ACCOUNTS
of chemical research

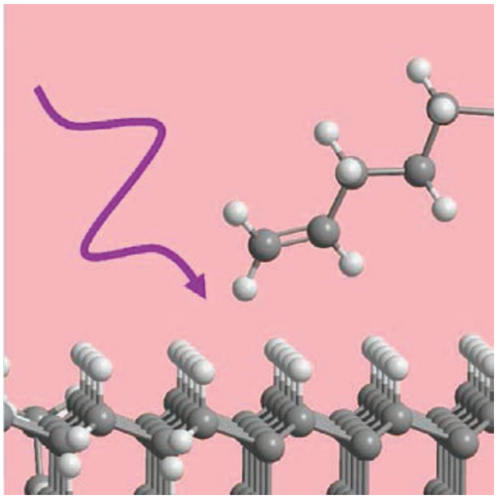
# Surface Chemistry for Stable and Smart Molecular and Biomolecular Interfaces via Photochemical Grafting of Alkenes

XIAOYU WANG, ELIZABETH C. LANDIS, RYAN FRANKING, AND
ROBERT J. HAMERS*

*Department of Chemistry, University of Wisconsin—Madison, 1101 University Avenue, Madison, Wisconsin 53706*

RECEIVED ON JANUARY 13, 2010

## CONSPECTUS



Many emerging fields such as biotechnology and renewable energy require functionalized surfaces that are "smart" and highly stable. Surface modification schemes developed previously have often been limited to simple molecules or have been based on weakly bound layers that have limited stability. In this Account, we report on recent developments enabling the preparation of molecular and biomolecular interfaces that exhibit high selectivity and unprecedented stability on a range of covalent materials including diamond, vertically aligned carbon nanofibers, silicon, and metal oxides.

One particularly successful pathway to ultrastable interfaces involves the photochemical grafting of organic alkenes to the surfaces. Bifunctional alkenes with a suitable functional group at the distal end can directly impart functionality and can serve as attachment points for linking complex structures such as DNA and proteins. The successful application of photochemical grafting to a surprisingly wide range of materials has motivated researchers to better understand the underlying photochemical reaction mechanisms. The resulting studies using experimental and computational methods have provided fundamental insights into the electronic structure of the molecules and the surface control photochemical reactivity. Such investigations have revealed the important role of a previously unrecognized process, photoelectron emission, in initiating photochemical grafting of alkenes to surfaces.

Molecular and biomolecular interfaces formed on diamond and other covalent materials are leading to novel types of molecular electronic interfaces. For example, electrical, optical, or electromechanical structures that convert biological information directly into analytical signals allow for direct label-free detection of DNA and proteins. Because of the preferential adherence of molecules to graphitic edge-plane sites, the grafting of redox-active species to vertically aligned carbon nanofibers leads to good electrochemical activity. Therefore researchers could graft electrocatalytic materials to carbon nanofibers to develop new types of selective electrocatalytic interfaces. Extending this chemistry to include metal oxides such as $TiO_2$ may lead to highly specific and efficient chemical reactions and new materials with useful applications in photovoltaic and photocatalytic energy conversion.

## 1. Introduction

Many emerging applications in fields such as biotechnology and renewable energy require functionalized surfaces that are "smart" and highly stable. For example, the integration of biomolecules such as DNA and antibodies onto surfaces provides new pathways for biological sensing that could allow real-time monitoring for pathogens.[1] Similarly, the integration of molecular catalysts or light-harvesting molecules onto electrodes could enhance the selectivity of photovoltaic and photocatalytic reactions of interest in renewable ener-

10.1021/ar100011f

gy.[2] A common need is the ability to prepare interfaces that are selective (i.e., that recognize a particular molecule or catalyze a particular reaction) and stable, able to withstand the challenging environments that practical implementations often demand.

Self-assembled monolayers on gold have been widely studied because gold–thiol chemistry provides a convenient pathway toward well-ordered molecular layers.[3−5] Yet, many emerging applications require semiconducting substrates or functional surfaces able to withstand higher temperatures, extremes of pH, high salt concentrations, and other harsh conditions. The integration of organic and biological molecules with covalent materials such as silicon and carbon presents new opportunities for making ultrastable highly selective surfaces. While silicon is the foundation of the microelectronics industry, carbon is a highly versatile material ranging from a transparent, wide bandgap semiconductor, diamond, to jet black, conductive carbon nanofibers. Metal oxides such as $TiO_2$ can also be highly stable and are of increasing interest in solar energy and photocatalysis. In each case, the challenge is to start with highly stable materials and make them "smart" by developing and implementing new surface modification strategies.

In this Account, we report recent and ongoing research on the formation of molecular interfaces to silicon, carbon, and metal oxides. We focus here on one particular route, the photochemical grafting of organic alkenes. This method is chosen because it has proven highly successful in forming (bio)molecular interfaces to several materials and because the resulting interfaces on carbon have exhibited excellent stability. Recent studies of underlying reaction mechanism have led to the discovery of a previously unrecognized process, photoelectron emission, as a key step in initiating the reaction, providing new mechanistic insights into the formation of the molecular layers.

## 2. A Starting Point: Covalent Molecular Interfaces to Silicon

Figure 1a outlines the procedure typically used for photochemical grafting of alkenes: an appropriate substrate is cleaned and prepared with a suitable termination; in most cases, the surface is terminated with hydrogen to provide coordinative saturation of all surface atoms. When a pure liquid alkene is dripped onto the sample and illuminated with ultraviolet light (typically at 254 nm), the molecules graft to the surface via their vinyl groups.[6−16] Studies using X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR) show that in most cases the grafting reactions are self-limiting, stopping after a coverage of approximately one monolayer, although multilayer formation is possible in some cases.[10,13,16] Figure 1b illustrates some of the molecules that have been successfully grafted. They include pure alkenes and molecules bearing additional functional groups. For example, trifluoroacetamide (TFAAD) and tBoc contain protected amine groups, providing routes to amine-terminated surfaces. Undecylenic acid methyl ester (UAME) is an excellent route to carboxylic acid-modified surfaces, and oligomers of ethylene glycol form protein-resistant surfaces.

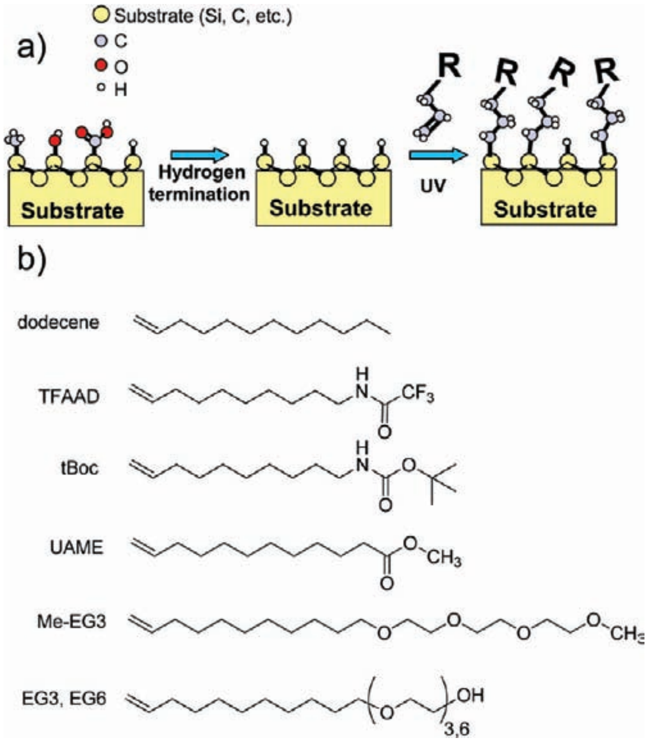


**FIGURE 1.** (a) Schematic illustration of the grafting of alkenes to covalent materials and (b) summary of some molecules that have been photochemically grafted to silicon and diamond surfaces.

The formation of covalent molecular interfaces began with early studies on silicon, motivated by silicon's central role in microelectronics. Initial studies grafted simple alkenes onto nanocrystalline silicon.[6,17] Shortly thereafter, we[8,9] and other groups[7,17] used this approach on single-crystal silicon and combined bifunctional molecules with multistep syntheses to covalently link DNA oligonucleotides to (111) and (001) surfaces of silicon.[8,9,18] Later studies extended this to making protein-resistant surfaces using ethylene glycol (EG) oligomers like those shown in Figure 1[19,20] and using mixed monolayers to create optimized protein-selective layers.[19] Because many functional groups such as primary amines, aldehydes, and carboxylic acid groups will react directly with H-terminated silicon under UV illumination, multistep synthesis on Si typically involves using protecting groups to stabilize the terminal group during the grafting step and then deprotecting after grafting to the surface.[8,9] This approach has been highly successful, enabling preparation of DNA-modified Si surfaces that exhibit high selectivity,[8,9,18,21] even able to detect single-base mismatches.[18]

While studies on silicon demonstrated the benefits of using photochemical grafting to prepare complex interfaces, the utility of silicon in aqueous environments is limited by the fact that penetration of water to the interface hydrolyzes Si−C and Si−O−C bonds, eventually removing the molecular layers from the substrate. This process can be slowed by using hydrophobic alkyl chains, but ultimately the molecular layers formed on silicon are only kinetically stable. To make truly *ultrastable* molecular layers, we realized that a different approach was needed, starting with materials with higher intrinsic stability. Seeking the ultimate in stability, we turned to diamond and other forms of carbon.

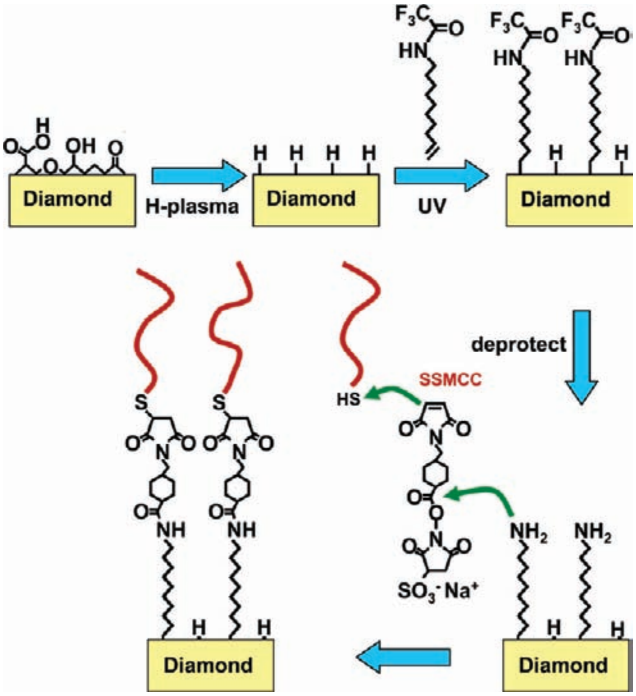


**FIGURE 2.** Schematic showing the steps in covalent bonding of DNA to diamond.

## 3. Ultrastable Molecular and Biomolecular Interfaces to Diamond

Carbon represents a versatile *suite* of materials whose properties can be tuned by controlling the hybridization.[22] In diamond, sp$^3$-hybridization and the high C−C bond strength lead to very high chemical stability and diamond's supreme position as the hardest known material. Diamond's semiconducting properties also enable the creation of hybrid bioelectronic devices similar to devices routinely made from silicon but with the potential for much greater stability. While diamond is sometimes considered an esoteric material, thin-film diamond coatings $<1\ \mu$m in thickness (consisting of intertwined nanocrystalline particles) can be easily and inexpensively deposited on a wide range of materials including metals, silicon, and transparent quartz; these diamond films yield the chemical stability of diamond in a practical and scalable manner. Similarly, amorphous and "hard" carbons with mixed sp$^2$−sp$^3$ hybridization can be deposited as thin-film coating materials that facilitate integration with a wider range of other materials.[22] Finally, nanostructured forms of carbon such as carbon nanofibers are made from sp$^2$-hybridized (graphitic) carbon and yield high surface-area materials with unusual electrical characteristics, described below.[23]

Carbon surfaces are typically cleaned using atomic hydrogen, yielding "H-terminated" surfaces that are very reproducible and stable.[24] The high stability of carbon-based materials makes them difficult to functionalize. Prior studies primarily used radical reactions of aryldiazonium salts.[25,26] Yet, in 2002 we made the surprising discovery that when covered with an alkene and illuminated with 254 nm light, alkenes graft to the diamond surface via the C═C group to form well-defined molecular layers.[10] This remarkable discovery has since formed the basis of numerous studies investigating the practical implementation and the fundamental mechanisms.

The outstanding properties of diamond as a robust substrate for functional surfaces were first demonstrated using DNA-modified diamond surfaces.[27] As shown in Figure 2, these were prepared by grafting an alkene bearing a protected amino group (TFAAD, depicted in Figure 1b) to H-terminated diamond; the grafted TFAAD was then deprotected and linked to thio-modified DNA oligonucleotides using the chemical linker SSMCC.[27] The stability and selectivity of the resulting DNA-modified surfaces were evaluated by exposing the DNA-modified diamond surfaces to repeated cycles of hybridization and denaturation using fluorescently labeled targets with complementary and noncomplementary sequences. Figure 3 shows a stability comparison with several other substrates of interest, including commercial amine-modified glass slides (Corning GAPS II), amine-terminated self-assembled monolayers on gold, and surfaces prepared by photochemically grafting layers to H-terminated Si(111) and to H-terminated glassy carbon. All of these examples started with amine-terminated

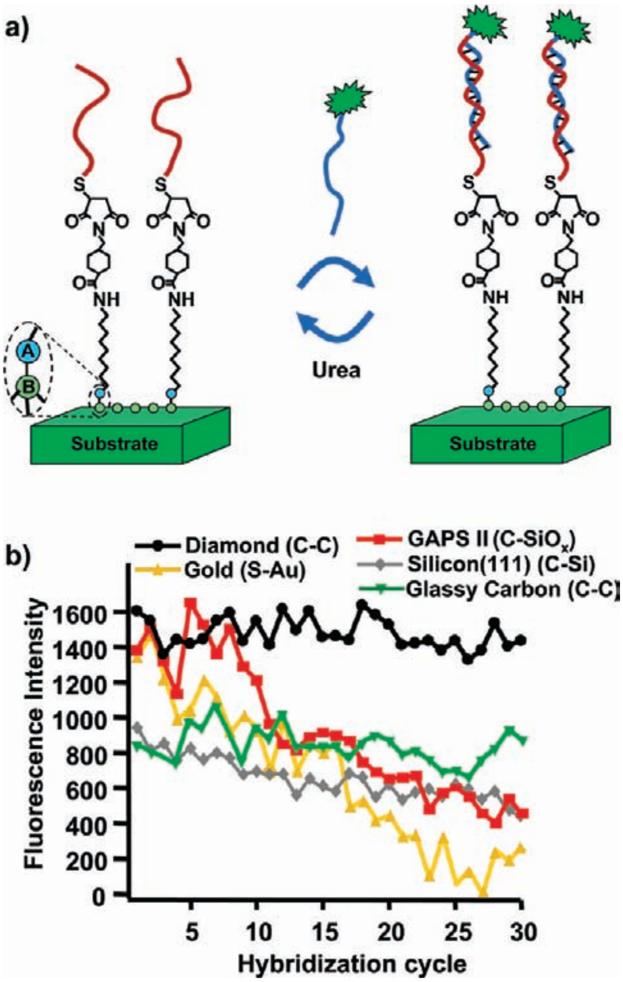


**FIGURE 3.** Stability of DNA-modified surfaces in repeated cycles of hybridization and denaturation using 8.3 M urea. Figure adapted from ref 27.

molecular layers and then used identical DNA chemistry. Consequently they have identical molecular structures except for the two atoms (labeled "A" and "B" in Figure 3a) that form the molecule−substrate interface.

Figure 3 shows that the two carbon substrates, diamond and glassy carbon, clearly exhibit superior stability.[10] Yet, that stability is not unique to diamond but is a consequence of the intrinsic stability of the C−C bonds formed at the interface and can therefore be extended to other forms of carbon. Subsequent studies have extended this work to link antibodies and other proteins to diamond,[20,28−30] to form protein-resistant and protein-selective surfaces,[19,20] and to create new types of bioelectronic sensing devices using the semiconducting properties of diamond.[30−32] Using carbon as a substrate enables preparation of a wide range of functional molecular and biomolecular layers with a high degree of functionality and with unprecedented stability

## 4. Mechanistic Studies of Photochemical Grafting of Alkenes

While the ability to prepare such highly functional and stable surfaces is remarkable from its utilitarian aspects, the initial grafting reaction is also intriguing from fundamental aspects. In particular, it is puzzling why the grafting reaction on diamond works at all, because at the wavelength used (254 nm) diamond and most organic alkenes are almost completely transparent. Early studies of alkene grafting to silicon had proposed a mechanism in which illumination with above-bandgap light creates electron−hole pairs (excitons) in the silicon, and the "holes" (electron vacancies) in the Si valence band would facilitate a reaction similar to a classical hydrosilylation reaction.[6,17] While very reasonable as a mechanism on silicon, diamond's large bandgap of 5.48 eV makes it transparent to light at wavelengths longer than 226 nm. This left us with the puzzling problem of how a transparent substrate and a transparent alkene can react when illuminated. In addition, the exciton mechanism cannot easily explain grafting on substrates with metallic properties such as carbon nanofibers and glassy carbon because these materials have very short exciton lifetimes.

One important clue to unraveling the mechanism was to examine how the rate of grafting varied with the electronic structure of the molecules. In particular, we hypothesized that if the rate-limiting step in grafting involved the terminal vinyl (C═C) group, then the reaction efficiency would be independent of the functional group at the other end. In reality, experiments on diamond[33,34] and amorphous carbon[12−15] revealed pronounced differences in rate between different molecules of similar size but having different terminal groups. For example, on diamond, TFAAD grafts quickly while tBoc grafts much more slowly (Figure 4a); grafting of 1-dodecene was not detectable under these conditions. Identical trends are observed on amorphous carbon[12−14] and carbon nanofibers.

To help understand these observations, density functional calculations were used to estimate the energies of the gas-phase molecular ionization potentials and electron affinities, and solvation energy corrections were applied to estimate the corresponding liquid-phase energies.[12,13,35] The results, depicted in Figure 4b, show that the bifunctional alkenes investigated all have similar donor levels (i.e., their ionization potentials are similar), but their acceptor levels (i.e., electron affinity) are quite different. Significantly, the trend of acceptor level energies exactly matches the observed trend of reactivity: the TFAAD molecule has the lowest-lying acceptor level because the trifluoroacetamide group is a good elec-

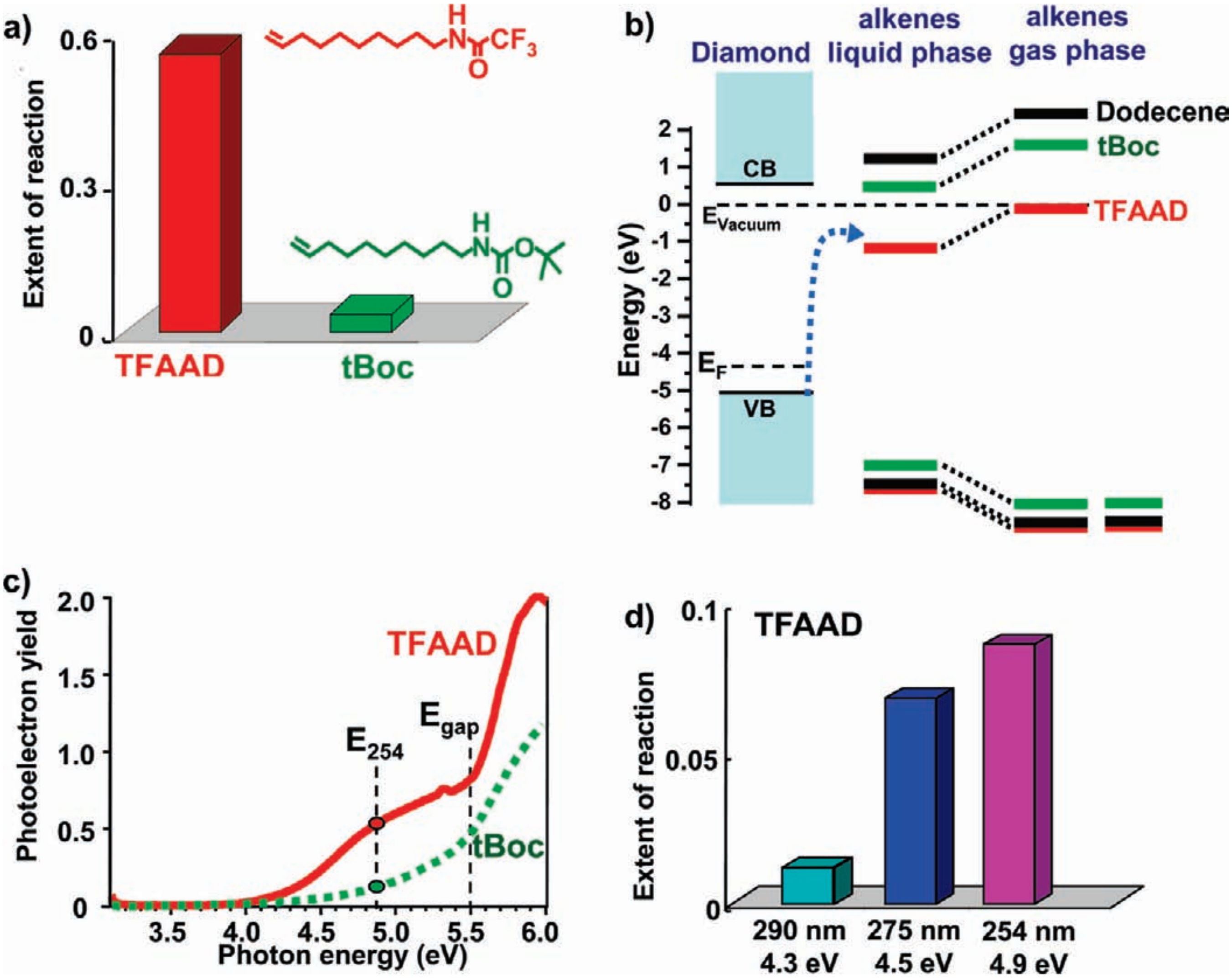


**FIGURE 4.** Photoemission initiation of grafting of alkenes to diamond: (a) relative reaction yields of TFAAD and tBoc on diamond using 254 nm light; (b) energy-level diagrams for donor and acceptor levels; (c) direct measurements of photoelectron emission from diamond into TFAAD and tBoc; (d) yield of TFAAD grafting to diamond at different wavelengths, normalized to constant photon fluence. Figure adapted from ref 34.

tron acceptor (lying well below the conduction band of diamond) and also has the highest reactivity. Other groups such as the *tert*-butyl oxycarbamate (tBoc) group and carboxylic acid methyl esters have higher-lying affinity levels and are less reactive, while pure alkenes are the poorest acceptors and the least reactive of the molecules studied.

These studies suggested that grafting on diamond is initiated by a photoemission process in which electrons are ejected from the valence band of diamond into acceptor levels of the adjacent alkenes. Indeed, this "internal photoemission" has recently been measured directly, as shown in Figure 4c. For TFAAD, significant photoemission yields are observed at energies well below the bandgap of diamond, with a threshold at ∼3.9 eV that is similar to the gap between the diamond valence band and the TFAAD affinity level in Figure 4b. The difference in photoelectron yield at 4.88 eV (254 nm) between TFAAD and tBoc corresponds closely to the differences in reactivity shown in Figure 4a. Similarly, measurements of grafting efficiency vs wavelength (Figure 4d) correspond closely to the photoemission yield. Definitive proof that photoelectron emission initiates grafting was provided by experiments showing that "seeding" a surface with a small amount of TFAAD greatly enhances the ability to graft otherwise poorly grafting molecules such as 1-dodecene.[13]

Figure 5 depicts the overall mechanism gleaned from these studies. Because the conduction band of diamond is very high in energy, the lowest-lying excitations involve direct electron transfer from diamond into the acceptor levels of the alkenes, as in Figure 4a. Additional studies show that the molecule that accepts the electron does not necessarily participate in sub-

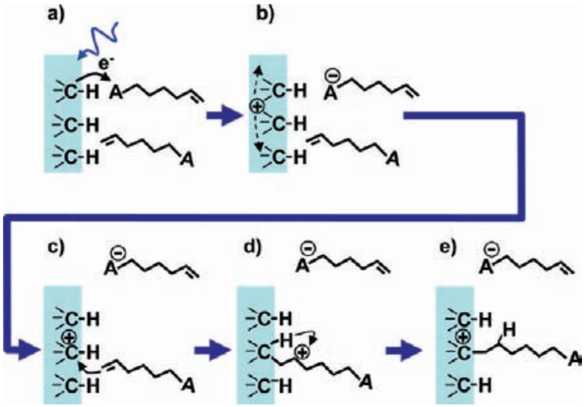


**FIGURE 5.** Schematic illustration of overall mechanism of photochemical grafting of alkenes on diamond: (a) initiation by photoemission, (b) possible lateral diffusion of holes, (c) nucleophilic attack by vinyl group on cationic diamond site, (d) possible hydride diffusion to restore 4-coordinate C atom at surface and neutralize molecular charge, leaving (e) final product.

sequent reaction steps: its primary role is to facilitate the photoelectron emission and the concurrent formation of valence-band holes (Figure 5b).[34] These valence band holes then undergo a nucleophilic attack by the electron-rich vinyl group of a second reactant molecule (Figure 5c). Subsequent steps to restore neutrality and eliminate radical sites are uncertain but might involve hydride transfer (as in Figure 5d) or radical propagation steps (not shown).

While our mechanistic studies were motivated by a desire to understand the mechanism on diamond, more recent studies have shown that this same initiation process, photoelectron emission, is also responsible for UV-initiated grafting on other forms of carbon[12−15] and even on silicon.[36] A key point common to all materials is that grafting of alkenes is induced by *holes* at the surface. Absorption of light in a bulk material creates electron−hole pairs, but the concentration of holes is limited by recombination. In contrast, the photoemission of electrons out of the material and into the adjacent liquid is likely *irreversible*; consequently, even if photoemission is a relatively inefficient process, each "hole" produced has a reaction probability approaching unity. The significance of this is underscored by the fact that experiments on amorphous carbon[12−15] and on carbon nanofibers[37] (which are both expected to have very short lifetimes for electron−hole pairs due to their metallic character), reveal similar trends in reactivity and wavelength dependence: TFAAD has the most facile reaction, tBoc slower, and pure alkenes the slowest. Finally, recent studies on very pure, float-zone refined silicon[36] show that when using 254 nm light the grafting rate again has the same dependence on molecular structure but is unchanged when the carrier lifetime is reduced 100-fold by intentionally introducing midgap recombination centers. This strongly suggests that even on silicon the UV-induced grafting is initiated by photoemission processes similar to those observed on diamond.

Ultimately these studies demonstrate that UV-induced photoemission is not limited to wide bandgap materials such as diamond, but is a more universal way of initiating grafting of alkenes to various carbon substrates. These factors have enabled formation of highly functional interfaces on amorphous carbon,[11−15] glassy carbon,[28] and vertically aligned carbon nanofibers,[37−42] facilitating the ability to take advantage of the unique properties of each form of carbon.

## 5. Optimizing Selectivity: Protein-Resistant and Protein-Selective Surfaces

Most early studies of biofunctionalized silicon and carbon were performed in pure buffer solutions where competitive binding is not significant. However, many applications require surfaces that can resist nonspecific binding of proteins or surfaces that have high affinity for desired target molecules while resisting others in complex media such as biological fluids. Self-assembled monolayers terminated with ethylene glycol (EG) subunits were known to resist protein binding on gold surfaces,[43] but it was not known whether photochemical grafting of short EG oligomers would be effective on diamond or whether other factors such as roughness of nanocrystalline diamond films (typically 10−100 nm) would obscure the effects. Figure 6 depicts data for nanocrystalline diamond films modified with four different surface treatments, interacting with four different proteins; these data show that even short oligomers such as EG6 are highly effective at reducing nonspecific binding of proteins.[19,20] Grafting of the EG6 oligomers reduces the nonspecific binding of avidin on nanocrystalline diamond to less than 0.02 monolayer,[19] a level similar to that observed with self-assembled monolayers on gold.[43] Moreover, diamond provides superior stability: a comparison of EG modified surfaces of diamond, silicon, and gold showed that immersion in water for 10 days produced no change in ability of EG-modified diamond surfaces to resist nonspecific binding, and XPS measurements showed no detectable change in the surface chemistry. In contrast, EG-modified silicon and gold samples both exhibited significant increases in nonspecific binding and evidence for partial loss of the EG layers.

The ultimate measure of the selectivity of a biomolecular interface is the ratio of specific binding (binding of a particular target molecule in solution) to nonspecific binding. By mak-

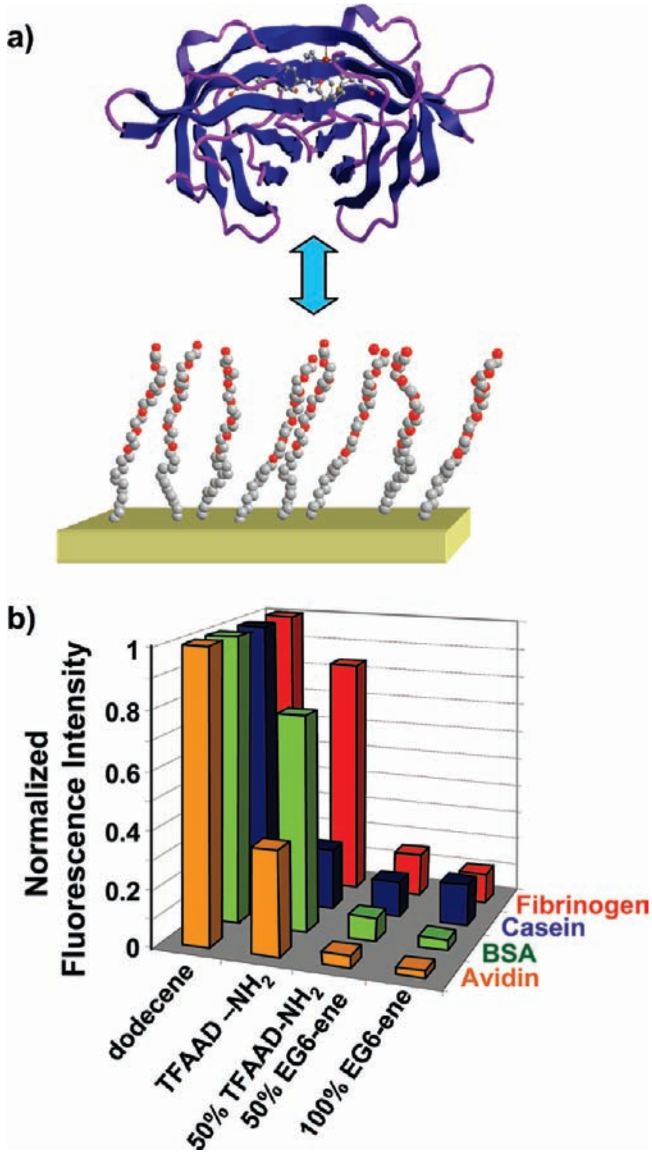


**FIGURE 6.** (a) Scale drawing of avidin being repelled by EG6-modified diamond surface and (b) measurements of nonspecific binding of four different proteins on diamond modified with different pure and mixed layers. Figure adapted from ref 19.

ing mixed monolayers in which molecules bearing a reactive group of interest (such as a protected amine for subsequent modification) are distributed among EG oligomers, one can significantly improve the overall ratio of specific to nonspecific binding (S/NS ratio). Experimental measurements using the biotin−avidin system showed that the monolayers formed using ~10% of a protected amine in 90% of ethylene glycol in the parent liquid yielded the best overall selectivity; these surfaces were able to selectively bind avidin even in serum.[19] These experiments demonstrate that multiple properties can be optimized using mixed monolayers.

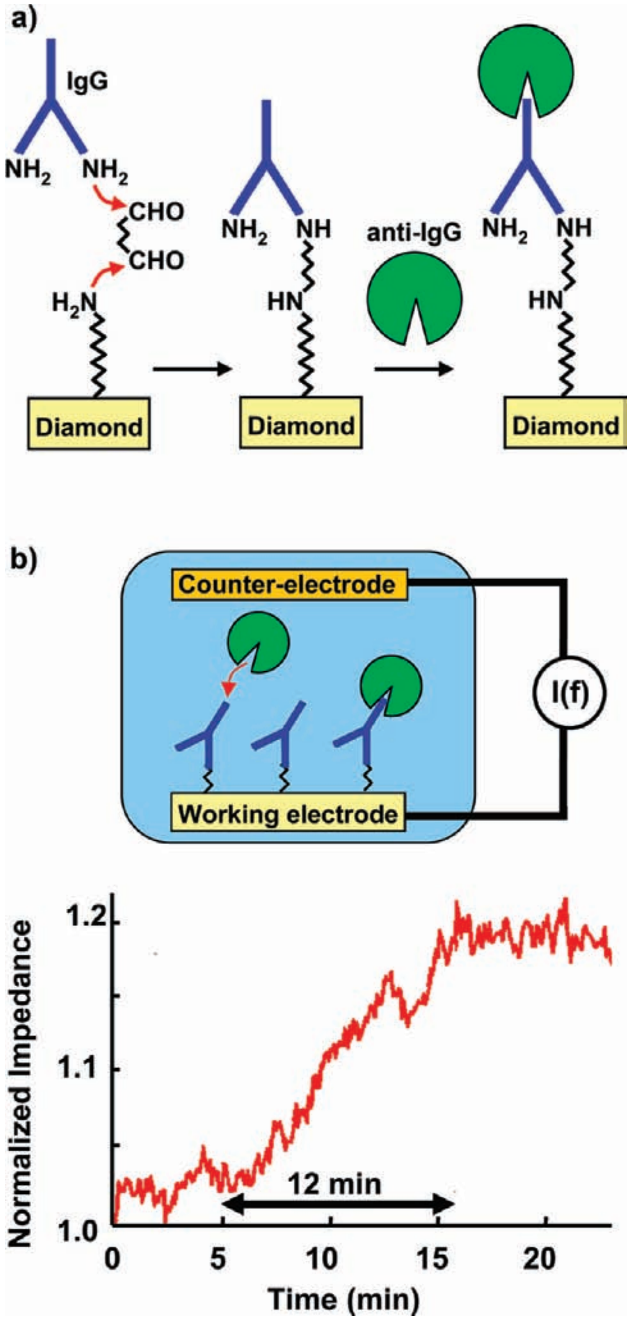


**FIGURE 7.** (a) Linking of IgG antibody to amine-modified diamond surface and subsequent recognition and bonding by anti-IgG and (b) impedance measurement showing real-time detection of recognition and binding of anti-IgG to IgG-modified diamond surface acting as the working electrode in a three-electrode impedance measurement (reference electrode not shown). Figure adapted from ref 29.

## 6. Covalent Biomolecular Interfaces for Chemical and Biological Sensing

One of the most intriguing applications of biomolecular surface chemistry on carbon is the potential development of label-free schemes to convert biological information directly into electrical,[28−32,44] electromechanical,[11] or optical[45] signals. Direct electronic transduction is possible through changes in the electrical impedance of the monolayers or, in the case of semiconducting substrates, changes in the conductivity of the semiconductor via a "field effect". In field effect devices, changes in the charge density near the semiconductor–liquid interface alter the conductivity in the semiconductor. These changes can be measured perpendicular to the interface via electrochemical impedance spectroscopy (EIS)[44,46,47] or parallel to the interface in a field-effect transistor to achieve label-free, real-time detection of biological binding events.[30] Figure 7 shows one example, in which human immunoglobulin G (IgG) was linked to a diamond surface and EIS measurements were used to directly detect the binding of the corresponding antigen, anti-IgG, to the surface-immobilized IgG molecules.[29]

Additional sensing schemes can also be enabled in which the binding of solution-phase targets to surface-bound probe molecules induce changes in the mechanical[11] or optical[45] properties. For these applications, amorphous carbon can be useful due to its ease of deposition. For example, the quartz-crystal microbalance (QCM) uses piezoelectric quartz crystals to detect submonolayer changes in mass. Coating a QCM crystal with a thin film of amorphous carbon and then using DNA chemistry like that described above enabled direct, real-time detection of DNA hybridization.[11] Similarly, very thin (<20 nm thick) amorphous carbon coatings on metal films can preserve the optical properties of the metal while leveraging the inherent stability of covalently grafted layers. This approach was used in recent studies of surface plasmon resonance (SPR) imaging of DNA–DNA binding and protein–DNA binding events.[45]

## 7. Emerging Applications of Covalently Grafted Molecular Layers in Renewable Energy

New applications for highly stable surfaces are emerging continually. Of particular interest are those related to renewable energy, such as electrocatalysis and solar-to-electrical energy conversion. In these areas, the electrical properties of the functionalized surfaces are of great importance. Two particular types of materials are currently of greatest interest: vertically aligned carbon nanofibers (VACNFs) and metal oxides, particularly $TiO_2$.

VACNFs are grown by plasma-enhanced chemical vapor deposition[48,49] and can be grown as individual fibers or as "forests" like those depicted in Figure 8a. VACNFs have a structure consisting of graphitic sheets in conical structures that nest inside one another to form a fiber. One consequence of this structure is that while conventional carbon nanotubes expose the basal plane of graphite along their sidewalls, transmission electron microscope (TEM) images (Figure 8b) show that VACNFs expose edge-plane sites every 1–2 nm along the nanofiber sidewalls.[37] Because electron-transfer rates at edge-plane graphite are $\sim 10^5$ times faster than those at basal planes,[50] VACNFs are expected to exhibit particularly good electron-transfer properties. However, VACNFs, like diamond, have little or no chemical selectivity of their own. Ongoing research is using molecular layers to tether redox-active moieties to VACNFs to enhance electron-transfer processes and electrocatalysis.

Studies using the redox-active protein cytochrome *c* and also using ferrocene as a model system have both demonstrated excellent electron-transfer characteristics even when linked through nominally insulating alkyl chains. For example, Figure 8c shows a cyclic voltammogram before and after linking aminoferrocene to VACNFs via an undecylenic acid monolayer. The peaks due to oxidation and reduction of ferrocene are clearly visible. Surprisingly, however, the molecular layers on VACNFs do not significantly alter the nanofiber–liquid capacitance. Additionally, the electron-transfer rates on VACNFs are nearly independent of the length of the alkyl chain tethering the redox group to the VACNF, rather than decreasing exponentially with molecular length as would be expected for electron tunneling through an alkyl chain. More detailed studies on VACNFs and conventional nanotubes show that photochemical grafting on VACNFs occurs selectively at the exposed graphitic edges.[37,42] As depicted in Figure 8d, this yields a rather "loose" layer characterized by a high degree of conformational flexibility. These experiments lead to a somewhat counterintuitive conclusion: that a less ordered or disordered molecular layer may perform better than dense, ordered molecular layers in augmenting electron-transfer processes at surfaces because in disordered layers the conformation flexibility of the molecule allows the redox-active groups to approach closer to the surface and because electron transfer processes can occur via through-solvent (similar to through-space) tunneling rather than through the alkyl chains.

A final emerging application of molecular layers involves molecular interfaces to metal oxides such as $TiO_2$ and ZnO. These are of increasing interest for applications in renewable energy such as solar conversion and photocatalysis.[2,51] Depending on the molecular structure and other physical and chemical properties of the interfaces of interest, molecular layers can play multiple roles: for example, they may augment

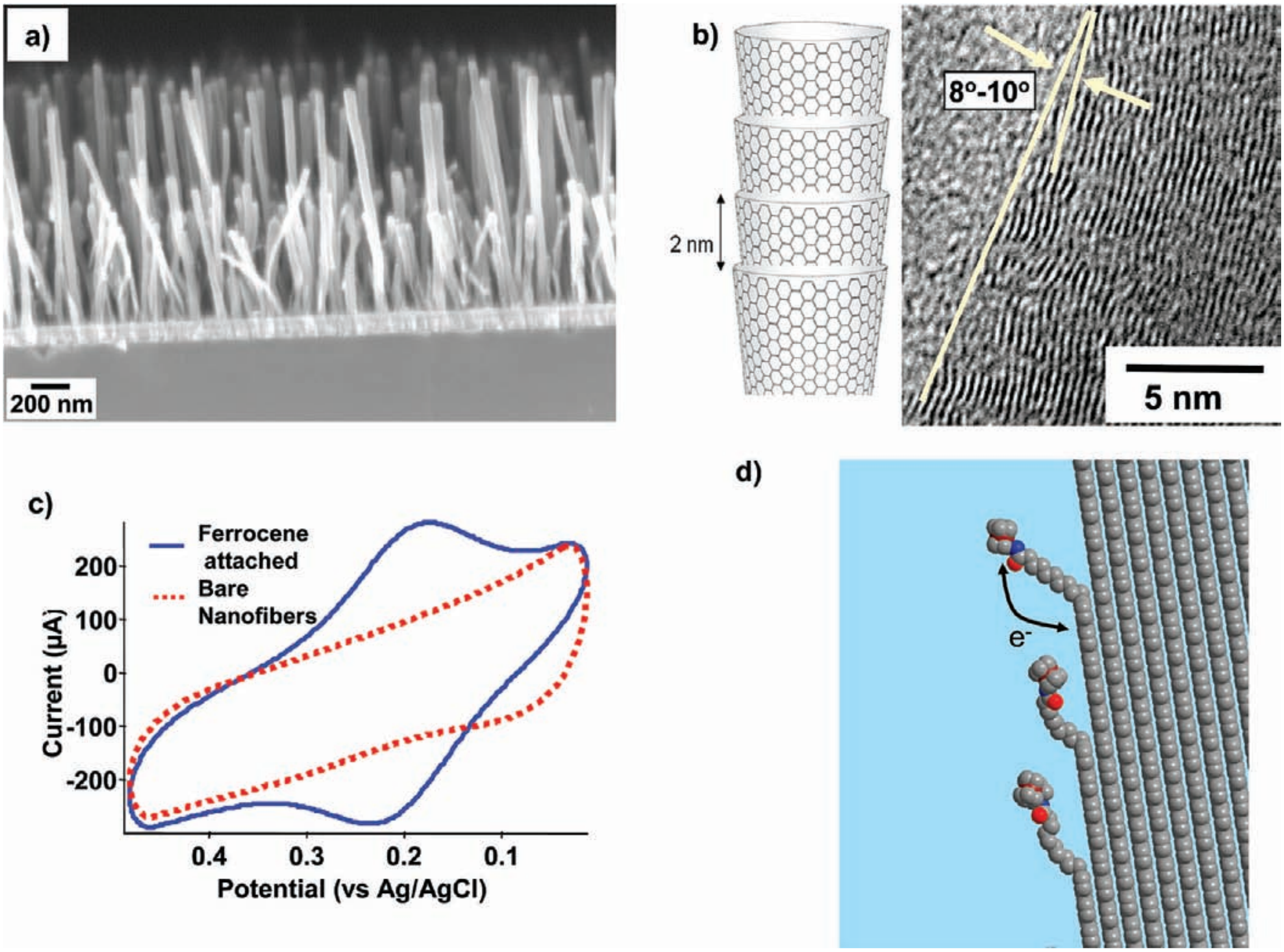


**FIGURE 8.** Grafting to vertically aligned carbon nanofibers: (a) SEM image of nanofibers; (b) high-resolution TEM image showing graphene sheets intersecting nanofiber edge at an angle of ~8°; (c) cyclic voltammetry of bare VACNFs and after grafting and functionalization with ferrocene, demonstrating increased Faradaic current but no change in capacitance; (d) molecular structure at VACNFs, showing preferential grafting at step edges and conformational flexibility of molecules that enhances electron transfer through the electrolyte instead of through the alkyl chains. Figure adapted from ref 42.

the construction of catalytic assemblies, they may act as insulators to block undesired electron-transfer processes, and they may provide molecular scaffolds to link light-harvesting or electrocatalytic reaction centers to electrode surfaces.

We have recently found that procedures like those described above will photochemically graft alkenes to nanocrystalline $TiO_2$ thin films and anatase $TiO_2$ single crystals.[16,52] A notable result shown in Figure 9 is that molecular layers grafted onto nanocrystalline $TiO_2$ for 54 days were able to withstand immersion in 80 °C deionized water and in 65 °C water at pH = 1 and pH = 10.3 with only minimal degradation.[16] While the electronic properties of the layers have not yet been characterized, the ability to extend molecular grafting from pure covalent materials such as silicon and carbon to more highly ionic materials such as metal oxides may further expand the range of potential applications enabled by versatile and highly stable chemistry.

## 8. Conclusions

Covalently grafted molecular layers provide the opportunity to create highly stable, functional interfaces on a wide range of materials. Photochemical grafting of alkenes has emerged as a versatile method for grafting functional molecular layers to a range of materials including silicon, various forms of carbon, and metal oxides. Detailed mechanistic studies have revealed that a previously unrecognized initiation process, photoelectron emission, is responsible for initiating the grafting process, providing an understanding of how the electronic structure of the substrate and of the reactant molecules impact the grafting process. Recent studies have demonstrated the

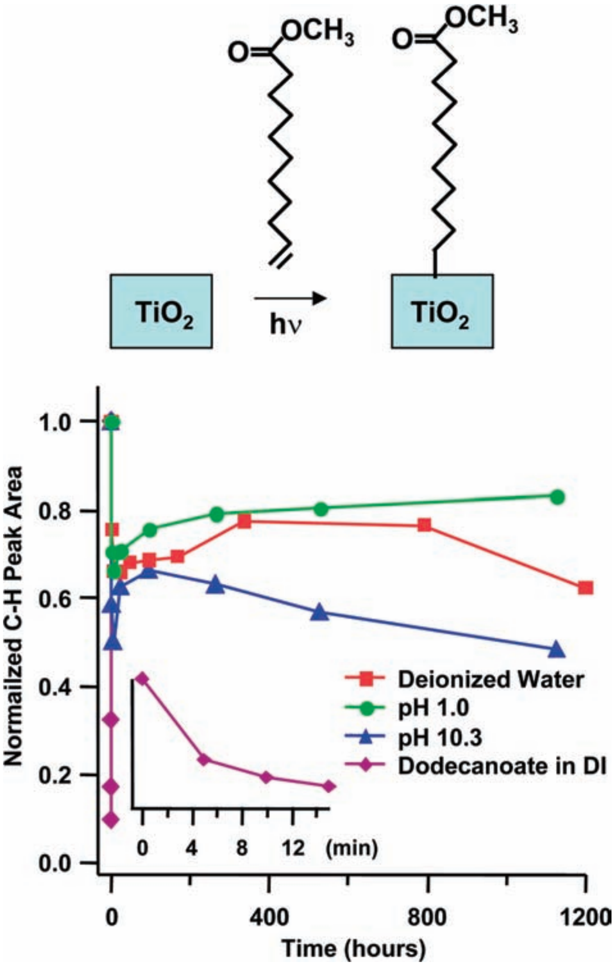


**FIGURE 9.** Photochemical grafting of undecylenic acid methyl ester to $TiO_2$ and stability of resulting molecular layer after immersion in water at different pH values for up to 54 days. The data also include a comparison with a simple linkage through a carboxylic acid group, using sodium dodecanoate, in purple. Note the much improved stability of the covalently grafted layers. Figure adapted from ref 16.

use of these layers to form ultrastable layers for biotechnology applications such as chemical and biological sensing. The extension of these methods to nanostructured carbons such as VACNFs and to metal oxides such as $TiO_2$ may lead to new applications in renewable energy and other fields of emerging importance.

*The work described here was supported in part by the National Science Foundation Grants CHE0314618, CHE0613010, CHE0911543, DMR-0210806, and DMR-0706559. The authors wish to acknowledge Drs. Wensha Yang, Tami L. Clare, Paula L. Colavita, Beth M. Nichols, Jeremy A. Streifer, and the many others who made significant contributions to the work described in this manuscript. The authors acknowledge fruitful collaborations and interactions with Dr. James Butler and Professor Lloyd M. Smith.*

## BIOGRAPHICAL INFORMATION

**Xiaoyu Wang** is a Ph.D. graduate student in Chemistry at the University of Wisconsin (anticipated graduation 2010). Her B.S. degree is in chemistry from Peking University.

**Elizabeth C. Landis** received her Ph.D. in Chemistry from the University of Wisconsin—Madison in May 2010 and is currently a postdoctoral fellow at Harvard University. She received her B.S. degree in Chemistry from Williams College.

**Ryan Franking** is a Ph.D. graduate student in the Materials Science Program at the University of Wisconsin (anticipated graduation 2011). He received his B.S. degree in Physics and Chemistry from Principia College.

**Robert J. Hamers** is the Wisconsin Distinguished Professor and Chair of the Department of Chemistry at the University of Wisconsin—Madison. His research interests include surface chemistry and photochemistry at semiconductors, nanotechnology, and electronic and optical properties of materials and interfaces.

## REFERENCES

1 Castner, D. G.; Ratner, B. D. Biomedical surface science: Foundations to frontiers. *Surf. Sci.* **2002**, *500*, 28–60.

2 Gratzel, M. Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells. *Inorg. Chem. Commun.* **2005**, *44*, 684–6851.

3 Nuzzo, R. G.; Allara, D. L. Adsorption of bifunctional organic disulfides on gold surfaces. *J. Am. Chem. Soc.* **1983**, *105*, 4481–4483.

4 Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. Fundamental-studies of microscopic wetting on oganic surfaces. 1. Formation and structural characterization of a self-consistent series of polyfunctional organic monolayers. *J. Am. Chem. Soc.* **1990**, *112*, 558–569.

5 Laibinis, P. D.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. Comparison of the structures and wetting properties of SAMs of n-alkanethiols on the coinage metal surfaces, Cu, Ag, Au. *J. Am. Chem. Soc.* **1991**, *113*, 7152–7167.

6 Stewart, M. P.; Buriak, J. M. Photopatterned hydrosilylation on porous silicon. *Angew. Chem., Int. Ed.* **1998**, *37*, 3257–3260.

7 Cicero, R. L.; Linford, M. R.; Chidsey, C. E. D. Photoreactivity of unsaturated compounds with hydrogen-terminated silicon(111). *Langmuir* **2000**, *16*, 5688–5695.

8 Strother, T.; Cai, W.; Zhao, X.; Hamers, R. J.; Smith, L. M. Synthesis and characterization of DNA-modified silicon (111) surfaces. *J. Am. Chem. Soc.* **2000**, *122*, 1205–1209.

9 Strother, T.; Hamers, R. J.; Smith, L. M. Covalent attachment of oligodeoxyribonucleotides to amine-modified Si (001) surfaces. *Nucleic Acids Res.* **2000**, *28*, 3535–3541.

10 Strother, T.; Knickerbocker, T.; Russell, J. N.; Butler, J. E.; Smith, L. M.; Hamers, R. J. Photochemical functionalization of diamond films. *Langmuir* **2002**, *18*, 968–971.

11 Sun, B.; Colavita, P. E.; Kim, H.; Lockett, M.; Marcus, M. S.; Smith, L. M.; Hamers, R. J. Covalent photochemical functionalization of amorphous carbon thin films for integrated real-time biosensing. *Langmuir* **2006**, *22*, 9598–9605.

12 Colavita, P. E.; Streifer, J. A.; Sun, B.; Wang, X. Y.; Warf, P.; Hamers, R. J. Enhancement of photochemical grafting of terminal alkenes at surfaces via molecular mediators: The role of surface-bound electron acceptors. *J. Phys. Chem. C* **2008**, *112*, 5102–5112.

13 Colavita, P. E.; Sun, B.; Tse, K. Y.; Hamers, R. J. Photochemical grafting of n-alkenes onto carbon surfaces: The role of photoelectron ejection. *J. Am. Chem. Soc.* **2007**, *129*, 13554–13565.

14 Colavita, P. E.; Sun, B.; Tse, K. Y.; Hamers, R. J. Photo-induced surface functionalization of carbon surfaces: The role of photoelectron ejection. *J. Vac. Sci. Technol., A* **2008**, *26*, 925–931.

15 Colavita, P. E.; Sun, B.; Wang, X. Y.; Hamers, R. J. Influence of surface termination and electronic structure on the photochemical grafting of alkenes to carbon surfaces. *J. Phys. Chem. C* **2009**, *113*, 1526–1535.

16 Franking, R. A.; Landis, E. C.; Hamers, R. J. Highly stable molecular layers on nanocrystalline anatase $TiO_2$ through photochemical grafting. *Langmuir* **2009**, *25*, 10676–10684.

17 Stewart, M. P.; Buriak, J. M. Exciton-mediated hydrosilylation on photoluminescent nanocrystalline silicon. *J. Am. Chem. Soc.* **2001**, *123*, 7821–7830.

18 Lin, Z.; Strother, T.; Cai, W.; Cao, X.; Smith, L. M.; Hamers, R. J. DNA attachment and hybridization at the silicon (100) surface. *Langmuir* **2002**, *18*, 788–796.

19 Clare, T. L.; Clare, B. H.; Nichols, B. M.; Abbott, N. L.; Hamers, R. J. Functional monolayers for improved resistance to protein adsorption: Oligo(ethylene glycol)-modified silicon and diamond surfaces. *Langmuir* **2005**, *21*, 6344–6355.

20 Lasseter, T. L.; Clare, B. H.; Abbott, N. L.; Hamers, R. J. Covalently modified silicon and diamond surfaces: Resistance to nonspecific protein adsorption and optimization for biosensing. *J. Am. Chem. Soc.* **2004**, *126*, 10220–10221.

21 Voicu, R.; Boukherroub, R.; Bartzoka, V.; Ward, T.; Wojtyk, J. T. C.; Wayner, D. D. M. Formation, characterization, and chemistry of undecanoic acid-terminated silicon surfaces: Patterning and immobilization of DNA. *Langmuir* **2004**, *20*, 11713–11720.

22 Robertson, J. Diamond-like amorphous carbon. *Mater. Sci. Eng., R* **2002**, *37*, 129–281.

23 Melechko, A. V.; Merkulov, V. I.; McKnight, T. E.; Guillorn, M. A.; Klein, K. L.; Lowndes, D. H.; Simpson, M. L. Vertically aligned carbon nanofibers and related structures: Controlled synthesis and directed assembly. *J. Appl. Phys.* **2005**, *97*, 041301.

24 Thoms, B. D.; Owens, M. S.; Butler, J. E.; Spiro, C. Production and characterization of smooth, hydrogen-terminated diamond C(100). *Appl. Phys. Lett.* **1994**, *65*, 2957–2959.

25 Allongue, P.; Delamar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Savéant, J. M. Covalent modification of carbon surfaces by aryl radicals generated from the electrochemical reduction of diazonium salts. *J. Am. Chem. Soc.* **1997**, *119*, 201–207.

26 Kuo, T. C.; McCreery, R. L.; Swain, G. M. Electrochemical modification of boron-doped chemcial vapor deposited diamond surfaces with covalently bonded monolayers. *Electrochem. Solid State Lett.* **1999**, *2*, 288–290.

27 Yang, W. S.; Auciello, O.; Butler, J. E.; Cai, W.; Carlisle, J. A.; Gerbi, J. E.; Gruen, D. M.; Knickerbocker, T.; Lasseter, T. L.; Russell, J. N., Jr.; Smith, L. M.; Hamers, R. J. DNA-modified nanocrystalline diamond thin-films as stable, biologically active substrates. *Nat. Mater.* **2002**, *1*, 253–257.

28 Lasseter, T. L.; Cai, W.; Hamers, R. J. Frequency-dependent electrical detection of protein binding events. *Analyst* **2004**, *129*, 3–8.

29 Yang, W. S.; Butler, J. E.; Russell, J. N.; Hamers, R. J. Direct electrical detection of antigen-antibody binding on diamond and silicon substrates using electrical impedance spectroscopy. *Analyst* **2007**, *132*, 296–306.

30 Yang, W.; Hamers, R. J. Detection of biological binding events using a diamond thin-film field-effect transistor. *Appl. Phys. Lett.* **2004**, *85*, 3626–3628.

31 Yang, W. S.; Butler, J. E.; Russell, J. N., Jr.; Hamers, R. J. Interfacial electrical properties of DNA-modified diamond thin films: Intrinsic response and hybridization-induced field effects. *Langmuir* **2004**, *20*, 6778–6787.

32 Yang, W.; Butler, J. E.; Russell, J. N., Jr.; Hamers, R. J. Electrochemical impedance studies of DNA modified diamond thin films. *Langmuir* **2004**, *20*, 6778–6787.

33 Wang, X.; Colavita, P. E.; Metz, K. M.; Butler, J. E.; Hamers, R. J. Direct photopatterning and SEM Imaging of molecular monolayers on diamond surfaces: Mechanistic insights into UV-Initiated molecular grafting. *Langmuir* **2007**, *23*, 11623–11630.

34 Wang, X.; Colavita, P. E.; Streifer, J. A.; Butler, J. E.; Hamers, R. J. Photochemical grafting of alkenes onto carbon surfaces: Identifying the roles of electrons and holes. *J. Phys. Chem. C* **2009**, *114*, 4067–4074.

35 Nichols, B. M.; Butler, J. E.; Russell, J. N.; Hamers, R. J. Photochemical functionalization of hydrogen-terminated diamond surfaces: A structural and mechanistic study. *J. Phys. Chem. B* **2005**, *109*, 20938–20947.

36 Wang, X.; Ruther, R. E.; Streifer, J. A.; Hamers, R. J. UV-induced grafting of alkenes to silicon surfaces: Photoemission versus excitons. *J. Am. Chem. Soc.* **2010**, *132*, 4048–4049.

37 Landis, E. C.; Klein, K.; Liao, A.; Pop, E.; Hensley, D.; Melechko, A.; Hamers, R. J. Covalent functionalization and electron-transfer properties of vertically aligned carbon nanofibers: The importance of edge-plane sites. *Chem. Mater.* **2010**, *22*, 2357–2366.

38 Baker, S. E.; Colavita, P. E.; Tse, K. Y.; Hamers, R. J. Functionalized vertically aligned carbon nanofibers as scaffolds for immobilization and electrochemical detection of redox-active proteins. *Chem. Mater.* **2006**, *18*, 4415–4422.

39 Baker, S. E.; Tse, K. Y.; Hindin, E.; Nichols, B. M.; Clare, T. L.; Hamers, R. J. Covalent functionalization for biomolecular recognition on vertically aligned carbon nanofibers. *Chem. Mater.* **2005**, *17*, 4971–4978.

40 Baker, S. E.; Tse, K. Y.; Lee, C. S.; Hamers, R. J. Fabrication and characterization of vertically aligned carbon nanofiber electrodes for biosensing applications. *Diamond Relat. Mater.* **2006**, *15*, 433–439.

41 Metz, K. M.; Goel, D.; Hamers, R. J. Molecular monolayers enhance the formation of electrocatalytic platinum nanoparticles on vertically aligned carbon nanofiber scaffolds. *J. Phys. Chem. C* **2007**, *111*, 7260–7265.

42 Landis, E. C.; Hamers, R. J. Covalent grafting of ferrocene to vertically aligned carbon nanofibers: Electron-transfer processes at nanostructured electrodes. *J. Phys. Chem. C* **2008**, *112*, 16910–16918.

43 Ostuni, E.; Chapman, R. G.; Holmlin, R. E.; Takayama, S.; Whitesides, G. M. A survey of structure—property relationships of surfaces that resist the adsorption of protein. *Langmuir* **2001**, *17*, 5605–5620.

44 Cai, W.; Peck, J. R.; van der Weide, D. W.; Hamers, R. J. Direct electrical detection of hybridization at DNA-modified silicon surfaces. *Biosens. Bioelectron.* **2004**, *19*, 1013–1019.

45 Lockett, M. R.; Weibel, S. C.; Phillips, M. F.; Shortreed, M. R.; Sun, B.; Corn, R. M.; Hamers, R. J.; Cerrina, F.; Smith, L. M. Carbon-on-metal films for surface plasmon resonance detection of DNA arrays. *J. Am. Chem. Soc.* **2008**, *130*, 8611–8613.

46 Souteyrand, E.; Cloarec, J. P.; Martin, J. R.; Wilson, C.; Lawrence, I.; Mikkelsen, S.; Lawrence, M. F. Direct detection of the hybridization of synthetic homo-oligomer DNA sequences by field effect. *J. Phys. Chem. B* **1997**, *101*, 2980–2985.

47 Souteyrand, E.; Martin, J. R.; Martelet, C. Direct detection of biomolecules by electrochemical impedance measurements. *Sensors Actuators, B* **1994**, *20*, 63–69.

48 Melechko, A. V.; McKnight, T. E.; Hensley, D. K.; Guillorn, M. A.; Borisevich, A. Y.; Merkulov, V. I.; Lowndes, D. H.; Simpson, M. L. Large-scale synthesis of arrays of high-aspect-ratio rigid vertically aligned carbon nanofibres. *Nanotechnology.* **2003**, *14*, 1029–1035.

49 Meyyappan, M.; Delzeit, L.; Cassell, A.; Hash, D. Carbon nanotube growth by PECVD: A review. *Plasma Sources Sci. Technol.* **2003**, *12*, 205–216.

50 Rice, R. J.; McCreery, R. L. Quantitative relationship between electron-transfer rate and surface microstructure of laser-modified graphite electrodes. *Anal. Chem.* **1989**, *61*, 1637–1641.

51 Galoppini, E. Linkers for anchoring sensitizers to semiconductor nanoparticles. *Coord. Chem. Rev.* **2004**, *248*, 1283–1297.

52 Li, B.; Franking, R.; Landis, E. C.; Kim, H.; Hamers, R. J. Photochemical grafting and patterning of biomolecular layers onto $TiO_2$ thin films. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1013–1022.