

# **Programming nanostructured soft biological surfaces** **by atomic layer deposition**

Imre Miklós Szilágyi<sup>1,2\*</sup>, Georg Teucher<sup>3</sup>, Emma Härkönen<sup>1</sup>, Elina Färm<sup>1</sup>, Timo Hatanpää<sup>1</sup>, Timur Nikitin<sup>1</sup>, Leonid Khriachtchev<sup>1</sup>, Markku Räsänen<sup>1</sup>, Mikko Ritala<sup>1</sup>, Markku Leskelä<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Helsinki, Helsinki, P.O. Box 55, FI-00014, Finland;

<sup>2</sup>Technical Analytical Chemistry Research Group of the Hungarian Academy of Sciences, Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Budapest, Szt. Gellért tér. 4., H-1111, Hungary; <sup>3</sup>Chemnitz University of Technology, Faculty of Natural Sciences, 09107 Chemnitz, Reichenhainer Straße 70, Germany

EMAIL: imre.szilagyi@mail.bme.hu

KEYWORDS: ALD, Biomimetic, Lotus, Photocatalysis, Superhydrophobic

## **ABSTRACT**

Here we present the first successful attempt to programme the surface properties of nanostructured soft biological tissues by atomic layer deposition (ALD). The nanopatterned surface of lotus leaf was tuned by 3-125 nm TiO<sub>2</sub> thin films. The lotus/TiO<sub>2</sub> composites were studied by SEM-EDX, XPS, Raman, TG-DTA, XRR, water contact angle and photocatalysis measurements. While we could preserve the superhydrophobic feature of lotus, we managed to add a new property, i.e. photocatalytic activity. We also explored how surface passivation

treatments and various ALD precursors affect the stability of the sensitive soft biological tissues. As we were able to gradually change the amount of nanopatterns of lotus, we gained new insights into how the hollow organic nanotubes on the surface of lotus influence its superhydrophobic feature.

## INTRODUCTION

The more we understand living systems, the more we adore the fascinating intelligence behind them. Mimicking the special morphologies, properties, functions and systems, which can be found in all creatures, is a hot field of science. Ranging from optics [1], sensors [2], medicine [3], solar [4], self-assembly [5], to catalysis [6]. etc, the biomimetic approach has proven to be a fruitful guide in many research areas. A major segment of biomimetics is to modify, coat or copy the surface of biological material. In this way, biological surfaces can be tailored for new applications or the working principles of their special features can be elucidated, and based on this artificial systems can be built, which model the desired properties of the biological surfaces [7,8].

Lotus leaf (*Nelumbo nucifera*) is one of the best-known examples in biomimetics, and it has inspired a whole industry of self-cleaning surfaces [9] Owing to the specially designed structures on its surface, i.e. microbumps covered with hollow nanotubes (Figure 1a-c), lotus leaf is the most superhydrophobic among all plants [10]. Researchers have tried both to make copies of its surface using lotus leaf as a template [11,12] and to build artificial models of it [13]. When lotus leaf was used as a template, first a negative replica was prepared by electroplating [11], or by nanoscale polymer casting [12]. Then this replica was filled with a polymer to provide a copy of the original lotus. A common feature of these template methods was that the copies exhibited almost the same extreme contact angles as lotus leaf, but these methods were not sensitive enough to be able to copy the hollow organic nanotubes on the lotus leaf surface. Therefore, a suitable method was still missing, which could copy the nanostructured surface of soft biological tissues with high precision.

Presently atomic layer deposition (ALD) seems to be almost the only choice, which could replicate exactly the nanopatterns of biological substrates. ALD is an ideal candidate to copy and program biological surfaces, as it allows deposition of uniform thin films on any 3D objects with thickness control of sub-nanometer precision [14,15]. ALD is based on successive, surface controlled reactions from the gas phase to produce thin films in the nanometer range with perfect conformality and process controllability [16]. Hence, ALD allows for new strategies in controlling the chemical and physical properties of nanoscale materials and synthesis routes to novel nanostructures [15,17]. One of the most sophisticated fields, where ALD can be used in

nanotechnology, is coating biological samples with thin films in order to tailor the properties of their nanostructured surfaces. The sensitive biological samples require low temperature ALD reactions, and only few such pilot studies have been conducted, e.g. ALD coating of tobacco mosaic virus and protein sphere (ferritin) [18], spider silk [19], butterfly wing [20], water strider leg [21], eye of the household fly [22], paper cellulose [23] and cotton [24] fibers. As a common feature, all these samples were dry, with a relatively robust structure. Rose petal [25] and legume [26] are the only examples, where plants were coated by ALD, however, these substrates were far from being nanopatterned, as the surface structures were in the micrometer range with only a few submicron features. Therefore, coating of nanostructured soft biological tissues by ALD has not been demonstrated, and the effect of ALD precursors on the stability of these soft biological substrates has not been investigated yet.

In this study, we present the first successful attempt to programme the properties of a truly nanostructured soft biological surface by depositing a few nm thick film on it by ALD. We have selected lotus leaf as an example for nanostructured soft biological tissues, and coated it with  $\text{TiO}_2$  nanofilms by ALD. Our aim was to add a new property, i.e. photocatalytic activity, while maintaining the superhydrophobic nature of lotus leaf. In this way, we could prepare a biological alternative of self-cleaning inorganic surfaces (smart windows, windscreens, building walls, etc).

## EXPERIMENTAL

*Preparation of lotus leaf composites.* Lotus leaves were received from the Botanical Garden of the University of Helsinki and needed special care during the measurements (Supporting information). The  $5 \times 5 \text{ cm}^2$  lotus leaf samples were put into the ALD reactor (Picosun Sunale R-150) as received.  $\text{TiO}_2$  ALD films were grown at  $65^\circ\text{C}$  using titanium isopropoxide,  $\text{Ti}(\text{iOPr})_4$  ( $60^\circ\text{C}$  evaporation temperature) and  $\text{H}_2\text{O}$ . The pulse and purge (purging gas:  $\text{N}_2$ ) sequences for both  $\text{Ti}(\text{iOPr})_4$  and  $\text{H}_2\text{O}$  precursors were two times 0.5 s pulse/1 s purge followed by 0.5 s pulse/15 s purge.  $\text{Al}_2\text{O}_3$  ALD film was grown using trimethylaluminium (TMA) and  $\text{H}_2\text{O}$  at  $65^\circ\text{C}$ . The pulse and purge (purging gas:  $\text{N}_2$ ) sequences for both TMA and  $\text{H}_2\text{O}$  precursors were five times 0.4 s pulse/1 s purge followed by 0.4 s pulse/15 s purge. 10" Si wafers were put under the lotus leaves for reference, and the film thickness was measured on them by X-ray reflectometry (Bruker D8 Advance). The ALD cycle numbers and film thickness for the  $\text{TiO}_2$

films were 100, 950, 2550 cycles and 3 nm, 45 nm, 125 nm, respectively, while for the 3 nm  $\text{Al}_2\text{O}_3$  film 30 cycles were used. The same growth rates were assumed for films on lotus leaf. The reference  $\text{Si}/\text{TiO}_2$  samples were used also in water contact angle and photocatalytic studies. Selected lotus leaves were fixated by immersing into 2,5 % glutaraldehyde solution (Sigma Aldrich, Grade I, 50 %) and 0.1 M Na Cacodylate buffer (pH = 7.4) for 24 h, and then rinsing with water.

*Characterization.* The morphology and composition of the samples was studied by a Hitachi S-4800 FESEM equipped with an Oxford INCA 350 EDX. XPS spectra were measured by a Physical Electronics Quantum 2000 instrument using Al  $K\alpha$  X-ray source (calibrated against the carbon 1s line at 248.8 eV). Raman spectra were recorded with a LabRam HR confocal microscope (Horiba Jobin Yvon) using excitation at 488 nm of an Ar-ion laser (0.1-1 mW at the sample), 100 $\times$  objective, and spectral resolution 2  $\text{cm}^{-1}$ . TG and single DTA curves of pure lotus leaf were measured in air (70  $\text{ml min}^{-1}$ ) with a Mettler-Toledo TGA850 device (10  $^{\circ}\text{C min}^{-1}$  heating rate, 2 mg sample mass, 70  $\mu\text{l}$   $\text{Al}_2\text{O}_3$  crucible).

*Contact angle and photocatalytic tests.* Water contact angle measurements of the lotus and lotus/ $\text{TiO}_2$  samples were conducted using a CAM 100 (KSV Instruments, Finland) device. The samples were irradiated with two parallelly arranged linear black lamps (General Electric, 20 W, UV range: 300-400 nm), and the contact angle values were measured again. Water contact angles of the  $\text{Si}/\text{TiO}_2$  and lotus/ $\text{Al}_2\text{O}_3$  samples were measured on a DSA30 (Krüss GmbH) instrument, and the consecutive UV irradiation of the samples was done by a circular black lamp (Sylvania, 22 W, UV emission peak at 350 nm).

For photocatalysis, 1 $\times$ 1  $\text{cm}^2$  pure or composite lotus leaf samples were put into 1 $\times$ 1  $\text{cm}^2$  sealed quartz cuvettes together with 2.9 ml of 0.03 mM methylene blue solution. The samples were irradiated with the same General Electric black lamps, as discussed previously. The UV-VIS spectra of the methylene blue solutions were measured by a HP 8453 UV-VIS spectrometer. At each UV-VIS measurement, the cuvettes were opened to air, so that the decomposition product gases could be released. The relative absorbance ( $A/A_0$ ), which is proportional to the methylene blue concentrations, was determined at 665 nm.

To study the photocatalytic activity of the planar  $\text{Si}/\text{TiO}_2$  composites, 1 $\times$ 1  $\text{cm}^2$  pieces of these samples were put into 1 $\times$ 1  $\text{cm}^2$  sealed quartz cuvettes together with 3 ml of methyl orange solution (14.286 mg / 1  $\text{dm}^3$ ). The samples were irradiated with the same Sylvania circular black

lamp, as discussed previously. The UV-VIS spectra of the methyl orange solutions were measured by a JASCO V-550 UV-VIS spectrometer. The relative absorbance ( $A/A_0$ ), which is proportional to the methyl orange concentrations, was determined at 464 nm.

## RESULTS AND DISCUSSION

Lotus leaves were coated with 3-125 nm thick  $\text{TiO}_2$  films using  $\text{Ti}(\text{O}^i\text{Pr})_4$  and  $\text{H}_2\text{O}$  as ALD precursors. The deposition temperature was only 65 °C. The nanostructures remained intact upon annealing at 65 °C in vacuum, while only  $\text{H}_2\text{O}$  was pulsed (Supporting information). In contrast, the chemical reaction with the Ti-precursor damaged the nanotubes seriously. When only 3 nm  $\text{TiO}_2$  was deposited, a great deal of the nanotubes were still present (Figure 1d), and with this thin  $\text{TiO}_2$  layer it was possible to preserve even the hollow structure of the organic nanotubes (Figure 1e). In the case of 45 nm  $\text{TiO}_2$  overlayer, only a small portion of the nanotubular features were preserved (Figure 1f). When 125 nm  $\text{TiO}_2$  was deposited (Figure 1g), the nanotubes disappeared completely, only the microbumps were visible, and the adhesion and stability of the  $\text{TiO}_2$  film was also reduced as the thick  $\text{TiO}_2$  film started to crack and peel off from the organic underlayer.

The presence of  $\text{TiO}_2$  on the lotus leaf surface was confirmed by several methods. Besides the usual elements in pure lotus, EDX showed that Ti was also present on the surface of the lotus leaf/ $\text{TiO}_2$  composites (Figure 1h) [27]. XPS also detected Ti, together with some elements of the lotus leaf (Figure 1i). The measured binding energy values for Ti were 458.0-458.3 eV (Figure 1j), which corresponds to  $\text{TiO}_2$  [28]. Pure lotus leaf and the lotus leaf/  $\text{TiO}_2$  composites had weak Raman signals (Figure 1k) suggesting that the as-deposited  $\text{TiO}_2$  film is essentially amorphous. However, when Raman measurements were done with higher laser energy, which crystallized  $\text{TiO}_2$ , strong anatase Raman peaks [29] were detected. Thus, Raman spectroscopy also confirmed indirectly the presence of  $\text{TiO}_2$ .

As an attempt to preserve a larger portion of nanotubes, selected lotus leaves were fixated in glutaraldehyde before the ALD process. However, already this chemical, which is used to fixate sensitive biological samples for electron microscopy, damaged the nanotubes on the top of the microbumps (Figure 2a).

To further study the effect of the metal organic ALD precursor, a 3 nm  $\text{Al}_2\text{O}_3$  film was grown on a fixated lotus leaf sample at 65 °C using trimethyl aluminium (TMA) and  $\text{H}_2\text{O}$  as precursors. TMA is considerably more reactive than  $\text{Ti}(\text{iOPr})_4$ , and the reaction between TMA and  $\text{H}_2\text{O}$  is highly exothermic. Thus, already after 30 ALD cycles the organic nanotubes disappeared completely, and the microbumps and the valleys between them were also severely damaged (Figure 2b).

We tried to remove the organic underlayer, so that a self-supported  $\text{TiO}_2$  replica of lotus leaf might be obtained. Based on the TG data (Figure 2c, in detail see Supporting information), lotus leaf decomposed and combusted completely at 530 °C in air. According to this, we annealed the lotus leaf/45 nm composite at 600 °C (in this sample the  $\text{TiO}_2$  layer was quite thick, but still some nanotubes were present). The results showed that the original micro- and nanostructures of the lotus leaf were completely destroyed, e.g. the  $\text{TiO}_2$  film at the microbumps opened up and broke into pieces (Figure 2d).

The contact angle measurements (Figure 3a-d) with water revealed that the lotus leaf/3 nm  $\text{TiO}_2$  composite was almost as superhydrophobic (153°) as pure lotus (157°). When the thickness of  $\text{TiO}_2$  was increased and the nanostructures on the surface disappeared, the contact angles decreased to 138° and 133° in the case of the lotus leaf/45 nm  $\text{TiO}_2$  and lotus leaf/125 nm  $\text{TiO}_2$  samples, respectively. In a recent study, when the nanopatterns of lotus were removed by annealing and only the microbumps were present, a similar decrease in the contact angle was observed [12]. In order to study further the effect of the nanopatterns and material of a surface on the wetting properties, we measured contact angles of 3, 45 and 125 nm  $\text{TiO}_2$  thin films deposited on Si substrates by the same ALD processes, as used in the case of the lotus substrates. The measured contact angles of the  $\text{TiO}_2/\text{Si}$  samples (93.2°, 95.8°, 94.2°, respectively) were close to the ones obtained previously for ALD deposited amorphous  $\text{TiO}_2$  films [30]. Compared to these, the significantly higher contact angles of the lotus/ $\text{TiO}_2$  composites can be clearly attributed to the nano- and micropatterns on the surface of the composites. The lotus/3 nm  $\text{Al}_2\text{O}_3$  sample also had a higher contact angle (120.8°), compared to planar amorphous  $\text{TiO}_2$  thin films. On this sample the nanopatterns were completely removed and the microbumps were damaged, but surface micropatterns were still partially present.

When the lotus leaf/ $\text{TiO}_2$  composites were irradiated with UV light for 2 h, the contact angles did not decrease significantly (Figure 3b-d), which is typical to ALD deposited amorphous  $\text{TiO}_2$  thin

films [30, 31]. In the case of the planar amorphous Si/TiO<sub>2</sub> thin films, the contact angles also showed only small decrease, i.e. in the case of the Si/3 nm TiO<sub>2</sub> sample the contact angle decreased from 93.2° to 86.8°.

The above results show that when a surface is adequately nanostructured, the nanopattern of the surface is decisive on the wetting properties and not the actual material of the surface.

The photocatalytic activity of the lotus leaf/TiO<sub>2</sub> composites was tested by decomposing aqueous methylene blue using UV light, and all composites were active photocatalysts (Figure 3e). The lotus leaf/45 nm composite, in which some nanotubes were still present but the TiO<sub>2</sub> layer was thick enough, was the most active photocatalyst. The lotus leaf/3 nm composite was almost as active, while the lotus leaf/125 nm composite, in which only the microbumps were preserved and had thus lower specific surface, had significantly lower activity.

The observed photocatalysis with the lotus/TiO<sub>2</sub> composites was a significant result, as the TiO<sub>2</sub> overlayers were essentially amorphous, according to the Raman measurements. In contrast to crystalline anatase or rutile phases, amorphous TiO<sub>2</sub> usually have little or no photocatalytic activity. However, recent results revealed that upon special conditions (e.g. hybrid type or composite TiO<sub>2</sub>) amorphous TiO<sub>2</sub> can have also pronounced photocatalytic activity [32]. The photocatalytic activity of the lotus/TiO<sub>2</sub> composites is supposed to be related to these cases, though XPS, EDX and Raman data do not show clear evidence of hybridization or composite materials. To investigate the source of the observed photocatalytic activity of the lotus/TiO<sub>2</sub> composites, the photocatalytic properties of the reference planar Si/amorphous TiO<sub>2</sub> composites were studied by decomposing aqueous methyl orange using UV light. The decomposition rate of methyl orange was very low in the case of the planar Si/TiO<sub>2</sub> samples, which had much smaller specific surface than the lotus/TiO<sub>2</sub> composites. However, the results showed that decomposition of methyl orange was somewhat enhanced by the Si/TiO<sub>2</sub> composites, compared to the photolysis of methyl orange irradiated by UV light (for details see Supporting information). Thus, the almost completely amorphous TiO<sub>2</sub> thin films, deposited by low temperature ALD, already had some photocatalytic activity, which was increased by growing these TiO<sub>2</sub> thin films on the nanopatterned lotus substrates.

Finally, we gained new insights into the working principles of superhydrophobic lotus leaf. In our study, we managed to gradually decrease the amount of organic nanotubes on the surface of lotus leaves by increasing the TiO<sub>2</sub> film thickness. In contrast, when lotus leaf was annealed in a



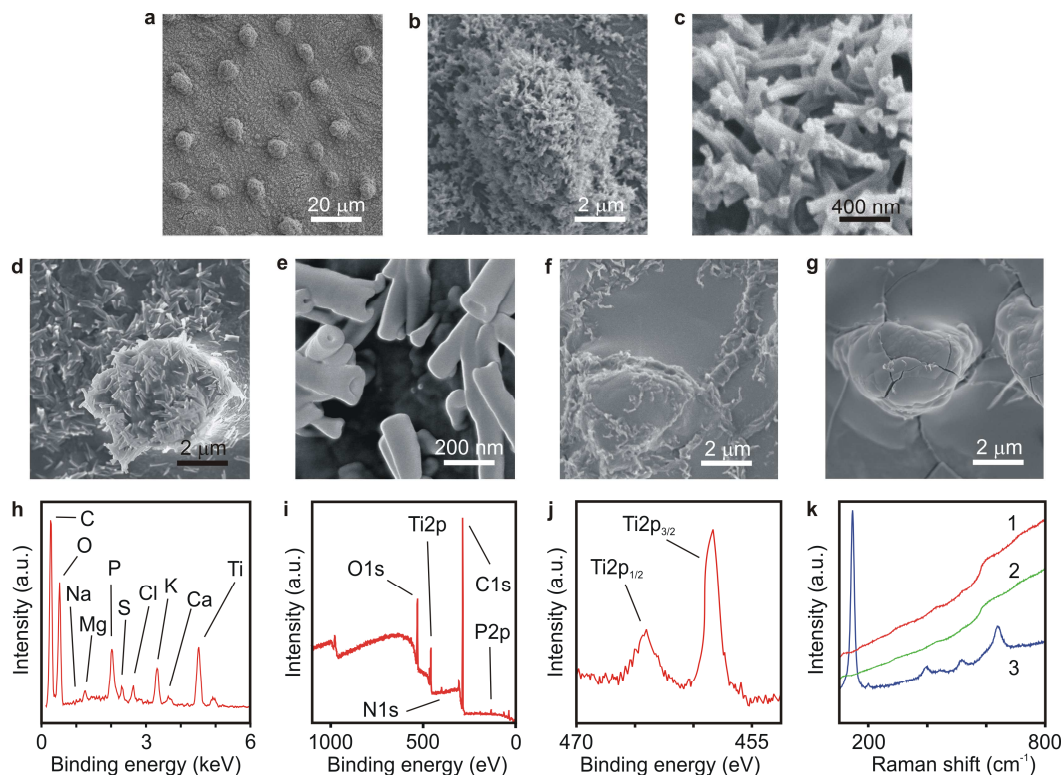
previous report, the only possibility was to completely remove the nanotubes [12], which resulted in the loss of the superhydrophobic feature. Based on our results, we think that possibly there are more organic nanotubes on the surface of lotus leaf, than the minimum number required for superhydrophobicity. When the number of nanotubes was decreased by 30-60 % (lotus leaf/3 nm  $\text{TiO}_2$ ), the contact angle ( $153^\circ$ ) was still similar to the case of pure lotus leaf ( $157^\circ$ ). We propose that the excessive number of organic nanotubes on lotus leaf provides a safety backup, i.e. if the nanotubes are partly damaged by e.g. excess heat from sunlight, the leaf can still maintain its self-cleaning feature.

## CONCLUSIONS

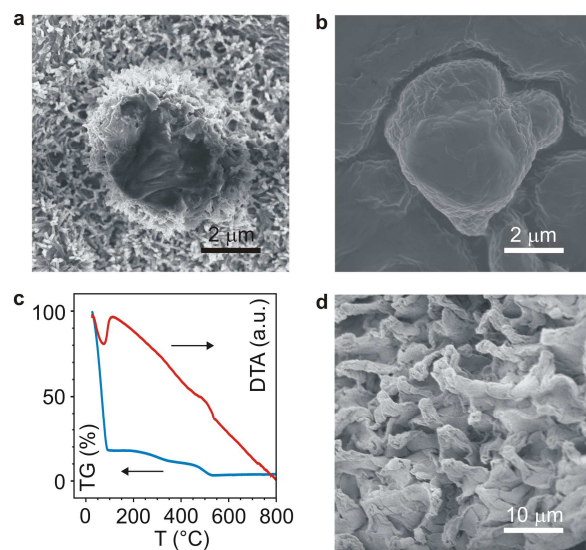
The obtained results demonstrate a new way of programming the surface properties of soft biological tissues. We modified the surface of lotus leaves by depositing  $\text{TiO}_2$  on it by ALD, and obtained a superhydrophobic and photocatalytic bionanocomposite. By varying the  $\text{TiO}_2$  film thickness, we could tailor the wetting and photocatalytic properties of the lotus/ $\text{TiO}_2$  material. With a 3 nm  $\text{TiO}_2$  film, even the hollow organic nanotubes on the surface of lotus leaves were preserved. In addition, as we managed to gradually change the amount of hollow organic nanotubes on the surface of lotus, we increased our understanding about how the superhydrophobic feature of lotus works. The obtained results demonstrate that the planned surface modification of nanostructured soft biological material (e.g. bacteria, various plant and animal soft tissues) is now potentially in our reach.

We have shown the limitations of ALD as well: reactions with the metal-organic ALD precursors can damage the very sensitive soft biological tissues. Additional surface treatments like fixation do not seem to help the situation. The solution is to use less reactive ALD metal-organic precursors. We did not succeed in preparing a self-supported replica of the lotus surface, as the removal of the organic underlayer damaged severely the as-deposited ALD film. However, if nanopatterned soft biological surfaces are copied by e.g. a polymer template method, a thin ALD film can be used as a protecting contact layer between the sensitive biological surface and the templating material, which can preserve the delicate biological nanostructures with high precision.

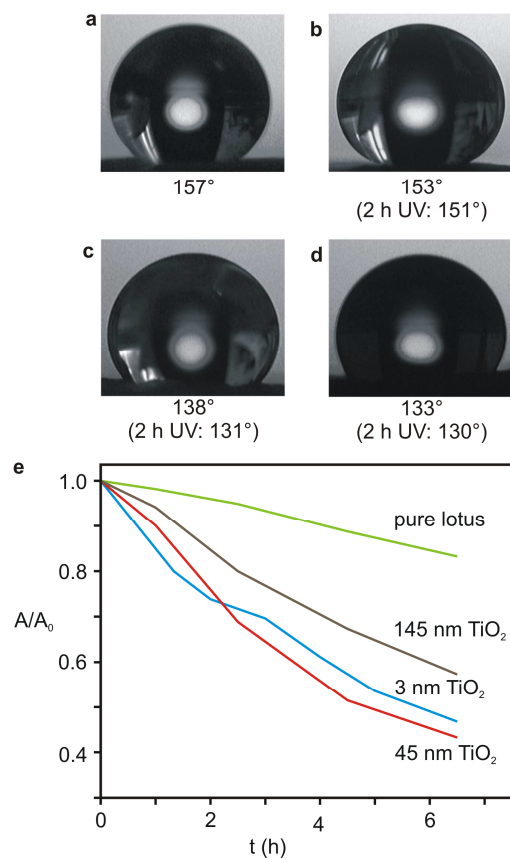
## FIGURES



**Figure 1.** Covering lotus leaf with TiO<sub>2</sub> thin films by ALD. SEM images of pure lotus leaf: (a) pattern of 5-10  $\mu\text{m}$  bumps on lotus leaf, (b) organic nanotubes covering the microbumps and the valleys between the bumps, (c) hollow structure of the 50-100 nm thick nanotubes. SEM images of the lotus leaf/TiO<sub>2</sub> composites: (d) a microbump of lotus leaf/3 nm TiO<sub>2</sub>, (e) preserved hollow nanotubes of lotus leaf/3 nm TiO<sub>2</sub>, (f) a microbump of lotus leaf/45 nm TiO<sub>2</sub>, (g) a microbump of lotus leaf/125 nm TiO<sub>2</sub>. (h) EDX spectrum of lotus leaf/45 nm TiO<sub>2</sub>. (i) Overall and (j) Ti2p XPS spectra of lotus leaf/45 nm TiO<sub>2</sub>. (k) Raman spectrum of pure lotus leaf (1) and of lotus leaf/45 nm TiO<sub>2</sub> at normal (2) and increased (3) laser power.



**Figure 2.** Additional surface treatments of lotus leaf. SEM images of a lotus leaf (a) fixated with glutaraldehyde solution and (b) after covering this sample with 3 nm Al<sub>2</sub>O<sub>3</sub> by ALD. (c) TG curve of lotus leaf in air. (d) SEM image of lotus leaf/45 nm TiO<sub>2</sub> annealed in air at 600 °C.



**Figure 3.** Tailoring the superhydrophobic and photocatalytic properties of lotus leaf/TiO<sub>2</sub>. Water contact angle measurements of (a) pure lotus leaf, (b) lotus leaf/3 nm TiO<sub>2</sub>, (c) lotus leaf/45 nm TiO<sub>2</sub> and (d) lotus leaf/125 nm TiO<sub>2</sub>. The numbers show the contact angles before and after (in brackets) 2 h irradiation with UV light. (e) Photocatalytic decomposition of aqueous methylene blue by the lotus/TiO<sub>2</sub> composites under UV light.

## SUPPORTING INFORMATION

Online supplementary data available from [stacks.iop.org/Nano](http://stacks.iop.org/Nano) (behavior of pure lotus leaf in vacuum, thermal decomposition of pure lotus leaf, special handling of lotus leaf, photocatalytic activity of planar Si/TiO<sub>2</sub> samples).

## ACKNOWLEDGMENTS

I.M.S. thanks for a Marie Curie Intra-European Fellowship (PIEF-GA-2009-235655) and a János Bolyai Research Fellowship of the Hungarian Academy of Sciences. The Raman studies were supported by the Finnish Centre of Excellence in Computational Molecular Science and the University of Helsinki Research Funds (HENAKOTO). We thank the Botanical Garden of the University of Helsinki, especially Mr. Leo Junikka, for providing the lotus leaf samples. Z. Hórvölgyi (Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, Hungary) is acknowledged for helping the water contact angle studies of the Si/TiO<sub>2</sub> and lotus/Al<sub>2</sub>O<sub>3</sub> samples.

## REFERENCES

- (1) Lee L P and Szema R 2005 *Science* **310** 1148
- (2) Scheibert J, Leurent S, Prevost A and Debrégeas G 2009 *Science* **323** 1503
- (3) Yoo J W, Irvine D J, Discher D E and Mitragotri S 2011 *Nature Rev. Drug. Discov.* **10** 521
- (4) Scholes G D, Fleming, G R Olaya-Castro A and van Grondelle R 2011 *Nature Chem.* **3** 763
- (5) Aksay I A, Trau M, Manne S, Honma I, Yao N, Zhou L, Fenter P, Elsenberger P M and Gruner S M 1996 *Science* **273** 892
- (6) Sels B, De Vos D, Buntinx M, Pierard F, Kirsch-De Mesmaeker A and Jacobs P 1999 *Nature* **400** 855
- (7) Razzak M and De Brabander J K **2011** *Nature Chem. Biol.* **7** 865
- (8) Ball P 2001 *Nature* **409** 413
- (9) Guo Z, Liu W and Su B L 2011 *J. Coll. Interf. Sci.* **353** 335
- (10) Cheng Y T, Rodak D E, Wong C A and Hayden C A 2006 *Nanotechnology* **17** 1359

- (11) Lee S M and Kwon T H J 2007 *Micromech. Microeng.* **17** 687
- (12) Sun M, Luo C, Xu L, Ji H, Ouyang Q, Yu D and Chen Y 2006 *Langmuir* **21** 8978
- (13) Yuan Z, Chen H, Tang J, Gong H, Liu Y, Wang Z, Shi P, Zhang J and Chen X 2007 *J. Phys. D* **40** 3485
- (14) Detavernier C, Dendooven J, Sree S P, Ludwig K F and Martens J A 2011 *Chem. Soc. Rev.* **40** 5242
- (15) Knez M, Nielsch K and Niinistö L 2007 *Adv. Mater.* **19** 3425
- (16) Leskelä M and Ritala M 2003 *Angew. Chem. Int. Ed.* **42** 5548
- (17) Kim H, Lee H B R and Maeng W J 2009 *Thin Solid Films* **517** 2563
- (18) Knez M, Kadri A, Wege C, Ulrich G, Jeske H and Nielsch K 2006 *Nano Lett.* **6** 1172
- (19) Lee S M, Pippel E, Gösele U, Dresbach C, Qin Y, Chandran C V, Bräuniger T, Hause G and Knez M. 2009 *Science* **324** 488
- (20) Huang J, Wang X and Wang Z L 2006 *Nano Lett.* **6** 2325
- (21) Ding Y, Xu S, Zhang Y, Wang A C, Wang M H, Xiu Y H, Wong C P and Wang Z L 2008 *Nanotechnology* **19** 355708
- (22) Huang J, Wang X and Wang Z L 2008 *Nanotechnology* **19** 025602
- (23) Kemell M, Pore V, Ritala M, Leskelä M and Lindén M 2005 *J. Am. Chem. Soc.* **127** 14178
- (24) Hyde G K, Park K J, Stewart S M, Hinstroza J P and Parsons G N 2007 *Langmuir* **23** 9844
- (25) Lee S M, Üpping J, Bielany A and Knez M 2011 *ACS Appl. Mater. Interfac* **3** 30
- (26) ) Zhao Y, Wie M, Lu Jun, Wang Z L and Duan X 2009 *ACS Nano* **3** 4009
- (27) Meng Z D, Peng M M, Zhu L, Oh W C and Zhang F J 2012 *Appl. Catal. B* **113-114** 141
- (28) Kuvarega A T, Krause R W M and Mamba B B 2011 *J. Phys. Chem. C* **115** 22110
- (29) Etacheri V, Seery M K, Hinder S J and Pillai S C 2010 *Chem. Mater.* **22** 3843
- (30) Kang H, Lee C S, Kim D Y, Kim J, Choi W, Kim H, 2011 *Appl. Catal. B* **104** 6.
- (31) Lee C S, Kim J, Son J Y, Choi W, Kim H, 2009 *Appl. Catal. B* **91** 628.
- (32) Huang J, Liu Y, Lu L and Li L 2012 *Res. Chem. Intermed.* **38** 487