydrogen-terminated. This termination confers a hydrophobic character to the surface with a water contact angle 94±2°. Photochemical oxidation of the BDD substrate yields a surface termination with a hydrophilic character. The contact angle value decreased significantly to 8°. Chemical esterification of the terminal hydroxyl groups with 4-azidobenzoic acid led to an increase in contact angle. A value of 57±2° was measured for the azide-terminated BDD surface. After clicking cyclophane groups to the azide terminated BDD surface, the contact angle dropped to 20±2°, as compared to 57±2° for the azide termination surface (Table 1), indicating that the cyclophane groups display a hydrophilic character.

2.2 X-ray photoelectron spectroscopy (XPS) analysis

Figure 3(a) displays the XPS survey spectrum of the azide terminated BDD surface. It shows a main peak at 285 eV due to C 1 s and a peak at 532 eV due to O 1 s. An additional peak at ~400 eV, characteristic of nitrogen (N 1 s) is also observed. High resolution XPS investigation of the N 1 s was performed (Figure 3(b)). Careful analysis showed two peaks at 401 and 406 eV, suggesting the presence of two nitrogen species in the azide-terminated monolayer, and reflects the differently charged nitrogen atoms in the azide group [19–21]. This indicates the success of the esterification reaction.

Table 1 Contact angles of diamond surfaces in the course of clicking

	H-BDD	HO-BDD	N_3-BDD	cyclophane-BDD
Contact angle	94±2°	8±2°	57±2°	20±2°

To investigate the changes in the surface composition after the introduction of the cyclophane functionality on the azide-terminated BDD surface, cyclophane-terminated BDD surface was also analyzed by XPS (Figure 4). XPS survey spectrum is shown in Figure 4(a). When compared with the XPS survey spectrum of the azide-terminated BDD surface (Figure 3), a new peak at 688 eV ascribed to F1s appeared after clicking cyclophane groups onto the azide-terminated BDD surface. The high resolution XPS spectrum of F 1 s is displayed in Figure 4(b). It consists of a single peak at 688 eV. Two expected peaks at 110 and 136 eV due to phosphorus atom were obeserved as expected for the cyclophane moieties. Figure 4(c) displays the high resolution XPS spectrum of N1s of the cyclophane modified BDD surface, showing two peaks at 399.4 and 401.6 eV corresponding to nitrogen in the form of 1,2,3-triazole and in the aromatic ring, respectively. All above indicates that cyclophane has been successfully clicked on the azide-terminated BDD surface.

2.3 Electrochemistry measurement

We have further exploited the electrochemical signature of the electroactive cyclophane moiety to investigate whether the cyclophane is grafted onto the BDD surface using click chemistry. The cyclic voltammogram of the cyclophane-terminated BDD surface recorded in acetonitrile (0.1 mol/L Bu_4NPF_6) (Figure 5) reveals the formation of two redox waves (absent in the azide terminated surface), presumably corresponding to the sequential formation of the diradical dication and fully reduced states of the cyclophane, respectively [11,22]. However, significant attenuation of the current was observed, which is consistent with surface inhibition due to the presence of either an overall low density surface grafting and/or the presence of defect domains. For further understanding, cyclic voltammograms of cyclophane solution on an azide modified BDD surface as well as on gold surface were investigated under the same conditions. Since two excellent redox waves were observed on gold surface, much

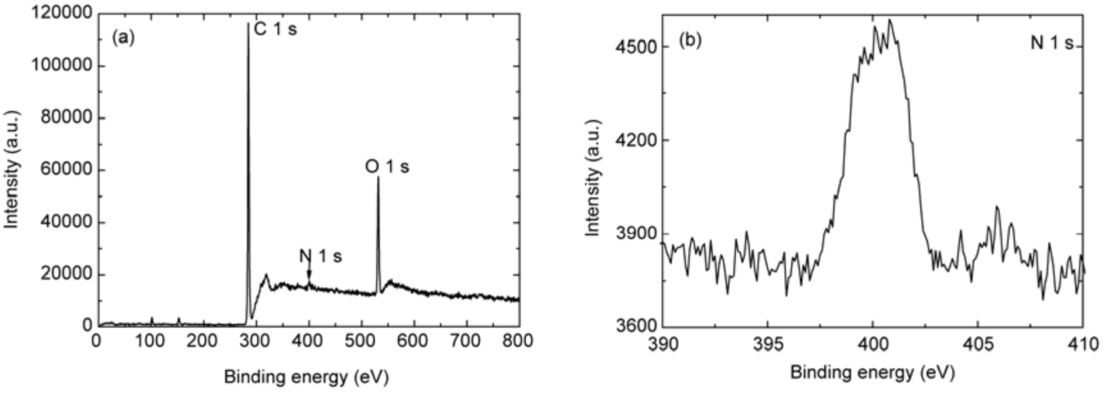

Figure 3 XPS survey spectrum of the azide-terminated BDD surface (a) and high-resolution XPS spectrum of the N 1 s peak (b).

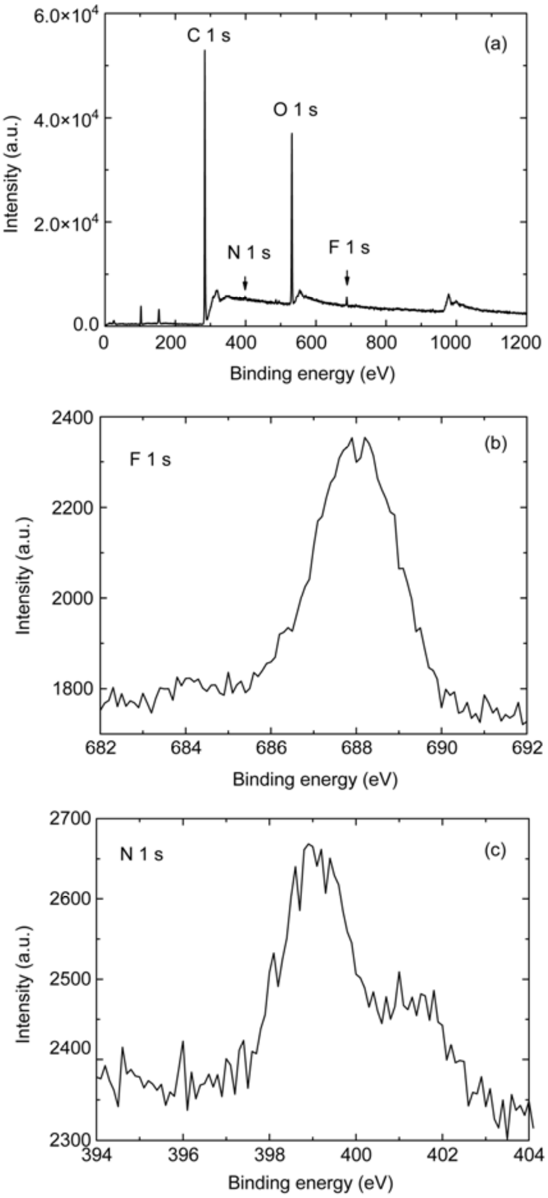

Figure 4 XPS survey spectra of cyclophane terminated BDD surface (a) high-resolution XPS spectrum of F 1 s (b) high-resolution XPS spectrum of N 1 s (c).

lower current on the former surface indicates a more blocked surface. As a whole, cyclophane covalently linked on BDD surface was further confirmed.

3 Conclusions

In conclusion, we have demonstrated that "click" chemistry can be successfully applied for coupling functional cyclophane bearing a terminal acetylene group to azide-terminated BDD surfaces. Because of the gentle nature of the procedure, the strategy developed in this work can be used as a general platform to prepare functionalized surfaces for various applications. Based on the successful linking of cyclophane to the azide-terminated BDD surface, we are currently exploiting the covalent coupling of the corresponding rotaxane and catenane onto azide terminated BDD surfaces using click chemistry. The applicability of this reaction scheme for coupling alkyne-terminated carbohydrates and other alkyne-functionalized molecules to flat supports is currently under investigation in our laboratory.

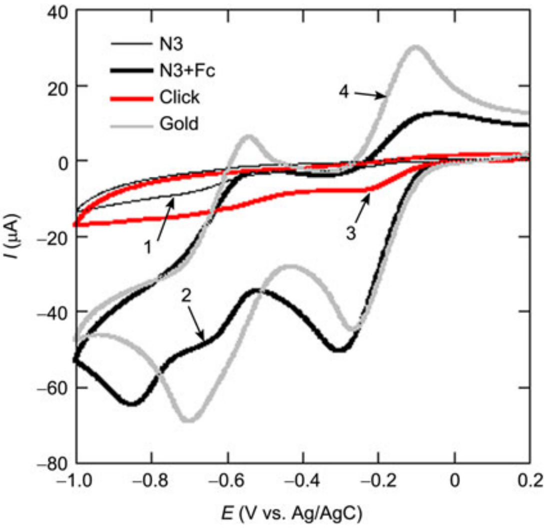

Figure 5 Cyclic voltammogram of azide modified BDD surface (curve 1), cyclophane solution on azide modified BDD surface (curve 2), cyclophane clicked BDD surface (curve 3), cyclophane solution on gold surface (curve 4) in acetonitrile (0.1 mol/L Bu_4NPF_6) solution. Scan rate: 0.1 V s^{-1}.

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