Structured Polymer Grafts on Diamond

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Abstract: In this work, a facile method for the preparation of structured and functional polymer grafts on diamond surfaces is described. Uniform poly(styrene) (PS) grafts with a thickness of ~110 nm were created directly onto oxidized ultrananocrystalline diamond (UNCD) surfaces by the self-initiated photografting and photopolymerization of bulk styrene with UV irradiation. The stable covalent bonding of the PS grafts allows polymer analogue reactions with drastic reaction conditions without noticeable detachment of the polymer coating. Thus, various functionalities, such as nitro, sulfonic, and aminomethyl groups have been successfully incorporated to the polymer grafts. Furthermore, the reactivity contrast between hydrogenated and oxidized UNCD surfaces allows for the preparation of structured polymer grafts. Finally, we have demonstrated the good reactivity and accessibility of the incorporated pendant functional groups.

Introduction

Diamond substrates, including single, poly, and nanocrystalline diamond, are very promising candidates for biotechnology and biosensing applications, due to their exceptional chemical stability, as well as excellent electrochemical properties and biocompatibility[1,2] Ultrananocrystalline diamond (UNCD), a recently engineered diamond composite,[3] has introduced new advantages such as smoothness, ease of large scale production, ability of integration with other materials, and low production cost. In addition, the particular electronic properties of UNCD make it possible to control the conductivity from the insulating to the metallic-like regime.[4] Therefore, there has been an increasing interest in using UNCD for biochemical applications.[5,6] However, the question remains regarding how to introduce chemical and biochemical functional groups to the inert and stable diamond surface in a well-defined way. So far, different strategies have been developed. Initially, fluorine- and

chlorine-terminated diamond surfaces were prepared by reaction with elemental fluorine[7] and chlorine.[8,9] Amino groups were introduced by amination of H-terminated diamond surfaces with a NH₃ plasma[10] or by UV irradiation in ammonia atmosphere.[11] Diamond can be oxidized by, e.g., anodic polarization,[12] oxygen plasma treatment,[13] or UV irradiation of the substrate in air.[14] Oxidized diamond surfaces can have hydroxyl, carbonyl, and ether surface groups, depending on the employed oxidation method. Further modification of oxidized diamond surfaces was achieved by reacting silane derivatives with the hydroxyl surface group.[12-15] Although silane monolayers on oxidized surfaces are widely used in the field of biomedical application, their poor stability in saline solutions at 37 °C makes them inappropriate for long-term applications.[16,17]

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(1) Swain, G. M.; Anderson, A. B.; Angus, J. C. *MRS Bull.* **1998**, *23*, 56–60.
(2) Bakowicz, K.; Mitura, S. J. *J. Wide Bandgap Mater.* **2002**, *9*, 261–272.
(3) Gruen, D. M. *Ann. Rev. Mater. Sci.* **1999**, *29*, 211–259.
(4) Bhattacharyya, S.; Auciello, O.; Birrell, J.; Carlisle, J. A.; Curtiss, L. A.; Goyette, A. N.; Gruen, D. M.; Krauss, A. R.; Schlueter, J.; Sumant, A.; Zapol, P. *Appl. Phys. Lett.* **2001**, *79*, 1441–1443.
(5) Yang, W. S.; Auciello, O.; Butler, J. E.; Cai, W.; Carlisle, J. A.; Gerbi, J.; Gruen, D. M.; Knickerbocker, T.; Lasseter, T. L.; Russell, J. N.; Smith, L. M.; Hamers, R. J. *Nat. Mater.* **2002**, *1*, 253–257.
(6) Hartl, A.; Schmich, E.; Garrido, J. A.; Hernando, J.; Catharino, S. C. R.; Walter, S.; Feulner, P.; Kromka, A.; Steinmuller, D.; Stutzmann, M. *Nat. Mater.* **2004**, *3*, 736–742.

(7) Freedman, A.; Stinespring, C. D. *Appl. Phys. Lett.* **1990**, *57*, 1194–1196.
(8) Sappok, R.; Boehm, H. P. *Carbon* **1968**, *6*, 283–288.
(9) Miller, J. B.; Brown, D. W. *Langmuir* **1996**, *12*, 5809–5817.
(10) Szunerits, S.; Jarna, C.; Coffinier, Y.; Delabouglise, D.; Boukherroub, R. *Electrochem. Commun.* **2006**, *8*, 1185–1190.
(11) Zhang, G. J.; Song, K. S.; Nakamura, Y.; Ueno, T.; Funatsu, T.; Ohdomari, I.; Kawarada, H. *Langmuir* **2006**, *22*, 3728–3734.
(12) Notsu, H.; Fukazawa, T.; Tatsuma, T.; Tryk, D. A.; Fujishima, A. *Electrochem. Solid-State Lett.* **2001**, *4*, H1–H3.
(13) Hernando, J.; Pourrostami, T.; Garrido, J. A.; Williams, O. A.; Gruen, D. M.; Kromka, A.; Steinmuller, D.; Stutzmann, M. *Diamond Relat. Mater.* **2007**, *16*, 138–143.
(14) Boukherroub, R.; Wallart, X.; Szunerits, S.; Marcus, B.; Bouvier, P.; Mermoux, M. *Electrochem. Commun.* **2005**, *7*, 937–940.
(15) Actis, P.; Manesse, M.; Nunes-Kirchner, C.; Wittstock, G.; Coffinier, Y.; Boukherroub, R.; Szunerits, S. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4924–4931.
(16) Wang, A. F.; Cao, T.; Tang, H. Y.; Liang, X. M.; Black, C.; Salley, S. O.; McAllister, J. P.; Auner, G. W.; Ng, K. Y. S. *Colloids Surf. B-Biointerfaces* **2006**, *47*, 57–63.
(17) Lud, S. Q.; Nikolaides, M. G.; Haase, I.; Fischer, M.; Bausch, A. R. *ChemPhysChem* **2006**, *7*, 379–384.

In the past few years, different methods for the controlled attachment of organic molecules to H-terminated diamond have been developed. Hamers' group[5] has reported on the photochemical functionalization of diamond with ω-alkenes. Using this approach, some of us demonstrated the covalent attachment of proteins on UNCD without loss of their biological function.[6] Carlisle et al.[18,19] reported on the electrochemically induced grafting of aryl diazonium derivatives on UNCD films. However, this technique results in the uncontrollable formation of multilayers. Recently, we reported on the formation of the first defined self-assembled monolayers (SAMs) of 4-nitrobiphenyl onto UNCD by the spontaneous grafting of 4-nitro-1,1′-biphenyl-4′-diazonium tetrafluoroborate in solution.[20]

The use of polymer coatings bearing multiple functions on a single grafted polymer chain, for instance, different responsive sites for (bio)sensing applications, is very attractive and has been demonstrated for various sensing principles.[21] However, only a few studies on polymer coatings covalently attached to diamond can be found in the literature. Li et al.[22] reported on the functionalization of oxidized nanodiamond particles via atom transfer radical polymerization (ATRP), Matrab et al.[18] reported on the ATRP of styrene and methyl methacrylate initiated by electro-grafted aryldiazonium salt on H-terminated UNCD, and Actis et al.[15] studied the electro-polymerization of pyrrole on oxidized boron-doped diamond electrodes modified by pyrrolyl units. In all of these studies, the surface had to be pre-modified with a more or less defined organic layer, following an established procedure to introduce surface grafting and initiator functions for the surface-initiated polymerization (SIP)—a common method also employed by some of us for the preparation of micro- and nanostructured polymer brushes using self-assembled monolayers (SAMs) of biphenyl thiols on gold.[23−25]

However, using a carbon substrate such as diamond offers the opportunity to directly introduce chemical functions or even a reactivity contrast by, e.g., different surface activation, such as hydrogenation or oxidation. Hence, the formation of defined reactive interlayers such as SAMs is no longer necessary, and the direct grafting of monomers on activated diamond surfaces can be realized in a one-step reaction. It has been shown that a broad variety of vinyl monomers can be directly grafted onto organic substrates such as polyolefines by self-initiated photografting and photopolymerization (SIPGP).[26,27] Surprisingly, this facile and very intriguing approach for the formation of stable and functional coatings has not received much attention so far.

Here, we present a straightforward method for the preparation of poly(styrene) (PS) coatings directly onto oxidized UNCD using the SIPGP approach with styrene as the monomer. Additionally, we investigated the preparation of structured polymer grafts on partially/structured oxidized UNCD surfaces. Moreover, we used different synthetic routes to incorporate functional groups into the polymer grafts by polymer analogue functionalizations of PS under quite drastic reaction conditions. We have confirmed the possibility of further modification of the polymer grafts, allowing the incorporation of additional functional molecules, such as fluorescent labels. This will open the way for designing more advanced biosensing schemes, incorporating multifunctional elements and with a higher loading capacity for biomolecules.

Methods

UNCD Substrates. Hydrogenated UNCD substrates were prepared as previously reported.[20] The surfaces were cleaned by thorough sequential rinsing with acetone, 2-propanol, and Millipore water and treated with oxygen plasma (Giga-Etch 100-E, TePla AG, Germany) for 300 s (200 W load coil power, pressure of 1.5 mbar). Under these conditions, the diamond surfaces have, among other functional groups such as carboxy or ether, hydroxyl surface groups.[13] The quality of the oxidation process was controlled by static water contact angle measurements ($\theta \leq 10°$). The structuring was performed using a S1805 Shipley photo resist that was spin-coated at 6000 rpm and a MJB3 mask aligner (SUSS MicroTec, Germany). The samples were then oxidized as described above and the photo resist removed by ultrasonification in acetone and 2-propanol (HPLC grade).

Self-Initiated Photografting and Photopolymerization (SIPGP). The hydrogen/oxygen patterned UNCD substrate was submerged in approximately 2 mL of freshly distilled and degassed styrene (Fluka) in a Duran glass photoreaction vial. Polymerization was allowed to complete within 16 h under constant irradiation with UV light ($\lambda_{max} = 350$ nm, 9.2 mW/cm^2) in a Rayonet Photochemical Reaction Chamber (Branford, Connecticut) at room temperature (RT). After photopolymerization, the samples were immediately cleaned by sequential ultrasonification in toluene, ethyl acetate and ethanol (all HPLC grade) for several minutes each.

Sulfonation of PS Grafts; Poly(styrene Sulfonic Acid) (PSSA). The poly(styrene) (PS) modified UNCD substrate was submerged in a solution of 1 mL acetic anhydride (Ac$_2$O) in 5 mL 1,2-dichloroethane. The solution was cooled by an ice bath and 0.36 mL of concentrated H$_2$SO$_4$ was slowly added. The solution was heated to 60 °C for 3 h. During the reaction, a phase separation of the solution was observed. The sulfonation of the PS grafts was only successful when the substrate was completely submerged in the lower phase. The substrate was removed from the reaction solution and thoroughly rinsed with 1,2-dichloroethane and deionized water.

Nitration of PS Grafts; Poly(nitrostyrene) (PNS). The PS modified UNCD substrate was submerged in a mixture of 1 mL conc. HNO$_3$ and 2.5 mL conc. H$_2$SO$_4$. The mixture was heated to 60 °C for 1 h. The substrate was removed and thoroughly rinsed with deionized H$_2$O (Millipore).

Amidoalkylation of PS Grafts; Poly((4-aminomethyl)styrene) (PAMS). The conversion of the PS to the PAMS grafts was performed following the synthetic route by Mitchell et al.[28] The PS modified UNCD substrate was submerged in a solution of 40 mg N-(hydroxymethyl)phthalimide (NHPI) in 5 mL dichloromethane (DCM) and 5 mL trifluoroacetic acid (TFA). Trifluoromethane sulfonate (0.09 mL) was added slowly under a dry N$_2$ atmosphere. The reaction was allowed to complete over night at RT. The substrate was removed and successively cleaned by ultrasonification in CF$_3$SO$_3$H/DCM (1:1), DCM, ethyl acetate, and ethanol to obtain poly(4-vinylbenzyl)phthalimide (PVBP)

(18) Matrab, T.; Chehimi, M. M.; Boudou, J. P.; Benedic, F.; Wang, J.; Naguib, N. N.; Carlisle, J. A. *Diamond Relat. Mater.* **2006**, *15*, 639−644.

(19) Jian, W.; Firestone, M. A.; Auciello, O.; Carlisle, J. A. *Langmuir* **2004**, *20*, 11450−11456.

(20) Lud, S. Q.; Steenackers, M.; Jordan, R.; Bruno, P.; Gruen, D. M.; Feulner, P.; Garrido, J. A.; Stutzmann, M. *J. Am. Chem. Soc.* **2006**, *128*, 16884−16891.

(21) Harsanyi, G. *Mater. Chem. Phys.* **1996**, *43*, 199−203.

(22) Li, L.; Davidson, J. L.; Lukehart, C. M. *Carbon* **2006**, *44*, 2308−2315.

(23) Schmelmer, U.; Jordan, R.; Geyer, W.; Eck, W.; Gölzhäuser, A.; Grunze, M.; Ulman, A. *Angew. Chem.-Int. Ed.* **2003**, *42*, 559−563.

(24) Schmelmer, U.; Paul, A.; Küller, A.; Steenackers, M.; Ulman, A.; Grunze, M.; Gölzhäuser, A.; Jordan, R. *Small* **2007**, *3*, 459−465.

(25) Steenackers, M.; Küller, A.; Ballav, N.; Zharnikov, M.; Grunze, M.; Jordan, R. *Small* **2007**, *3*, 1764−1773.

(26) Deng, J. P.; Yang, W. T.; Rånby, B. *Macromol. Rapid Commun.* **2001**, *22*, 535−538.

(27) Wang, H. L.; Brown, H. R. *Macromol. Rapid Commun.* **2004**, *25*, 1095−1099.

(28) Mitchell, A. R.; Kent, S. B. H.; Engelhard, M.; Merrifield, R. B. *J. Org. Chem.* **1978**, *43*, 2845−2852.
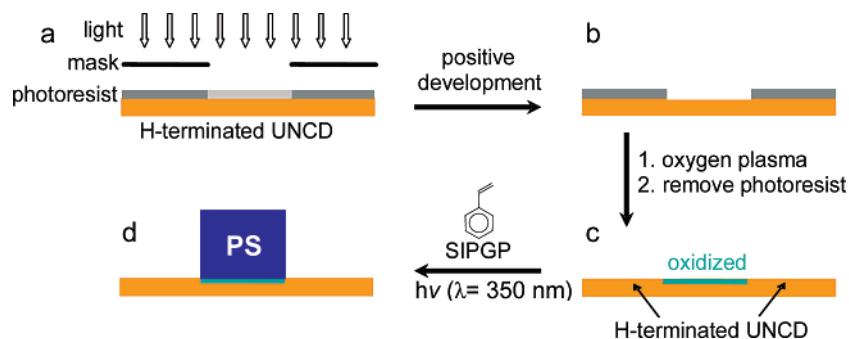
Figure 1. Preparation of structured PS grafts on UNCD. (a) H-terminated UNCD substrate is structured by a spin-coated photoresist (PMMA). (b) The substrate was exposed to an oxygen plasma and the photoresist removed (c). (d) PS grafts were selectively formed on the oxidized UNCD surface regions by UV-induced SIPGP of styrene.

grafts. PAMS grafts were obtained by refluxing the PVBP coated substrate in 5 mL of ethanol containing 5% hydrazine dihydrate for 16 h. The substrate was finally cleaned by ultrasonification in ethanol.

Fluorescent Labeling of PAMS Grafts (PAMS-R). The PAMS modified UNCD substrate was submerged in a 10 mM rhodamine B isothiocyanate solution in ethanol for 3 days in the dark at RT. The surface was cleaned by ultrasonification in ethanol.

X-ray Photoelectron Spectroscopy (XPS). The XPS measurements were performed on 12 mm^2 non-patterned UNCD samples. XPS was carried out under ultrahigh vacuum conditions (2×10^{-9} mbar). The XPS system was equipped with a Mg Kα X-ray source (1253.6 eV; X-ray current: 10 mA; X-ray Voltage: 10 kV) and a Escalab MK II analyzer. The spectra were recorded at an angle of 49° between the incident X-ray beam and the electron detector. The peak areas for the determination of the surface atom composition were calculated by the integration of a Voigt fit (80% Gaussian and 20% Lorentzian).

Infrared Spectroscopy (IR). IR spectroscopy was performed on modified 12 mm^2 unstructured oxidized UNCD samples using a IFS 55 Bruker instrument equipped with a DRIFT setup from SpectraTech and an MCT detector. For each spectrum with a spectral resolution of 4 cm^{-1}, 550 scans were accumulated. For each measurement, background spectra were recorded on freshly oxidized UNCD samples.

Atomic Force Microscopy (AFM). AFM scans were obtained with a Nanoscope IIIa scanning probe microscope from Veeco Instruments using standard tips in tapping mode. The average roughness (rms) was calculated from a 5 μm^2 area.

Fluorescence Microscopy. The fluorescence microscopy images were obtained with an Axiovert 200M Zeiss AG microscope equipped with a ORCA-ER camera (Hamamatsu Photonics Japan). The sample was irradiated using a 00 filter set (530−585 nm). The cross section analysis was obtained by pixel analysis of the 256 bit black and white fluorescence image using the *Image J* software package.

Results and Discussion

In Figure 1, the preparation of structured poly(styrene) (PS) grafts on ultrananocrystalline diamond (UNCD) is schematically outlined. A freshly hydrogenated UNCD substrate surface was patterned with 20-μm wide parallel stripes by conventional photolithography and the exposed areas oxidized by oxygen plasma. After this treatment, hydroxyl groups are expected on the plasma-exposed surface area.[13] After thorough cleaning the photoresist stripes, the substrate was submerged in bulk styrene and irradiated for 16 h with UV-light of a spectral distribution between 300 and 400 nm ($\lambda_{max} = 350$ nm) for the self-initiated photografting and photopolymerization (SIPGP). Finally, all physisorbed polymer was carefully removed by thorough cleaning under ultrasonic irradiation in several solvents.

The resulting substrate topography was investigated by atomic force microscopy (AFM). The AFM scan in Figure 2 shows
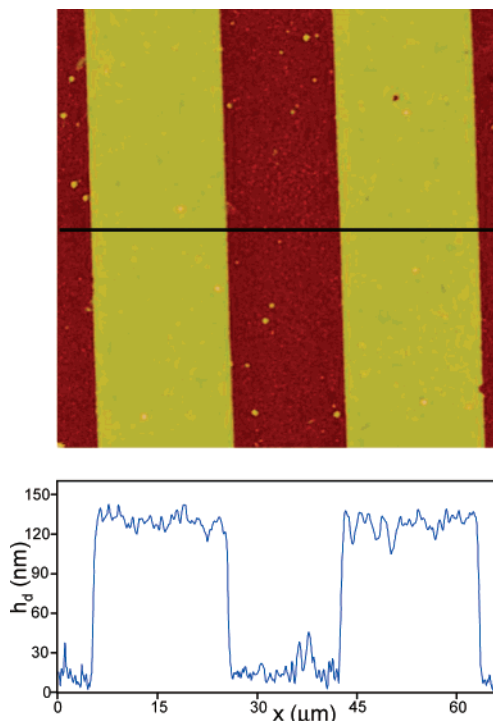

Figure 2. AFM scan (70 × 70 μm^2) along with a section analysis of the patterned PS grafts on UNCD. Photopolymerization by UV irradiation ($\lambda_{max} = 350$ nm). Irradiation time: 16 h. Polystyrene layer thickness: 109 ± 9 nm. The native UNCD regions have a roughness of 9.6 nm rms, the PS coated regions of 6.0 nm rms.

that the SIPGP of styrene resulted in patterns, previously determined by the patterned oxidation. At the oxidized areas, stripes with a relative height of 109 ± 9 nm were formed. Furthermore, the surface roughness of the native UNCD substrate (rms 9.6 nm) was rendered by the additional polymer layer, showing a lower average roughness value of 6.0 nm (rms).

The modified substrates were further analyzed by infrared (IR) and X-ray photoelectron spectroscopy (XPS). In the IR spectrum (Figure 3a), the characteristics fingerprints of poly-(styrene) (PS) are observed: the stretching vibrational modes of aromatic groups (ν(CH): ∼3030 cm^{-1}; ν(CC): 1430−1610 cm^{-1}) and modes from methylene groups with a maximum at 2923 cm^{-1}.[29] The XPS characterization (see spectra in Figure 3b) corroborates that the SIPGP of styrene resulted in the formation of PS grafts on UNCD.

(29) Hesse, M. M., H.; Zeeh, B. *Spektroskopische Methoden in Der Organischen Chemie*; Georg Thieme Verlag: Stuttgart, Germany, 1995.
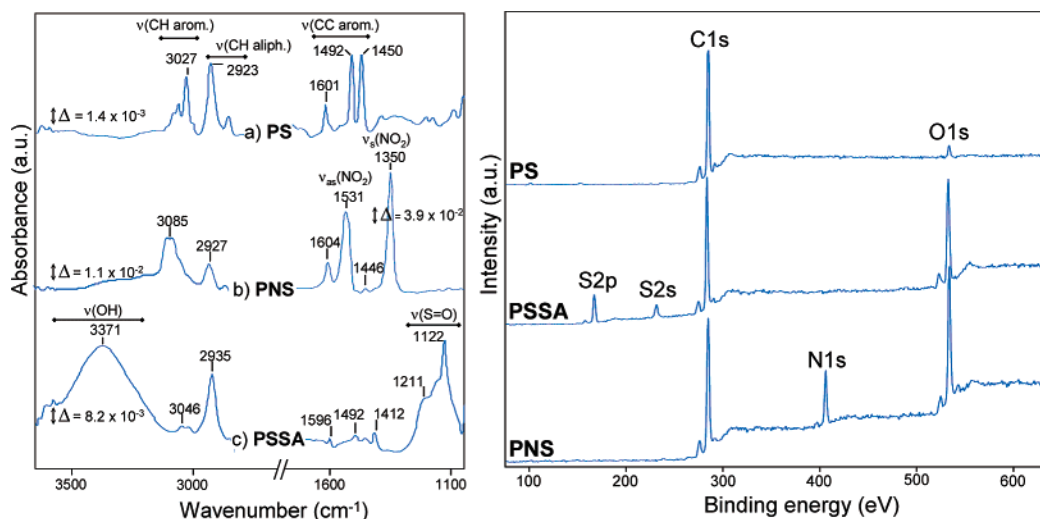
Figure 3. IR spectra and XPS survey scans of PS, PNS and PSSA grafts on oxidized UNCD. (a) The upper IR spectrum shows characteristics fingerprints of PS: the stretching vibrational modes of aromatic groups (ν(CH aromatic) and ν(CC)) and from methylene groups ((ν(CH/CH$_2$ aliphatic)). The IR spectrum of the aminated PS graft (PNS) reveals the two bands characteristics of the symmetric (ν_s(NO$_2$)) and asymmetric (ν_{as}(NO$_2$)) vibration modes of aromatic nitro groups. The sulfonated PS spectrum shows one broad absorption band characteristic of the sulfonic acid ν(OH) stretching mode and two intense bands corresponding to the ν(S=O) stretching modes of aromatic sulfonic acid. (b) Survey scans of PS, PSSA and PNS grafts. For the PS grafts only C1s and O1s peaks are visible; the O1s is attributed to water adsorption. In addition to the O1s signal, the XPS spectrum of nitrated PS grafts (PNS) reveals the N1s peak expected for the nitro group, while S2p and S2s peaks are observed for PSSA grafts.

The formation of polymer grafts occurs via the SIPGP process.[26,27] In this mechanism, the monomer absorbs a photon and acts as a photosensitizer to activate a surface functional group by hydrogen abstraction. The radical formed on the surface initiates a free radical surface-initiated polymerization (SIP) of the monomer. The formation of PS grafts on the oxidized areas can be explained by the energy difference required for the hydrogen radical abstraction from the oxidized and hydrogenated surface areas. For the H-terminated (100) diamond surface, the theoretical bond dissociation energy (BDE) of C–H was calculated by Petrim et al.[30] using density functional theory to be 401.5 kJ·mol^{-1}, whereas the BDE for the O–H functions, as present in the oxidized UNCD surface, is only 71 kJ·mol^{-1} as calculated using the same model.[31] This significant difference of the BDEs for the prominent functional groups of the two surface areas is, in our view, the reason for the formation of PS grafts on oxidized UNCD. Hence, a very facile technique for the direct polymer modification of diamond surfaces is now available, and the reactivity difference between H-terminated and oxidized diamond surfaces directly allows the preparation of structured polymer grafts on diamond. From these results alone, the formation of a thinner polymer coating on the H-terminated areas cannot be ruled out completely. However, as shown later (see discussion of fluorescence microscopy), the grafting occurs exclusively on the oxidized UNCD surface areas.

Polymer Analogue Reactions. Although a broad variety of vinyl monomers can be grafted by SIPGP, the preparation of polymer grafts with pendant functionalities can be prepared directly by polymer analogue reaction. In contrast to many other substrate/polymer graft combinations, the present system should be of unique chemical stability, because the polymer should be attached via a stabile ether or, after a radical reaction cascade, direct C–C bond to the diamond surface. Thus, polymer analogue reactions might be possible which would otherwise

result in detachment of the polymer chain from the surface or etching/dissolution of the substrate material.

In Figure 4, the various polymer analogue reactions of PS grafts on UNCD such as the nitration with fuming nitric acid,[32] the sulfonation with a mixture of concentrated sulfuric acid and acetic anhydride (acetylsulfuric acid)[33] and the amidoalkylation to poly((4-aminomethyl)styrene) (PAMS) grafts are outlined. Note that some reactions on the polymer coatings are performed for several hours in concentrated acids at 60 °C.

First, the impact of the polymer analogue reaction with the quite drastic reaction conditions upon the polymer layer homogeneity was monitored by AFM measurements. Neither the nitration nor the sulfonation of PS grafts on UNCD resulted in a detectable loss of the polymer coating. The coatings appeared homogeneous after the reactions and the cleaning procedures. Although the oxidized UNCD surfaces have a roughness of 16.5 nm rms, the PS coating displayed a lower rms of 9.2 nm. Nitration and sulfonation resulted in PNS and PSSA coatings with an even smother surface with rms values of 5.1 and 5.5 nm, respectively.

The successful conversion of the grafted PS to poly-(nitrostyrene) (PNS) and poly(styrenesulfonic acid) (PSSA) were confirmed by IR spectroscopy and XPS (Figure 3a and b).

After nitration of the PS layer, two strong absorption bands at 1350 cm^{-1} and 1531 cm^{-1} appears in the IR spectrum of PNS, characteristic for the symmetric (ν_s(NO$_2$)) and asymmetric (ν_{as}(NO$_2$)) vibration modes of aromatic nitro groups.[29] The sulfonated PS spectrum shows one broad absorption band centered at 3371 cm^{-1}, characteristic for the sulfonic acid ν-(OH) stretching mode and two intense bands between 1100 cm^{-1} and 1250 cm^{-1} corresponding to the ν(S=O) stretching modes of aromatic sulfonic acid.[29,34]

A quantitative analysis of the nitration and sulfonation reaction was performed by XPS. Survey scans of PS, PSSA

(30) Petrini, D.; Larsson, K. *J. Phys. Chem. C* **2007**, *111*, 795–801.
(31) Larsson, K., Private Communication.

(32) Zenftman, H. *J. Am. Chem. Soc.* **1950**, (MAR), 982–986.
(33) Tran, Y.; Auroy, P. *J. Am. Chem. Soc.* **2001**, *123*, 3644–3654.
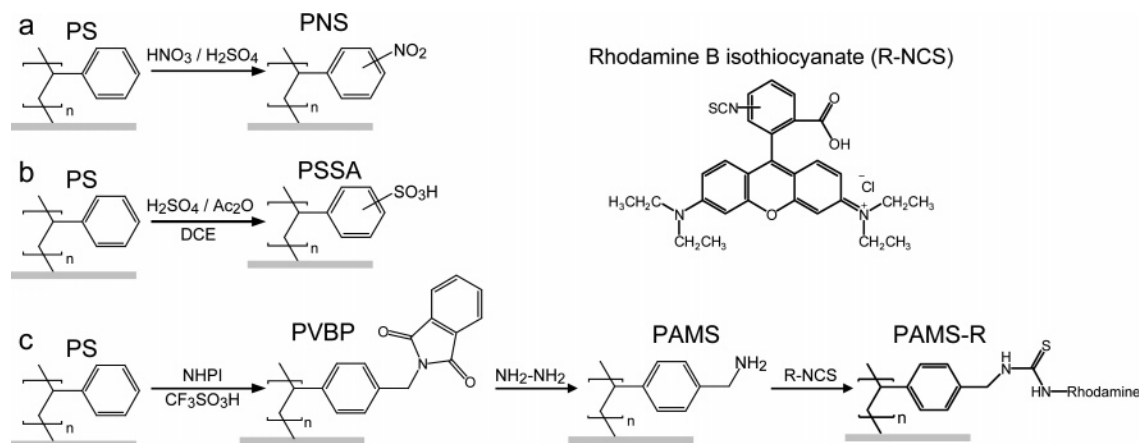(34) Nasef, M. M.; Saidi, H. *Appl. Surf. Sci.* **2006**, *252*, 3073–3084.

Figure 4. Outline of the different polymer analogue reactions of PS grafts reported in this work. (a) Nitration of PS grafts with fuminic nitric acid results in poly(nitrostyrene) (PNS) grafts. (b) Sulfonation by acetylsulfuric acid results in poly(styrene sulfonic acid) (PSSA) grafts. (c) Amidoalkylation of PS grafts results in poly((4-aminomethyl)styrene) (PAMS) grafs. In addition, the schematic also shows the grafting of the fluorescent label rhodamine B to PAMS grafts.

Table 1. Surface Atom Composition of the Polymer Grafts as Obtained by XPS

polymer	C	O	N	S
PS	8	0.46		
PNS	8	3.58	2.66	
PSSA	8	4.33		0.98[a]

[a] Average of the S composition determined by the S2p (0.88) and S2s peak (1.08).

and PNS grafts are shown in Figure 3b. The C1s and O1s peaks are centered at 285 and 533 eV, respectively. The N1s peak present in the PNS spectrum is centered at 406 eV, which additionally corroborates the successful introduction of a nitro group.[35] The S2p and S2s signal centered at 168 and 232 eV, respectively, can be attributed to the aromatic sulfonic acid group of PSSA. These assignments are in agreement with earlier reports and unambiguously prove the successful polymer analogue sulfonation of the PS grafts.[34]

The surface atom composition was calculated by the area of the XPS peaks taking into account the sensitivity factors (Table 1), and assuming a homogeneous functionalization of the polymer. The approximate S/C ratio of 1/8 for PSSA, calculates to an average substitution degree of one sulfonic acid group per phenyl ring. As apparent from Table 1, the surface-atom composition of PS and PSSA grafts have slightly higher oxygen content than expected. This is a common observation and is most likely explained by the presence of strongly absorbed water or organic solvent, used during the substrate cleaning process.

The N/C ratio for the PNS layer of 2.66/8 calculates to a substitution of 2.66 nitro groups per phenyl group, whereas the O/C ratio of 3.58/8 calculates to a slightly lower substitution degree of 1.89. Under the chosen reaction conditions, the introduction of approximately two nitro groups per aromatic ring of PS is in agreement with the literature. It is known that a first nitro substitution occurs in the para position, and a second substitution in the ortho position.[32]

It is important to note that the XPS measurements do not give the atomic composition of the entire polymer layer but only from the upper few nanometers. The emission intensity in XPS measurements is lower for functionalities located deeper

in the material, due to inelastic scattering of electrons. Reorganization within the polymeric layer may influence the measured composition (e.g., the measured S/C ratio in PSSA grafts may be higher than the average S/C ratio in the entire polymer layer due to the interaction between sulfonic acid groups and air humidity).

These first results show the major advantage of this approach, in which polymer grafts are covalently attached to the substrate via chemically stable links. This allows the further functionalization of the polymer grafts without the common constraints with respect to the reaction conditions.

Aminomethyl derivatives of cross-linked PS resins are widely used for solid-phase organic synthesis and many synthetic routes were developed for further functionalization of these resins.[36] The conversion of the PS grafts to the poly((4-aminomethyl)-styrene) (PAMS) grafts (Figure 4c) was performed following the synthetic route developed by Mitchell et al.[28] and is a versatile candidate for the direct chemical incorporation of complex bioorganic molecules, such as peptides or proteins, into polymer coatings on diamond.

As outlined in Figure 4c, PS grafts on UNCD are amidoalkylated by the Tscherniac-Einhorn reaction with *N*-(hydroxymethyl)phthalimide (NHPI) resulting in poly(4-vinylbenzyl)-phthalimide (PVBP) coating. In a second step, the phthalimide group was hydrazinolysed to give PAMS grafted on UNCD.

The successful reaction was confirmed by IR spectroscopy (Figure 5). Two strong absorption bands at 1712 cm^{-1} and 1770 cm^{-1}, characteristic for the carbonyl stretching vibrational modes ν(C=O(N)) of the phthalimide moiety, are clearly observed.[37] The hydrazinolysis of the poly(4-vinylbenzyl)phthalimide (PVBP) grafts is confirmed by the absence of these absorption bands and the appearance of a broad absorption band centered at 3357 cm^{-1} and the shoulder at 3291 cm^{-1}, characteristic for the asymmetric and symmetric amino stretching modes ν(NH$_2$). The distance of 66 cm^{-1} between the symmetric and asymmetric absorption band is in agreement with earlier reports.[29] The successful hydrazinolysis in refluxing ethanol shows that the

(35) Eck, W.; Stadler, V.; Geyer, W.; Zharnikov, M.; Golzhauser, A.; Grunze, M. *Adv. Mater.* **2000**, *12*, 805–808.

(36) Dörwald, F. Z. *Organic Synthesis on Solid Phase*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2002.

(37) Gravano, S. M.; Borden, M.; von Werne, T.; Doerffler, E. M.; Salazar, G.; Chen, A.; Kisak, E.; Zasadzinski, J. A.; Patten, T. E.; Longo, M. L. *Langmuir* **2002**, *18*, 1938–1941.
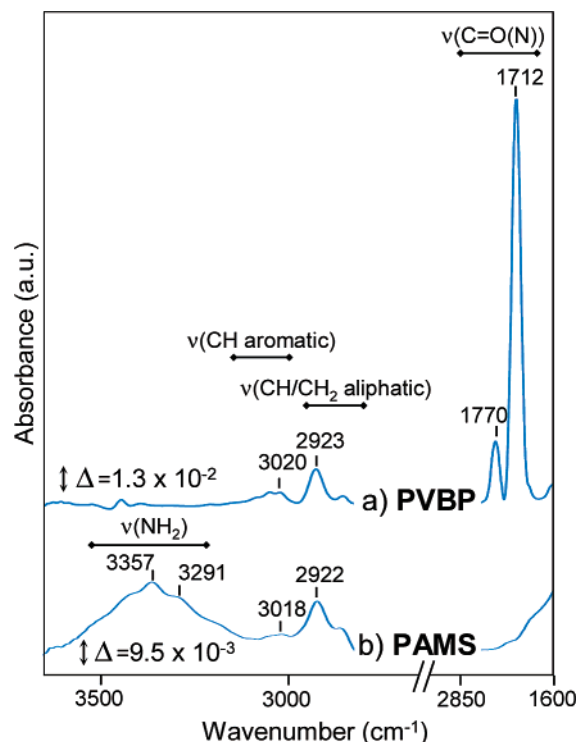
Figure 5. IR spectra of poly(4-vinylbenzyl)phthalimide (PVBP) grafts (upper spectrum) and of poly((4-aminomethyl)styrene) (PAMS). In addition to the fingerprints of poly(styrene), stretching vibrational modes of aromatic groups, ν(CH aromatic): ∼3020 cm^{-1}, and of methylene groups, ν(CH aliphatic): ∼2923 cm^{-1}, the IR spectrum of the PVBP grafts shows two strong absorption bands at 1712 cm^{-1} and 1770 cm^{-1}, which are characteristic for the carbonyl stretching vibrational modes ν(C=O(N)) of the phthalimide moiety. The hydrazinolysis of the poly(4-vinylbenzyl)-phthalimide (PVBP) grafts is confirmed by the absence of these absorption bands in the IR spectrum of the PAMS grafts, and the appearance of a broad absorption band centered at 3357 cm^{-1} and the shoulder at 3291 cm^{-1}, characteristic for the asymmetric and symmetric amino stretching modes ν(NH$_2$).

polymer grafts are also stable under strong reducing reaction conditions.

To demonstrate that the aminomethyl group can be functionalized even with steric demanding organic molecules, PAMS grafts created on microstructured oxidized UNCD surfaces were additionally functionalized with the fluorescence label rhodamine B isothiocyanate (RBITC) (Figure 4c). After the reaction and thorough cleaning of the substrate, fluorescence microscopy shows a strong fluorescence signal exclusively at the PAMS structures, corresponding to the originally oxidized UNCD surface areas (Figure 6a). We conclude that RBITC is covalently bonded to the PAMS grafts via the thiourea bond. The experiment shows that even large molecules can effectively be bonded within the polymer grafts.

The effective fluorescent labeling reaction of the modified polymer coating can be used to detect even thin polymer layer that might be formed also on the H-terminated UNCD substrate areas. As discussed above for Figure 1, the relative height difference of the patterend PS coated UNCD displayed a height difference of ∼110 nm, which indicates at least a preferred grafting of PS onto the oxidized UNCD areas. However, this height difference is relative and does not exclude the formation of a thinner PS coating on the hydrogenated UNCD. In order to control the presence of polymer grafts on the hydrogenated UNCD regions of patterned substrates, we compared the
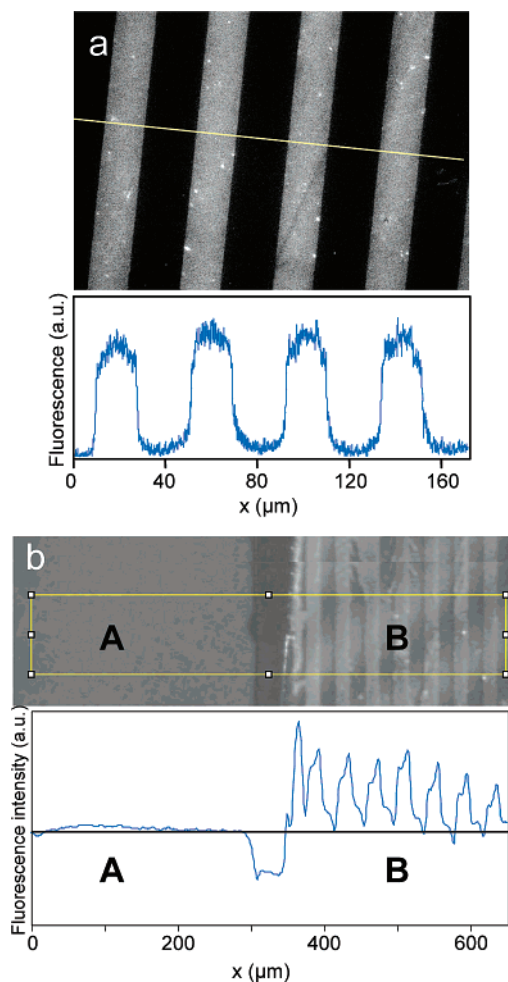

Figure 6. Fluorescence microscopy characterization of structured PS grafts on UNCD. (a) Fluorescence image and section analysis of a patterned oxidized UNCD surface, functionalized with PAMS grafts and labeled with rhodamine B isothiocyanate. The bright regions correspond to the oxidized surface areas (compare with Figure 2). (b) Fluorescence microscopy image and average section analysis of a native hydrogenated UNCD sample as reference (A) and a patterned PAMS-R graft on UNCD (B).

fluorescence signal of the dark regions in Figure 6a (corresponding to non oxidized UNCD areas) and the fluorescence signal of a H-terminated UNCD reference sample to which the photografting process was not applied but was reacted with rhodamine B. Figure 6b directly compares the fluorescence intensity of a native UNCD substrate next to a patterned PMAS-R graft. The fluorescence intensity of the native UNCD is the same as of the H-terminated UNCD areas of the patterned substrate. Because even submonolayer coverage of rhodamine B should give a significant signal,[38] it can be stated that under the conditions used in this work, the SIPGP of styrene occurs *exclusively* on oxidized UNCD surfaces.

Conclusions

The direct self-initiated photografting and photopolymerization (SIPGP) of styrene onto oxidized UNCD surfaces results in homogeneous and extremely stable poly(styrene) coatings with a thickness of about 110 nm. The grafting occurs only on oxidized areas and not on hydrogenated UNCD, allowing the preparation of structured polymer coatings on diamond. Fur-

(38) Tsukanova, V.; Lavoie, H.; Harata, A.; Ogawa, T.; Salesse, C. *J. Phys. Chem. B* **2002**, *106*, 4203−4213.

thermore, various polymer analogue reactions with quite drastic reaction conditions can be performed such nitration, sulfonation, and amidoalkylation, and stable functional polymer grafts are obtained. The introduced polymer pendant chemical functions are accessible for the coupling of large molecules such as rhodamine B.

With this facile technique, a broad variety of chemical functions can be directly coupled to diamond. Due to the stability and biocompatibility of the substrate and the stable grafting of the polymer coating, this method enables the fabrication of a broad variety of functional surfaces for modern technologies. This includes sensor array fabrication for biomedical applica-tions as well as high-throughput experimentation in materials science and catalysis.

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