Communication

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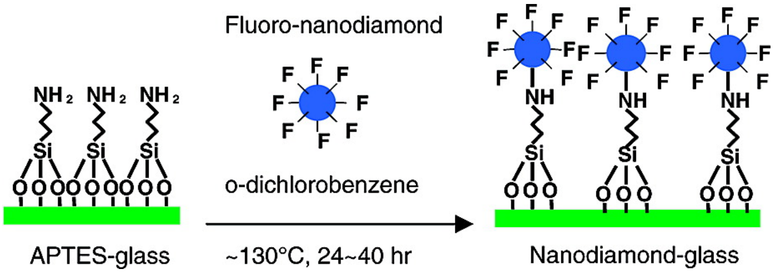

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Fluorinated Nanodiamond as a Wet Chemistry Precursor for Diamond Coatings Covalently Bonded to Glass Surface

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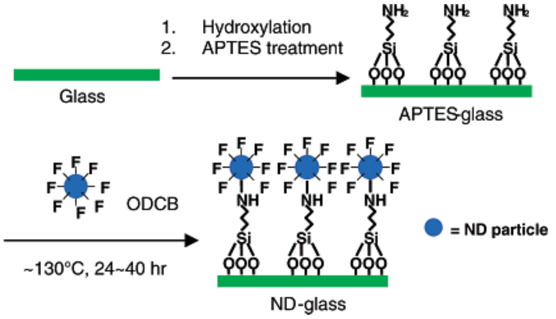
Diamond has been attracting tremendous attention due to a wide range of extreme properties exhibited by this material.[1,2] During the past decade, the areas of diamond applications have been significantly expanded through coating the diamond particles onto solid substrates by developed thin films growth techniques.[3] Currently, the most common group of methods to fabricate diamond thin films utilizes chemical vapor deposition (CVD), involving a gas-phase chemical reaction occurring above a solid surface and resulting in deposition and nucleation growth of diamond on that surface.[1] While various CVD methods differ in details, they all share common experimental features such as the need for specialized and costly instrumentation (reactors, vacuum furnaces, heaters, or plasma generators) and extreme reaction conditions, for example, a temperature range of 1000−1400 K and precise control of gas flow for growing either micro- or nanocrystalline diamond films. These methods also require the substrate to be resistant to high temperature and to possess modest reactivity with carbon. Therefore, development of an alternative approach utilizing mild reaction conditions and a low-cost methodology for coating substrate surface with diamond is of significant importance. Herein, we report a method of nanodiamond (ND) coating on glass surface through the reaction of fluorinated nanodiamond (fluoro−ND) powder with the amino-functionalized glass surface. This novel approach is based on the wet chemistry process (solution reaction) occurring at low temperature and resulting in a robust covalent bonding of tiny fluoro−ND crystals to the substrate.

In our work, we used a commercially available nanoscale diamond powder (Nanostructured and Amorphous Materials, Inc.; >97% purity) prepared by detonated explosion synthesis.[4] The powder consists of 1−2 μm-sized clusters built of aggregated tiny (3.5−6.5 nm) diamond nanocrystals. During the recent study,[5] we have developed a method for direct fluorination of this powder to produce fluoro−ND. This ND derivative shows an improved solubility in polar solvents, a dramatically reduced particle agglomeration, and an ability of chemical displacement of fluorine by amino reagents and other nucleophiles. These experimental results precipitated the idea of conducting a wet chemical reaction between fluoro−ND and terminal amino groups of the functionality attached to the glass surface by using a silane coupling agent, 3-aminopropyltriethoxysilane (APTES), commonly applied for surface modification of a range of materials.[6] This approach is illustrated in Scheme 1. By implementation of this methodology, diamond particles are not grown on the substrate like in CVD, but are attached to the substrate surface through a molecular linker, APTES. Covalent Si−O−Si bonds can be formed between the linker and the substrate after hydrolysis of the APTES ethoxy groups followed by condensation reaction with the numerous OH groups pregenerated on the surface. Fluoro−ND is then reacted with the surface-immobilized APTES terminal amino groups followed by elimination of HF and formation of the C−N−C bonds to provide coupling to the substrate.

Scheme 1. Reaction Steps for Coating Glass with Fluoro−ND



The fluoro−ND was prepared by fluorination of nanodiamond powder through a reported procedure.[5] After this treatment, the nanodiamond cluster size is significantly decreased (to a few tens of nanometers) with particle surfaces terminated by fluorine atoms. EDX data indicated that the F/C ratio in fluoro−ND, used as a precursor in further coating experiments, was 9.3/100. In our previous studies, we already established the reactivity of fluoro−ND toward the $-NH_2$ group in ethylenediamine.[5] However, in the present work, to obtain assurance that fluoro−ND can also efficiently react with the NH_2 group in APTES, the reaction of a fluoro−ND suspension solution in anhydrous 1,2-dichlorobenzene (ODCB) with the added slightly excess amount of APTES was carried out first. The reaction mixture was stirred at 130 °C for 24 h, then cooled to room temperature, and filtered.

ATR-FTIR spectra (Figure 1) provide clear evidence for the occurrence of this reaction. Thus, the prominent peak of the C−F stretch at 1340 cm^{-1} in fluoro−ND (a) almost entirely disappears after the reaction, and new peaks corresponding to the IR features of APTES−ND derivative, $\{(EtO)_3Si(CH_2)_3NH\}_x$−ND, are observed (b). This is confirmed by EDX analysis indicating the decrease of fluorine content in the latter sample from 9.3 to just 1.2 per 100 carbons.

The glass coating process was carried out as follows. A glass microscope slide (1 × 1 cm) was cleaned in piranha etch (7:3 v/v 98% H_2SO_4/30% H_2O_2) at 90 °C for 1 h, rinsed in ultrapure water (Milli-Q system, Millipore), and blow-dried with a stream of filtered N_2. Thereafter, the substrate was immersed in a fresh 85 mM solution of APTES in ethanol for 30 min, then washed with ethanol, gently dried under N_2 stream, and cured in a vacuum oven at 100 °C for at least 2 h to allow the APTES molecules to fully condense onto the glass surface. Then, the substrate was immersed in a fluoro−ND suspension in ODCB prepared in a small vial. The vial was placed in the oven and kept there at 130 °C for 24−40 h. After that, the substrate was rinsed with ethanol and then sonicated in ethanol for 30 min to remove all unbonded particles deposited on the surface. Finally, the substrate was dried for further characterization measurements.

Figure 2 shows the AFM images of glass surface taken before and after coating. The APTES-treated glass substrate (Figure 2a) is mostly smooth, showing only a few spots that may be caused by dust or surface defects. After the reaction with fluoro−ND, the

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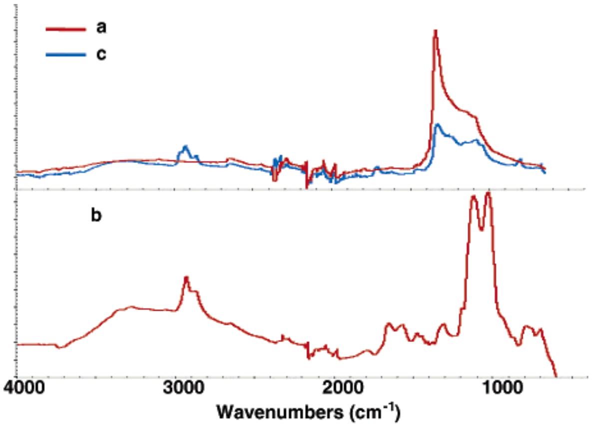

Figure 1. ATR-FTIR spectra of fluoro−ND powder before (a) and after the reaction with APTES (b) and hydrazine (c).

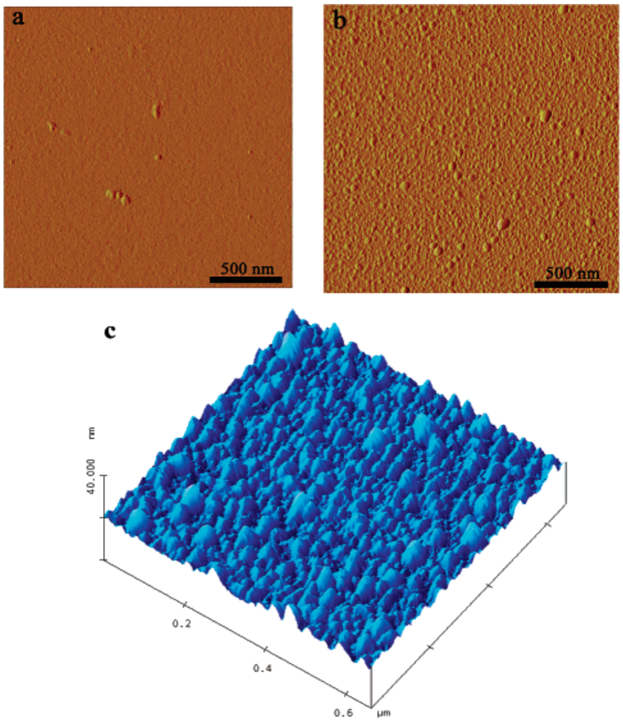

Figure 2. AFM images of APTES−glass surface taken before (a) and after coating the reaction with fluoro−ND (b and c).

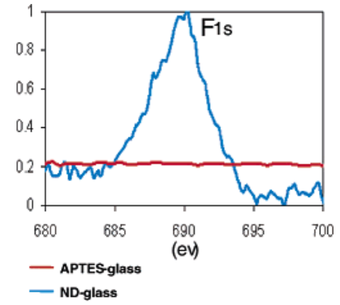

Figure 3. XPS F1s peak.

Table 1. XPS Elemental Analysis (at. %)

	APTEX–glass	ND–glass		APTEX–glass	ND–glass
Si2p	26.1	21.0	Nls	1.1	0.4
Ols	63.0	50.5	Fls	0	2.1
Cls	9.8	26.0			

surface becomes rough at the nanoscale (Figure 2b), due to the attached ND particles. The three-dimensional image of this sample, shown in Figure 2c, provides a more detailed vision of the surface morphology. The surface-bonded fluoro−ND particle sizes range from 10 to 40 nm. They are closely packed, although not quite fully covering the surface. SEM was also used for surface characterization, providing images consistent with the AFM data.

XPS analysis gives further evidence for the fluoro−ND particles coating the glass surface. First, it shows the appearance of a fluorine F1s peak after the coating (Figure 3). Since fluorine substituents, which are located in fluoro−ND crystals on the side opposite to the glass surface, will not react with the surface terminal amino groups, the residual fluorine should remain on the coated surface. Therefore, the detection of a fluorine peak helps to establish the presence of diamond on the surface. Second, a huge increase of carbon atomic percentage measured by elemental analysis (Table 1) can also be related only to the diamond coating.

To confirm that the particles are covalently bonded to the surface, two additional coating procedures were tested. In one case, bare glass substrate was held in fluoro−ND solution for 24−40 h at 130 °C. In the other case, APTES-functionalized glass was kept in contact with solubilized fluoro−ND for the same period of time but at room temperature. Thereafter, ultrasonication in ethanol for 30 min of both samples was done after coating. The samples were characterized by AFM and XPS, which have shown no diamond present in each sample. This comparison indicates that the film coating can be obtained only when the conditions (such as heating) for the reaction between solvated fluoro−ND and amino-functionalized surface are maintained and covalent bonds are formed during the reaction.

The surface-bonded fluoro−ND can be further modified by chemical substitution and removal of residual fluorine. For example, treatment of fluoro−ND powder with the anhydrous hydrazine, N_2H_4 (98%, Aldrich),[7] resulted in removal of most of the fluorine and partial reduction of the C−F to the C−H bonds, as indicated by the IR spectrum (Figure 1c). The similar treatment of fluoro−ND coated on glass also led to its defluorination, in this case to such a low fluorine content that it was virtually undetectable by the XPS.

In summary, we have presented a cost-effective method for coating glass surface with covalently attached diamond particles by using wet chemistry lab techniques. The fabricated nano-thin monolayers can be further functionalized, for example, by biomolecules for sensor device applications or by diamines for subsequent bonding of multiple nanodiamond particle layers for protective coatings. The developed method can be extended to nanodiamond coating of various substrates, such as quartz, silicon, metals, and other materials. These experiments are currently in progress.

Acknowledgment. This work was supported by the Texas Advanced Technology Program and the Robert A. Welch Foundation.

Supporting Information Available: Raman spectrum of fluoro−ND, and SEM images of APTES-functionalized glass surface taken before (a) and after (b) reaction with the solubilized fluoro−ND. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Thirty milligrams of fluoro−ND was placed in 10 mL of anhydrous hydrazine and was then sonicated for 1 h.

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