Communication

Self-assembled Monolayers of *n*-Hexadecanoic Acid and *α*-Hydroxyl *n*-Hexadecanoic Acid on Titanium Surfaces

CHEN, Hai-Gang[a](陈海刚)   WU, Xue-Dong*,[a](乌学东)   YU, Qin-Qin[a](虞勤琴)
YANG, Sheng-Rong[b](杨生荣)   WANG, Da-Pu[a](王大璞)   SHEN, Wen-Zhong[c](沈文忠)

[a] *School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China*
[b] *State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, Gansu 730000, China*
[c] *Laboratory of Condensed Matter Spectroscopy and Opto-Electronic Physics, Department of Physics, Shanghai Jiaotong University, Shanghai 200240, China*

n-Hexadecanoic acid (HA) and *α*-hydroxyl *n*-hexadecanoic acid (HHA) are shown to spontaneously assemble on Si-supported titanium surfaces. Contact angle measurements, reflection absorbance IR, AFM and XPS characterizations are performed to examine the physical and chemical states of attached monolayers. The results show that the two amphiphiles tend to form disordered monolayers on titanium surfaces. The HHA headgroups are believed to form polydentate coordination with Ti, which is more chemically stable than the bidentate coordination of HA. All the facts of characterization indicate that HHA monolayer has more surface coverage than HA monolayer.

Keywords   self-assembled monolayers, surface chemistry, polydentate coordination, titanium surface

During the last two decades, people have paid much interest in the chemistry of self-assembled monolayers (SAMs), which shows powerful applications in the fields of biosensors and tailored surfaces. Particularly, two types of SAMs, *i.e.*, thiols/thiolates on gold and silanes on siliceous surfaces, have been extensively investigated in both basic research and their applications.[1] However, the available techniques could not offer a versatile protocol in view of the chemical variety of engineered material surfaces, such as metal surfaces. Therefore, it is necessitated to extend the current SAMs families and de-

velop new ways to attach organic monolayers on those substrates. Titanium and its alloys are very important biomaterials owing to their outstanding mechanical performances and excellent biocompatibility. Recently, some routes to attach organic monolayers on titanium and TiO_2 surfaces have been developed. McCathy *et al.*[2] studied the monolayers of hydridosilanes on titanium surfaces. However, this method should be conducted very carefully and has poor reproducibility thanks to the sensitivity of hydridosilanes. Spencer *et al.*[3,4] studied the SAMs of dodecyl phosphates on various titanium/TiO_2 surfaces from aqueous solution. In this paper, we design a new route to covalently attach organic monolayers on titanium surfaces under mild conditions, namely self-assembled monolayers of *n*-hexadecanoic acid (HA) and *α*-hydroxyl *n*-hexadecanoic acid (HHA) on titanium surfaces. Although SAMs of fatty acids on the surfaces of Ag, Cu, and Al, as well as their corresponding oxides surfaces, have been investigated,[5] no similar work deals with the titanium surfaces, which is chemically different from the IB group metals.

Experimental

The titanium surface was prepared by vacuum sputtering of highly pure titanium in a thickness of 200 nm on

single polished Si(111) wafer. The substrates were pre-treated using cold Piranha solution (98% H_2SO_4 : 30% $H_2O_2 = 7:3$, V/V) for 60 min to activate the surfaces. Then the samples were immersed in a 1 mmol/L solution of HHA in ethanol or HA in n-hexane for 24 h at room temperature, respectively. Finally, the samples were rinsed with ethanol and n-hexane, respectively, and blown dry with nitrogen.

The static contact angles were measured with a contact measuring apparatus in which a video camera was e-quipped to capture the picture of the drop as soon as 2 μL of pure water was dropped on the surface of a sample. At least three drops at different positions on each slide were used for the reported angle readings.

Reflection absorbance infrared spectra (RAIR) were obtained with a Nicolet Nexus 870 spectrometer equipped with an MCT detector cooled with liquid nitrogen. Spectra were collected in a grazing angle mode with a fixed angle of 80° using p-polarized light. All spectra are reported as $-\lg(R/R_0)$, where R is the reflectivity of the substrate with monolayer and R_0 is the reflectivity of the reference. A freshly Piranha solution pretreated substrate was used as a reference. All the spectra were obtained with an average of 1024 scans with a resolution of 4 cm^{-1}. Atomic Force Microscopy (AFM) measurements were carried out with a NanoScope III a scanning probe micro-scope (Digital Instruments, Inc.). The measurements were performed in air at room temperature in contact mode.

X-Ray photoelectron spectroscopy (XPS) analyses were performed using a PHI 5702 multifunctional X-ray photoelectron spectrometer. Spectra were collected at a base pressure of 10^{-7} Pa using Al Kα source operating at 250 W. The pass energy of the analyzer was set at 29.35 eV. Spectra were fitted using Gaussian-Larentzian functions. The energy scale was referenced to aliphatic hydro-carbon C_{1s} signal at 284.6 eV.

Results and discussion

From the static contact angle measurements, it was observed that the original titanium surface was a bit hy-drophobic, whose water contact angle was around 88°. In fact, we failed to form SAMs on such surfaces with im-mersion method if no pretreatment was adopted. This in-dicates that it is necessary to perform surface hydroxyla-tion before the formation of SAMs. After pretreated with Piranha solution, it becomes completely hydrophilic (the

water static angle decreases to 12°), which results from the formation of Ti—OH groups on the surface. The as-prepared HA and HHA monolayers exhibit a water static angle of 99° and 109°, respectively. This strongly implies that HAA monolayer covers more densely than HA mono-layer on titanium surface. The contact angle of HHA monolayer is as high as that of well packed monolayers obtained from other similar alkyl-terminated surfactants.[6]

Fig. 1 represents the RAIR spectra of HA and HAA monolayers. The peaks for C—H stretching (2960—2850 cm^{-1}) in the high frequency region confirm the presence of alkyl chain groups on the surfaces. The peaks at 2869 cm^{-1} and 2962 cm^{-1} are attributed to ν_s (CH$_3$) and ν_a(CH$_3$), respectively. The peak frequencies for ν_s(CH$_2$) and ν_a(CH$_2$) appear at 2856 cm^{-1} and 2927 cm^{-1}, which
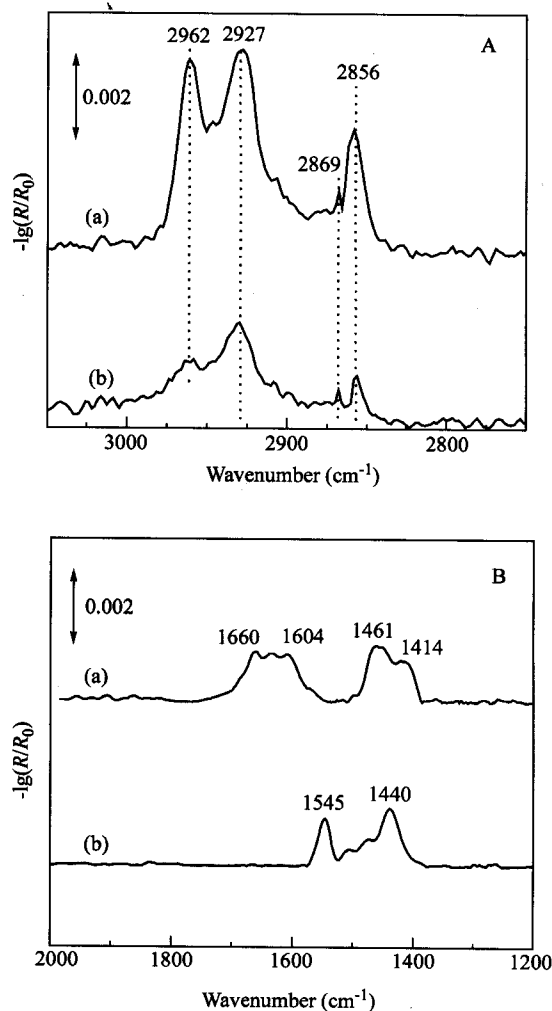

Fig. 1   Reflection-absorbance IR spectra of (a) HAA and (b) HA SAM on TiO$_2$ surface. A: high-frequency region, B: low-frequency region.

are higher than those for highly ordered crystalline SAMs.[6] It is known that the stretching frequencies of —CH$_2$— can reflect the packing structures of monolayers. In general, the peaks at 2850 cm^{-1} for ν_s(CH$_2$) and 2918 cm^{-1} for ν_a(CH$_2$) indicate a crystalline state and well-ordered structure; while peaks at 2856 and 2927 cm^{-1} imply disordered and liquid-like structure.[7] The results suggest that those monolayers formed on titanium surfaces are in disordered liquid-like state. It might lie in the surface lattice of titanium dioxide. Normally, titanium surface tends to form an amorphous oxide layer, which would result in the disorder of grafted alkyl chains. It can also be found that the intensity of C—H stretching of HHA monolayer is stronger than that of HA monolayer, which also implies that HHA molecules pack more densely than the HA moelcules. As to the low frequency region, two obvious peaks for HA monolayer at 1440 cm^{-1} and 1545 cm^{-1} can be assigned to ν_s(RCOO$^-$) and ν_a(RCOO$^-$), respectively. The separation between symmetric and asymmetric vibration of carboxylate ion is about 105 cm^{-1}, indicating carboxylate chelating with Ti in bidentate form (Scheme 1).[8] The coordination of HAA with Ti is more complicated. No RO—H stretching band (generally at 3440 cm^{-1} in HHA crystalline) could be detected in the RAIR spectra, which suggests that the α-hydroxyl group would chemically bind with Ti^{4+} and tend to form a stable five-membered ring when collaborating with

Scheme 1

Ti$\langle$ O ... $\rangle$C—R
      O
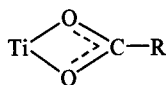
carboxyl. Differing from that of HA monolayer, the peak region assigned to ν_s(RCOO$^-$) and ν_a(RCOO$^-$) of HHA monolayer is significantly broadened, ranging from 1414 cm^{-1} to 1461 cm^{-1} for ν_s(RCOO$^-$) and from 1604 cm^{-1} to 1660 cm^{-1} for ν_a(RCOO$^-$). It can be inferred that equalization between C = O and C—O bonds in RCOO$^-$ ion is weakened, $i.\,e.$, the chemical states of the two oxygen atoms in RCOO$^-$ are not identical. The binding structure is illustrated in Scheme 2, one oxygen atom would completely bind with Ti, and the other one would partially act as an electron pair donator to form a coordinating bond with respect to the d^0 orbital of Ti (IV). Notably, in the case of HHA monolayer, the head groups can bind with the surface Ti atoms through polydentate linkage, which is more chemically stable than the monodentate and bidentate ones.

Scheme 2

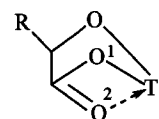R—$\langle$ O
         O^1
         O^2—Ti

Fig. 2 shows the AFM images of Piranha treated Ti surface (a), HA monolayer (b) and HHA monolayer (c). The root mean square (RMS) roughness of bare titanium is about 1.2 nm over a 2 μm × 2 μm. After HA and HHA monolayers formed on the surfaces, the RMS roughness is about 1.5 nm. It can be observed that HHA tends to form more uniform and denser monolayer than HA.

The chemical states of monolayers can be observed from XPS analyses. As shown in Figs. 3 (a)—(d), the
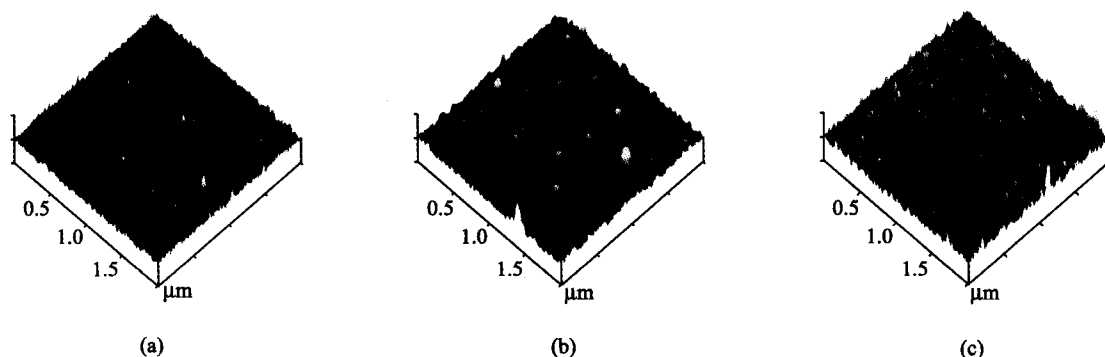

(a)   (b)   (c)

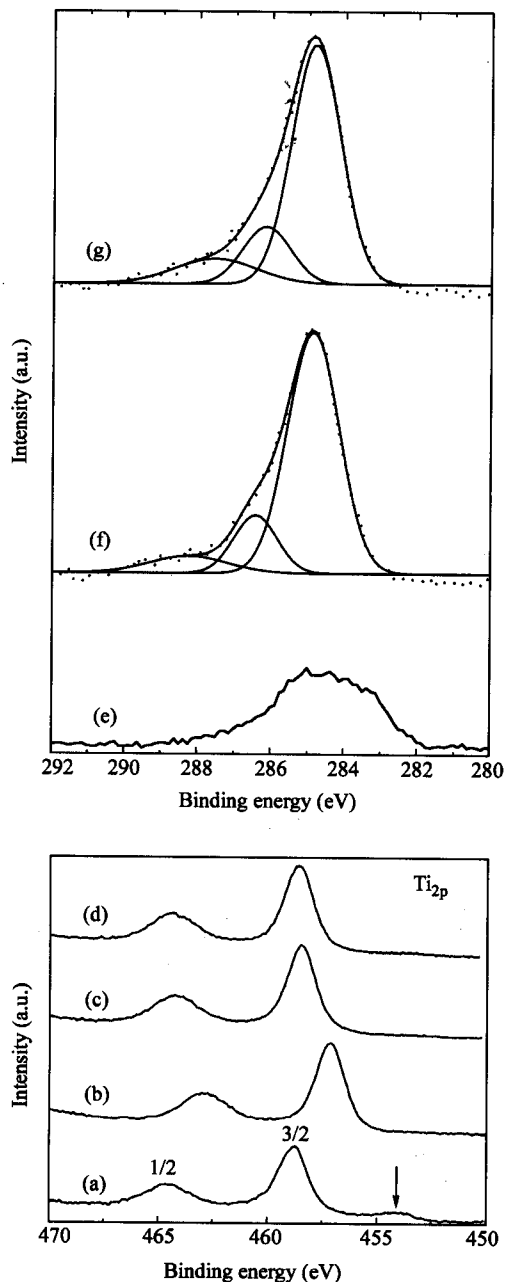**Fig. 2** AFM images of (a) Ti surface, (b) HA monolayer and (c) HHA monoalyer.

Fig. 3   XPS spectra of Ti_{2p}: (a) bare titanium substrate, (b) pretreated TiO_2, (c) HA monolayer on TiO_2, (d) HHA monolayer on TiO_2, and C_{1s}: (e) bare titanium substrate, (f) HA monolayer, and (g) HHA monolayer.

binding energy of Ti_{2p} of a clean bare titanium substrate contains two strong peaks at 464.6 eV and 458.7 eV, which are typical peaks of $Ti_{2p}^{1/2}$ and $Ti_{2p}^{3/2}$ for TiO_2. Besides mentioned above, a small peak at 453.8 eV can also be found, which is assigned to the free titanium

component. After treated with Piranha solution for 60 min, two obvious changes can be observed. The first is the disappearance of the small peak at 453.8 eV, indicating no existence of free titanium. Secondly, the peaks of $Ti_{2p}^{1/2}$ and $Ti_{2p}^{3/2}$ for TiO_2 undergo a shift of about 1.6 eV to lower positions, appearing at 462.8 eV and 457.1 eV, respectively. This shift can also be observed from the O_{1s} data. We attribute these changes to the surface charging effect caused by the emission of electrons under X-ray bombardment.[9,10] After HA or HHA self-assembled on titanium surface, the Ti_{2p} peaks return back to their typical positions (458.5 eV and 464.3 eV), which suggests that attached organic layers make the surfaces more difficult to be charged.

The XPS patterns of C_{1s} are shown in Figs. 3 (e)—(g). The C_{1s} peaks of bare titanium substrate is broad and irregular, which is attributed to trace hydrocarbon contaminations. After HA or HHA self-assembled on titanium surfaces, the intensity of C_{1s} peaks is significantly strengthened. A peak at 284.6 eV, which is assigned to long aliphatic chain, dominates the C_{1s} spectrum for self-assembled monolayer of HA. The other two peaks at around 286.4 eV and 288.2 eV can be attributed to $C—O$ and $C = O$, respectively. The C_{1s} spectrum for HHA SAM exhibits similar peak positions except for some difference in relative peak intensities from that of HA after fitting. It contains more $C—O$ component because of the presence of α-hydroxyl group in the self-assembled molecules. From Table 1, for Piranha pretreated surface, it can be found that the O_{1s} peak at 528.6 eV is associated to TiO_2, and the peak at 530.5 eV is associated to hydroxide or hydroxy species on the surface. However, in the case of self-assembled monolayers, three peaks could be found at 530.1 eV, 531.6 eV and 532.4 eV, which

Table 1   XPS analyses of O_{1s} after fitting with Gaussian-Larentzian functions

Sample	Binding energy (eV)	Relative component (%)	Attribution
Pretreated TiO_2	528.6	59.0	TiO_2
	530.5	41.0	Ti—OH
	530.0	79.9	TiO_2
HA-SAM	531.6	10.8	Ti—OH
	532.5	9.3	COO^-
	530.1	77.5	TiO_2
HHA-SAM	531.6	8.1	Ti—OH
	532.4	14.4	$C—O$ or COO^-

are attributed to TiO$_2$, Ti—OH, and COO$^-$ or C—O, respectively.[4] The relative intensity of Ti—OH component decreases in the order of pretreated TiO$_2$, HA-SAM, and HHA-SAM (from 41%, to 10.8%, and to 8.1% respectively). This tendency also reflects that HHA monolayer owns more surface coverage than the HA monolayer, which is consistent with the contact angle measurement and RAIR results.

From above, it can be concluded that both n-hexadecanoic acid and α-hydroxyl n-hexadecanoic acid can spontaneously form self-assembled monolayers on titanium surfaces. However, these monolayers are in disordered liquid-like state owing to the amorphous oxide upper-layer. From surface characterizations, HHA monolayer shows more surface coverage than HA monolayer because HHA tends to form polydentate coordination (five-membered ring), which is more chemically stable than the bidentate coordination (four-membered ring) of HA.

References

1   Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.

2   Fadeev, A. Y.; McCarthy, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 12184.

3   Tosatti, S.; Michel, R.; Textor, M.; Spencer, N. D. *Langmuir* **2002**, *18*, 3537.

4   Huang, N. P.; Csucs, G.; Emoto, K.; Nagasaki, Y.; Kataoka, K.; Textor, M.; Spencer, N. D. *Langmuir* **2002**, *18*, 252.

5   Tao, Y. T. *J. Am. Chem. Soc.* **1993**, *115*, 4350.

6   Tao, Y. T.; Hietpas, G. D.; Allara, D. L. *J. Am. Chem. Soc.* **1996**, *118*, 6724.

7   Laibinis, P.; Whitesides, G. M.; Parikh, A. N.; Tao, Y. T.; Allara, D. L.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152.

8   Wu, X. D.; Wang, D. P.; Yang, S. R. *J. Colloid Interface Sci.* **2000**, *222*, 37.

9   Pinzari, F.; Ascarelli, P.; Cappelli, E.; Giorgi, R.; Turtu, S. *Appl. Surf. Sci.* **2000**, *156*, 1.

10 Masuda, Y.; Sugiyama, T.; Lin, H.; Seo, W. S.; Koumoto, K. *Thin Solid Films* **2001**, *382*(1—2), 153.

(E0206041   PAN, B. F.; DONG, H. Z.)