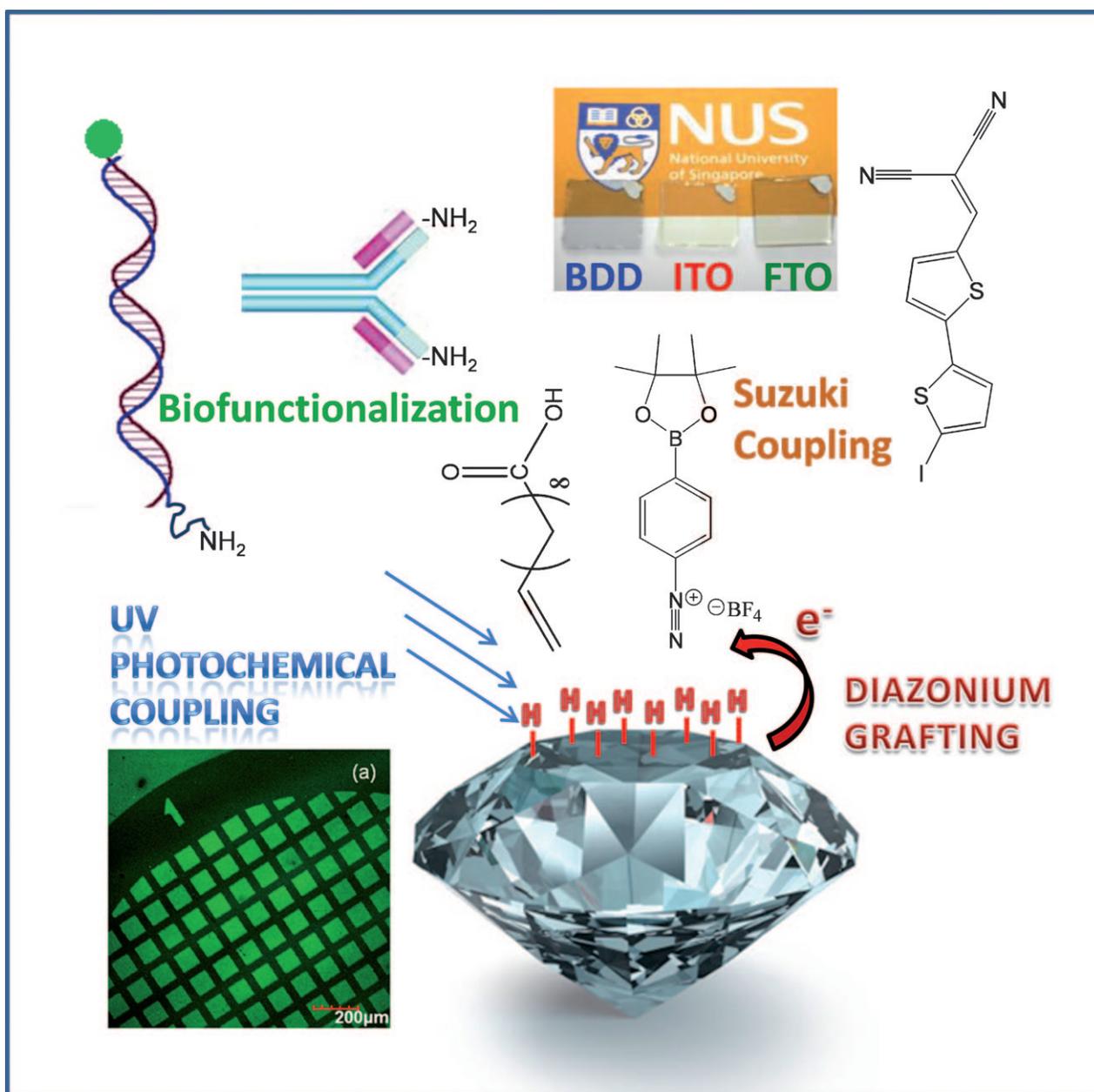# FOCUS REVIEWS

The Chemistry of C−H Bond Activation on Diamond

Yu Lin Zhong and Kian Ping Loh*[a]

Abstract: The surface of hydrogen-terminated diamond resembles a solid hydrocarbon substrate. Interestingly, the C−H bonds on the diamond surface are not as unreactive as that of saturated hydrocarbon molecules owing to its unique surface electronic properties. The invention of C−H bond activation and C−C coupling reactions on the dia- mond surface allows chemists to develop powerful chemi- cal transistors, biosensors, and photovoltaic cells on the di- amond platform.

Keywords: chemical vapor deposition · C−H activation · diamond · surface chemistry · Suzuki coupling

1. Introduction

Owing to its rarity, extraordinary hardness, and brilliance, diamond has always been valued in human civilizations as gemstones. Since it is a carbon allotrope residing in Group 4 of the periodic table with Ge and Si, there is no inherent reason why diamond cannot be used in electronics.[1] In the last ten years, there has been rapid progress in the chemical vapor deposition of diamond thin films with a view towards developing thermal management solutions or high-power electronics.[2] The electronic properties of diamond can be varied from insulating (intrinsic diamond) to conductive using boron (p-type) or phosphorous (n-type) doping. In ad- dition to these bulk properties, a high surface conductivity has been detected on intrinsic hydrogen-terminated dia- mond surfaces,[3] which has been used in chemical field- effect transistors[4] or solution-gated biosensors.[5] Owing to its transparency, wide electrochemical potential window, and chemical robustness, diamond has also been evaluated as a platform for biosensing[6] or photovoltaics.[7] With further engineering of the diamond material, it was shown that ver- tically aligned diamond nanowire DNA sensors can easily surpass the detection limit on conventional gold electrode with extremely good stability.[8] More intriguingly, diamond holds the key in unlocking practical quantum photonic devi- ces owing to the low level of decoherence intrinsic in dia- mond.[9]

In almost all cases, maintaining the correct surface termi- nation on diamond is essential to obtain the highest desired performance. For biosensing and photovoltaic applications, functionalization of the diamond surface is usually needed, and that is where the chemical reactivity of the diamond sur- face has to be considered. This Focus Review considers the latest development in C−H bond activation on diamond.

2. Properties of the Hydrogen-Terminated Diamond

A schematic of the diamond lattice can usually be found in most high-school chemistry textbooks as an introduction to the directional and specific sp^3 bonding in tetrahedrally bonded solid-state carbon. The take-home message for the student is that the C−C bond strength is one of the strongest in nature, and the directional and specific bonds in the dia- mond lattice imparts great mechanical strength on the mate- rial. While the schematic shows a picture of the bulk lattice, most textbooks fail to mention what happens when the sp^3 bonds at the surface truncate at the air–solid interface. Unlike graphite, the diamond surface has to be truncated by hydrogen to maintain the sp^3 integrity. As-grown synthetic diamond films produced by chemical vapor deposition, as well as natural diamond polished in the presence of olive oil,[10] are hydrogen-terminated. It took a decade and many surface chemistry studies for scientists to correlate the unique electronic and chemical properties of diamond with the presence of surface-bound hydrogen. Today, physicists and electrical engineers appreciate that this monolayer of surface hydrogen imparts a whole new dimension of chemis- try on the diamond surface.

The surface of hydrogenated diamond resembles a contin- uous sp^3-bonded alkane molecule (Figure 1). How difficult is it to activate this C−H bond for reactions? The classical methods for dehydrogenation required a chemical group to be adjacent to the targeted C−H bond, which is clearly absent in diamond. The chemical inertness of diamond sur- face arises from these strong localized bonds which resemble saturated hydrocarbons; these systems have no low-lying empty orbitals or filled orbitals of high energy that could participate in chemical reactions. For this reason diamond electrodes possess an electro- chemical potential window as wide as 4 electron volts before oxygen and hydrogen evolu- tion.[11]

However, there is an interest- ing twist for diamond compared to hydrocarbons, such that the hydrogen-terminated diamond surface can be more susceptible to photochemical activation than alkanes. To begin, the presence of C−H bonds on the
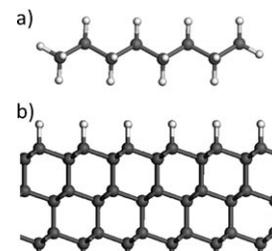

Figure 1. a) Ball-and-stick drawing of octane and b) H- terminated diamond lattice.

[a] Dr. Y. L. Zhong, Prof. Dr. K. P. Loh
Department of Chemistry
National University of Singapore
3 Science Drive 3, Singapore 117543
Fax: (+65) 6779-1691
E-mail: chmlohkp@nus.edu.sg

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surface creates a surface dipole that lowers the vacuum level beneath the conduction band minimum of diamond, producing the condition of negative electron affinity (NEA).[12] Such NEA properties can also be found for diamondoid molecules based on the variants of adamantine ($C_{10}H_{16}$).[13] The large binding energy splitting between one shell and the next in these hydrocarbons places low-lying empty levels beneath the vacuum level, such that the ionization energy for removing electrons is much reduced compared to molecules with positive electron affinity. The signature of NEA in hydrogen-terminated diamond is the lower-than-band-gap threshold energy for electron ejection.[14] The photoelectron threshold energy of 4.4 eV for the onset of secondary electron emission from the diamond surface is smaller than the band gap of diamond at 5.5 eV. This low energy threshold arises from the energy gap between the valence-band maximum and the vacuum level, which is situated 1.1 eV below the conduction-band minimum (Figure 2). This property has
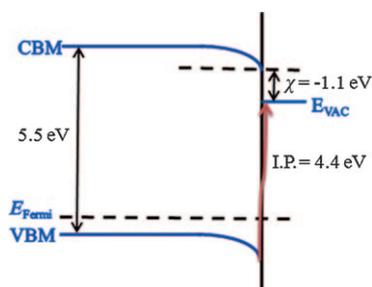

Figure 2. Typical energy level diagram of boron-doped H-terminated diamond exhibiting negative electron affinity.

Kian Ping Loh *obtained his PhD from the Physical and Theoretical Chemistry Laboratory, University of Oxford, in 1997 and did his postdoctoral work in the National Institute for Materials, Tsukuba, Japan during 1997–1998. Both his PhD and postdoctoral work concerned the surface chemistry of diamond, a dedicated research field he has worked for more than ten years. He is currently leading the diamond research effort at the National University of Singapore.*

Yu Lin Zhong *received his B.Appl.Sc (Hons) in Applied Chemistry from National University of Singapore (NUS) in 2005. During this, he joined Prof. Kian Ping Loh's group as an undergraduate research student and thereafter continued as a PhD candidate. He was the NUS President Graduate Fellow and the recipient of the Best Graduate Researcher Award 2009. He is currently a Postdoctoral Research Associate with Prof. Steven L. Bernasek at Princeton University, focusing on the surface chemistry on silicon.*

stimulated interests in the use of diamond as a cold cathode.[15] The implication for chemistry is that hydrogenated diamond has a low work function and is a good electron donor. The photochemical activation of diamond with UV light may allow electron ejection and radicalization of reactants that have vinyl groups, thus allowing C−C coupling on the surface (see below).

Diamond is well known as a perfect insulator, and an insulating surface is not conducive for electron ejection. It turns out that a second surprise is that the presence of surface hydrogen induces an "insulator-to-metal" transition on nominally undoped diamond.[16] Owing to the low work function of hydrogenated diamond, the transfer of electrons from diamond to hydrated protons in solution gives rise to hole accumulation in diamond, resulting in a p-type surface conductivity.[17] Chakrapani and Angus reported the interactions of hydrogen-terminated, macroscopic diamonds and diamond powders with aqueous solutions of controlled pH and oxygen concentration.[18] They showed that electron transfer between the diamond and an electrochemical reduction/oxidation couple involving oxygen in aqueous phase is responsible for the surface conductivity. Essentially what this means is that although bulk diamond is insulating, the surface of diamond can be conducting when it is wetted or exposed to acidic gases in humid environment. It has been reported that a low concentration of NO_2 in air is able to induce sheet carrier concentration on the order of $2 \times 10^{14} \text{ cm}^{-2}$ on diamond.

Both the NEA and p-type conducting effect on diamond can be reversed when the hydrogen terminations on the diamond are replaced by oxygen.[19] Oxidation of the diamond surface can be achieved by exposure to oxygen plasma or thermal annealing at elevated temperatures in an oxygen-rich environment. The surface of diamond becomes terminated by oxygen functionalities such as ether, epoxy, or hydroxyl groups. By changing the termination from hydrogen to oxygen on diamond, the surface conductivity vanishes and charge transfer from the surface is inhibited by its positive electron affinity. Therefore by controlling the surface termination on diamond, the reactivity of the diamond surface can be tuned.

3. Photochemical Activation of the C−H Bond

The presence of surface conductivity, coupled with the ease of electron transfer from the diamond surface, has important implications for its surface reactivity. Owing to the NEA of diamond, the use of sub-band-gap light of 254 nm (4.9 eV) is sufficient to activate the C−H bond for C−C coupling with vinyl-group-containing molecules. The photochemical functionalization is a surface-mediated photochemical reaction initiated by the photoejection of electrons from the H-terminated diamond to the alkene liquid phase. Oxidized diamond surface with higher ionization potential is inactive to UV photochemical functionalization. Figure 3 shows that the UV photochemical activation on diamond begins with a
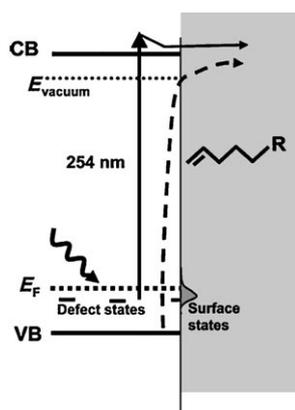
Figure 3. Proposed mechanisms for ejection of electrons into liquid phase: excitation from occupied defects and/or surface states to the conduction band followed by diffusion and emission (solid arrow); direct photoemission from valence band to the vacuum level (dashed arrow). Reproduced with permission from reference [20].

UV photoexcited electron from diamond ejected into the LUMO of the vinyl group which is positioned near the vacuum level in the solvated form, thus creating radical anions in the liquid phase.[20]

Some of these nucleophilic radical anions may abstract H atoms from the surface to produce a surface carbon dangling bond which then couples to the alkene moiety of the liquid-phase molecules and transfers the radical to it. The grafted molecule bearing the radical can initiate a polymerization process with another alkene moiety, abstract a proton from any molecule in the liquid phase, or abstract a hydrogen atom from the diamond surface which is conveniently located next to it. From careful AFM characterization of the functionalization growth process by Yang et al.,[21] it was observed that the grafted film formation is a 2D process until a monolayer is reached and from which a slow but continuous multilayer formation proceeds. This implies that the grafted molecule bearing a reactive radical will preferably abstract an adjacent H atom on the diamond surface and propagates sideward from this "nucleation" center until a monolayer is formed before the start of slow cross-polymerization. The slow cross-polymerization may be due to the increased ionization potential for completely functionalized diamond surface, which sets a high barrier for the photoelectron to

be emitted. The mechanism of the whole photochemical functionalization process is presented in a step-by-step schematic drawing as shown in Figure 4.

The photochemical coupling method has been deployed to couple DNA linkers on the diamond surface for constructing biosensors. There are many different functionalization strategies for diamond surface that have been developed over the years and have been reviewed by Szunerits and Boukherroub.[22] Stutzman,[23] Nebel,[24] and Krüger[25] have written review papers focusing on the biofunctionalization chemistry. Herein, we aim to focus on the diamond-based chemical reactions between functional organics and diamond surface that result in the formation of highly stable C−C bonds which can also be viewed as an extension of the diamond surface lattice.

The attachment of DNA to H-terminated diamond surface begins with UV photochemical coupling of a long-chain ω-unsaturated amine, protected with the trifluoroacetamide functional group, followed by deprotection to yield the long-chain amine functionalized diamond surface. It was then reacted with a hetero-bifunctional crosslinker before finally coupling to the thiol-modified DNA. The most convincing advantage of using diamond is the bonding stability of DNA to diamond in which there was no sign of degradation after repeated hydridzation/denaturing cycles, in comparison to other electrodes.[6a] We have successfully demonstrated the direct UV photochemical coupling of undecylenic acid without a protecting group on diamond in contrast to previous failed attempts with unprotected amine.[26] In comparison with the tedious method of using a protected form of unde-
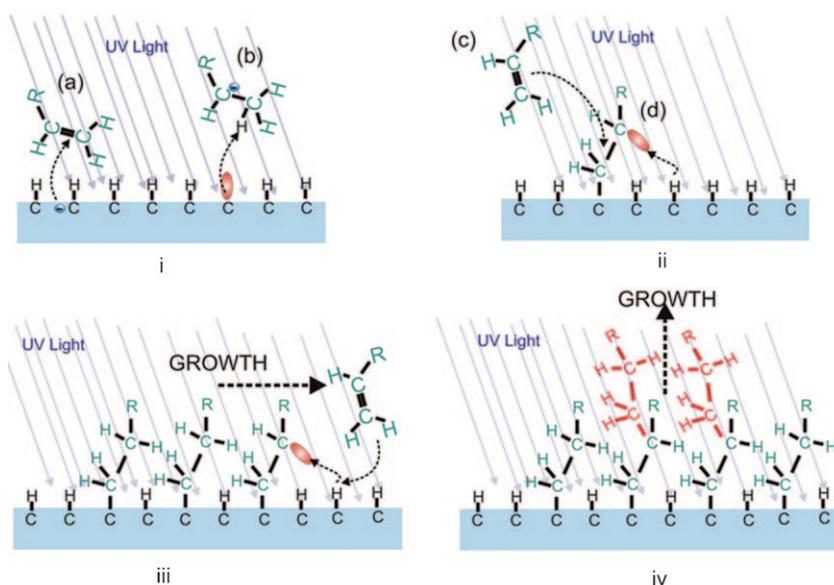

Figure 4. Schematic grafting of the diamond surface by amines. i) The generation of radical anions by electron transfer from diamond to the olefin (a); the nucleophilic properties of the radical causes a hydrogen abstraction (b), which results in a surface carbon dangling bond. ii) The dangling bond reacts with an olefin molecule to form a diamond-carbon/olefin-carbon bond (c). This olefin abstracts a hydrogen atom from the diamond surface (d), which is a new site for olefin addition. iii) The hydrogen abstraction reaction results in a chain reaction. iv) In case of extended illumination, a 3D growth sets in that is due to cross-polymerization of olefin molecules. Reproduced with permission from reference [21].

cylenic acid (UA), trifluoroethylundecenoate (TFEU), the direct method was found to form a higher density of carboxylic acid groups on diamond as characterized and confirmed by a variety of techniques. The lower grafting efficiency of TFEU is attributed to the bulky protecting group and inevitable damage caused to the monolayer by the use of strong base during the deprotection step.[27] The successful UV photochemical patterning of diamond surface was achieved through a photomask with undecylenic acid, and the functionalized areas were directly coupled to amine-modified DNA via the generic carbodiimide coupling chemistry. The immobilized DNA was then hybridized to the fluorescein isothiocyanate (FITC)-labeled complementary and the resultant patterned fluorescence image is shown in Figure 5.
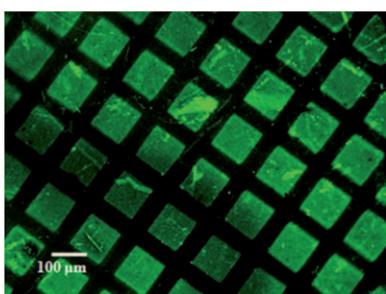

Figure 5. Patterned fluorescence images of fluorescein isothiocyanate (FITC)-labeled DNA immobilized on undecylenic acid functionalized diamond and subjected to repeated denaturation–rehybridization cycles (three cycles).

4. Diazonium Grafting Chemistry

Although the UV photochemical functionalization is a convenient method for coupling linear aliphatic chains terminating with a single vinyl group, it is not so useful to couple conjugated molecules with selectivity because the presence of more than one unsaturated bond in the reactant results in nonselective pathways of attachment to the surface in the presence of UV activation. Conjugated molecules include a large class of organic dyes, where the coupling to diamond is useful for developing photovoltaic devices. To prevent uncontrolled radical reactions, alternative C−C coupling reactions have to be developed for conjugated aryl molecules.

Conjugated molecules have some advantages compared to the saturated alkyl chains. First, the presence of π–π stacking in aryl compounds affords denser packing of the monolayer compared to the alkyl monolayer. Moreover, the delocalized electrons in aryl linkers afford a lower resistance compared to the alkyl linker, which is essen-

tial if diamond is to be used as electrode materials in organic electronics. Therefore, it is desirable to consider a generic method which allows the direct wiring of conjugated aryl molecules on diamond with good specificity.

One way of functionalizing the hydrogenated diamond surface is by simply placing organic molecules on the surface followed by photochemical or thermal activation. For example, the direct insertion of diaryl carbenes into hydrogenated diamond has been demonstrated. To avoid difficulties in the handling of highly reactive compounds, the carbene is generated in situ from the thermal decomposition at 400 K of a thin film of the corresponding diaryl diazomethane precursor deposited at the diamond interface.[28]

One of the most versatile methods is the spontaneous or electrochemical functionalization of diamond with aryldiazonium salt. The aryldiazonium salt can be synthesized "on demand" by the electrochemical grafting of in situ generated aryldiazonium salts.[29] The challenge for aryldiazonium reduction is in the difficulty to limit the reaction to a monolayer. A comprehensive review by Pinson and Podvorica[30] discussed monolayer grafting achieved by the careful control of grafting parameters such as the amount of charge supplied using short time constant potential attachment and the concentration of aryldiazonium salt. Nebel and co-workers compared the grafted organic film of 4-nitrobenzene on diamond by using cyclic voltammetry and constant potential attachment with AFM characterization.[31] They found that the cyclic voltammetry attachment formed a thick organic layer of up to 80 Å owing to the three-dimensional growth scheme as shown in Figure 6. By employing the constant potential attachment for 600 s, a thin and compact film was formed as sufficient time was given to allow π–π stacking interactions between neighboring molecules, which favors two-dimensional growth on the surface.

Furthermore, the energy offset between the chemical reduction potential of the different aryldiazonium salts and the valence band maximum of the diamond determines the reactivity of the aryldiazonium salts. For example, a monolayer of 4-bromobenzene can be achieved by the constant potential method,[32] but the same process produced a 25-Å-thick layer of 4-nitrobenzene.[31] The differences can be traced to the different chemical reduction potential of the salt. The use of spontaneous aryldiazonium grafting and the importance of stacking interactions were also demonstrated

Figure 6. Nitrophenyl groups at an initial stage of attachment grow three-dimensionally (3D) as shown here schematically, forming layers of varying heights and densities. Layer thicknesses of up to 80 Å are detected for cyclic voltammetry attachment after five cycles, whereas the layer becomes denser and only about 25 Å thick in the case of constant potential attachment. Reproduced with permission from reference [31].

by Lud et al.[33] in the formation of a biphenyl self-assembled monolayer on doped ultrananocrystalline diamond. We have compared the diazonium salt grafting reactions using cyclic voltammetry, constant potential, and spontaneous attachment of 4-nitrophenyl aryldiazonium and we found that the spontaneous grafting method resulted in a self-limiting monolayer formation.[34] More significantly, the spontaneous grafting method is applicable to undoped H-terminated diamond but not undoped oxygenated diamond owing to the presence of a surface conductivity layer only in the former. In order to overcome the inertia for electron transfer from oxygenated diamond to the aryldiazonium salt, a radical initiator such as ammonium iron sulphate hexahydrate (AISH) was added in the aryldiazonium solution, which results in the successful functionalization of undoped oxygenated diamond. Based on this discovery, we have extended the application of radical initiator-assisted spontaneous aryldiazonium functionalization to the unreactive oxidized nanodiamond powder with great success.[35]

The different reactivity of diazonium coupling on hydrogenated or oxygenated diamond implies that selective coupling on the surface can be achieved if the diamond surface is first prepatterned with oxygenated and hydrogenated domains. For example, the grafting of 4-nitrophenyl diazonium (4NPD) salt occurs selectively on the hydrogenated domains only. This was performed in acidic aqueous electrolyte, which was found to be a more favorable medium than organic solvent in forming a thinner yet compact nitrophenyl organic film.[36] Alternatively, UV photochemical patterning with hydrophobic alkenes can first be performed to block off the exposed area. Thereafter, the typical stepwise surface biofunctionalization scheme[37] was performed to couple probe DNA on the previously unexposed area, as shown in Figure 7. Hence, by using with a combination of UV photochemical coupling and aryl diazonium coupling steps, we demonstrated that both positive and negative images of DNA can be patterned on the diamond wafer (Figure 8).

The diazonium coupling can be extended to more interesting organic dyes. We synthesized a tailor-made molecular pyridinium dye bearing a terminal aniline group which was diazotized and grafted to doped diamond surface via the electrochemical reduction of in situ generated aryldiazonium
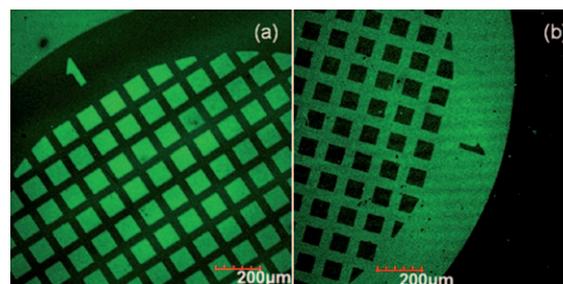

Figure 8. a) "Positive" DNA patterned fluorescent image produced by utilizing undecylenic acid as a biolinker. b) "Negative" DNA patterned fluorescent image achieved by using trifluoroethylundecenenoate (TFEU) as a blocking agent, followed by biofunctionalization of the unexposed area via the diazonium grafting chemistry.

dye.[38] The molecular dye functionalized diamond was used as a platform for electrostatic self-assembly of polyoxometalates as shown in Figure 9. In this case, the use of the long bulky aryldiazonium compound resulted in the formation of a self-limiting bilayer thickness even though excessive reduction cycles were employed. This is due to the blocking of electron transfer from diamond electrode through the long molecular dye, which prevented further reduction and grafting growth. The hydrophobic nature and limited solubility of the molecular dye in aqueous solution may also have enhanced the packing density of the molecular film. The introduction of a molecular wire with a positively charged pyridinium end allows the electrostatic assembly of modular nanosystems on diamond, that is, for example, porphyrin-based redox systems.

The UV photochemical functionalization is well suited for photopatterning of insulating alkyl chains whereas the direct wiring of conjugated aromatics can be easily achieved with the diazonium salt grafting followed by Suzuki coupling. The combination of these functionalization methods can be used for the fabrication of more-complex devices. For example, dielectric films constructed of long alkyl chains can first be patterned on the hydrogenated diamond surface via UV photochemical functionalization. Next, molecular wires can be simply attached onto those unpatterned areas via spontaneous aryldiazonium attachment.
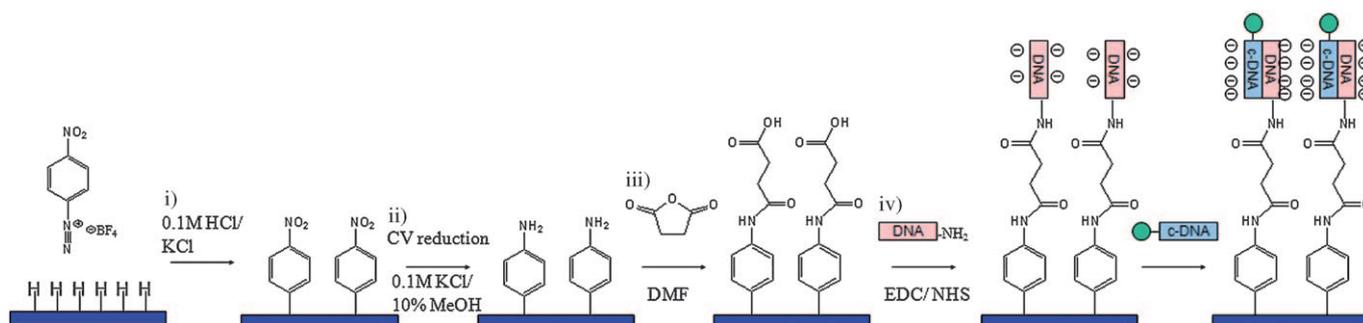

Figure 7. Biofunctionalization of diamond via diazonium grafting chemistry. i) Functionalization of H-terminated diamond with 4-nitrophenyl diazonium (4NPD) salt in aqueous acidic solution. ii) Electrochemical reduction of ntirophenyl to aimnophenyl. iii) Coupling of succinic anhydride linker. iv) EDC/NHS coupling of probe DNA.
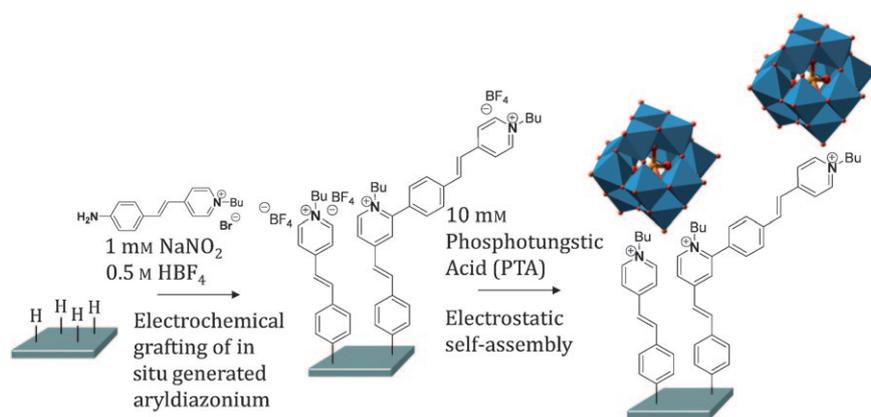
Figure 9. Electrochemical grafting of in situ generated aryldiazonium dye followed by electrostatic self-assembly of phosphotungstic acid (PTA).

compared to dye coupled onto typical optically transparent electrodes such as indium tin oxide (ITO)[40] and fluorine-doped tin oxide (FTO). Furthermore, the dye-coupled diamond electrode also showed higher photoconversion efficiency owing to the matching energy levels between dye and diamond, which demonstrates the advantage of diamond in the field of photoelectrochemistry.

5. Surface Suzuki Coupling

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.[39] 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.

We have investigated the optimal conditions for the generation of bromophenyl or phenylboronic acid functional groups on diamond surface, to be used as a synthon for Suzuki cross-coupling to the respective phenylboronic acid or bromophenyl.[34] The advantage of this approach is that it is highly specific and eliminates any possible multilayer film formation. As a proof of concept, we chose to couple 2-fluorobiphenyl boronic acid (2FBB) to the bromophenyl-functionalized surface as shown in Figure 10. The successful coupling was confirmed with a reaction yield of 87% by monitoring the bromine and fluorine marker from XPS. More importantly, the thickness of the adlayer on single crystal diamond was characterized by AFM scratching before and after Suzuki coupling to 2FBB. The line profile across the unscratched area and scratched trench shows an increase in height of the adlayer which agrees well with the height of a grafted 2FBB molecule (1.40 nm), calculated by density functional theory (DFT). This also proves that the Suzuki-coupled mesogenic molecule is standing upright on the diamond surface.

From Figure 11, the application of the versatile surface Suzuki coupling is seen in the coupling of various conjugated "donor–acceptor" dyes on arylboronic ester functionalized diamond surface, as seen in our recent work.[7] Such a surface coupling scheme can be extended to other organic coupling reaction such as Heck coupling or Sonogashira coupling with the appropriate surface-grafted synthons and reaction conditions. The interface between diamond and the coupled molecules is highly stable as evident from the higher photostability exhibited on dye-coupled diamond
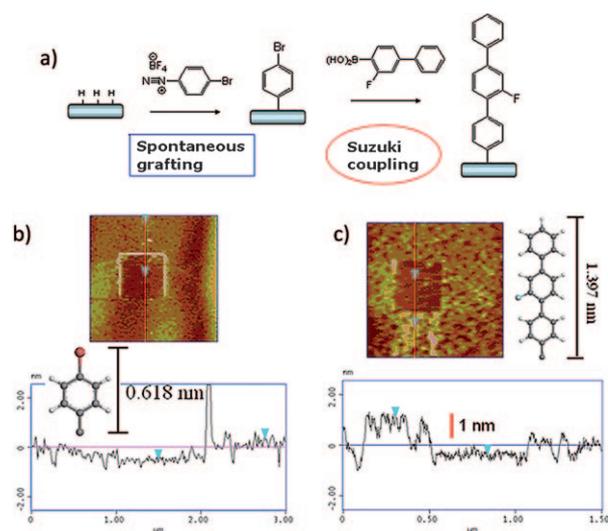

Figure 10. a) Schematic drawing of spontaneous aryldiazonium functionalization with 4-bromophenyldiazonium salt (4BrPD) followed by surface Suzuki coupling to 2-fluorobiphenyl boronic acid (2FBB). b) AFM image of scratched area on 4BrPD-functionalized diamond and line profile through the scratched area showing a depth of 0.6 ($\pm$0.2) nm, in close agreement with the calculated molecular length of 0.618 nm. c) AFM image of scratched area after coupling to 2FBB and line profile through the scratched area showing a depth of 1.5 ($\pm$0.3) nm, in close agreement with the calculated molecular length of 1.397 nm.

Oligothiophene-linked fullerene dyad systems have received considerable attention due to the efficient photoinduced electron transfer from the oligomer to the covalently attached fullerene moiety.[41] In such molecular assemblies, the oligothiophene segment acts as the photoactive electron donor while fullerene behaves as an effective electron acceptor. Owing to close proximity of the electron donor and acceptor moieties, these molecular dyads typically undergo fast charge separation upon photoexcitation, giving rise to high photoconversion efficiency. In this work, we constructed donor–acceptor molecular dyads comprising bithiophene as photoactive electron donor and a fullerene or dicyano moiety as the electron acceptor on a boron-doped diamond
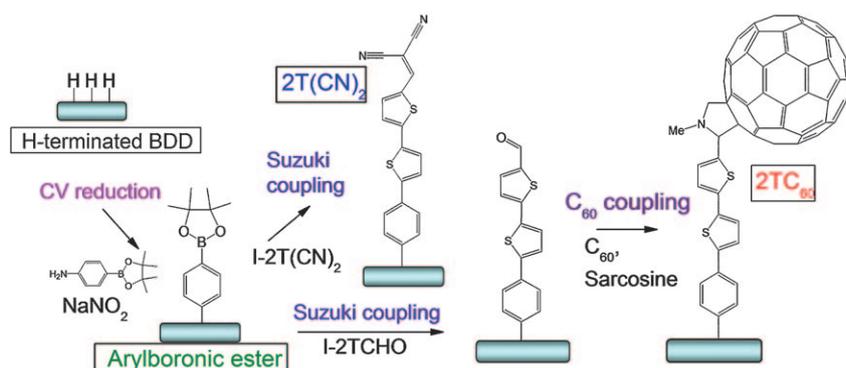
6. Conclusion

Hydrogen termination of diamond surface transforms it into a two-dimensional solid hydrocarbon template. Owing to the unique electronic properties imposed by hydrogen termination, the C−H bond on diamond can be readily activated for C−C coupling reactions by UV photochemical functionalization or spontaneous aryldiazonium attachment. The advantage of di-
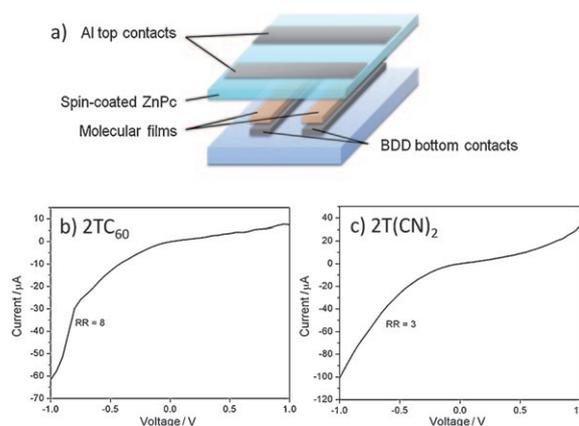

Figure 11. Schematic drawing of surface functionalization with arylboronic ester and Suzuki coupling scheme of bithiophene-C_{60} (2TC_{60}) and bithiophene-dicyano (2T(CN)$_2$) on boron-doped diamond (BDD) thin film.

platform. This is an interesting structure because fullerene, a high electron affinity molecule, is coupled onto diamond, a negative electron affinity material, via a conjugated molecular wire. It is easy to predict that the direction of the preferred electron flow is from diamond to fullerene.

The boron-doped diamond (BDD) substrate was first functionalized with arylboronic ester using cyclic voltammetry between +0.5 V and −0.5 V (vs. Ag/AgCl) with a scan rate of 100 mV s^{-1}. A solution of 5 mM arylboronic ester was prepared in 0.1 M HCl and purged with N$_2$ gas for at least 15 min prior to the experiment. The arylboronic ester functionalized diamond substrate was rinsed thoroughly and sonicated in Nanopure water, THF, and hexane to remove any physisorbed molecules. Suzuki coupling of bithiophene to diamond was carried out by heating arylboronic ester functionalized diamond in a solution containing 50 μmol 5-(5-iodothiophene-2-yl)thiophene-2-carbaldehyde (I-2T-CHO), 0.5 mg NaOAc, and 0.5 mg [Pd(PPh$_3$)$_4$] in argon-purged methanol at 60 °C overnight. The substrate was sequentially rinsed and sonicated in methanol, toluene, THF, and hexane to remove any physisorbed molecules. C$_{60}$ was grafted onto 2T-CHO-functionalized diamond by refluxing the substrate in a solution of 10 mg C$_{60}$ and 5 mg N-methylglycine in 10 mL argon-purged 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 C$_{60}$ molecules.

The molecular systems were investigated using the sandwich device configuration with cross-bar contacts. Figure 12 shows the I–V characteristics of bithiophene-C_{60} (2TC_{60}) and bithiophene-dicyano (2T(CN)$_2$). Under light illumination, both molecular dyads displayed prominent rectifying behavior with higher conductivity when the BDD substrates were negatively biased. The preferred direction of electron flow is from bithiophene to the electron acceptor moieties. The rectification ratios (RR) of 2TC_{60} and 2T(CN)$_2$ are 8 and 3, respectively, where RR = I(−1.0 V)/I(+1.0 V). Stronger rectification effect can be observed in 2T-C_{60} whereas higher current magnitudes are observed in 2T(CN)$_2$. 2T(CN)$_2$ exhibits higher currents than 2TC_{60} owing to the fact that its frontier orbitals are delocalized over the entire molecule.

Figure 12. a) Schematic drawing of sandwich device fabrication. b,c) Sandwich device I–V results for bithiophene-C_{60} (2TC_{60}) and bithiophene-dicyano (2T(CN)$_2$). Voltage bias was applied to BDD bottom contact.

amond is its chemical robustness which gives rise to very strong C−C bonds at the interface that are resistant to oxidation or hydrolysis. The diamond substrate is superior in this regard when compared with the silicon surface which is unstable against oxidation and hydrolysis. Transparent and conducting diamond can be deployed as an electrode in photovoltaics when an organic dye is coupled on the surface. The UV photochemical activation scheme is compatible with the lithographical grafting of polymer or printable organic electronic circuits on diamond, so there is good potential of developing molecular electronics on the diamond platform.

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