

## LETTERS

### Use of Photoreactive Sol–Gel Interfaces To Form Robust Low-Surface-Energy Fluoropolymer–Silica Nanocomposite Coatings

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A new method for the formation of tightly bound, low-surface-energy nanocomposite coatings on glass and other hydroxylated surfaces is reported. This technique involves the initial deposition of a porous vanadia–silica sol–gel thin film on the surface of the substrate. These coatings act as reactive interfaces for the photopolymerization of vinyl monomers. Using this interface, polyvinylidene fluoride (PVF2)–silica nanocomposite coatings on quartz were fabricated. These coatings were found to be extremely robust and yielded a surface whose energy was close to that of pure PVF2.

Modification of the surfaces of glass, metal, and other substrates is of considerable practical importance in the control of wettability and tribological properties and to increase resistance to deleterious environments.<sup>1</sup> Prominent among the methods used to modify surfaces is the deposition of organic films to form a barrier and to impart the particular properties of the organic material to the surface.<sup>2</sup> Such coatings can be organic polymers deposited from solution or by hot melt techniques, or small molecules attached by methods such as silane coupling chemistry.<sup>3</sup> Recently, studies of organic–inorganic nanocomposites have indicated that the inherent robustness and thermal stability of this class of materials may recommend them for a number of applications including that of protective coatings.<sup>4</sup>

We report here a new method for the formation of tightly bound, low-surface-energy coatings on glass and other hydroxylated surfaces. The initial step in the technique involves the deposition of a porous vanadia–silica sol–gel thin film on the surface of the substrate. This step is followed by the photopolymerization of fluorinated vinyl monomers in the sol–gel

coating to yield a robust fluoropolymer–silica coating. This approach is based on previous studies that have shown that isolated vanadia sites are facile photocatalysts for the polymerization of vinyl and acetylenic monomers.<sup>5,6</sup> When photopolymerization is carried out on monomers inside the pores of a vanadia–silica xerogel, a polymer–silica composite structure is produced. Since the polymer phase is constrained by the pores of the xerogel which are on the order of 10–100 Å, the resultant materials are nanocomposite structures.<sup>7</sup> We determined that this photopolymerization process is retained in thin films of this material where irradiation in the presence of organic monomers results in the formation of polymer–silica coatings (Scheme 1). Using this approach we have successfully formed polyvinylidene fluoride (PVF2)–silica coatings on quartz and other substrates.

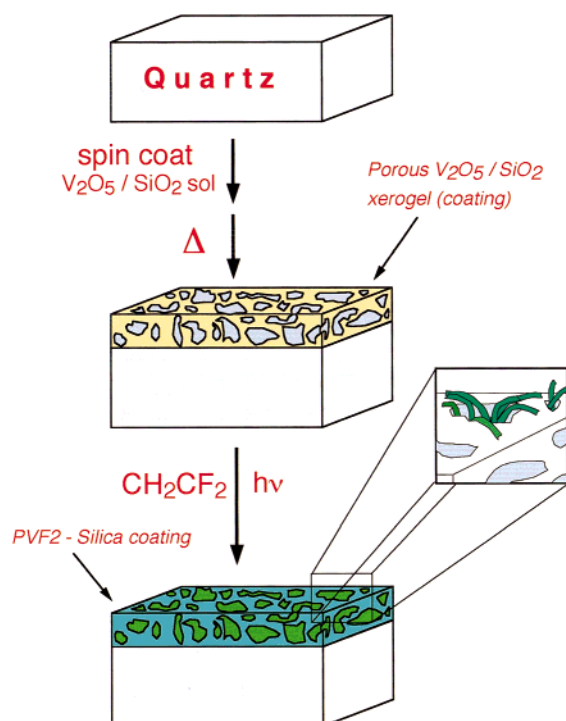
In a typical preparation, substrates of fused quartz were coated with vanadia–silica sols containing 10 mol % vanadium (moles V/(moles V + moles Si)). Prehydrolyzed stock solutions were made by the addition of a substoichiometric amount of water (1:1 water:silicon) to a solution of 10 mol % oxovanadium tris(isopropoxide) and tetramethylorthosilicate (2.87 M) in methanol. HCl was added in a 0.3:1 mole ratio with silicon.<sup>8</sup> The solutions were stirred overnight, at which point water was added

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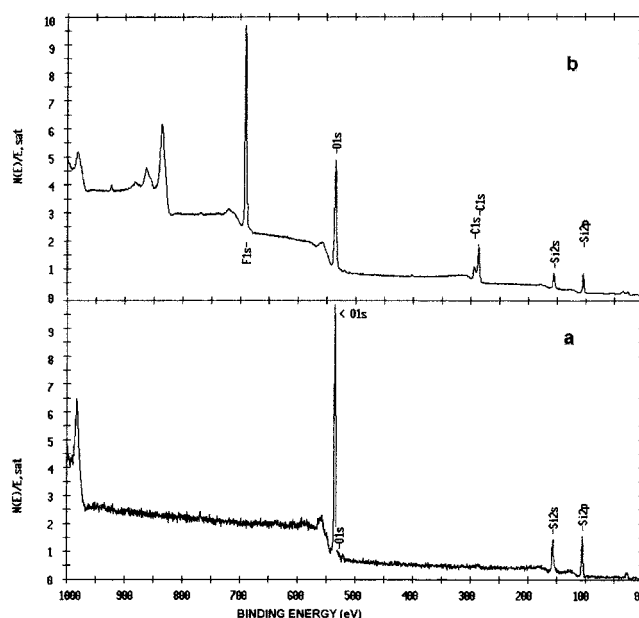
## SCHEME 1



to bring the water:silicon ratio to 3:1. Uniform thin films of  $\sim 1 \mu\text{m}$  thickness (determined by scanning electron microscopy) were made by spin coating ( $\sim 2000$  rpm) measured aliquots ( $100 \mu\text{L}$ ) of the vanadia-silica sol onto the quartz substrates. After addition, the sol was allowed to spin off and evaporate. The substrates were dried at  $150^\circ\text{C}$  and then heated to  $500^\circ\text{C}$  under oxygen.

Photolysis of the coated substrates in the presence of condensed vinylidene fluoride resulted in the incorporation of PVF2 into the surface layer. In a typical polymerization, vanadia-silica coated substrates, dried at  $200^\circ\text{C}$  just prior to use, were placed in a sealed pressure vessel equipped with a quartz window. Gaseous vinylidene fluoride was introduced into the vessel and then, with cooling, condensed into a thin layer of liquid over the sample. Irradiation was carried out over a period of 2 min with a high pressure 200 W Hg/Xe lamp equipped with a  $\lambda \geq 285$  nm cutoff filter. Control experiments verify that no polymerization occurs in the absence of the photocatalytic sol-gel coating.

Surface analysis of the coated quartz substrates was carried out by X-ray photoelectron spectroscopy (XPS).<sup>9</sup> Figure 1 shows XPS survey scans of the surface of vanadia-silica coated substrates before and after photolysis in the presence of vinylidene fluoride. The incorporation of fluorocarbon into the surface of the irradiated sample is apparent from the presence of a strong peak at 692 eV corresponding to the 1s electron binding energy of fluorine.<sup>10</sup> In addition, two different carbon 1s peaks are observed at 294 and 287 eV. The position of these peaks agrees quite closely with the C(1s) binding energies observed for the  $-\text{CF}_2-$  and  $-\text{CH}_2-$  groups, respectively, in pure PVF2.<sup>11</sup> Integration of the peaks, with application of the appropriate sensitivity factor gives the elemental surface composition (Table 1). The carbon-to-fluorine ratio shows a slight excess of carbon while the ratio of the  $-\text{CH}_2-$  to  $-\text{CF}_2-$  carbon peaks, obtained from multiplexing the C(1s) region, is 2.1:1. This differs from the 1:1 ratios expected for pure PVF2 but is consistent with cross-linking and dehydrofluorination of



**Figure 1.** X-ray photoelectron spectra of a quartz substrate coated with a vanadia-silica xerogel coating (a) prior to and (b) after photolysis in the presence of vinylidene fluoride.

**TABLE 1: Elemental Composition**

element	concentration (%)	
	V/Si coating	PVF2/V/Si coating
Si(2p)	24.98	8.05
O(1s)	72.49	24.93
V(2p) <sup>a</sup>	2.53	0.74
C(1s)		33.84
F(1s)		32.44

<sup>a</sup> Vanadium concentration determined from deconvolution of the V(2p) peak from under the O(1s) satellite.

**TABLE 2: F and Si Composition as a Function of XPS Takeoff Angle**

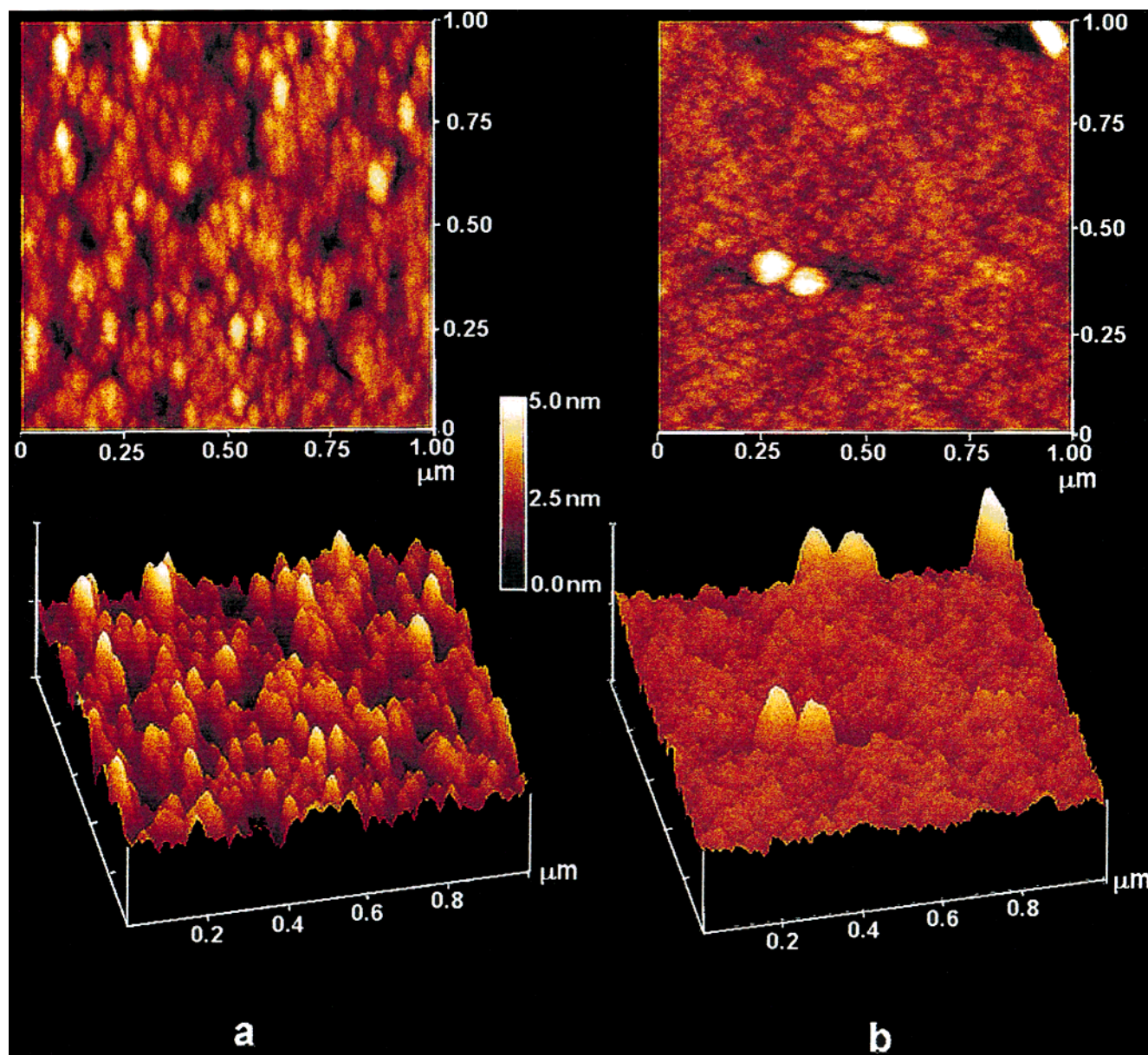
takeoff angle( $^\circ$ )	penetration depth (nm) <sup>a</sup>	Si(%)	F(%)	F/Si
85	6.2	14.18	39.26	2.77
65	2.3	13.08	40.00	3.06
45	1.7	7.92	58.53	7.39
25	1.1	5.74	57.65	10.04

<sup>a</sup> Estimated (ref 13) as  $\text{depth} = 3\lambda \sin \theta$  ( $\lambda$  = x-ray wavelength;  $\theta$  = takeoff angle).

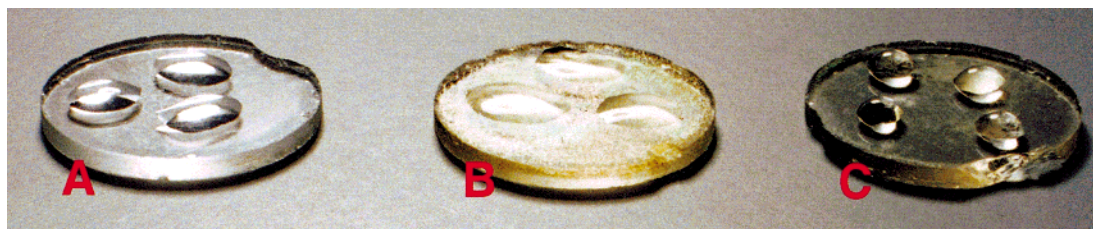
the polymer during photolysis.<sup>12,13</sup> XPS spectra reported for radiation-cross-linked PVF2 are virtually identical to the photopolymerized materials with a C/F ratio greater than 1 and a decrease in the amount of  $-\text{CF}_2-$  observed in the spectrum.<sup>14</sup>

The XPS data for the PVF2-coated substrates indicates that carbon and fluorine are the dominant species at the surface with relatively low ( $\leq 8\%$ ) amounts of silicon observed. This suggests that the PVF2 is not only filling pores of the xerogel film but is also forming a polymer layer on the surface of the coating. Further evidence for this is provided by the XPS takeoff-angle dependence of the F/Si ratio (Table 2). This ratio ranges from 2.77 to 10.04 over an angular range from  $85^\circ$  to  $25^\circ$ , indicating that, at the surface, fluorine is present preferential to silicon. This is consistent with a surface PVF2 layer on the order of several nanometers in thickness.<sup>15</sup>

The microscopic structure of these surfaces can be observed by atomic force microscopy (AFM).<sup>16</sup> Figure 2 shows AFM images of a quartz substrate coated with a  $\sim 1 \mu\text{m}$  vanadia-silica film and an identically coated substrate in which vinyl-



**Figure 2.** Atomic force micrographs, collected in Tapping Mode, of the surface of a quartz substrate coated with a vanadia-silica xerogel coating (a) prior to and (b) after photolysis in the presence of vinylidene fluoride.



**Figure 3.** Water drops on the surface of quartz disks (a) uncoated and coated with a vanadia-silica xerogel coating (b) prior to and (c) after photolysis in the presence of vinylidene fluoride (diameter of disks is 2 cm).

nylidene fluoride has been deposited. Imaged on the same scale, the surfaces are dramatically different. The material containing no polymer was significantly rougher with a rms roughness of 0.637 nm compared to 0.296 nm for the PVF2 coating.<sup>17</sup> As seen in the image (Figure 2a) the surface of the sol-gel coated sample has sharp surface structures of  $\sim 60$  nm in diameter. This microstructure is similar to the interior of bulk silica xerogels and has been observed previously in monolithic vanadia/silica materials.<sup>7</sup> The space between these structures,

which commence at  $\sim 20$  nm and taper to  $< 5$  nm at the limit of the range of the probe, constitutes the more mesoporous region of the xerogel. As seen in Figure 2b, the polymer containing sample is significantly smoother with few well-defined structural features. We suggest that the differences result from polymer filling of the porous regions between the silica features, which acts to smooth the surface. Taken together, these studies suggest that, upon infusion of the vinyl monomer and subsequent photopolymerization, the xerogel fills with polymer until it



emerges from the pores and forms a thin layer on the surface (Scheme 1, inset). It should be noted, however, that these studies have been restricted to surface analysis techniques and the properties of the composite in the interior is not directly known.

For these coatings to be useful, they have to be robust and significantly alter the surface properties of the substrate. As can be seen in Figure 3, water droplets bead up dramatically in the PVF2 coated substrates suggesting that the surface energy is significantly lower. Contact angle measurements, made using the captive bubble method to obtain advancing angles, gave values of  $38(\pm 4)^\circ$  and  $28(\pm 5)^\circ$  for the blank quartz substrate and the sol-gel coated substrate, respectively, while the PVF2-coated sample had a value of  $86(\pm 2)^\circ$ .<sup>18</sup> In comparison, the contact angle of neat PVF2 is reported to be  $82(\pm 2)^\circ$ .<sup>19</sup> The coatings also appear to be quite robust. They were impervious to routine handling and rubbing. More quantitatively, the coating adhesion was tested using the ASTM standard tape test (D 3359-78, method A), where no delamination or removal was observed.<sup>20</sup> In more chemically deleterious tests (i.e., exposure to refluxing  $\text{CCl}_4$  for several hours) some loss of polymer was observed.

We believe that this technique represents an interesting new approach to the modification of glass and other surfaces. While we have demonstrated this approach for PVF2, it should be of general utility for a range of organic polymers, which will permit the engineering of specific surface properties. In addition, the fact that it is a photoinitiated reaction suggests that it will also be amenable to photolithographic patterning.

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