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Photo-oxidation Studies of 4-(Chloromethyl)phenyltrichlorosilane on Silicon and Titanium Oxides

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The rates of photo-oxidation of 4-(chloromethyl)phenyltrichlorosilane (CMPS) formed on titanium oxide (TiO_2) and silicon oxide (SiO_2) substrates were studied. The optimized self-assembly of CMPS films on SiO_2 and TiO_2 were investigated which subsequently used for comparing photochemical reactions by exposing samples under deep UV of 254 nm. Upon the UV irradiation, the tail group of CMPS monolayers; chloro benzyl group is converted to aldehyde group and further exposure leads to the formation of polar group (carboxylic acid) which generates surfaces with a high surface free energy and a hydrophilic character. Analyses of contact angle, Fourier transform infrared and X-ray photoelectron spectroscopy (XPS) were performed to monitor the products generated upon UV irradiation. It was found that highly efficient and rapid photo-oxidation was observed for CMPS on TiO_2, a complete conversion within minutes compared to CMPS on SiO_2. The use of TiO_2 has shown that the rate is thrice faster than SiO_2 which is efficient as a photocatalytic oxidation. The resulting carboxylic group terminated surface was subsequently derivatized using 2-amino-1,1,1-trifluoroethane (TFEA). Contact angle and XPS measurements of post-derivatization indicated that the surface functionalization was extensive.

Keywords: Self-assembled monolayers, 4-(Chloromethyl)phenyltrichlorosilane, Photo-oxidation, Titanium oxide, Photocatalyst.

INTRODUCTION

Self-assembled monolayers (SAMs) represent one particular class of organic thin film chemisorbed onto surface of solids such as Au [1], Ag [2], SiO_2 [2,3], Al_2O_3 [4], TiO_2 [5,6] and GaN [7] that are increasingly used as templates for the construction and the subsequent study of nanoscale features [2,3,5]. The surface properties of a SAM are governed by the tail groups of the molecules. It can be altered to produce new surface chemistries which offer a range of applications, from microelectronicto biotechnology fields [8]. A photochemical method is one of the modification approaches that significantly offer advantages to transform initial tail groups to reactive ones [3,5,9,10]. This involved various surface monolayer conversion, including the conversion of alkylthiolates to alkysulfonates [11], photoconversion polyethylene glycol surface to aldehyde [12] and photodecomposition of alkylsiloxane [9]. As the micro-devices are reduced down to the nanoscale, modified surface properties have gained more and more importance and generated further interest in the interactions between functional/biological molecules at surfaces.

Irradiation of alkanethiol has previously been performed by Leggett and co-workers [11]. It is suggested that photo-oxidation of the thiols leads to the formation alkylsulfonate ($R-SO_3$) species. The interaction that exists between the alkylsulfonate group and the gold surface is particularly weak in comparison with the strong sulfur-gold interaction and thus, the oxidised species is readily displaced by either rinsing or through submerging the modified SAM into a solution of an opposing thiol [11,13].

However, there is not much study performed on photo-irradiation of silanes monolayer. The photo-oxidation of alkyl silane on SiO_2 has been reported to follow zero-order kinetics, resulting the scission of alkyl chain instead of head group of Si. This is likely due to the presence of OH radical and atomic oxygen that generated from the dissociation of ozone under UV irradiation in air [14]. Compared to alkanethiols, large amount of energy and prolong of irradiation time are required to decompose and oxidize alkylsiloxane monolayers [9]. Nevertheless, the problem of using high energy of UV is that the ability of light used to deteriorate the surface of monolayers. Therefore, a photocatalyst is required to accelerate the rate of photo-irradiation of silane monolayer which remains tail groups reactive. Titanium oxide has been comprehensively used in photochemical studies for its unique characteristics as photocatalysts. Recently, studies have shown a rapid decomposition of alkylsiloxane on TiO_2 rather than based on silicon oxide. TiO_2 semiconductor in fact generates electron-holes pairs.

Highly reactive species such as OH and O_2 radicals are produced upon UV irradiation due to O_2 scavengers, being used to oxidize and decompose most organic compounds.

The purpose of this paper is to examine the rates of photooxidation of 4-chloromethylphenyl tricholorosilane (SAM-1) covalently bonded on SiO_2 and TiO_2. The protocol involves (i) the self-assembly approach to give quality and reproducible monolayers (ii) the use of ultraviolet light at the wavelength of 254 nm to oxidize and convert chloromethyl terminated surfaces SAM-1 to carboxylic acid group SAM-2 (iii) the immobilization of trifluoroacetic anhydride onto SAM-2 to monitor the reactivity of functional groups upon UV exposure. This demonstrates the utility of the functionalized groups for bioelectronic applications and in particular due to growing interest in using silicon devices in biotechnology.

A proposed mechanism of 4-(chloromethyl)phenyltrichlorosilane (CMPS) oxidized is shown in Fig. 1 [10]. It shows several reactions that lead to the photolytic cleavage of the C-Cl bond by UV irradiation. The final product produced is carboxyl group at which aldehyde and methyl radical groups are yielded as intermediate.

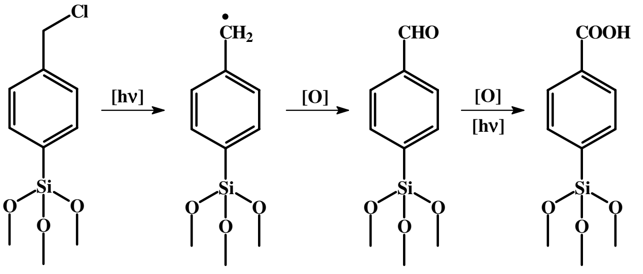

Fig. 1. Proposed photo-oxidation mechanism of CMPS SAMs towards UV exposure of 254 nm wavelength in the presence of sufficient oxygen in air

EXPERIMENTAL

N-type (100) doped silicon wafer 22 × 22 mm; Nr.1 microscope glass slides were purchased from Aldrich Chemicals and Thermo Scientific, respectively and were used as solid substrates. 4-Chloromethylphenyltrichlorosilane (CMPS) (> 95 %), hydrochloric acid (fuming 37 %) and titanium tetra isopropoxide (TTP) were purchased from Gelest, Inc., R&M Chemicals and Aldrich Chemicals, respectively. Absolute ethanol solution was purchased from HmbG Chemicals. Triton X-100 and TiO_2 nanopowder were obtained from Acros Organics and Degussa AG respectively. 2-Amino-1,1,1-trifluoroethane (TFEA) was purchased from Aldrich. Gloves bags (model X-17-17) were purchased from Glas-Col.

Surface topography and roughness were characterized using atomic force microscopy (Q-Scope 250, Quesant Instrument Corporation). Elemental analysis was carried out by Fourier transform infrared (FT-IR). X-ray photoelectron spectroscopy (XPS) was measured with. Contact angle data were obtained using ThermoCahn Dynamic Contact Angle (DCA300).

Substrate cleaning: 22 mm × 22 mm of microscope glass slides and 10 mm × 10 mm silicon wafers were immersed in hydrochloric acid (aq.) for 24 h followed by rinsing with ethanol and dried with nitrogen gas to remove organic contaminants.

Preparation of dry toluene: Molecular sieves were placed in a flask closed tightly with a rubber subseal. The tap of the flask was attached to an oxygen free nitrogen gas source. A solution of toluene was then transferred to the flask by injection through the subseal and left for 24 h to allow a complete dried solution [14].

Preparation of TiO_2 thin films: TiO_2 sol was prepared using a system containing an alkoxide compound; titanium tetra isopropoxide (TTP), hydrochloric acid (HCl), ethanol, distilled water and Triton X-100 (surfactant) [15-17]. The molarity of alkoxide in HCl, ethanol and water are 1:1.1:10:10 mole ratio, respectively. The concentration of water to alkoxide was 0.8 % (w/w). The system was added based on the following sequence; TTP into a solution of ethanol, HCl and water (stirred for 2 h) and then added 10 drop of Triton X-100. The mixture was stirred for few hours at room temperature. The resulting sol-gel was transparent with yellowish colour. Spin-coating method has been applied for the growth of TiO_2 thin films on substrates. The spinning operation was conducted at 500 rpm for 20 s. The substrates-TiO_2 coated was heat-treated at 70 °C for 5 min in an oven. The spinning and heat treatment was repeated for a uniform and full coverage of sol to the substrates.

Self-assembled monolayer preparation: The substrates were placed in a beaker and immersed 0.2 M CMPS dissolved in dry toluene. Due to air sensitivity of silane, the preparation was performed in a glove bag and purged with nitrogen. The samples were then removed and rinsed with toluene and ethanol to remove excess reactants and dried with nitrogen gas. The samples were sonicated for 10 min in ethanol and dried with nitrogen gas.

Photo oxidation of CMPS: The samples of CMPS SAMs on SiO_2 and TiO_2 were placed into a closed chamber with an attached UV lamp (4500 $\mu W/cm^2$, Model 11SC-1). The wavelength of the UV lamp was 254 nm with the power of keep it together the value and unit.

Surface derivatization with 2-amino-1,1,1-trifluoroethane (TFEA): The photomodified samples were then undergone a derivatization reactions. The process proceeds with the 3-(dimethylamino)-1-ethylpropylcarbodiimide (EDC) reacting with the carboxylic acid and coupling N-hydroxysuccinimide (NHS), to form the active ester intermediate. The surface subsequently reacts with amine groups from TFEA compound. The surfaces were immersed in a solution of 1 mM TFEA in ethanol for several hours. The samples were then rinsed with ethanol and dried with nitrogen gas.

RESULTS AND DISCUSSION

The formation of reproducible monolayers remains challenging as the tendency of silanols to polymerize. Therefore, it is highly dependent on a variety of parameters [18]. One of the factors; time of immersion is widely studied and important to control surface coverage limit and to develop the time required to achieve uniform coverage of CMPS on TiO_2 and SiO_2, analysis of contact angle as a function of immersion time were performed. The changes in the water contact angle of CMPS on SiO_2 and TiO_2 substrates are shown in Fig. 2. The contact angle data of CMPS on silicon and titanium oxide is relatively similar. The contact angle of CMPS-coated TiO_2 rapidly increases and closely reaches to a constant maximum value after 180 min of immersion. Meanwhile, CMPS-coated SiO_2 shows initially a slow deposition of monolayers on the surfaces where the reaction reached the limiting value within 200 min. The constant value of water contact angle of CMPS monolayers is around 79° as in agreement with values from ordered and compact CMPS SAMs [10]. The growth of CMPS monolayers on TiO_2 substrate seems to be faster than that on the SiO_2, suggesting a rapid condensation on TiO_2 due to lower electronegativity of titanium. This is supported with condensation rate of inorganic-organic materials that is dependent on electronegativity of metal atom [19].

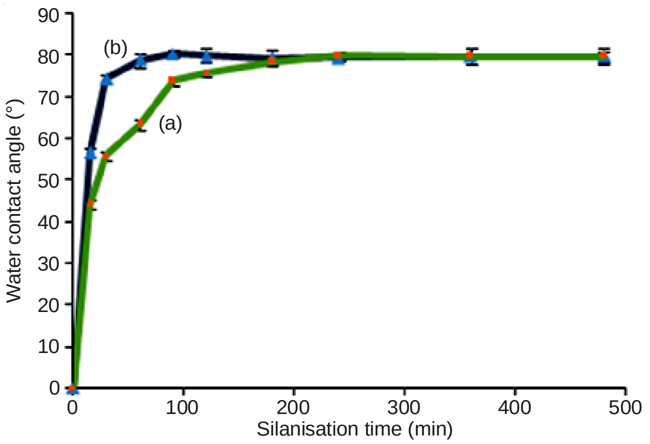

Fig. 2. Water contact angle of CMPS on (a) SiO_2 and (b) TiO_2 substrates as a function of silanization time

Fig. 3 shows the AFM images of surface coverage of substrates (TiO_2 and SiO_2) and CMPS monolayers adsorbed on each substrate (CMPS/TiO_2 and CMPS/SiO_2). The flat surfaces of TiO_2 and SiO_2 substrates are replaced by a fine textured morphology of CMPS after optimized condition; 3 h immersion time. This suggests the formation of completed uniform and smooth films with no silane polymerization occurs on the both substrates. AFM roughness measurements were carried out to support this hypothesis. The values were found to increase from 0.359 to 1.003 nm and 0.349 to 1.022 nm for CMPS/TiO_2 and CMPS/SiO_2, respectively, indicating similar chemical characteristic of silane attached on titanium oxide and silicon oxide substrates.

To provide further support on the hypothesis, the CMPS formed successfully on TiO_2 and SiO_2 were confirmed by means of XPS. Shown in Fig. 4(a) and 4(b) are the high resolution scans of C1s of CMPS on TiO_2 and SiO_2, respectively. The spectra were fitted into 2 components, corresponding to the C-C or C-H hydrocarbon peak at 285.0 eV and the C-Cl shoulder at 287.2 eV, resulting in a good agreement between the experimental and theoretical compositions.

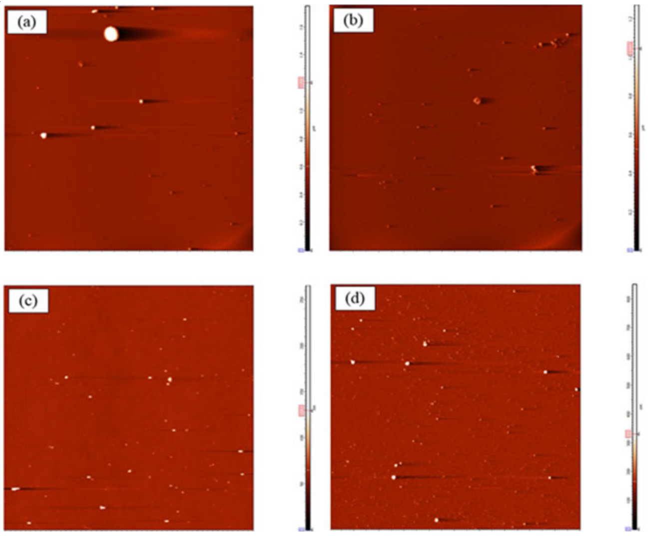

Fig. 3. AFM image for (a) Bare TiO_2 (b) Bare SiO_2 (c) CMPS/TiO_2 and (d) CMPS/SiO_2. Image size: 10 μm × 10 μm. AFM image resolution: (a) 1.20 μm (b) 1.04 μm (c) 0.13 μm (d) 0.33 μm

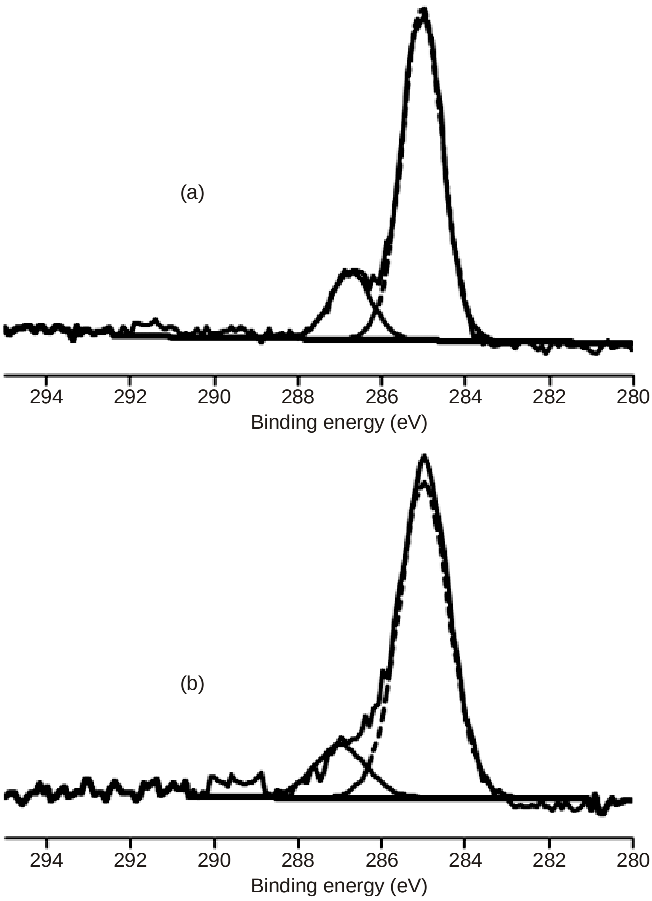

Fig. 4. XPS C 1s narrow scan of 4-chloromethyltrichlorosilane monolayer adsorbed on (a) TiO_2 and (b) SiO_2

Photochemical oxidation of CMPS SAMs on TiO_2 and SiO_2: The samples were subjected to UV irradiation to identify the nature of surface photoproducts formed during irradiation. The contact angle and FT-IR data were used to monitor the photo-oxidation process of a monolayer when the CMPS is irradiated with UV. Varying the irradiation time can control the surface composition of the CMPS monolayer. Fig. 5 shows the variation in the of water contact angle of CMPS monolayer on TiO_2 and SiO_2 against UV irradiation time. For both samples, a fall in water contact angle values can be observed from 79° to 22°. The decreasing values suggested the conversion of chloro benzyl tail group to hydrophilic surfaces; aldehyde. Further reduction was examined, suggesting the surface coverage is replaced by carboxylic groups. By comparison with CMPS on SiO_2 and CMPS monolayer on TiO_2. The presence of titanium oxide is responsible for the fast effect of photo-oxidation benzyl tail group. The completed conversion of benzyl group to carboxylic surfaces is observed when the lines in the graph reached the plateau at the value of 20 °C. FT-IR kinetic test study on the formation of carboxylic acid upon UV irradiation demonstrated the broad peak appeared in the range of 3200 and 3500 cm^{-1}, corresponding to C-OH asymmetric stretch mode. The intensity of bands emerged is measured in percent transmittance. Fig. 5b shows the percentage of transmittance of UV irradiated CMPS SAMs on (i) TiO_2 and (ii) SiO_2. A significant rise in percentage is observed after 10 min UV exposure for CMPS on TiO_2, with increasing illumination time, the value increases. However, the observation is in contrary to CMPS on silicon oxide. The slow hike of percentage suggests the slow conversion of chloro group to carboxyl surfaces.

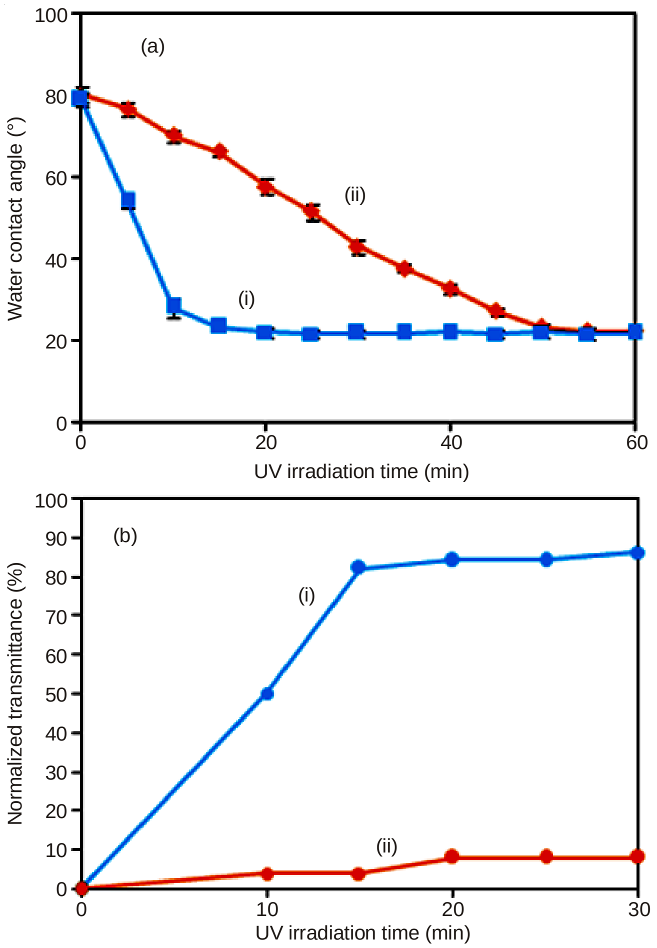

Fig. 5. (a)Variation of water contact angle and (b) Normalized transmittance of CMPS SAMs on (i) SiO_2 and (ii) TiO_2 towards various UV exposure time

The data indicate that TiO_2 efficiently converts the tail group of CMPS SAMs to carboxyl group 3 times faster than SiO_2 due to wide band gap that is activated by UV light. The electron holes provide a strong oxidation power thus produced a highly oxygen species such as OH and O_2 radicals [9]. The species resulting from electron scavenging process play an important role in oxidation and decomposition of organic compounds [20]. Oxygen is produced *via* water oxidation on TiO_2 nanoparticles. The photochemical process produced superoxides to generate an addition amount of hydroxyl radicals [21]. The formation of radicals can be shown in the following equations:

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \quad (1)$$

$$O_2 + e^- \longrightarrow O_2^{\bullet -} \quad (2)$$

$$O_2 + H^+ \longrightarrow HO_2^{\bullet} \quad (3)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \quad (4)$$

$$H_2O_2 + e^- \longrightarrow OH^{\bullet} + OH^- \quad (5)$$

For further characterization of the surface photo-irradiation process, chemical analysis was performed by X-ray photoelectron spectroscopy. Fig. 6(a) and 6(b) shows narrow scans of C 1s of the surface on TiO_2 and SiO_2, respectively after UV exposure. The peak at a binding energy 285 eV indicative of carbon bound to carbon (C-C). The new peak was observed at 289.1 eV after the samples were exposed to UV light which is attributed to ester bond (O-C=O).

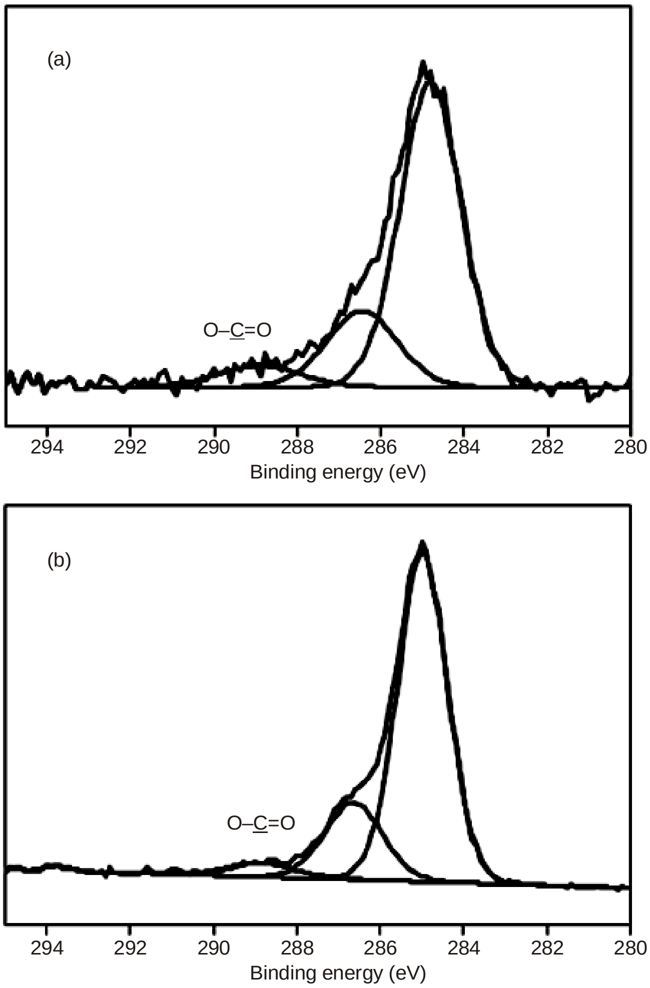

Fig. 6. High resolution scan C 1s of UV Irradiated CMPS SAMs on (a) TiO_2 and (b) SiO_2

Surface derivatization of carboxylic terminated surface with 2-amino-1,1,1-trifluoroethane (TFEA): The reactivity of carboxylic acid surfaces generated upon UV irradiation is monitored by coupling the surface with TFEA molecules. This is a quick test to retain the surface reactivity for subsequent biological immobilization, anticipating that the activated carboxylic formed are sufficiently reactive to selective and covalently bind primary amines on the biological molecules. The surface was firstly activated using a carbodiimide (EDC) reagent in combination with N-hydroxysuccinimide (NHS) followed by TFEA coupling reaction.

Fig. 7(a) shows the variation in the advancing contact angle plotted as function of reaction time for COOH group surface derivatised with a 1 mM of TFEA solution. The reaction reached a limiting value within 8 h, indicating the complete reaction between carboxylic group and TFEA molecules. The successful reaction was confirmed by X-ray photoelectron spectroscopy (XPS), as shown in Fig. 7(b). The peak at keep the value and unit together shift relative to the saturated hydrocarbon signal, 285 eV represents to O-C(O)CF_3 group. However, it is noticeable that the ratio area of CF_3 and C-N is not as expected as theoretical value which is 1:1, suggesting incomplete derivatization of the molecules. The most likely explanation is probably due to steric hindrance that caused to the size of the CF_3 groups [20].

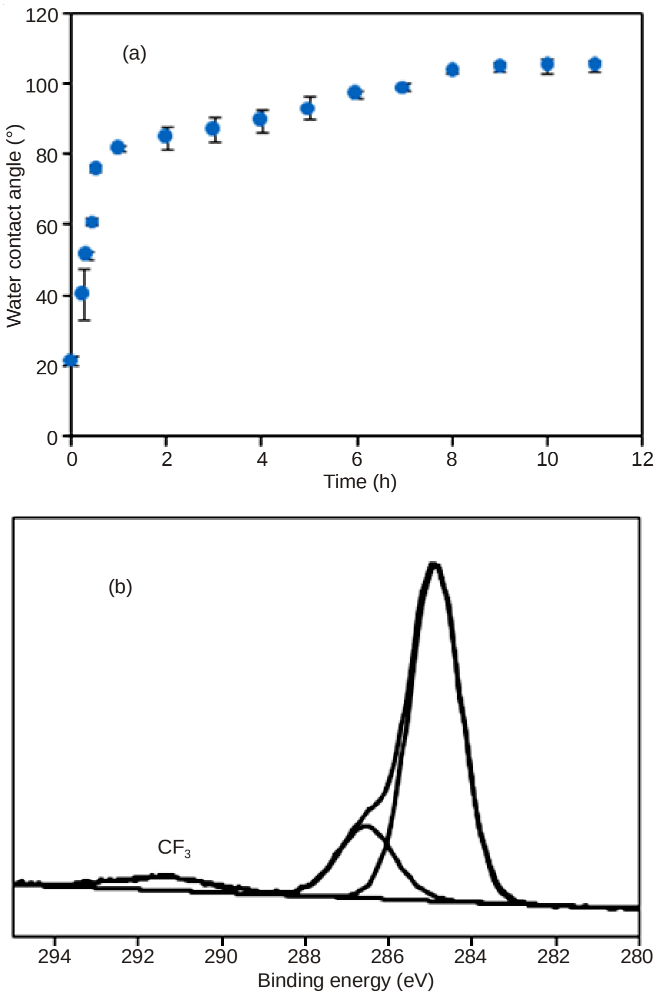

Fig. 7. (a) Variation of water contact angle of the function describing the surface coverage by carboxylic acid group of UV post irradiated CMPS on TiO_2 exposed to a 1 mM solution of TFEA for varying time periods (b) Narrow scan of C 1s of sample following exposure to a 1 mM solution of TFEA for 8 h

Conclusions

The photo-oxidation of 4-(chloromethyl)phenyltrichlorosilane (CMPS) based on self-assembled monolayers (SAMs) formed on TiO_2 and SiO_2 has been studied using AFM, XPS, FTIR and contact angle analysis. The parameter to produce a good quality of monolayer has been investigated and the optimum conditions of silanization reaction are fixed throughout the experiment. Based on the studies, the oxidation rate of chloromethylphenyl group is accelerated by TiO_2 layer. The tail group is rapidly and efficiently decomposed to carboxyl group during UV irradiation. These can be supported by the data and analysis from XPS, FTIR and contact angle.

In surface derivatization, the surface was modified with TFEA in order to retain the reactivity of aldehyde tail group upon a protein immobilization as the primary amine on the protein are selectively and covalently bind with aldehydes tail group.

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