Wet-chemical approach for the halogenation of hydrogenated boron-doped diamond electrodes

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Brominated and chlorinated boron-doped diamond electrodes were prepared through a radical substitution reaction and reacted further with alkyl-Grignard reagents.

Much attention is currently being paid to the chemical modification of solid substrate surfaces due to their utility as model systems for understanding electron transfer in molecular electronics, bioelectronics, and sensors, among other applications. Immense research effort has been devoted especially to functionalising semiconductor surfaces. In the case of silicon, various strategies for the introduction of diverse functionalities can be readily employed.[1] Still, the chemical stability of the semiconductor/organic interface is limited as surface-active electronic defects are easily formed. Some of these disadvantages can be overcome by using diamond. The use of diamond has gained remarkable interest in different research areas due to its excellent mechanical properties, outstanding chemical stability and good electrical conductivity upon doping.[2]

Novel reactions with organic molecules expand the perceptions and perspectives of the surface reactivity of diamond. The possibility of chemically modifying diamond films has been exploited in depth in the last fifteen years. Various strategies based on chemical, photochemical and, in the case of doped diamond, on electrochemical concepts have been proposed.[3] Halogenation in the gas phase was one of the first surface modifications investigated on diamond. Fluorine and chlorine atoms directly react with diamond and allow surface halogenation.[4–6] The conditions necessary to generate atomic species are rather vigorous and corrosive (*e.g.* Cl_2/400–500 °C; F_2/470 °C).[5,6] Milder conditions can be used during photochemically initiated gas phase halogenation.[7–9] To date, the only report on the halogenation of diamond in the liquid phase has been reported by Ikeda *et al.* in 1998,[10] who chlorinated diamond powder with sulfuryl chloride (SO_2Cl_2) aided by the radical initiator 2,2-azobiisobutyronitrile (AIBN) at 50 °C and also brominated diamond powder using Br_2 at 50 °C in chloroform. The development of simple and controllable solution-based procedures for halogenation of continuous diamond films is thus still sought after.

We report here, for the first time, the feasibility of brominating and chlorinating hydrogenated boron-doped diamond (H-BDD) interfaces using *N*-bromo- and *N*-chlorosuccinimide (NBS and NCS), respectively (Fig. 1). Brominated and chlorinated surfaces are obtained *via* a radical substitution reaction of C–H groups on diamond with bromine and chlorine radicals. The conditions for the halogenation involve refluxing in anhydrous CCl_4 in the presence of a radical initiator, such as benzoyl peroxide to result in Br-BDD and Cl-BDD interfaces.†

Contact angle measurements were used to follow the changes in surface wetting properties due to surface functionalisation. As-deposited diamond showed a water contact angle of 93 ± 2°, as is expected for a surface terminated with hydrophobic C–H bonds. Chemical grafting of electron withdrawing groups to the diamond interface does not influence significantly the wetting properties. Contact angles of 87 ± 2° and 85 ± 2° are obtained for the Br-BDD and Cl-BDD interfaces, respectively. The values are comparable to those reported in the literature for diamond surfaces halogenated using plasma treatment.[11] The high contact angles give a first indication that oxidation has not taken place preferentially under such reaction conditions, as this would result in contact angles <10°. The stability of the interfaces was determined by following the change of contact angle over time. After 14 days of atmospheric exposure the contact angles determined were still within the error range, indicating that both interfaces are fairly stable in air. When immersed in water for 2 days, the contact angles decreased to 83 ± 2° for Br-BDD and to 81 ± 2° for Cl-BDD.

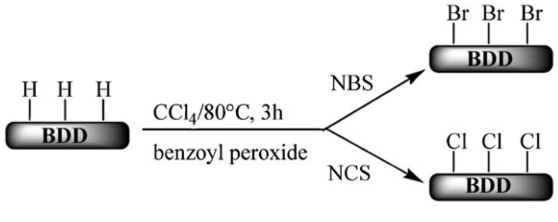

Fig. 1 Halogenation of H-BDD through radical substitution reaction using NBS and NCS.

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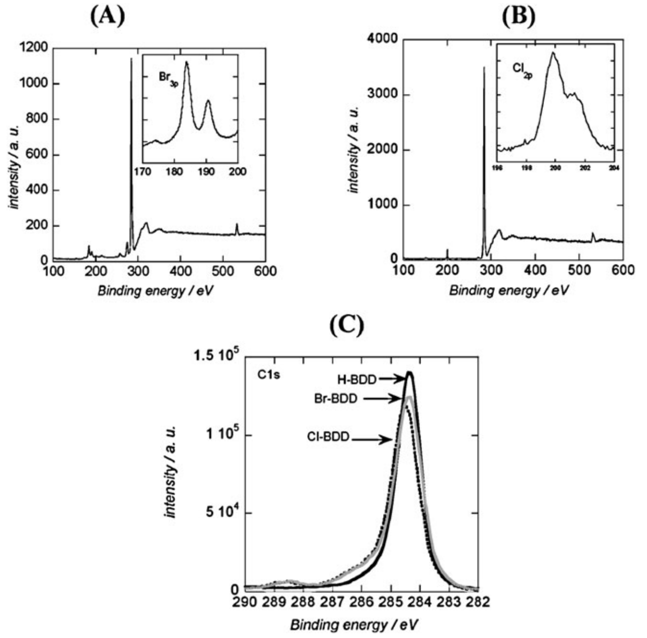

Fig. 2 XPS survey of (A) brominated and (B) chlorinated diamond surfaces. The insets correspond to the high-resolution XPS of Br 3p and Cl 2p; (C) high-resolution XPS of the C 1s band of as-deposited BDD (black), Br-BDD (grey) and Cl-BDD (black dotted)

X-Ray photoelectron spectroscopy (XPS) was used to analyse the chemical composition and the nature of the chemical bonding on the diamond surface before and after chemical modification.

The XPS survey of as-deposited BDD displays a main peak for C 1s at 285 eV and a very small peak at 532 eV for O 1s with a O/C ratio of 0.30. The presence of oxygen is most likely due to the partial oxidation of the BDD surface during its handling. After reaction with NBS and NCS, additional peaks at 183.9 and 190.5 eV due to Br 3p and at 199.8 and 201.3 eV due to Cl 2p are observed (Fig. 2). The atomic concentration ratio Br/C and Cl/C are estimated to be 0.18 and 0.15, respectively. The values are comparable to those reported by Kondo *et al.*[11] The O/C ratio after halogenation increased to 0.98 for Br-BDD and 1.01 for Cl-BDD, indicating that some oxidation is taking place during halogenation. High-resolution XPS (Fig. 2C) of the C 1s band indicates the formation of C=O groups (288.6 eV). The shoulder at ~286.3 eV is due to the formation of C–X (X = Br, Cl) and C–O bonds.

Furthermore, we studied the electrochemical properties of the modified BDD surfaces using $[Fe(CN)_6]^{3-/4-}$ as the redox couple in solution. Fig. 3A shows the *i–E* curves in an aqueous solution of 10 mM $Fe(CN)_6^{4-}$ in 0.1 M KCl recorded on H-BDD, Br-BDD and Cl-BDD electrodes. A significant decrease of the apparent rate constant is observed for the halogenated BDD electrodes, being similar to that of UV/ozone oxidized interfaces.[12] In the case of Cl-BDD, the standard electrochemical potential shifted to more anodic values. In contrast to F-BDD, where a window of ideal polarisability of 5 V could be recorded,[13,14] Cl-BDD and Br-BDD diamond surfaces show electroactive windows similar to that of H-BDD (Fig. 3B).

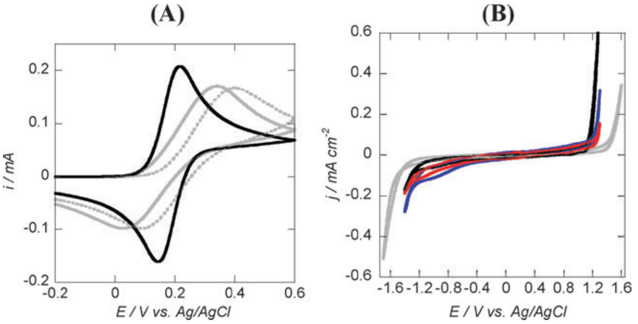

Fig. 3 Cyclic voltammograms of BDD electrodes in an aqueous solution of (A) $Fe(CN)_6^{4-}$ (10 mM) in KCl (0.1 M): H-BDD (black), Br-BDD (grey), Cl-BDD (grey dotted); (B) KCl (0.1 M): H-BDD (black), Br-BDD (blue), Cl-BDD (red), UV/ozone oxidised-BDD (grey); scan rate: 50 mV s^{-1}.

The chemical reactivity of the halogenated BDD surfaces was further investigated by exposing the brominated BDD surface to a Grignard reagent (Fig. 4). A similar strategy has been reported for the alkylation of chlorinated diamond[10] and Si surfaces.[15] The Br-BDD was immersed in an anhydrous THF (20 ml) and 10 ml of 1 M $C_{10}H_{21}MgBr$ in diethyl ether. The mixture was heated for 72 h in a constant temperature bath set at 80 °C. The resulting surface was rinsed at room temperature with 1% CF_3COOH solution in THF, Milli-Q water, sonicated in methanol and dried under a stream of nitrogen.[16] The contact angle of the resulting interface increased to 100 ± 2°, due to the hydrophobic character of the long alkyl chain. The value is in agreement with contact angles between 100–108 °C reported for chemically modified silicon and perfluorodecyl silane modified polycrystalline diamond surfaces.[12] The water contact angle is known to depend on surface morphology together with surface chemical composition.

The decyl-terminated BDD ($C_{10}H_{21}$-BDD) surface was further characterized by cyclic voltammetry using $Fe(CN)_6^{4-}$ as the redox couple in solution (Fig. 5). Attenuation of the current is observed which is consistent with surface inhibition due to the presence of a long alkyl chain on the surface and is comparable to perfluorodecyl-terminated BDD.[3] The current signal is however rather intense suggesting that the electrode is not fully blocked. This points towards either a overall low-density surface grafting and/or the presence of defect domains.

The results presented here demonstrate for the first time an easy-to-perform and controllable formation of Br-BDD and Cl-BDD on surfaces. The interest of halogen-functionalised BDD is in the high reactivity of the surface-bound halogens that can be utilised for the introduction of other surface functionalities. This was demonstrated by exposing Br-BDD to alkyl-Grignard reagents.

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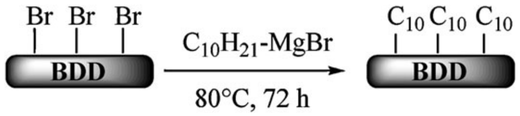

Fig. 4 Alkylation of a brominated BDD surface using $C_{10}H_{21}MgBr$.

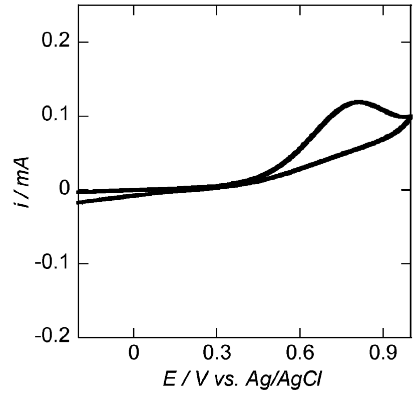

Fig. 5 Cyclic voltammogram of $C_{10}H_{21}$-BDD electrode in an aqueous solution of $Fe(CN)_6^{4-}$(10 mM) in KCl (0.1 M): scan rate: 50 mV s^{-1}.

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Notes and references

† H-BDD was immersed in a CCl_4 (20 mL) solution of benzoyl peroxide (0.1 mmol), *N*-bromosuccinimide (NBS, 2 mmol) or *N*-chlorosuccinimide (NCS, 2 mmol) and heated to 80 °C for 6 h under nitrogen atmosphere. The samples were subsequently washed with CCl_4, ethanol and water and dried under a nitrogen stream.

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