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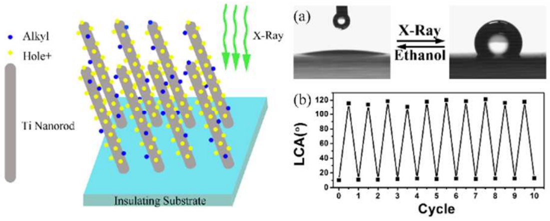

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X-ray Irradiation induced Reversible Wettability Modification of Titanium NRAs

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Reversible transition between hydrophilicity and hydrophobicity of Ti NRAs induced by alternate X-ray irradiation and ethanol immersion was revealed. The wettability modification was attributed to the chemisorption of alkyl group onto TNRAs surface from airborne molecular.

Introduction

Smart surfaces with reversible wettability transitions under external stimuli have recently generated extensive interests due to potential applications in various fields [1,2]. Different approaches have been put forward to achieve novel wetting behaviour, (e.g. superhydrophilicity, superhydrophobicity and superoleophilicity), by focusing on the two dominant factors on wettability of surfaces, *i.e.* surface roughness and chemical states [3]. Among these studies, bio-inspired nanostructure materials have been the state-of-the-art since rough surfaces with nanoscale are more sensitive to environmental stimuli [4-6]. Nanostructure surfaces within different material systems have been successfully fabricated by the glancing angle deposition (GLAD) and oblique angle deposition (OAD) method, due to their advantages on large area fabrication, substrate insensitivity and all-material appliance [7,8]. Because of the rough and porous character, efficient wettability modifications of those films have been realized, especially those stimulated by chemical surroundings [9].

The control of wettability by light stimuli of ultraviolet (UV) and visible light have been extensively studied in the literatures [10-13], while those by X-ray illumination is by far less investigated. X-ray, which is of smaller wavelength, is reported to be efficient stimuli to generate chain scission in organic materials [14]. Moreover, piezoelectric materials will surface-charged by positive charged holes (h^+) as X-ray could generate electron-hole separation and the X-ray photoelectron emit. Together with their larger penetration, X-rays are thus supposed to have different impact on materials than UV/Vis light. Among the studies on X-ray generated wettability manipulation, Kwon *et al* focused on the photoelectric effect [15] while Weon *et al* emphasized on the chain scission generation [16]. Though both works have obtained remarkable wettability modification upon X-ray stimuli, no reversible transition without artificial chemi-introduction was realized.

Transition metals such as Ni, Pd, Pt, Fe, Co, Rh, Cu and Ti have been widely used as catalytic media upon organic industry and scientific research [17-18]. Benefit from the porous character with larger specific surface area, nanostructured catalysts have presented better efficiency. Titanium alloy, on the other hand, has drawn great attentions during last few decades because of their unique biocompatibility [19]. As well developed biocompatible implants, realization of the reversible wettability modification on titanium under external stimuli are of great importance with the potential application in drug delivery and payload release [20].

In this communication, inspired by the considerations above, we deposited Titanium nanorod arrays (Ti NRAs) using OAD approach and remarkable wettability modification of the films was achieved upon X-ray irradiation.

Experimental

Ti NRAs of 300 nm in length were deposited by oblique angle deposition (OAD) method using an e-beam evaporation instrument onto n-Si (100) wafers and quartz substrates, respectively. Both substrates were ultrasonicly cleaned by ethanol/deionized water and dried by flowing nitrogen. For OAD, large substrate tilting angle of 85 ° was set to form glancing incidence flux of titanium vapor. Evaporations were performed at a base pressure of 10^{-8} Torr and deposition rate was program controlled at 0.5nm/s with e-beam power supply of ~ 1KW.

Structure and morphology of the as-received Ti NRAs films was characterized *ex situ* by X-ray diffraction (XRD) (Rigaku Dmax 2500V), field emission scanning electron microscope (FE-SEM) (JSM-7001F) and high resolution transmission electron microscope (HRTEM) (JEOL 2011). SEM observations were performed at a 45° tilting angle of film cross-section. X-ray irradiations were performed by PHI-5400 using Mg source under the vacuum of 10^{-9} Torr while collecting the XPS signals at the same time. Typical duration of X-ray illumination was set to be 10 min with X-ray power supply of 200W. Contact angle measurements were performed by the sessile drop method [21] on OCA 15pro system with tilting stage. The "as-placed" contact angles were firstly measured by deploying a drop and recorded

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in real time till the droplet reach stability. The advancing and receding angles were then image-recorded and measured by tilting the test stage till the droplet start rolling. The contact angle value was obtained as an average of five measurements recorded on different surface locations for each sample with the deionized water volume set to be 3μL. Each CA measured sample was ethanol cleaned and flowing nitrogen dried before X-ray irradiation process to exclude the influence of water on XPS chamber.

Results and Discussion

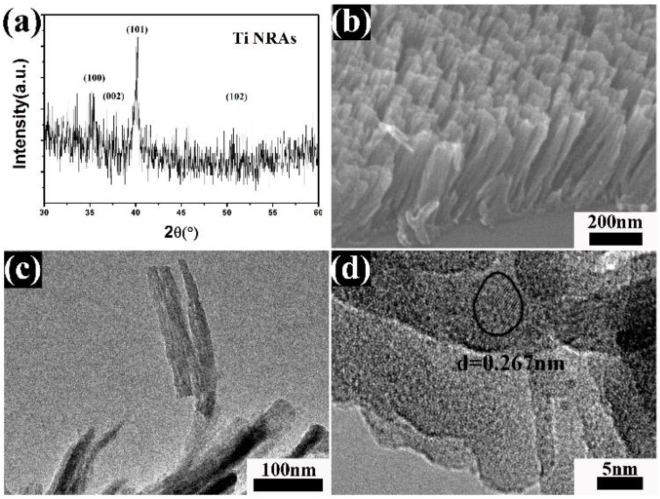

Figure 1 XRD (a), FE-SEM (b) and HRTEM (c, d) characterizations of Ti NRAs by OAD

The crystal structure and morphology of as-received Ti NRAs films were studied by XRD, FE-SEM and HRTEM. One sees from Fig. 1(a) that the film is poor crystallized as all the reflection peaks have weak intensity. All the peaks can be assigned to hexagonal α phase of Titanium (JCPDS 44-1294). FE-SEM observation revealed well-separated structure of the nanorod arrays. Single nanorod is of 300 nm in length and 30-50 nm in diameter. TEM observation confirmed the separation while HRTEM revealed nano-crystalline of Ti nanorod with lattice fringe correspond to (0002) plane detected. As-received Ti NRAs on both substrates are hydrophilic and hydrophilicity can be well kept by at least 10 days as shown in Fig. S1. Prolonged storage in ambient atmosphere will lead to monotonic increase of the contact angles (both advancing and receding) by the continuous absorption of the carbon-based molecule [22].

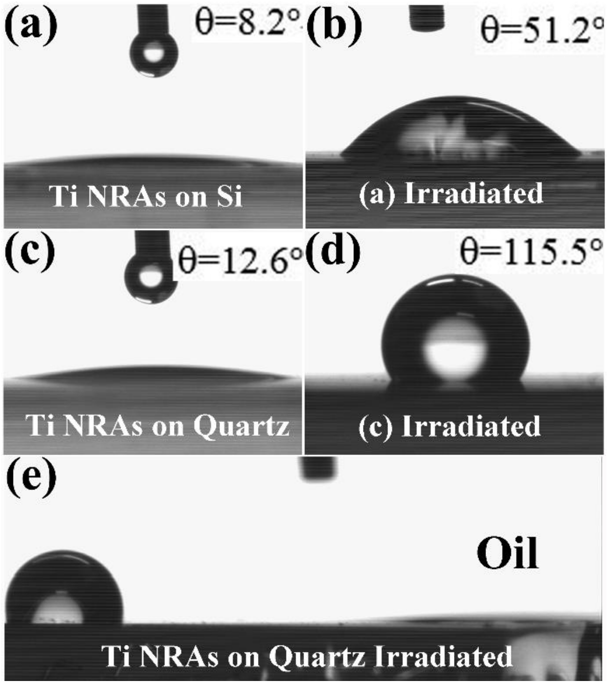

Figure 2 Wettability modification introduced by X-ray irradiation to Ti NRAs on silicon (a, b) and quartz (c, d, e) substrate, respectively. The hydrophobicity and oleophilicity was achieved at the same time on X-ray irradiated Ti NRAs on quartz and shown in 2(e)

Fig. 2 illustrated the wettability transition upon X-ray irradiation of Ti NRAs on Si & quartz substrates, respectively. For Ti NRAs on Si, the contact angle increase from 8.2° to 51.2° while those on quartz presented hydrophilic-hydrophobic transition upon X-ray irradiation by "as-placed" contact angle modified from 12.6° to 115.5°. For X-ray irradiated Ti NRAs on quartz, the corresponding advancing and receding angle evolved to value of 130° and 107°， respectively. It's noteworthy that by adding an extra quartz beneath the silicon substrate during X-ray irradiation, the wettability of Ti NRAs on silicon showed the same transition as Ti NRAs on quartz did. Once achieved hydrophobicity upon irradiation, the contact angles (the as-placed, advancing and receding angles) of Ti NRAs can be kept for more than 30 days. Oleo-wettability of the films were also characterized and showed in Fig. 3(e). All the samples with or without irradiation were superoleophilic as CA of oil is less than 10°. It's clearly illustrated by Fig. 2(e) that for the X-ray irradiated Ti RNAs, hydrophobicity and oleophilicity can be achieved at the same time. Various X-ray powers of 50W, 100W, 200W and 260W were also applied and it turned out that the wettability of irradiated sample is power-independent within the scope as the contact angle have a fluctuation between 112° and 117°. The transition was also found to be X-ray duration independent between 5min and 60min. Wettability of blank silicon and quartz upon X-ray irradiation revealed no observed variance of silicon and certain change of quartz (Fig. S2). Room temperature *in situ* oxidation of Ti NRAs with duration of 30min were performed by introducing floating oxygen into the deposition chamber. The oxidation process also introduced certain modifications of contact angle upon irradiation (Fig. S3). As the morphology of the NRAs kept unchanged when suffering the oxidization process, the capillary effects of Ti NRAs are invariable which then highlight the chemical modification nature of the Ti NRAs upon irradiation.

As highlighted in Fig. 3, the wettability modification showed good reversible transition. Reversible transition can be easily realized by immersion of the irradiated sample into ethanol. The immersion into ethanol would have no influence on the nanostructure while may dissolve the attached molecule, after which the film restitute to be hydrophilic as the as-received one. By cycling the irradiation, process illustrated in Fig. 2 generated and re-introduce chemical modification on the Ti NRAs surface, the film then turn from superhydrophilic to hydrophobic.

Comprehensive investigations of the as-received results suggested that X-ray irradiation introduce wettability evolution of the Ti NRAs films by surface chemical modification on insulating quartz substrate.

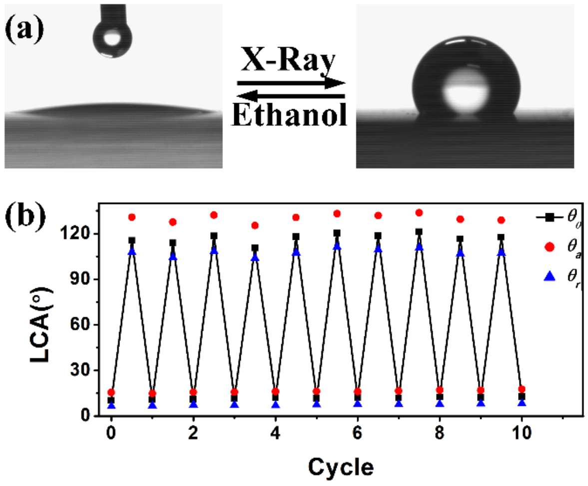

Figure 3 Revisable hydrophilic-hydrophobic transitions of Ti NRAs on quartz substrate upon X-ray irradiation and ethanol immersion. θ_0 refers to the as-places contact angle while θ_a and θ_r to advancing and receding angle, respectively.

Meanwhile, Ti NRAs on conductive Si substrates show no remarkable changes. Similar wettability deterioration have been observed by Aronov *et al* in their work of low energy electron irradiated thermo-oxide Silicon in vacuum [23]. Though the mechanism is complicated, they denoted the final wettability changes to alkyl group formation on the top surface. Interestingly, alkyl group are concurrently both strongly hydrophobic and oleophilic which is in accordance with our results in Fig. 2(e). Also, good solubility of alkyl group into organic solvent can well interpret the hydrophobic-hydrophilic transition upon ethanol immersion during cycle transition in Fig. 3. Considering that alkyl group have the static contact angle of about 110° [24, 25], we then cautiously reach the conclusion that upon X-ray irradiation, alkyl group was introduced to the surface of Ti NRAs and responsible for the wettability manipulation.

In his review paper, F. Zaera have presented that alkyl halides chemisorb molecularly on transition metal surfaces and the scission of carbon-halogen bond can be easily activated photolytically to yield adsorbed alkyl moieties [26]. Other works have devoted the organometallic approach that C=C/C-H chain scissions can be generated by X-ray illumination and catalyzed by transition metal to form alkyl moieties, the as-generated moieties would then be trapped by positive charged holes [27]. Noticing that definite concentration of Carbon were found on all studied samples during irradiation by X-ray, the alkyl group formation was qualified possible during the X-ray irradiation. Direct observation of XPS peaks assigned to Ti-C bond during irradiation in Fig. 4(b, d) strongly support the hypothesis of alkyl formation.

Possible mechanism of alkyl group formation on Ti NRAs upon X-ray irradiation are proposed and illustrated in Fig. 5. Four indispensable factors contribute to the modification are highlighted in Fig. 5, *i.e.* X-ray irradiation, Ti NRAs, substrate conductivity and ultrahigh vacuum (UHV).

X-ray here is the dominating factor by generating the electron-hole separation. With the photoelectrons emit, variations of the charged behaviour were realized depending on the conductivity of substrates, *i.e.* positive charged hole (h^+) will be neutralized on conducting substrate (n-Si), while accumulate on the insulating surface. From the XPS signals collected during irradiation, significant peak shift to higher binding energy (284.6eV to 290.5eV for C1s) was observed in results from insulating quartz substrates (Fig. 4b) while no changes can be detected in those on n-silicon wafer (Fig. 4a). The continuous X-ray illumination and h^+ can generate chain scission of the surface absorbed molecule on insulating substrate while only X-ray generation can be realized for sample on silicon [28]. Moreover, suggested by the variation between blank silicon and quartz upon irradiation (Fig. S2), the h^+ would be key factor on the acquisition of the as-produced moieties. The mechanism was supposed to be the trapping centre of h^+ for the anion alkyl moieties with unpaired electron and then promote the reaction.

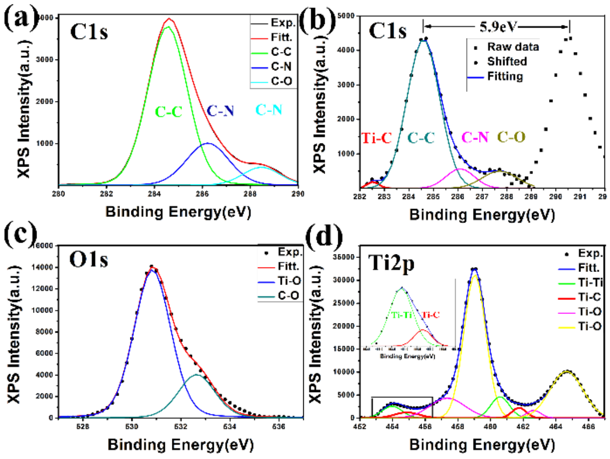

Figure 4. High resolution XPS spectrum and peak fit of C1s from Ti NRAs on Silicon (a) and quartz (b). Corresponding peaks are fitted and highlighted, among which Ti-C bond from Ti NRAs on quartz can be confirmed.

Ti NRAs play three different roles and all the factors were correlated to the rough structure. Firstly and conceivably, the rough surface favoured the surface absorption of organic molecules. Secondly, implied by difference between as-received and the *in situ* oxidized film upon irradiation, elemental titanium play dominate role on the transition. Since transition metal have been efficient catalysts during the reaction in chemical industry, titanium catalyzed the X-ray/h^+ generated chain scission of absorbed organic to form alkyl moieties. The rough nature would also benefit the catalyst process by larger specific surface area. Lastly, once alkyl group formed onto Ti NRAs, single nanorod turn to be hydrophobic. By following the Wenzel Model, rough morphology of a hydrophobic surface will enlarge the contact angles [29].

The proposed mechanism then can fit all the results and variations quite well. Ti NRAs on quartz showed larger modification upon X-ray irradiation than those on silicon (Fig. 2) as h^+ contribute to the generation of chain scission and alkyl moieties acquisition. Similar variation have been revealed between blank silicon and quartz while without the molecule absorption and contact angles enlargement effects of Ti NRAs, modification degree have a remarkable decline (Fig. S2). The catalytic effects of Ti upon transition was highlighted as *in situ* oxidized film show rather smaller response (Fig. S3) while the response itself confirm the contribution of h^+.

Another important factor easily ignored was the ultrahigh vacuum (UHV). From Fig 4(c), one sees that the O1s spectrum can be well fitted to O-Ti (top surface) and O-C (absorbed molecules) bond without other chemical states. On one hand, UHV can exclude the existence of H_2O and O_2 which will greatly hinder the chain scission, while on the other hand it limit the absorbed molecule amount on Ti NRAs. Furthermore, the diminishment of H_2O from UHV eliminate the formation of hydroxyl which will contribute to the wetting behaviour and then lead to contact angle decrease.

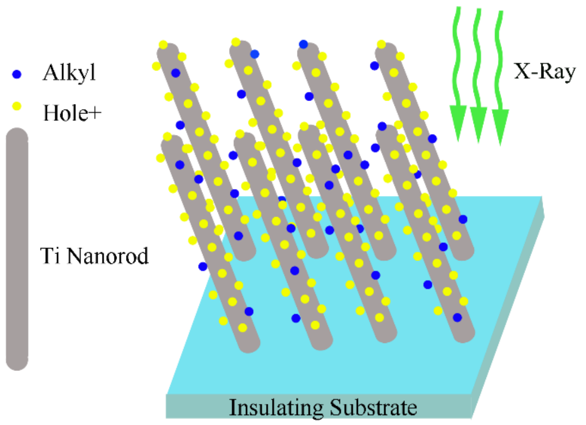

Figure 5. Mechanism of alkyl group formation introduced by X-ray irradiated Ti NRAs on insulating substrate

Conclusions

In summary, reversible transition between hydrophilicity and hydrophobicity have been achieved on Ti NRAs films on insulating quartz substrate upon X-ray irradiation and ethanol cleaning. Combined indispensable factors of X-ray illumination, catalyzed Ti nanostructure, insulating substrate and UHV contribute to the transition by promoting alkyl formation onto film surface from absorbed molecules.

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Notes and references

(1) Xin, B. W.; Hao, J. C., Reversibly Switchable Wettability. *Chem. Soc. Rev.* 2010, 39, 769-782.
(2) Drelich, J.; Chibowski, E.; Meng, D. D.; Terpilowski, K., Hydrophilic and superhydrophilic surfaces and materials. *SOFT MATTER* 2011, 7, (21), 9804-9828.
(3) Feng, X. J.; Jiang, L., Design and Creation of Superwetting/Antiwetting Surfaces. *Adv. Mater.* 2006, 18, 3063-3078.
(4) Yao, X.; Song, Y. L.; Jiang, L., Applications of Bio-Inspired Special Wettable Surfaces. *Adv. Mater.* 2011, 23, 719-734.
(5) Wang, J. X.; Zhang, Y. Z.; Wang, S. T.; Song, Y. L.; Jiang, L., Bioinspired Colloidal Photonic Crystals with Controllable Wettability. *Acc. Chem. Res.* 2011, 44, 405-415.
(6) Drelich, J., Marmur, A. Physics and applications of superhydrophobic and superhydrophilic surfaces and coatings. *SURFACE INNOVATIONS* 2014, 2(4) 211-227.
(7)Zhou, Q.; He, Y.; Abell, J.; Zhang, Z.; Zhao, Y., Optical Properties and Surface Enhanced Raman Scattering of L-Shaped Silver Nanorod Arrays. *J. Phys. Chem. C* 2011, 115, 14131-14140.
(8) Ni, J.; Zhu, Y.; Wang, S. H.; Li, Z. C.; Zhang, Z. J.; Wei, B. Q., Nanostructuring HfO2 Thin Films as Antireflection Coatings. *J. Am. Chem. Soc.* 2009, 92, 3077-3080.
(9) Tsoi, S. F.; Fok, E.; Sit, J. C.; Veinot, J., Surface Functionalization of Porous Nanostructured Metal Oxide Thin Films Fabricated by Glancing Angle Deposition. *Chem. Mater.* 2006, 18, 5260-5266.
(10) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T., Light-induced Amphiphilic Surfaces. *Nature* 1997, 388, 431-432.
(11) Feng, X. J.; Zhai, J.; Jiang, L., The Fabrication and Switchable Superhydrophobicity of TiO2 Nanorod Films. *Angew. Chem. Inter. Ed.* 2005, 44, 5115-5118.
(12) Caputo, G.; Nobile, C.; Kipp, T.; Blasi, L.; Grillo, V.; Carlino, E.; Manna, L.; Cingolani, R.; Cozzoli, P. D.; Athanassiou, A., Reversible Wettability Changes in Colloidal TiO2 Nanorod Thin-film Coatings under Selective UV Laser Irradiation. *J. Phys. Chem. C* 2008, 112, 701-714.
(13) Yan, B.; Tao, J. G.; Pang, C.; Zheng, Z.; Shen, Z. X.; Huan, C.; Yu, T., Reversible UV-light-Induced Ultrahydrophobic-to-Ultrahydrophilic Transition in an alpha-Fe2O3 Nanoflakes film. *Langmuir* 2008, 24, 10569-10571.
(14)Heister. K.; Zharnikov, M.; Grunze, M.; Johanssom, L. S. O.; Ulman, A., Characterization of X-ray Induced Damage in Alkanethiolate Monolayers by High-Resolution Photoelectron Spectroscopy, *Langmuir* 2001, 17, 8-11.
(15) Kwon, Y. B.; Weon, B. M.; Won, K. H.; Je, J. H.; Hwu, Y.; Margaritondo, G., X-ray-Induced Changes in Wettability. *Langmuir* 2009, 25, 1927-1929.
(16) Weon, B. M.; Kwon, Y. B.; Won, K. H.; Yoo, J.; Je, J. H.; Li, M.; Hahn, J. H., Ablation and Deposition of Poly(dimethylsiloxane) with X-Rays. *ChemPhysChem* 2010, 11, 115-118.
(17) Bissember, A. C.; Lundgren, R. J.; Creutz, S. E.; Peters, J. C.; Fu, G. C., Transition-Metal-Catalyzed Alkylations of Amines with Alkyl Halides: Photoinduced, Copper-Catalyzed Couplings of Carbazoles. *Angew. Chem. Inter. Ed.* 2013, 52, 5129-5133.
(18) Vidal, I.; Melchor, S.; Alkorta, I.; Elguero, J.; Sundberg, M. R.; Dobado, J. A., On the Existence of Alpha-Agostic Bonds: Bonding Analyses of Titanium Alkyl Complexes. *Organometallics* 2006, 25, 5638-5647.
(19)Liu, X. Y.; Chu, P. K.; Ding, C. X., Surface Nano-Functionalization of Biomaterials. *Mater. Sci. Eng. R* 2010, 70, 275-302
(20) Song, Y. Y.; Roy, P.; Paramasivam, I.; Schmuki, P., Voltage-Induced Payload Release and Wettability Control on TiO2 and TiO2 Nanotubes. *Angew. Chem. Inter. Ed.* 2010, 49, 351-354.
(21) Drelich, J. Guidelines to measurements of reproducible contact angles using a sessile-drop technique. *SURFACE INNOVATIONS* 2013, 1(4) 248-254.
(22) Boinovich, L., Emelyanenko, A., Pashinin, A., Lee, C.H., Drelich, J., Yap Y.K., Ori, Origins of Thermodynamically stable superhydrophobicity of Boron Nitride nanotubes coatings *LANGMUIR* 2012**,** 28, 1206-1216.
(23) Aronov, D.; Molotskii, M.; Rosenman, G., Charge-Induced Wettability Modification. *Appl. Phy. Lett.* 2007, 90, 10410410.
(24) Peczonczyk, S.L.; Mukherjee, J.; Carim A.I.; Maldonado, S., Wet Chemical Functionalization of III-V Semiconductor Surfaces: Alkylation of Gallium Arsenide and Gallium Nitride bya Grignard Reaction Sequence. *Langmuir* 2012, 28, 4672-4682
(25) Cho. K.L.; Wu, A.H.F.; Liaw, I.I.; Cookson, D.; Lamb, R.N.; Wetting Transitions on Hierarchical Surfaces. *J. Phys. Chem. C.* 2012, 116, 26810-26815
(26) ZAERA, F., Preparation and Reactivity of Alkyl-Groups Adsorbed on Metal-Surfaces. *Acc. Chem. Res.* 1992, 25, 260-265.
(27) Zaera, F., An Organometallic Guide To The Chemistry of Hydrocarbon Moieties on Transition Metal Surfaces. *Chem. Rev.* 1995, 95, 2651-2693.
(28) Roy, P.; Berger, S.; Schmuki, P., TiO_2 Nanotubes: Synthesis and Applications. *Angew. Chem. Inter. Ed.* 2011, 50, 2904-2939.
(29) Wenzel, R. N., Resistance of Solid Surfaces to Wetting by Water. *Ind.&Eng. Chem.* 1936, 28, 988-994