FULL PAPER

Chiral Thin Films of Metal Oxide

Hagay Moshe,^[a] Maarten Vanbel,^[b] Ventsislav Kolev Valev,^[b, c] Thierry Verbiest,^[b] David Dressler,^[d] and Yitzhak Mastai^{*[a]}

Abstract: In this paper, we describe for the first time the synthesis of new chiral nanosized metal oxide surfaces based on chiral self-assembled monolayers (SAMs) coated with metal oxide (TiO₂) nanolayers. In this new type of nanosize chiral surface, the metal oxide nanolayers enable the protection of the chiral self-assembled monolayers while preserving their enantioselective nature. The chiral nature of the SAM/ TiO₂ films was characterized by variety of unique techniques, such as secondharmonic generation circular dichroism (SHG-CD), quartz crystal microbalance, and chiral adsorption measure-

Keywords: chirality • enantioselective crystallization • enantioselectivity • second-harmonic generation • self-assembled monolayers

Introduction

In recent years, chirality^[1-4] and chiral surfaces^[5-13] have been found to play an important role in nanotechnology, for example, in chiral nanoscale surfaces and nanoparticles. Generally, chiral solid surfaces can be derived from chiral bulk structures that expose chiral, enantioselective surfaces, such as quartz and other crystalline materials (typically covalent inorganic oxides).^[14] Another category of chiral solid surfaces is composed of crystalline solids produced from materials with achiral bulk structures. Such chiral surfaces are based on single crystals of metals (with bcc or hcp crystal structures)^[7] that expose high Miller indices with periodic arrays of steps, terraces, and kinks. Finally, the most common method for the preparation of chiral surfaces is the adsorption of chiral molecules, typically onto metallic surfa-

 [a] H. Moshe, Prof. Y. Mastai
Department of Chemistry and the Institute of Nanotechnology Bar-Ilan University, Ramat-Gan 52900 (Israel)
Fax: (+972) 3-7384053
E-mail: mastai@.biu.ac.il

[b] M. Vanbel, Dr. V. K. Valev, Prof. T. Verbiest Katholieke University of Leuven Department of Chemistry (Belgium)

[c] Dr. V. K. Valev University of Cambridge Cavendish Laboratory Nanophotonics Centre JJ Thomson Ave, Cambridge CB3 0HE (UK)

[d] Dr. D. Dressler
Department of Chemical Engineering
Massachusetts Institute of Technology, Cambridge (USA)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201300760.

shown. Our working hypothesis that it is feasible to design chiral surfaces based on a chiral SAM/metal oxide nanolayer hybrid system is supported by our previous research^[15] and that of other research groups^[16,17] who showed that chirality

that of other research groups^[16,17] who showed that chirality can be templated in metal oxides to form chiral materials such as nanoporous alumina nanofilms and mesoporous silica chiral structures. The first demonstration of the preparation of chiral metal oxide surfaces was reported by the group of Jay A. Switzer.^[18] In a series of articles^[18-20] they showed that chiral surfaces of CuO can be electrodeposited onto achiral substrates (e.g., gold) using solution-templating agents, such as tartaric acid and amino acids, to direct the chiral growth of metal oxide surfaces.

Chem. Eur. J. 2013, 19, 10295-10301

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY ONLINE LIBRARY

- 10295

ments with circular dichroism spectroscopy. The chiral resolution abilities of the SAMs coated with metal oxide (TiO_2) nanolayers were investigated in the crystallization of a racemic mixture of threonine and glutamic acid. Our proposed methodology for the preparation of nanoscale chiral surfaces described in this article could open up opportunities in other fields of chemistry, such as chiral catalysis.

ces. The resulting surface is chiral if the adsorbed molecules retain their chirality.

Although chiral surfaces based on SAMs or other organic (or polymeric) surfaces exhibit highly enantiospecific properties, they still suffer from many restrictions, such as low thermal stability and poor chemical and mechanical characteristics, which limit their usefulness for chemical applications, particularly for enantioselective catalysis and chiral separation. In this paper, we propose a new innovative type of stable, chiral nanosized metal oxide surface. The structure and chirality of this type of chiral surface is based on chiral self-assembled monolayers (SAMs) coated with nanosized films of metal oxide materials. The idea underlying this new design of nanochiral surfaces is that the ceramic nanolayers coating the chiral SAMs protect the chiral SAMs that would otherwise be destroyed under the reactions conditions, thereby preserving their enantioselective nature. In Figure 1, the overall structure of the new nanoscale hybrid chiral surfaces based on chiral SAMs and ceramic nanolayers is shown.



SAM/ ceramic nanolayers chiral surfaces

Figure 1. Illustration of the design and the synthesis paths for the new chiral SAM/ceramic nanolayer surfaces.

Generally, many inorganic metal oxides, such as silica, zeolite, alumina, zirconia, ZnO, clay, and others, can be used as supports for chiral SAMs. In this study, we decided to use TiO_2 to form protective nanolayers for the chiral SAMs, since its synthesis does not demand high temperatures that could harm the chiral SAMs. Various growth techniques can be applied to synthesize ceramic nanolayers on chiral SAMs such as vacuum-based methods (CVD and MOCVD) or chemical solution methods including sol–gel, electrochemical deposition, and hydrothermal synthesis. However, in this work we utilize the atomic layer deposition (ALD) technique^[21] since it provides excellent thickness control and produces very dense and uniform layers.

Results and Discussion

The first step in the synthesis of this type of nanochiral surface requires the preparation of chiral SAMs. Generally, chiral SAMs can be produced by reacting gold substrates with thiols that feature chiral groups at the tail terminus. Gold films of 50 nm thickness were deposited on mica substrates using a high-vacuum sputtering technique. AFM measurements of the gold films show very smooth films with an average root-mean-square (RMS) roughness of 5 Å and with typical gold grain sizes of 60 nm (see Figure S1 in the Supporting Information). X-ray diffraction measurements of the gold films indicate strong orientation of the gold films along the (111) crystal plane (see Figure S2 in the Supporting Information).

For the chiral SAMs, we used enantiomers of cysteine and glutathione. The chiral SAMs were formed on the gold surfaces by immersing the gold substrates in 10 mm solutions of cysteine or glutathione in water overnight. The formation and structure of the chiral SAMs on the gold surfaces were verified using various techniques. X-ray photoelectron spec-

troscopy (XPS) of the chiral SAMs on the gold surface shows typical Au 4f (81 eV), N 1s (398 eV), and C 1s (282 eV) peaks (see Figure S3 in the Supporting Information). In addition, the sulfur (S 2p) peak seen at 159 eV is attributed to the S–Au bond. Finally, contact angle measurements of the bare gold (contact angle of 67°) and of the Dor L-cysteine SAMs (contact angle of 18° and full spread for glutathione) indicate the formation of homogenous self-assembled monolayers on the gold surfaces.

 TiO_2 films were grown by ALD using $[Ti{N(CH_3)_2}_4]$ as the precursor, following a process described previously.^[22,23] Briefly, films were grown on 2.5×2.5 cm chiral SAM substrates; the ALD reactor was operated at a pressure of about 0.1 Torr, and Ar was used as a carrier gas and for purging between precursor pulses. The TiO₂ precursor was evaporated at 75°C and precursor pulse lengths of 0.2 and 0.06 s were used. In order to examine the properties of the deposited metal oxide films, we employed several techniques. First, after film deposition, we ran AFM measurements that showed no increase in the surface roughness of the surfaces, indicating the formation of uniform films. The thickness of the TiO₂ film was measured by ellipsometry and cross-sectional transmission electron microscopy (TEM) and found to be (10 ± 0.1) nm. The TEM cross-section images shown in Figure 2 revealed that the TiO₂ films prepared by ALD nucleated efficiently on the SAMs and formed a very smooth and conformal film. Furthermore, selected area electron diffraction of the TiO₂ film confirmed the amorphous nature of the films. We have to emphasize that the stability of the chiral SAM under ALD conditions and during the deposition are very critical.^[24] Furthermore, it is known from the literature^[25] that metal deposition (e.g., Ti) on functionalized self-assembled alkane thiols by chemical vapor deposition (CVD) can lead to the formation of metal clusters on the surface due to direct metal-carbon bonds with the surface, without altering the structure of the self-assembled monolayer. Therefore, we examined the stability of the chiral SAMs under low-pressure and high-temperature (100°C) ALD conditions. The XPS measurements revealed that the chiral SAMs are stable under these conditions. Moreover, we performed two cycles of ALD to obtain two layers of TiO₂ and ran XPS measurements on this sample (see Figure S4 in the Supporting Information). The XPS measurements show a peak at 457 eV, which corresponds to the formation of Ti 2p, together with typical peaks attributed to the SAMs. Additionally, we measured the chemical composition of the 10 nm TiO₂ film by XPS to eliminate the possibility that cysteine diffused to the outer surface of the TiO₂. These measurements show only the presence of Ti and O, without S residues from the chiral SAM. Finally, it is found from electron microscopy and Xray diffraction measurements that the TiO₂ film has an amorphous structure. Thus, based on the above results, we have shown that nanosized amorphous TiO₂ films of controlled thicknesses can be grown on chiral SAMs by ALD.

The next stage of this research focuses on evidence of the chirality of the SAM/metal oxide nanosurfaces. Generally,

10296 -

FULL PAPER



Figure 2. Cross-sectional high resolution TEM image of ALD TiO $_2$ films deposited on chiral SAMs of L-cysteine.

several techniques^[26] can be used to study the chiral nature of nanosized surfaces, such as chiral AFM, STM, secondharmonic generation (SHG), and isothermal titration calorimetry.^[27] However, due to the unique structure of our nanosized chiral surfaces, we are rather limited in the techniques that can be used to prove the chirality of these surfaces. In this work, we have selected several techniques, namely quartz crystal microbalance (QCM), second-harmonic generation circular-dichroism (SHG-CD) spectroscopy, enantioselective crystallization, and chiral adsorption measurements, as the methods to study the chirality of the SAM/TiO₂ nanolayer surfaces.

The first indication of the chiral nature of the chiral SAM/TiO₂ nanofilms comes from the second-harmonic generation-circular dichroism (SHG-CD) technique. SHG-CD is a surface-sensitive nonlinear-optical-activity effect that results in a different SHG efficiency for left- and right-circularly polarized fundamental excitation light.^[28] The SHG-

CD effect is then expressed as $\Delta I(2\omega) = I(2\omega)_{\text{left}} - I(2\omega)_{\text{right}}$, with $I(2\omega)_{\text{left, right}}$ being the SHG intensity with left- or rightcircularly polarized excitation. In our experiments, a fundamental beam at 800 nm was incident at 45° on the sample and the s-polarized second-harmonic light was detected in a reflection geometry. The ellipticity in the polarization of the fundamental light was continuously modulated by a quarter wave plate while simultaneously detecting the s-polarized component of the second-harmonic light (400 nm). The result is shown in Figure 3, in which the SHG intensity is



Figure 3. SHG intensity versus quarter wave plate rotation angle. Top: Dand L-cysteine on gold; bottom: D- and L-cysteine on gold covered with TiO₂. The solid lines are theoretical fits using the formalism described in the Supporting Information.

plotted versus the rotation angle of the quarter wave plate (QWP). At QWP angles of 45°, the fundamental light is left-circularly polarized, and at 135° it is right-circularly polarized. The samples used were D-cysteine, L-cysteine, and DL-cysteine SAMs on gold and on gold covered with TiO₂. It is clear from Figure 3 that for the enantiomerically pure samples of cysteine on gold, there is a distinct difference in SHG efficiency for left- and right-circularly polarized excitation (45° and 135° QWP angle), clearly indicating the presence of chirality. Furthermore, the polarization curves for the L- and D-samples are almost mirror images, as one would expect for opposite enantiomers. Noteworthy is the dramatic difference in the polarization curves from the samples on gold and those covered with TiO₂. An analysis of the polarization curves shows that chiral contributions to the SHG response change upon addition of the TiO₂ layer, while the achiral contributions do not change (see Supporting Information).

Assuming that addition of the TiO_2 does not significantly change the packing of the cysteine SAM, this implies that the TiO_2 is chiral. Note also that while the samples on gold show a SHG-CD response that changes sign between the enantiomers, this is not the case for the samples covered

www.chemeurj.org

with TiO₂. This can be attributed to the presence of several chiral interfaces contributing to the nonlinear optical response. In that case, a change in enantiomer of the SAM does not necessarily imply a change in the SHG-CD sign of the TiO₂ layer. The racemic samples all show a much smaller chiral contribution to the SHG response (see Figure S5 in the Supporting Information) that can be attributed to small defects in the optical components used.

A EUROPEAN JOURNAL

Additional evidence for the chiral nature of the chiral SAM/TiO₂ nanofilms comes from quartz crystal microbalance (QCM) measurements. Previous studies showed that QCM can be used to demonstrate chiral discrimination of enantiomers on thin chiral films.^[29,30] QCM with dissipation monitoring kinetic^[31] adsorption measurements were performed on the TiO₂ chiral films by flowing an undersaturated solution of valine enantiomers (0.7 g/10 mL in deionized water) over the surface of the chiral TiO₂ thin films. Figure 4 shows the adsorption/desorption profile of L- and



Figure 4. Quartz microbalance (QCM) adsorption/desorption profile of L- and D-valine onto TiO₂ L- and D-cysteine nanofilms.

D-valine on TiO₂ L- and D-cysteine chiral films. Due to the unique and new structure of our chiral SAM/TiO₂ nanofilms, the interpretation of the QCM results using commonly used models, such as the Voigt model, for calculations of the thickness of adsorption are not applicable. Therefore, we simply used the Saurbrey equation $\bar{[32]}$ to calculate the mass of the valine enantiomers adsorbed onto the chiral SAM/ TiO₂ nanofilms. Results of the QCM measurements are shown in Figure 4. These measurements show a difference of about 50 ng between the adsorption of L- and D-valine onto the TiO₂/L-cysteine surface, which indicates there is preferential adsorption of D-valine onto the L-imprinted TiO₂ SAMs of L-cysteine and is proof of enantioselective adsorption. Similar results were observed in the adsorption of valine enantiomers onto a TiO2/D-cysteine surface. The racemic solution (DL) of valine showed the same behavior on the SAM of L- and D-cysteine TiO₂ surfaces.

Finally, we employ enantioselective crystallization experiments to prove the chirality of the SAM/TiO₂ films. Our reason for employing crystallization is based on the idea that if these surfaces are indeed chiral, crystallization of chiral systems on them will result in enantioselectivity. The basic assumption is that enantiospecific chiral surfaces act as selective chiral centers for the crystallization of the enantiomer with a chirality equivalent to that of the surface. In order to examine the chirality of the SAMs/TiO₂ surfaces we studied the crystallization of DL-glutamic acid (racemic system) and DL-threonine (conglomerate). All crystallization experiments were conducted from supersaturated solutions of the amino acids in deionized water at room temperature. The surfaces were placed vertically in the crystallization solutions and macrosized crystals were crystallized at the surfaces. The crystals were gently removed from the surfaces; the enantiomeric excess (ee) in crystals both on the surface and from bulk solutions were measured separately, in order to determine the amount of chiral separation. In the first set of experiments, we studied the crystallization of DL-threonine onto L- or D-cysteine SAM/TiO2 surfaces and L-glutathione SAM/TiO₂, and the results of those experiments are shown in Figure 5.



Figure 5. Enantiomeric excess in DL-threonine crystallization experiments on the chiral SAM/TiO₂ surfaces.

As can be seen from Figure 5, in a controlled crystallization experiment of DL-threonine in solution and on Au–TiO₂ (10 nm) surfaces, no enantioselective crystallization is observed and the *ee* is negligible (ca. 1.3% *ee*). Furthermore, in an additional series of controlled crystallization experiments performed on the SAMs on gold alone, no enantioselective crystallization is observed. In contrast to the control crystallization, optical measurements of crystals that were collected from L-cysteine and L-glutathione SAM/TiO₂ surfaces show *ee* of 38.3 and 19%, respectively, of the L enantiomer. In a similar DL-threonine crystallization experiment done on D-cysteine, enantioselective crystallization is observed with an *ee* of 13.2% for the D enantiomers. These experiments clearly demonstrate the chiral nature and the chiral recognition of the cysteine SAM/TiO₂ surfaces.

In the next set of experiments, we studied the crystallization of a racemic system of DL-glutamic acid. It is known that DL-glutamic acid can crystallize in two forms: the conglomerate form, known as anhydrous DL-glutamic acid, and the racemic compound, known as DL-glutamic acid monohydrate.^[33] The anhydrous and monohydrated forms of DL-glutamic acid have different crystal habits, and therefore their formation can also be studied using SEM and X-ray diffraction. In the Supporting Information, Figure S6 displays an SEM image of crystals crystallized on the L-glutathione SAM/TiO₂ surface. The crystals grown on the L-glutathione SAM/TiO₂ exhibit a platelike morphology, characteristic of the conglomerate form of DL-glutamic acid. In addition, the X-ray diffraction spectrum (see Figure S7 in the Supporting Information) of the crystals grown on the L-glutathione SAM/TiO₂ surface displays peaks at $2\theta = 10.3$, 13.6, 20.6, 21.4, 21.8, and 32.8°, which correspond to the (020), (011), (040), (101), (111), and (042) planes of the conglomerate DL-glutamic acid, as reported in the literature.^[34] However, it should be mentioned here that we did not observe chiral resolution on the chiral-SAM-coated TiO₂ nanofilms. Nevertheless, based on previous studies^[35] it is know that stabilization of the conglomerate form of chiral system is usually due to selective chiral interactions between the surfaces and the crystal interfaces of the conglomerate.

In the final stage of this research, we selected CD spectroscopy as a tool for exploring the chiral binding, selectivity, and chiral recognition of enantiomers to the chiral SAM/ metal oxide surfaces. As a representative case to demonstrate the chiral recognition ability, D- and L-threonine were used to investigate the selective chiral interactions with the surface chirality of the chiral SAM/metal oxide surfaces. The chiral adsorption measurements were carried out by taking an aqueous solution containing 10 mM of the L or D enantiomer of threonine and 2.5×2.5 cm of L-cysteine SAM/ TiO₂ surfaces were added to these solutions. The optical activities of the solution were measured with time at a wavelength of $\lambda = 209$ nm. The representative plots of adsorption dynamics (Q) versus time of L- and D-threonine obtained from optical CD experiments are shown in Figure 6. As can be seen, the amount of adsorbed L-threonine Q (mmol) increases rapidly as a function of time while the amount of the adsorbed D-threonine remains almost constant. These results clearly demonstrate the stereoselective uptake of the L enantiomers by the chiral SAM/metal oxide surfaces and display a significant difference in the adsorption kinetics of the enantiomers.

Overall, the chiral nature of the chiral SAM/metal oxides has been demonstrated by the above crystallization and optical experiments. However, it is clear that further experiments need to be carried out in order to understand the chirality of these surfaces in detail and in particular the chiral templating mechanism, which remains an important open question. We assume that the origin of the chirality of the TiO₂ films is due to the chiral sites of the SAM that serve as templates for the nucleation of TiO₂, leading to chiral templating of the TiO₂ films. We suppose that the chiral templating of the TiO₂ occurs through a similar mechanism to templating chirality in other materials, such as mo-

FULL PAPER



Figure 6. CD measurements of D- and L-threonine solutions after L-cysteine SAM/TiO₂ surfaces were added. The CD was measured for the solutions and used to calculate the amount of adsorbed threonine Q(mmol).

lecularly imprinted polymers^[36,37] and chiral mesoporous materials.^[15,38] The structure of self-assembled monolayers of cysteine on gold has been studied and suggests that the surface interaction involves the thiol-gold bonding and leads to the direct exposure of the chiral molecules on the surface, making it easily accessible for interactions with the TiO₂ precursor. It should be noted that R. Schillinger et al. reported^[39] that L-cysteine has higher hydrogen affinity to the Au (17 11 9) surface, as compared with D-cysteine, that reflects the enantiospecific adsorption of cysteine molecules on a chiral gold surface. However, in our work we use standard Au (111) surfaces, and we therefore assume that L- and D-cysteine have identical adsorption structures on the gold surface. We presume that the nucleation on the chiral sites of the SAM induce a chiral arrangement of the whole TiO₂ film, leading to chirality of the films. This also agrees with our observations that films with thicknesses higher than 10 nm lose their chiral nature, probably because the chiral induction is limited to a short range of about 10 nm.

To summarize, in this article we described the development of an entirely new class of chiral surfaces. The existing methods to characterize chirality in our chiral surfaces are very limited, however we used a variety of techniques, such as SHG-CD, QMB, and CD spectroscopy, as tools for exploring the chiral recognition and chiral enantioselective crystallization. All the above techniques clearly demonstrated that the chiral SAMs/TiO₂ films are chiral. Nevertheless, it should be noted that the SHG-CD and QMB measurements give a strong indication that the films are chiral, yet those measurements did not show "reversed symmetry" between the two enantiomers. It is clear that further study and model development are required to fully understand those measurements. On the other hand, the crystallization and the CD spectroscopy experiments clearly demonstrated enantiospecific adsorption and crystallization on the chiral nanosized metal oxides surfaces.

www.chemeurj.org

Conclusion

In conclusion, in this paper we described the development of an innovative type of chiral surface based on a nanoscale hybrid system of chiral SAMs coated with metal oxide nanolayers. We demonstrated the chiral nature of those hybrid systems of chiral SAMs with metal oxides nanolayers by employing various analytical techniques, such as quartz crystal microbalance, second-harmonic generation circular dichroism (SHG-CD), circular dichroism spectroscopy, and chiral crystallization. It should be emphasized that due to the unique structure of nanoscale hybrid systems of chiral SAMs coated with metal oxide nanolayers, the present techniques for measuring the chirality of these systems with nanoscale resolution are very limited. We utilized SHG-CD and quartz crystal microbalance measurements that clearly demonstrated that the SAM/TiO₂ surfaces are chiral. Although the resulting enantiomeric excess in crystallization on the SAM/metal oxide nanosurfaces is not yet very high, the basic principles of chiral discrimination by these surfaces has been demonstrated, so future studies with optimized film architectures and chiral functions might result in significant improvements of the chiral discrimination of those hybrid systems. Experiments on chirality go back for many years, but the knowledge in this field, particularly at the nanoscale and of surfaces, is still rather limited. We believe that the approach presented in this paper is highly significant for the development of a new type of chiral surface for enantioselective chemistry. Moreover, our results on chiral nanosize metal oxide films may provide significant progress in the understanding of the structure and nature of chiral surfaces. Finally, our proposed methodology for the preparation of nanochiral surfaces can open up opportunities in other fields of chemistry, such as chiral catalysis, analytical chemistry, and surface science.

Experimental Section

Gold films were deposited on mica, KAl₂(AlSi₃O₁₀)(OH)₂. Typically, a 50 nm thick layer of gold (99.995%) was sputtered on freshly cleaved mica sheets at a pressure of approximately 1×10^{-3} mbar with a deposition rate of (0.5 nm s⁻¹).

Chiral SAMs were formed on the gold surfaces by immersing the gold substrates overnight in 10 mM solutions of D-, L-cysteine or L-glutathione in deionized water. After removal from the solutions, the chiral SAM surfaces were washed thoroughly with water and blown dry with nitrogen. **Atomic layer deposition (ALD)**: The samples were introduced into the ALD system (Cambridge, Fiji F200). The TiO₂ thin films were deposited onto chiral SAM surfaces using a [Ti{N(CH₃)₂]₄] precursor and water. Ar served as both the carrier and the purging gas. Thin films of TiO₂ were grown on the chiral SAMs at 373 K under 1×10^{-2} Torr. The ALD cycle consisted of 0.2 s exposure to [Ti{N(CH₃)₂]₄] (evaporated at 348 K), 10 s Ar purge, and a 0.06 s exposure to water. A total of 125 ALD circles were used to obtain TiO₂ films with a thickness of (10 ± 0.1) nm.

SHG-CD: The second-harmonic-generation experiment was carried out using a $Ti-Al_2O_3$ laser at the fixed fundamental wavelength of 800 nm with an average power output of 70 mW. The pulse length and repetition rate were 120 fs and 82 MHz, respectively. The polarization of the incident beam on the sample was controlled by a polarizer and half-wave

plate. Subsequently, the beam passed through a quarter-wave plate, which rotated over 360 degrees. This enabled a change in polarization from linearly polarized light, through elliptical polarization, to circularly polarized light. The incident beam was cleared of unwanted visible light by a RG665 filter and then focused on the sample to a spot of approximately 40 μ m. The angle of optical incidence was 45° on the sample. The generated photons of the half wavelength (400 nm) in reflection were then filtered through two BG39 filters, which blocked the fundamental beam. An analyzer was placed after the sample to vary the output second-harmonic beam. This output beam was detected with a photomultiplier tube and analyzed with a photon counter. The SHG polarization curves were analyzed according to the procedure described in the Supporting Information.

Enantioselective crystallization: In all crystallization experiments analytical grade amino acids (>99.9%) were purchased from Sigma Aldrich and used as received. For pL-threonine crystallization, experiments were conducted with supersaturated solutions DL-threonine (7.5 g) was suspended in deionized water (25 mL). Thereafter, the solution was heated to 75°C and stirred until it was completely dissolved and left to cool to room temperature. Finally, the chiral surfaces were placed vertically in the crystallization solutions. Macrosized crystals crystallized at the chiral surfaces were considered and removed manually from the chiral surfaces; the enantiomeric excess (ee) in both crystals crystallized on the surfaces and from the bulk crystallization solutions were measured separately, in order to determine the amount of chiral separation. Specific light rotation was measured with a JASCO digital polarimeter (Model P-1010 $\lambda =$ 589 nm, $\pm 0.05^{\circ}$ accuracy) using a cylindrical quartz cell (5 mL, L= 50 mm) at room temperature by dissolving the crystals in water. For the DL-glutamic acid crystallization, experiments were conducted as described above form supersaturated solutions of DL-glutamic acid (1.25 g) in deionized water (25 mL).

Scanning electron microscope (SEM) images were obtained with a FEI instrument-Inspect S model at acceleration voltages of 5, 15, and 30 kV. High-resolution transmission electron microscope (HR-TEM) images were taken with a 2100 JEOL microscope working at a voltage of 200 kV; images were recorded on CCD 4×4k camera (Gatan), and EDS chemical analysis was performed with a Thermo electron group system. XPS analysis: XPS analyses were performed in a Kratos AXIS-HS spectrometer, using a monochromatized $Al_{K\alpha}$ source. Survey and high resolution spectra were acquired at 75 or 150 W, respectively. All data acquisitions were performed at detection pass energies of 40-80 eV. All XPS measurements were carried out at room temperature, under vacuum conditions of (1.0-3.0) 10⁻⁹ Torr. Spectra were acquired with a low electron flood gun for charge neutralization. The spectrometer energy scale was routinely calibrated according to the ISO TC/201 SC7 international procedure for binding energy (BE) with Au 4f 7/2 83.98 and Cu 2p 3/2 932.67. Spectra binding energy were not corrected for charging shifts. Data processing was done with VISION software (Kratos).

Quartz crystal microbalance measurements with dissipation monitoring (QCM-D) were performed with AT-cut quartz crystals mounted in an E1 system (Q-sense AB, Gothenburg, Sweden). Gold crystals (catalog number QSX301) coated with L-cysteine SAM/TiO₂, having a fundamental resonant frequency of about 5 MHz, were purchased from Q-Sense AB. All QCM-D experiments were performed under flow-through conditions using a digital peristaltic pump (IsmaTec, IDEX) operating in sucking mode. The pump tubing was connected to a glass vial containing the studied solutions that were injected into the sensor crystal chamber at 0.1 mLmin⁻¹. The normal Q-sense AB instrument mass sensitivity in liquid is 1.8 ng cm⁻².

Circular dichroism spectra in the near UV or visible range were recorded with a Jasco J-815 spectropolarimeter. For UV (190–260 nm) measurements, 10 mM aqueous solutions of the L- or D-threonine after 2.5×2.5 cm of L-cysteine SAM/TiO₂ surfaces were added to these solutions for 0, 10, 20, 40, 60, 90, or 120 min.

Powder X-ray diffraction patterns of DL-glutamic acid were acquired with a Bruker AXS D8 Advance diffractometer with $Cu_{K\alpha}$ (λ =1.5418 Å) operating at 40 kV and 40 mA. Data were collected from 2θ = 10 to 40° with a step size of 0.01°.

10300 -

Acknowledgements

H.M. would like to acknowledge the BIU Department of Chemistry for funding. We thank Dr. Moshe Herzberg from the Zuckerberg Institute for Water Research at Ben-Gurion University of the Negev for quartz microbalance measurements. T.V. acknowledges support from the KU Leuven (GOA research grant). This research was supported by the Israel Science Foundation (grant No. 660/07).

- [1] R. Raval, Chem. Soc. Rev. 2009, 38, 707-721.
- [2] Y. Mastai, Chem. Soc. Rev. 2009, 38, 772-780.
- [3] G. Coquerel, D. B. Amabilino in *Chirality at the Nanoscale: Nano*particles, Surfaces, Materials and more (Ed.: D. B. Amabilino), Wiley-VCH, Weinheim, 2009, pp. 305–348.
- [4] J. Zhang, M. T. Albelda, Y. Liu, J. W. Canary, *Chirality* 2005, 17, 404–420.
- [5] S. M. Barlow, R. Raval, Surf. Sci. Rep. 2003, 50, 201-341.
- [6] S. Barlow, R. Raval, *Curr. Opin. Colloid Interface Sci.* 2008, 13, 65–73.
- [7] A. J. Gellman, ACS Nano 2010, 4, 5-10.
- [8] R. M. Hazen, D. S. Sholl, Nat. Mater. 2003, 2, 367-374.
- [9] J. D. Horvath, A. J. Gellman, Top. Catal. 2003, 25, 9–15.
- [10] J. D. Horvath, A. Koritnik, P. Kamakoti, D. S. Sholl, A. J. Gellman, J. Am. Chem. Soc. 2004, 126, 14988–14994.
- [11] J. N. James, D. S. Sholl, Curr. Opin. Colloid Interface Sci. 2008, 13, 60–64.
- [12] A. G. Mark, M. Forster, R. Raval, ChemPhysChem 2011, 12, 1474– 1480.
- [13] S. M. Barlow, R. Raval, Curr. Opin. Colloid Interface Sci. 2008, 13, 65–73.
- [14] Progress in Biological Chirality (Eds.: G. Pályi, C. Zucchi, L. Caglioti), Elsevier, Oxford 2004.
- [15] A. Gabashvili, D. D. Medina, A. Gedanken, Y. Mastai, J. Phys. Chem. B 2007, 111, 11105–11110.
- [16] S. Marx, D. Avnir, Acc. Chem. Res. 2007, 40, 768-776.
- [17] T. Delclos, C. Aimé, E. Pouget, A. Brizard, I. Huc, M.-H. Delville, R. Oda, *Nano Lett.* **2008**, *8*, 1929–1935.

- [18] J. A. Switzer, H. M. Kothari, P. Poizot, S. Nakanishi, E. W. Bohann-
- an, *Nature* **2003**, *425*, 490–493. [19] E. W. Bohannan, H. M. Kothari, I. M. Nicic, J. A. Switzer, *J. Am.*
- *Chem. Soc.* **2004**, *126*, 488–489.
- [20] R. V. Gudavarthy, N. Burla, E. A. Kulp, S. J. Limmer, E. Sinn, J. A. Switzer, J. Mater. Chem. 2011, 21, 6209–6216.
- [21] S. M. George, Chem. Rev. 2010, 110, 111-131.
- [22] S.-M. Lee, E. Pippel, U. Gösele, C. Dresbach, Y. Qin, C. V. Chandran, T. Bräuniger, G. Hause, M. Knez, *Science* 2009, 324, 488–492.
- [23] C. Lin, F.-Y. Tsai, M.-H. Lee, C.-H. Lee, T.-C. Tien, L.-P. Wang, S.-Y. Tsai, J. Mater. Chem. 2009, 19, 2999–3003.
- [24] E. K. Seo, J. W. Lee, H. M. Sung-Suh, M. M. Sung, Chem. Mater. 2004, 16, 1878–1883.
- [25] K. Konstadinidis, P. Zhang, R. Opila, D. Allara, Surf. Sci. 1995, 338, 300–312.
- [26] Q. Chen, N. V. Richardson, Annu. Rep. C 2004, 100, 313-347.
- [27] A. Shval, Y. Mastai, Chem. Commun. 2011, 47, 5735-5737.
- [28] S. Sioncke, T. Verbiest, A. Persoons, Mater. Sci. Eng. R 2003, 42, 115–155.
- [29] C. Xu, S. C. Ng, H. S. O. Chan, Langmuir 2008, 24, 9118-9124.
- [30] H.-S. Guo, J.-M. Kim, S.-M. Chang, W.-S. Kim, *Biosens. Bioelectron.* 2009, 24, 2931–2934.
- [31] M. Rodahl, F. Höök, B. Kasemo, Anal. Chem. 1996, 68, 2219-2227.
- [32] G. Sauerbrey, Z. Phys. 1959, 155, 206-222.
- [33] M. Ejgenberg, Y. Mastai, Chem. Commun. 2011, 47, 12161-12163.
- [34] J. J. Verbist, M. S. Lehmann, T. F. Koetzle, W. C. Hamilton, Acta Crystallogr. Sect. B: 1972, 28, 3006–3013.
- [35] D. H. Dressler, I. Hod, Y. Mastai, J. Cryst. Growth 2008, 310, 1718– 1724.
- [36] G. Wulff, Angew. Chem. 1995, 107, 1958–1979; Angew. Chem. Int. Ed. Engl. 1995, 34, 1812–1832.
- [37] T. Takeuchi, J. Haginaka, J. Chromatogr. B 1999, 728, 1-20.
- [38] S. Fireman-Shoresh, S. Marx, D. Avnir, Adv. Mater. 2007, 19, 2145– 2150.
- [39] R. Schillinger, Ž. Šljivančanin, B. Hammer, T. Greber, *Phys. Rev. Lett.* 2007, 98, 136102.

Received: February 26, 2013 Published online: June 21, 2013

FULL PAPER