Suzuki Coupling of Aryl Organics on Diamond

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Received December 26, 2007. Revised Manuscript Received February 7, 2008

We demonstrate a facile method for the Suzuki coupling of aryl molecules on the diamond surface. This is a more versatile alternative compared to previous coupling methods based on alkene linkers because it opens up possibilities for the application of diamond in molecular electronics and photovoltaics. The diamond surface is premodified with aryldiazonium salt in order to functionalize it with aryl halide or aryl boronic acid, and these are then used as synthons in the subsequent Suzuki coupling to aryl molecules. This method is highly specific and can be used for the uninterrupted molecular conjugation of diamond to a large class of organic molecules. As a proof of concept, we also demonstrate a diamond−fullerene photocurrent converter by using Suzuki coupled oligothiophene as the conjugated linker between diamond (electron donor) and fullerene (electron acceptor).

I. Introduction

Boron doped diamond thin films have now emerged as important electrode materials and biosensing platforms owing to their chemical robustness, optical transparency, wide electrochemical potential window, and biocompatibility. However, most applications require the functionalization of the inert diamond surfaces to attach biomolecular probes for biorecognition events.[1] Methods such as photochemical coupling with alkenes,[2] as well as electrochemical modification via reduction of aryldiazonium salts,[3] had been applied successfully for the biofunctionalization of diamond. Methods based on the photochemical coupling of alkenes are restricted mainly to alkyl compounds, since the presence of aromaticity in the target adsorbates will open up non-selective pathways of attachment to the surface in the presence of UV activation. Although alkyl linkers serve the purpose of tethering probe biomolecules on the surface, there are several disadvantages compared to the choice of conjugated aryl compounds as biolinkers or self-assembly layers. First, in terms of the stability of the biofunctionalized interface, a denser, hydrophobic interface will prevent the hydrolysis of the interfacial bonds arising from the infiltration of water molecules to the interface. In this case the presence of $\pi-\pi$ stacking in aryl compounds affords denser packing of the monolayer compared to the alkyl monolayers. Second, the delocalized electrons in aryl linkers afford a greater efficiency in charge transfer compared to the alkyl linker, and this is essential if diamond is to be used as electrode materials in organic electronics. Therefore, it is desirable to consider a generic method which allows the C−C coupling of a wide range of aryl molecules on diamond with good specificity. The electrochemical reduction of aryldiazonium salts is a very convenient way of derivatizing the surface with simple aryl molecules.[4,5] Aryldiazonium salts have been used to functionalize various metals and semiconductors[6] for applications in fields ranging from combinatorial chemistry to molecular electronics.[7]

Functionalization of diamond with aryldiazonium salts was first reported by Kuo et al.,[8] and much interest was generated subsequently.[9] While the aryldiazonium reduction method is a convenient way for the derivatization of surfaces, one drawback is the difficulty to limit the reaction to a monolayer.

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The control of layer thickness during aryldiazonium coupling depends on several factors. A comprehensive review by Pinson and Podvorica[10] discussed monolayer grafting achieved by the careful control of grafting parameters such as the amount of charge supplied during electrochemical grafting and the concentration of aryldiazonium salts. A Monte Carlo simulation of attaching 4-bromobenzene on Si(111) performed by Allongue et al.[11] indicated that the formation of organized domains is related to the higher probability of grafting a molecule in the neighborhood of a first attached molecule, arising from $\pi-\pi$ stacking interactions between neighboring adsobates. The importance of stacking interactions was also demonstrated by Garrido et al.[12] in the formation of biphenyl self-assembled monolayers on doped ultrananocrystalline diamond. In addition, the chemical reduction potential of the different aryldiazonium salts with respect to the Fermi level of the solid surface controls the extent of reaction. For example, a monolayer of 4-bromobenzene can be achieved by constant potential method, but the same process produced 25 Å thick layer of 4-nitrobenzene.[13] This is possibly due to the slower attachment kinetics of 4-bromophenyl diazonium salt (4BrPD) which allows time for the intermolecular stacking of ordered monolayers.

On the other hand, the Suzuki coupling reaction is a synthetic method for the synthesis of biaryls from aryl halides and aryl boronic acids in the presence of a palladium catalyst and base.[14] This cross coupling reaction can be used to couple a wide range of reagents and hence has wide applicability in the synthesis of pharmaceutical drugs and in the preparation of conjugated aromatic polymers or oligomers for use in organic light emitting diodes. Pd-catalyzed cross-coupling reactions have been applied successfully for the functionalization of single-walled carbon nanotubes (SWCNT), using iodophenyl functionalized SWCNT as the synthons.[15] In this work, we investigated the optimal conditions for the generation of bromophenyl or phenylboronic acid functional groups on diamond, to be used as a synthon for cross-coupling to the respective phenylboronic acid or bromophenyl. We found that intrinsic diamonds which are effective insulators in air can be spontaneously derivatized with diazonium salts to obtain a surface monolayer of phenylbromide, and these can be used later for Suzuki cross-coupling with aryl organics. The advantage of this approach is that it is highly specific and does not require potential-controlled electrochemical grafting so the multilayer film formation process is suppressed.

II. Experimental

Chemical Reagents. All chemicals purchased were of the purest grade and used as received from Sigma-Aldrich unless otherwise stated. All solvents used for reaction and rinsing were of HPLC grade unless otherwise stated. 5-(5-iodothiophene-2-yl)thiophene-2-carbaldehyde (I-2T-CHO) was synthesized and characterized by MALDI-TOF and NMR (see Supporting Information). All dilutions and the preparation of redox electrolytes for electrochemical work were made with Nanopure water (18.0 MΩ cm).

Diamond Substrates. Undoped nanocrystalline (u-NCD) diamond of 2.5 μm thickness was deposited on p-doped Si(001) substrates which have been pretreated in a diamond powder/isopropanol slurry with an ultrasonic technique. The deposition was performed by a modified hot filament process with a CH_4 concentration of 2.91% in hydrogen. The substrate temperature as measured by a thermocouple (type K, Chromel/Alumel) was about 780 °C. These u-NCD were used throughout the experiments unless otherwise stated. The 50 μm thick polycrystalline boron doped diamond (BDD) films were grown on *p*-type Si substrates in a commercial 2.45 GHz microwave plasma reactor (Astex) using methanol and boron oxide mixtures. The BDD samples had a surface resistance of 10 Ω cm, and the boron doping level was approximately 10^{20} cm^{-3}. These BDD samples were used for electrochemical experiments due to their high conductivity.

Acid cleaning and hydrogen plasma cleaning of diamond were performed for all diamond samples. Metallic impurities were first removed by hot aqua regia ($HNO_3/HCl = 1:3$), followed by the removal of organic impurities from the diamond samples using hot "piranha" solution ($H_2O_2/H_2SO_4 = 1:3$) at 90 °C for 1 h. This will result in an oxidized diamond surface as evident in the increased hydrophilicity. H-termination of diamond samples was performed by microwave hydrogen plasma treatment using 800 W microwave power and 300 sccm of hydrogen gas flow for 15 min.

Reaction Conditions. Functionalization of diamond samples with aryl diazonium salts was carried out using three different methods, namely, (1) cyclic voltammetric scan technique applied between +0.5 and −0.5 V (vs Ag/AgCl) with a scan rate of 100 mV/s or (2) constant potential technique at +0.2 V (vs Ag/AgCl) for 5 s; or (3) spontaneous functionalization technique with varying immersion times between 15 and 120 min. All functionalization experiments were carried out in a solution of 5 mM aryldiazonium salt in 0.1 M HCl which was purged with N_2 gas for at least 15 min, unless otherwise stated. For electrochemical reduction of in situ generated aryldiazonium salt, 5 mM of target aniline was diazotized with an equivalent molar amount of $NaNO_2$ in N_2 gas-purged 0.5 M HCl, which was directly used for cyclic voltametric scan from +0.5 to −0.1/−0.5 V (vs Ag/AgCl) at a scan rate of 100 mV/s. After modifications, the substrates were sequentially rinsed and sonicated in Nanopure water, THF, and hexane to remove any physisorbed molecules.

For Suzuki coupling, all preparations were performed in a glovebox. For coupling of arylbromide functionalized diamond to target arylboronic acid, the functionalized diamond with 50 μmol of arylboronic acid, an equivalent molar amount of sodium acetate (NaOAc), catalytic amount of $Pd(PPh_3)_4$ (0.5 mg, 0.43 μmoles), and 2 mL of Ar purged methanol were added into a rubber septum sealed conical flask, which was then heated at 60 °C for 12 h. For coupling of arylboronic ester functionalized diamond to target arylbromide, the reaction condition was similar except that a catalytic amount of NaOAc (0.5 mg, 6.1 μmol) was added instead. To link the oligothiophene to diamond, arylboronic ester functionalized diamond was heated at 60 °C for 12 h in a solution of 50 μmol 5-(5-iodothiophene-2-yl)thiophene-2-carbaldehyde (I-2T-CHO), 0.5 mg of NaOAc, and 0.5 mg of $Pd(PPh_3)_4$ in argon-purged methanol. After all the coupling reactions, all substrates were sequentially rinsed and sonicated in methanol, toluene, THF, and hexane to remove any physisorbed molecules.

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To form the C_{60}-linked oligothiophene modified diamond, C_{60} was linked to 2T-CHO coupled diamond by refluxing the substrate in a solution of C_{60} (10 mg, 14 μmol) and *N*-methylglycine (5 mg, 56 μmol) in 10 mL of toluene under N_2 atmosphere for 24 h. After coupling, the substrate was sequentially rinsed and sonicated in toluene, THF, and hexane for at least 30 min to remove any physisorbed molecules.

Instrumentations. X-ray photoelectron spectroscopy (XPS) was performed with a Phobios 100 electron analyzer (SPECS GmbH), using an unmonochromated Mg Kα X-ray source (1253.6 eV). The pass energy of the hemisphere analyzer was set at 50 eV for wide scan and 20 eV for narrow scan, while the takeoff angle was fixed normal to the sample. Static secondary ion mass spectrometry (SSIMS) was carried out in a TOF-SIMS IV instrument using low ion dose of less than 10^{-12} ions/cm^2. It was equipped with a time-of-flight ion mass analyzer with a mass resolution above 7000. The ion beam source used was Ga ion with beam energy of 25 keV and a pulse width of 25 ns. The positive spectra obtained were normalized against Ga ion intensity, and the negative spectra were normalized against total counts.

Atomic force microscopy (AFM) scratching experiments were performed using a NanoMan AFM system (Veeco Instruments and Process Metrology) operating under contact mode. A large force of >120 nN was employed to scratch an area of 1 μm^2 or 500 nm^2 with complete removal of grafted organic, while a very slight force of <0.3 nN was used subsequently for direct imaging. Contact mode cantilevers with a typical resonant frequency of 13 kHz and a force constant of 0.2 N/m were applied in this study. Loading forces during the scratching experiments were calculated from force curve measurements for each cantilever.

All electrochemical measurements were carried out with an Autolab PGSTAT30 potentiostat (Eco Chemie B.V.) in a single-compartment Teflon cell with three-electrode configuration system: a diamond working electrode, Ag/AgCl reference electrode (3.0 M KCl), and a Pt mesh counter electrode. Top contact on the diamond sample surface was made through an Au-plated probe. For all electrochemical experiments, a small area (0.07 cm^2) of the diamond surface was exposed to the electrolyte through a Viton O-ring, unless otherwise stated. For electrochemical grafting of in situ generated diazonium salt, contact was made to a corner of the BDD sample, and it was partially immersed in electrolyte to allow functionalization of a larger area.

Photoelectrochemical measurements were performed in a N_2 saturated 0.1 M Na_2SO_4 solution containing 5 mM methyl viologen (MV2+) as an electron carrier, using the modified BDD as a working electrode in a typical three-electrode configuration system. The light source employed was a 150 W halogen lamp (NOVAFLEX Fiber Optic Illuminator from World Precision Instruments).

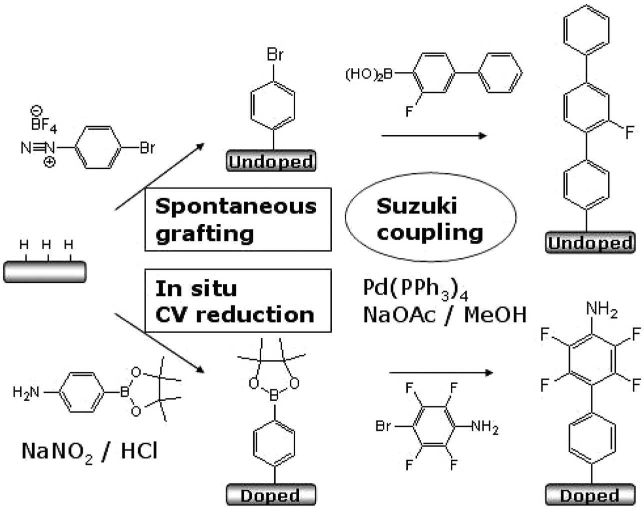
III. Results and Discussion

Spontaneous Grafting. As shown in Scheme 1, the first step in the reaction scheme requires the generation of either bromophenyl or phenylboronic ester on the diamond surface, and these are the synthons needed for subsequent Suzuki cross coupling reactions. The initial experiments examined the thickness of the chemically grafted phenyl groups, since a well-controlled monolayer is preferred for the layer-by-layer extension of the organic layers. Three methods of grafting 4-nitrophenyl diazonium salt (4NOPD) on boron-doped diamond (BDD), namely, cyclic voltammetric (CV) reduction, constant potential attachment (CPA), and spontaneous grafting (SG) by simple dipping, were attempted. The electroactive nitrophenyl groups allowed the titration of surface coverage by calculating the amount of charge transferred during CV. The surface coverage, τ, of the 4-nitrobenzene formed can be estimated from equation 1, where the integrated area under the reduction peak, *Q*, could be used for estimating the coverage of the nitro groups

$$\tau = Q/(nFA) \tag{1}$$

($n = 6$ is the number of electrons transferred during the electrochemical reduction of nitro to amine groups, *F* is the Faraday constant $= 9.65 \times 10^4$ C equiv^{-1}, and *A* is the area of exposed diamond electrode $= 0.07$ cm^2). From Figure 1, the surface densities of the nitro group grafted using three CV cycles and 5 s of constant potential reduction were in the range of 1×10^{15} molecules·cm^{-2}. Longer treatment time did not increase the coverage significantly. Spontaneous grafting (SG) that occurred within 120 min of immersion resulted in surface densities ranging from 6.0 to 8.8×10^{14} molecules·cm^{-2}. An ideal close-packed monolayer surface coverage was calculated by Pinson and Podvorica[10] to be 8×10^{14} molecules·cm^{-2}; therefore, within the margins of

Scheme 1. Two Functionalization Routes Using Aryldiazonium Salts, followed by Suzuki Coupling with Aryl Organics



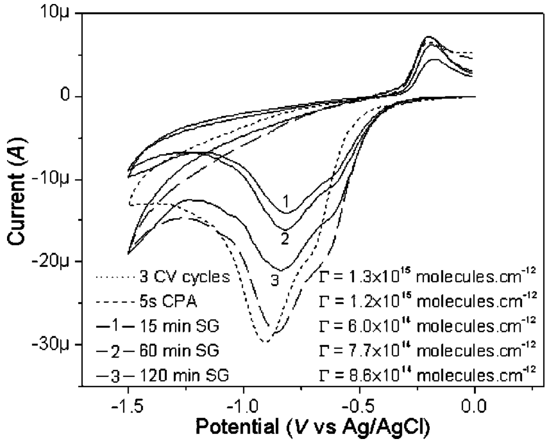


Figure 1. Comparison of NO_2 reduction peak of diamond samples functionalized by three cyclic voltammetric (CV) cycles (dotted line), 5 s of constant potential attachment (CPA) (dashed line), and spontaneous grafting (SG) for 15 min (solid line 1), 60 min (solid line 2), and 120 min (solid line 3). Surface coverage, τ, was calculated from respective integrated reduction peak using eq 1.

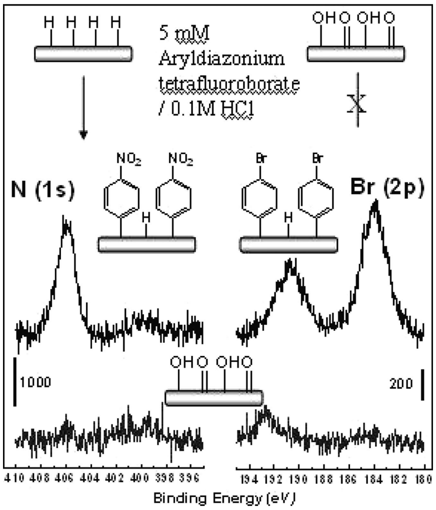


Figure 2. XPS characterization of spontaneous functionalization of 4-nitrophenyldiazonium tetrafluoroborate ($4NO_2PD$, left column) and 4-bromophenyldiazonium tetrafluoroborate (4BrPD, right column) on H-terminated undoped nanocrystalline diamond (u-NCD:H, top row) and oxidized undoped nanocrystalline diamond (u-NCD:O, bottom row).

error, a limiting monolayer can be grafted on the substrate independent of the different methods applied, with the spontaneous coupling method producing a coverage closer to the monolayer limit, as opposed to multilayer growth.

The spontaneous functionalization method is advantageous because it can be applied on intrinsic (undoped) diamond (resistance >100 GΩ). The spontaneous coupling of nitrophenyl as well as bromophenyl diazonium salts was found to be facile on these electrically insulating substrates if the surfaces of these samples were hydrogen-terminated. Simply by immersing undoped H-terminated nanocrystalline diamond (u-NCD:H) in 5 mM 4-bromophenyldiazonium tetrafluoroborate (4BrPD)/0.1 M HCl solution for 2 h, covalently grafted bromophenyl groups were formed on the surface, as evidenced by the XPS Br 3p peaks shown in Figure 2. To verify the actual thickness of the functionalized organic layer, AFM scratching experiments[16] were conducted on the functionalized single crystal diamond, C(100). By using a large force of >120 nN, an area of 1 μm^2 was scratched with complete removal of grafted organic.[13] Thereafter, direct imaging with contact mode AFM was performed with a very slight force of < 0.3 nN. A line profile was drawn through the scratched trench and perpendicular to the tip scanning direction so as to minimize error due to artifacts along the scanning direction. From Figure 3, the line profile shows a height difference of 0.6 (±0.2) nm between the unscratched area and scratched trench, which agrees well with the height of a bromobenzene molecule (0.618 nm) calculated by density functional theory (DFT). This shows that spontaneous functionalization of intrinsic diamond allows the formation of a self-assembled monolayer (SAM) in contrast to most electrochemical methods which result in multilayer formation. To prove that the applied force was gentle enough for nondestructive imaging, the same area can be repeatedly scanned and a reproducible image could be obtained each time.

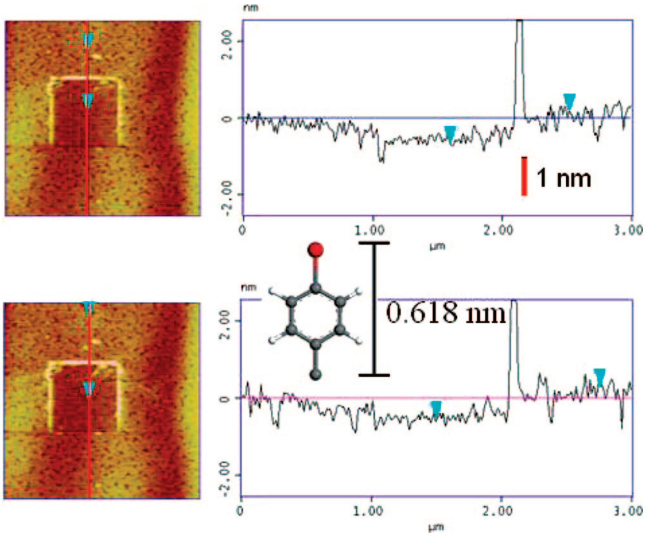


Figure 3. Top: Contact mode AFM image of a scratched area on 4-bromophenyldiazonium tetrafluoroborate (4BrPD)-functionalized C(100) and a line profile through the scratched area showing a depth of 0.6 (±0.2) nm. Bottom: Repeated scan of the same area. Model showing the calculated height of grafted bromobenzene to be 0.618 nm.

We found that the occurrence of the spontaneous coupling reaction depends critically on the nature of surface termination on the diamond, as well as the electrical conductivity of the diamond. Based on the generally accepted grafting mechanism, a phenyl radical is produced directly through an electron transfer from the diamond to the aryldiazonium salt in concert with the cleavage of dinitrogen.[10] At first sight, the fact that electron transfer can proceed from intrinsic diamond is intriguing. However, it is well-known that the surface conductivity and electron affinity on the diamond surface can be tuned by changing the surface terminating groups.[17] An intrinsic diamond can develop a *p*-type surface conducting channel following exposure of the hydrogenated diamond surface to the humid environment. This is due to the presence of a hole accumulation layer which arises from electron transfer between the diamond and an electrochemical redox couple involving oxygen, as explained by Angus et al. recently.[18] Such remarkable insulator-to-metal transition of intrinsic diamond when it is immersed in a redox electrolyte had been explained by Nebel et al. previously using electrochemical methods.[19] A switch from insulating to conducting behavior of diamond will occur if the chemical potential of the electrolyte is below the valence band maximum of diamond, such that valence electrons can tunnel into the adsorbate levels to give rise to equilibration. On the other hand, O-termination causes a depletion of the hole accumulation layer and increases the surface resistance. Accordingly, we found that, on intrinsic diamond, the spontaneous coupling of aryldiazonium salts is facile when the surface is H-terminated, but the reaction is completely

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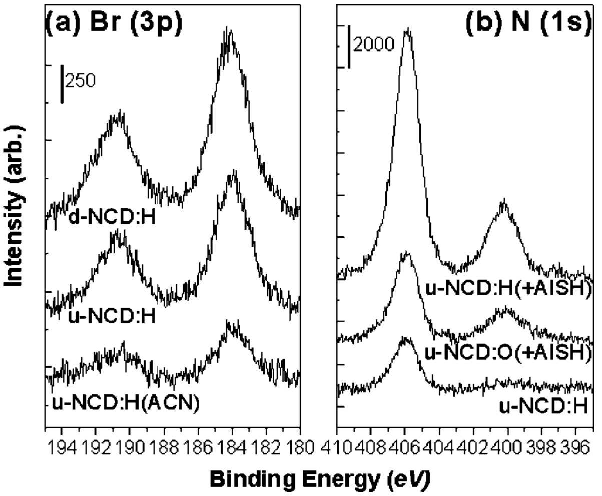

Figure 4. (a) From top down: XPS Br 3p spectra of doped H-terminated NCD (d-NCD:H) and undoped H-terminated NCD (u-NCD:H) functionalized with 5 mM of 4-bromophenyldiazonium tetrafluoroborate (4BrPD) in 0.1 M HCl or acetoniltrile (ACN). The doped sample showed higher reactivity than the intrinsic sample. (b) From bottom up: N 1s spectra of u-NCD:H functionalized with 5 mM 4-nitrophenyldiazonium tetrafluoroborate ($4NO_2PD$); undoped oxidized NCD (u-NCD:O) functionalized with 5 mM $4NO_2PD$ + ammonium iron(II) sulfate hexahydrate (AISH); and u-NCD:H functionalized with 5 mM $4NO_2PD$ + AISH. The addition of AISH increases the grafting efficiency with the diazonium salts.

inhibited when it is O-terminated, as shown in Figure 2. For intrinsic diamond which has attained some degree of *p*-type conductivity in solution, the surface conductive layer is only a few angstroms thick, and the charge transfer rate is limited by the small densities of carriers. Thus, the spontaneous transfer of electrons to initiate the reduction of the aryldiazonium salt can only proceed if the surface has sufficient conductivity and can be expected to be self-limiting at a monolayer due to the increase in charge transfer resistance across the interface when an organic monolayer formed on the surface. To further illustrate the key role of substrate surface conductivity, spontaneous coupling of 4-bromophenyldiazonium tetrafluoroborate (4BrPD) was attempted on lightly doped H-terminated nanocrystalline diamond (d-NCD:H) under the same conditions. XPS analysis as shown in Figure 4a now shows higher Br 3p peak intensity compared to the intrinsic samples (u-NCD:H), implying a direct relationship between dopant level (density of carriers) and grafted functional group density. In addition, the coupling efficiency was much lower when the grafting of the aryldiazonium salts was carried out in acetonitrile (ACN) compared to acidic media, as evidenced by the lower Br 3p intensity detected for the former. In acidified water, the surface conductivity of diamond is higher due to "surface transfer" doping to acceptor-like states induced by hydroxonium ions, and such a process is weaker in acetonitrile. A schematic illustrating the equilibration of the Fermi level and chemical potential following the transfer of valence band electrons from the diamond into electrolyte is shown in Figure 5a. Figure 5b shows the position of the chemical potentials of various aryldiazonium salts relative to the valence band of diamond.

Similarly, when 4-nitrophenyldiazonium tetrafluoroborate ($4NO_2PD$) was used, the spontaneous coupling occurred only on H-terminated diamond (u-NCD:H) and not on the oxygenated ones (u-NCD:O), as seen in Figure 2. The N 1s spectrum of u-NCD:H shows only a single peak at 406 eV due to the nitro group, the peak at 400 eV attributable to the reduced amine group, which is inevitably present on electrochemically functionalized surface (e.g., constant potential or CV methods), is conspicuously absent here, indicating that spontaneous coupling of aryldiazonium salts on intrinsic diamond is a more controlled way of introducing nitro groups without the concomitant reduction accompanying electrochemical methods. As depicted in Figure 5b, both the reduction chemical potential of $4NO_2PD$ and that of 4BrPD are lower than that of the valence band maximum of diamond when referenced to the vacuum level,[20] suggesting that electron transfer from diamond to both electrolyte species is thermodynamically feasible. However, the higher electron affinity of oxygenated diamond places its valence band maximum below the chemical potential of these electrolyte species; therefore, there is an energy barrier for electron transfer to these species, which explains the lack of spontaneous coupling on oxygenated diamond.

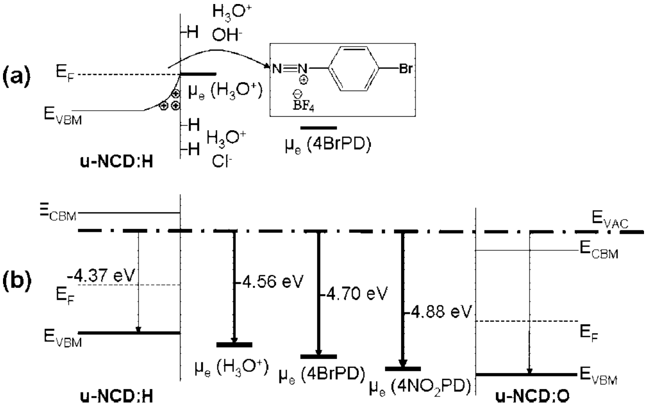

Figure 5. (a) Schematic description of spontaneous reduction of 4-bromophenyldiazonium tetrafluoroborate (4BrPD) on undoped H-terminated NCD (u-NCD:H). The reaction is facilitated by the surface conductive layer induced by acidic water. (b) Energy level diagram for u-NCD:H, undoped oxidized NCD (u-NCD:O), and reduction chemical potentials of hydroxonium ions (H_3O^+), 4BrPD, and 4-nitrophenyldiazonium tetrafluoroborate ($4NO_2PD$) in solution.

In order to overcome the inertia for electron transfer from oxygenated diamond to $4NO_2PD$, a radical initiator such as ammonium iron(II) sulfate hexahydrate (AISH) was added. In this case, the coupling of nitrophenyl could be achieved on oxygenated diamond, as shown in Figure 4b. When AISH was added during the spontaneous grafting of $4NO_2PD$, on u-NCD:H, the intensity of NO_2 peak in XPS was observed to be four times higher than when it was not added. Thus, AISH helps to reduce the aryldiazonium salt and generate phenyl radical for surface grafting. However, the addition of AISH brought about the appearance of a lower binding energy N 1s peak at 400 eV assignable to the NH_2 groups, which is evidence of excessive reduction of the aryldiazonium salt and formation of multilayers. More investigation and fine-tuning of reaction conditions are required to elucidate the role of AISH and optimization of the organic layer.

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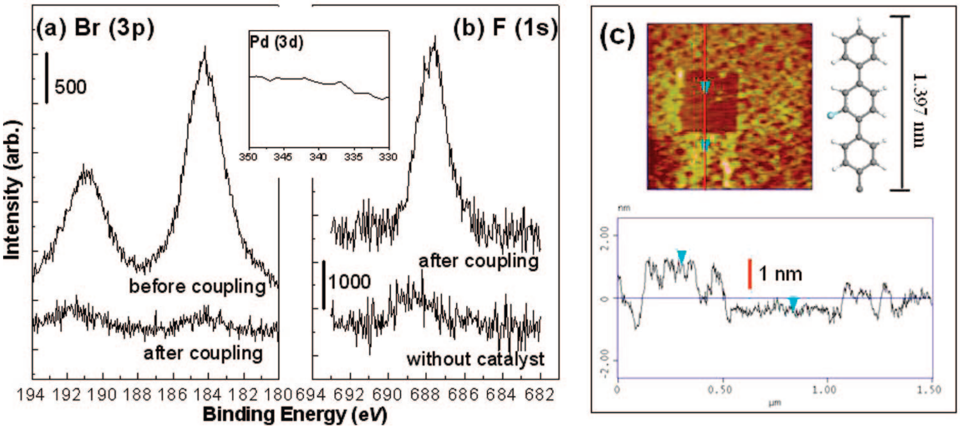

Figure 6. (a) XPS Br 3p spectrum of 4-bromophenyldiazonium tetrafluoroborate (4BrPD) functionalized undoped NCD (u-NCD) before and after Suzuki coupling to 2-fluorobiphenyl boronic acid (2FBB). (b) XPS F 1s spectrum of 4BrPD functionalized u-NCD after Suzuki coupling to 2FBB; the lower spectrum is a control experiment where no Pd catalyst was added. Inset: Zoom-in wide scan spectrum showing the absence of Pd 3d peaks (~335 to 340 eV) after Suzuki coupling. (c) Contact mode AFM image of scratched area on 4BrPD functionalized C(100) after coupling to 2FBB and line profile through the scratched area showing a depth of 1.5 (±0.3) nm, in close agreement with the calculated molecular length of 1.397 nm.

Surface Suzuki Coupling. The bromophenyl coupled surface provides an excellent solid phase platform for further C−C extension via Suzuki coupling (refer Scheme 1). As a proof of concept, we chose to couple 2-fluorobiphenyl boronic acid (2FBB) to the bromophenyl functionalized surface, where the successful coupling was confirmed by monitoring the fluorine marker in XPS. From Figure 6, the success of the Suzuki coupling is evidenced by the vanishingly weak intensity of the Br signal, which is accompanied by the appearance of F 1s peak. After correcting for the respective atomic sensitivity factors, the reaction yield calculated from the $\mathrm{F_{(aftercoupling)}/Br_{(beforecoupling)}}$ ratio is 87%. The yield of this heterogeneous reaction is comparable to coupling reactions performed in homogeneous solution.[21] It is noteworthy that our reaction conditions produced no detectable Pd catalyst contamination after the Suzuki coupling reaction. To prove that 2FBB did couple via Suzuki coupling, a control experiment was performed without using the Pd catalyst, and XPS results showed negligible F 1s signal. In order to verify the thickness of the coupled adlayer, AFM scratching experiment similar to what was described previously was performed on a C(100) substrate after Suzuki coupling to 2FBB. As shown in Figure 7, the line profile shows an increased height difference of 1.5 (±0.3) nm between the unscratched area and scratched trench which agrees well with the height of a grafted 2FBB molecule (1.397 nm) calculated by density functional theory (DFT). This proves that the Suzuki coupled mesogenic molecule is standing upright on the diamond surface.

Our testing showed that the Suzuki coupling conditions on bromophenyl functionalized diamond work well with most of the commercially available boronic acids. In order to demonstrate the concept of "uninterrupted" conjugation between adsorbate and substrate, we selected the molecule of pyrene for Suzuki coupling. Surfaces attached with pyrene molecules have many applications ranging from chemical sensing[22] to photosensitization of substrate,[23] but they are often linked to the surface through an alkyl chain. The uninterrupted conjugation of pyrene via Suzuki coupling was tested using pyrene boronic acid as an example. Using TOF-SIMS to analyze the surface bound species, we concluded that pyrene boronic acid was successfully coupled to 4BrPD functionalized diamond with direct conjugation (see Figure S1, Supporting Information). This is because in addition to the observation of peak fragments corresponding to the pyrene ions ($m/z = 200$) the peak fragments of phenylpyrene ion ($m/z = 276$) could also be detected. Since the phenyl moieties originated from the diamond surface before the Suzuki coupling, this proved that the pyrene was linked to the surface via the aryldiazonium derivatized phenyl linker, forming an uninterrupted conjugation system to diamond.

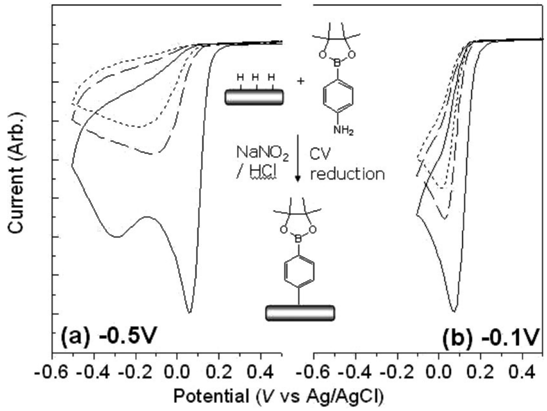

Figure 7. In situ electrochemical generation of boronic ester derivatized aryldiazonium salts, showing three CV reduction cycles (first cycle, solid line; second cycle, dashed line; and third cycle, dotted line) with applied CV between (a) +0.5 V to –0.5V and (b) +0.5 V to –0.1 V, at a scan rate of 100 mV.

CV Reduction of in Situ Generated Aryldiazonium Salts. To expand the versatility of Suzuki coupling, the generation of arylboronic ester on the diamond surface as

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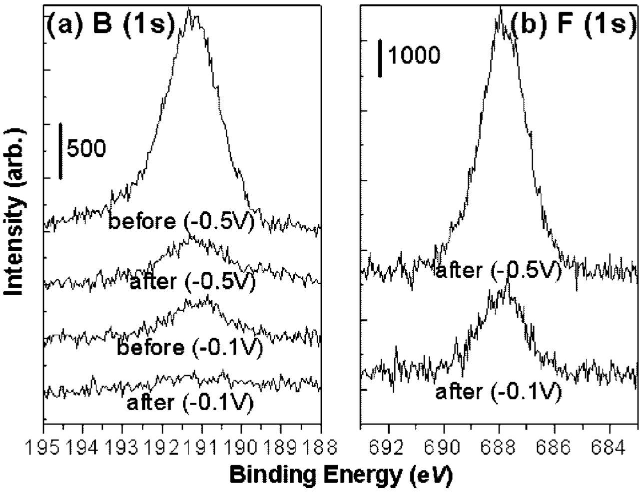

Figure 8. XPS spectra of BDD functionalized by electrochemically generated arylboronic ester generated by CV cycling to −0.1 or −0.5 V, showing (a) B 1s and (b) F 1s before and after Suzuki coupling to 4-bromotetrafluoroaniline (4BrTFA).

an alternative synthon to couple with aryl halides was also attempted, in accordance to the second Suzuki coupling route shown in Scheme 1. One problem is that boronic acid derivatized aryldiazonium salt is not commercially available, so we attempt to generate boronic ester derivatized aryldiazonium salt by diazotization of 4-aminophenylboronic ester (4APBE) with an equivalent mole of $NaNO_2$ and followed by electrochemically grafting the in situ generated aryldiazonium salt on the diamond surface. In this case a conducting diamond sample has to be used as the substrate. As shown in Figure 7, the first CV cycle exhibits a well-defined reduction peak at 0.07 V (vs Ag/AgCl) which can be assigned to the formation of the aryl radical. The intensity of this reduction peak decreases in the second and third CV cycles, which is suggestive of the passivation of the diamond surface by the electrochemically grafted layer.[4] Moreover, the thickness, or density, of the grafted layer could be controlled by varying the cathodic potential during CV. For example, the XPS spectrum of the diamond surface as shown in Figure 8 shows that by cycling to −0.5 V, and the intensity of the boron signal due to the surface arylboronic ester functionality was five times that of cycling to −0.1 V.

After generating the arylboronic ester on the diamond surface, Suzuki coupling to 4-bromotetrafluoroaniline (4BrTFA) was carried out, where the F signal provides a good fingerprint marker in XPS. Typically, a higher coverage of tetrafluoroaniline (after −0.5 V) was obtained on the diamond sample which had been premodified with a higher coverage of arylboronic ester, as evident in the higher F 1s intensity detected in XPS (Figure 8), although the F intensity does not scale linearly with coverage of the surface arylboronic acid due to steric hindrance. Based on the increase in F 1s and N 1s intensity, we calculated the F 1s/N 1s ratio to be 3.9, which correlates well with molecular formula of 4BrTFA. From the XPS C 1s spectrum of arylboronic ester-functionalized BDD before and after Suzuki coupling, a chemically shifted peak at 289 eV attributable to the C−F aromatic carbon in 4BrTFA can be discerned (see Figure S2, Supporting Information). The presence of 4BrTFA on the diamond surface was further confirmed by the electrochemical characteristics of this redox active species. By performing CV on the 4BrTFA-coupled diamond using 0.1 M KCl as electrolyte, a redox peak at around 0.5 V (vs Ag/AgCl), attributable to hydroxyaminobiphenyl/nitrosobiphenyl reversible reduction−oxidation, could be observed. This is analogous to previous reports of 4-aminobiphenyl molecule grafted on UNCD.[12]

Diamond-Based Organic Solar Cell. To test the usefulness of the Suzuki coupled organic-diamond platform for the charge transfer system involving diamond as the electron donor and fullerene as the acceptor, we selected oligothiophene as the conjugated linker between fullerene and diamond. Starting from the arylboronic ester functionalized BDD platform, we performed Suzuki coupling to 5-(5-iodothiophene-2-yl)thiophene-2-carbaldehyde (I-2T-CHO). This was followed by the linking of C_{60} to the carbaldehyde moieties present on the terminal ends with *N*-methylglycine (2T-C_{60}), as shown in Figure 9. The success of Suzuki coupling step can be seen in the almost complete disappearance of B 1s peak and corresponding appearance of the S 2p peak after Suzuki coupling to I-2T-CHO. After the linking to C_{60} with *N*-methylglycine, there was a slight decrease in S 2p signal due to attenuation by the top C_{60} molecules and increase in N 1s peak due to incorporation of *N*-methylglycine linker. Furthermore, the presence of C_{60} on the surface was confirmed by the appearance of a chemically shifted shoulder from the bulk diamond peak and the appearance of C_{60} valence states in the UPS He I spectrum (see Figure S3, Supporting Information).

As a proof of concept, we performed photoelectrochemical measurements using the C_{60}-linked oligothiophene-modified BDD (modified BDD) as the working electrode in a typical three-electrode electrochemical system. The photocurrent versus applied voltage curves show increased photocurrent intensity on the modified BDD at negative bias (see Figure S4, Supporting Information). When a H-terminated BDD without any surface modification was used as the control, no photocurrent response was obtained. This agrees with the mechanism that upon light generation of the electron−hole pair in the chromophore, the separated electron flows toward the electron-withdrawing C_{60}[24] and hence negative bias favors such a flow. In Figure 10, the strong photocurrent response of C_{60}-linked oligothiophene-modified BDD contrasts markedly with the absence of photocurrent response on hydrogen terminated BDD. Furthermore, we observed highly stable photocurrent conversion during our preliminary testing (see Figure S5, Supporting Information), which we attribute to the strong interfacial C−C covalent bonding and robustness of the Suzuki coupling scheme in building a molecular charge transfer network on diamond. More detailed studies concerning the action spectrum and quantum efficiency will be carried out and reported in a later paper.

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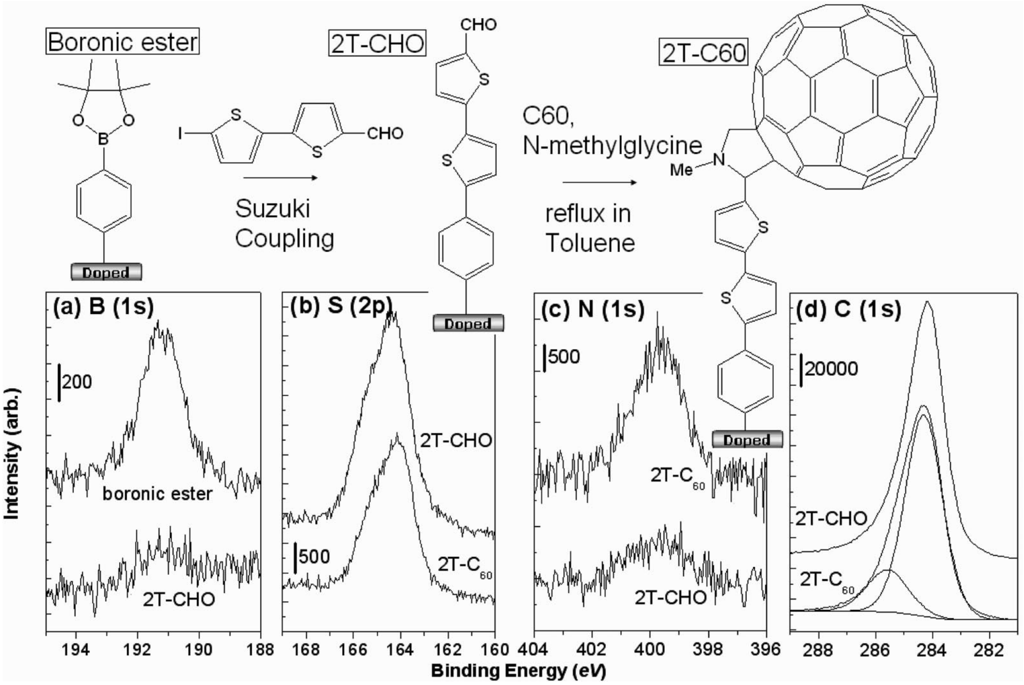

Figure 9. (a) XPS B 1s spectrum of arylboronic ester functionalized BDD generated by five cycles of CV reduction to −0.2 V and after Suzuki coupling to 5-(5-iodothiophene-2-yl)thiophene-2-carbaldehyde (2T-CHO) and XPS spectra showing (b) S 2p, (c) N 1s, and (d) C 1s of the 2T-CHO coupled BDD (2T-CHO) and (d) after linking to C_{60} with *N*-methylglycine (2T-C_{60}).

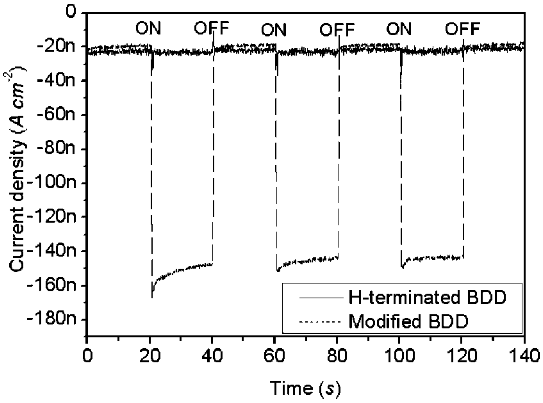

Figure 10. Photocurrent response of H-terminated BDD (solid line) and C_{60}-linked oligothiophene-modified BDD (dashed line) in 5 mM methyl viologen/0.1 M Na_2SO_4 solution at −0.1 V bias (vs Ag/AgCl).

IV. Conclusion

In this work, we have demonstrated a generic method to couple aryl molecules on diamond surfaces using a combination of aryldiazonium salt derivatization and Suzuki coupling steps. This method is highly versatile and specific compared to the photochemical coupling method using alkyl linkers. The reactions involving bromophenyl as the synthon to couple to target phenyl boronic acids could be carried out on intrinsic hydrogenated diamond, using simple wet solution chemistry. Because spontaneous derivatization does not require electrical or photochemical activation, we predict that these surface processing methods may also work well on detonation or high-pressure−high-temperature nanodiamond powder. In other words, this method of coupling aryl molecules should have general validity on all types of diamond surfaces. Furthermore, we observed that the spontaneous coupling of aryldiazonium salts could proceed on intrinsic diamond with hydrogen terminations but not on oxygenated diamond. Fundamentally, this may be related to the energy barrier in interfacial charge transfer on surfaces with different electron affinities and conductivities. The addition of a radical initiator such as AISH can promote diazonium salt derivatization of oxygenated diamond, although in this case the extent of the reaction is more difficult to control.

We have also explored the possibility of grafting arylboronic ester on diamond through electrochemical reduction of in situ generated aryldiazonium salt and demonstrated that this offers another feasible pathway to the Suzuki coupling of aryl halides on diamond. The successful demonstration of Suzuki coupling methods in this work, which is especially useful for aryl molecular systems, that is, fused ring systems, molecular dyes, or polymers, opens up new possibilities for the applications of diamond in molecular electronics and photovoltaics. For example, we have successfully constructed a diamond−oligothiophene−fullerene system using the chemistry described here and demonstrated the photocurrent conversion effect involving charge transfer across the diamond (donor)−oligothiophene (linker)−fullerene (acceptor) interface.

Acknowledgment. K.P.L. will like to acknowledge the support of MOE-ARF Academic Grant R-143-000-275-112: Electrochemical Surface Science study of Functional Biomolecular Scaffolds on Nanodiamond.

Supporting Information Available: Synthesis procedures for 5-(5-iodothiophene-2-yl)thiophene-2-carbaldehyde. TOF-SIMS spectra, XPS C 1s spectra, UPS He I spectra, cyclic voltammograms, and photocurrent response of functionalized/modified diamond (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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