Sub-micrometer polarimetry of chiral surfaces using near-field scanning optical microscopy†

David H. Dressler, Asher Landau, Arie Zaban and Yitzhak Mastai*

Received (in Cambridge, UK) 23rd November 2006, Accepted 8th January 2007
First published as an Advance Article on the web 23rd January 2007
DOI: 10.1039/b617139g

In this work we have studied the optical activity of chiral crystal surfaces with polarized near-field scanning optical microscopy (NSOM); our studies clearly demonstrated that polarized NSOM can be utilized to determine chirality at crystal surfaces.

Chirality is a natural phenomenon, which differentiates an object from its own mirror image. Chirality is of prime significance, as most of the biological macromolecules have particular chirality that is correlated with their biological activity. Many processes used in chemical production involve solid surfaces and can be made enantioselective by using chiral surfaces. In the past decades chiral surfaces[1–7] have received attention for their potential applications in chiral selection such as in stereoselective chemical synthesis, separation of chiral compounds, crystal growth, protein adsorption, and optical activity. It is clear that measuring chirality of surfaces is critical for further development of chiral surfaces for various applications and to the basic understanding of the nature of chirality. In recent years a variety of methods[8] have been developed, which allow us to characterize the structures of chiral surfaces and rationalize the interaction between adsorbate molecules and chiral substrates. Those techniques include for instance: low-energy electron diffraction (LEED), X-ray photoelectron diffraction, chiral AFM,[9] and STM,[10] and electrochemical oxidation.[11]

The direct optical activity measurements of chiral surfaces and crystals by a polarimeter are practically difficult. This difficulty was overcome using HAUP[12,13] (High Accuracy Universal Polarimeter) which improved the errors resulting from birefringence in optical measurements and introduced an automatic data analyzer. However actual HAUP measurements are not as simple as routine polarimetry in solutions, since the optical properties, including optical activity, show anisotropy for each crystal plane. Other optical methods to examine chiral surfaces include reflection–absorption infrared spectroscopy (RAIRS),[14] second-harmonic generation (SHG)[15] and polarimetry with optical microscopy.[16] However so far all experiments using polarized light on chiral surfaces have been carried out on larger areas of a few μm and the characterization of chiral surfaces at submicronic scale is very limited.

Here we report a new method for the determination of surface chirality based on the use of polarized near-field scanning optical microscopy (NSOM). Near-field optical microscopy[17–19] has been a field of rapid growth in the past years that provided numerous examples of chemical surfaces and biological systems analysis with high resolution of *ca.* 50 nm. The use of NSOM to perform spectroscopic measurements such as emission, absorption and transmission provides a rich set of tools to probe sample properties at nano scale. In recent years polarization NSOM[20–22] techniques have been developed to control the polarization properties in the near field. Polarization-modulation NSOM can be used to gain information about surfaces such as: liquid crystals organization, thin film analysis, optical anisotropy, magneto-optical effects and surface polarimetry. Polarization NSOM imaging can also aid in distinguishing between real optical effects and those arising from large topographical changes. Polarization-modulation NSOM techniques have also been used to read, write, and characterize single magnetic bits.

To investigate the chirality of surfaces we developed a new type of reflection polarization NSOM as shown schematically in Fig. S1 (see supporting information). A laser source (λ = 488 nm) is used as the light source; the light passes through a half wave plate to the NSOM tip in a polarized state. The resulting linearly polarized light is coupled into a bent single-mode optical fiber. In our experiment we use NSOM tips with extinction ratios of 1 : 20. The light emitted from the tip aperture and reflected from the sample is collected by a microscope objective lens. The collected light then travels up the microscope column where a circular analyzer is inserted (dichroism mode) before the light reaches a photomultiplier tube. Experiments described here are performed in the illumination reflection mode. In this geometry, linear polarized light exits from the probe aperture vertically to the surface and serves as the light source. After the near-field light interacts with the chiral surfaces, the light scattered and reflected from the surfaces is collected in the far field. After collection of the light, a polarization analyzer with extinction ratio of 6000 : 1 is used to selectively measure the transverse polarization component of the collected light. We selected the minimum polarized light emerging from the optical fiber as the zero point of polarization of the system.

To demonstrate the chiral discrimination capability of the polarized NSOM, we must select model systems for chiral surfaces. Generally, chiral surfaces[23] can be produced by chiral templating of organic molecules, derived from naturally chiral bulk crystalline structures, and also produced from achiral bulk structures such as metals. In this work, we chose chiral surfaces derived from enantiomerically pure crystals of amino acids, namely L- or D-histidine. Enantiomerically pure L- and D-histidine crystals were grown onto Au (111) substrates from supersaturated solutions at room temperature. Enantiomerically pure histidine crystals grown on Au surfaces crystallized as prism shaped crystals with approximate dimensions of *ca.* 10 μm as examined by scanning electron microscopy (see Fig. 2B). In addition the X-ray diffraction

---

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel. E-mail: mastai@mail.biu.ac.il

† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/b617139g

patterns of the L- or D-histidine crystals on Au surfaces match the ones reported in the literature.[24]

The enantiomerically pure D- and L-histidine were used as our model system for chiral surfaces to demonstrate chiral detection by polarized NSOM. We have to point out that although our model for chiral surfaces is based on microsize crystals, the chirality detection of the NSOM is obtained only from a depth of *ca.* 300 nm of the chiral surfaces. Fig. 1 presents the NSOM polarization dependence of light reflected from the surfaces of L and D crystals of histidine.

As one can see from Fig. 1 the intensity of light reflected from the chiral surfaces as a function of the analyzer angle is sinusoidal to a high degree of accuracy. Furthermore the two enantiomeric crystals display approximately maximum reflection intensities at opposite angles of rotation, namely analyzer angle. This type of symmetrical optical behavior is characteristic for the optical activity of enantiomers and it is observed for all analyzer angles. For example, the maximum reflection intensity for the L crystals is obtained at an analyzer angle of *ca.* 30° while the NSOM maximum reflection intensity for the D crystals is observed at *ca.* 150° (corresponds to −30°). Those results demonstrate the capability of our method to measure chirality at surfaces, which can be employed for the determination of chirality of crystal surfaces.

We have to mention that the NSOM light polarization results were not influenced by various crystal parameters such as: morphology, crystal size, crystal thickness or orientation. Light can also undergo polarization by reflection from surfaces particularly for metallic surfaces; the extent to which polarization occurs is dependent upon the angle at which the light approaches the surface and upon the material which the surface is made of. However since in our work the polarization dependence of the Au (111) surface is set as the reference point for zero polarization of the system we can neglect those effects.

The ability to simultaneously acquire topography and NSOM images is of great importance in correlation and study of chiral surfaces. Fig. 2 shows line profiles of the NSOM reflection intensity taken at the maximum analyzer angle (*ca.* 30°) and topography as acquired over the same area of L-histidine crystal of 10 μm × 10 μm.

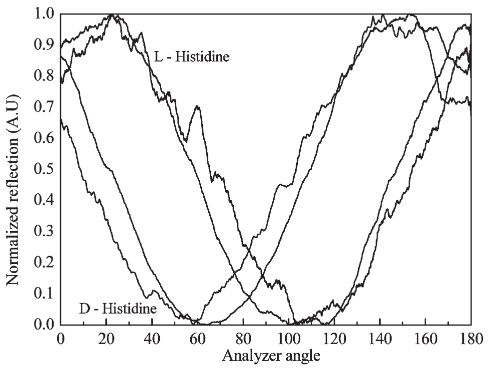

Fig. 1 Line profiles of the reflection intensity of enantiomeric crystals of histidine *vs.* analyzer degree (NSOM in reflection mode).

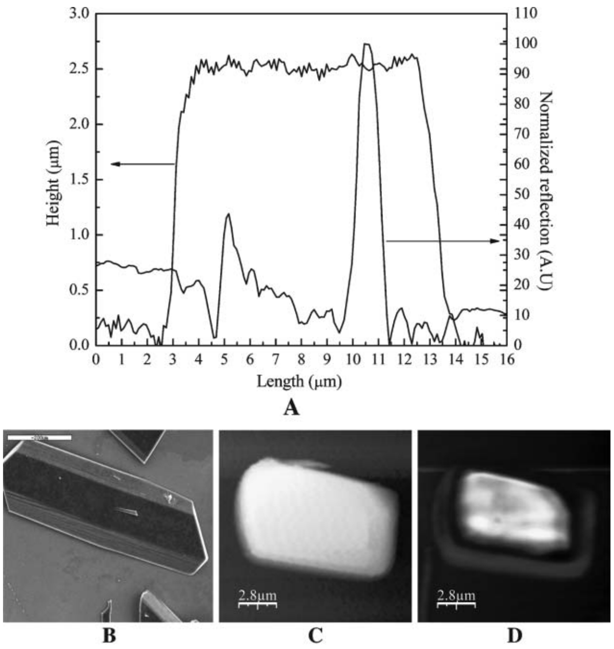

Fig. 2 (**A**) NSOM and topography line profiles taken from the same region of L-histidine crystal as indicated by vertical line indicated on the images shown in **C**; (**B**) scanning electron microscope image of L-histidine; (**C**) topography image; (**D**) polarized NSOM image taken at max. reflection of 30°.

What is of most interest from those images is the lack of correspondence between the optical polarization and topographic data. As can be seen the topographic image indicates that the crystal surface is topographically smooth. The total topographic z-height variation is less than 4 nm and the noise of the topographic profile is less than 2 nm. In contrast to the topographical results, the optical results reveal marked variation in the intensity of the reflected light along the crystal. At the crystal edges the intensity of the reflected light increases/decreases rapidly, probably due to the orientation of the NSOM tip and the crystal surface. However along the crystal plane we obtain optical reflection that is different from that expected from a homogeneous chiral surface. We should mention that in similar measurements done at different analyzer angles, *e.g.* 80° and 120°, the same inhomogeneous behavior of the reflected light was observed. The source of the modification in the optical reflection along the crystal surfaces is not clear to us yet but it may be due to a number of effects. For instance, it is possible that the heat of the NSOM probe provides enough thermal energy to cause the molecules on the surface to rotate or even to evaporate. It should be mentioned that similar results, namely optical modification in light reflection, that are independent of topographic modification were reported in the case of liquid crystal surfaces.[25] Finally, in order to evaluate the sensitivity of our method for the determination of chirality of surfaces, we decided to measure chirality of self assembled multilayers of chiral molecules. Chiral self assembled multilayers of D- or L-cysteine on thin Au (111) films were prepared. Under these experimental conditions we achieved well-defined chiral multilayers with a thickness of approximately 5 layers (*ca.* 6 nm) as confirmed by ellipsometry measurements. We were unable to determine the surface chirality of those self assembled multilayers using our NSOM method due to the low optical activity signal reflected from those surfaces.

In this work we have studied the near-field optical response of chiral crystal surfaces. Our studies clearly demonstrate that polarized NSOM can be utilized to determine chirality at crystal surfaces. The sensitivity of this method allows us to measure chirality of nanoscale objects and could be useful for chiral identification of nanostructures. Furthermore, the possibility of using NSOM to probe chirality can be applied in many other fields in which the NSOM technique is used, such as polymers and biological systems. Finally the possibilities to simultaneously measure the optical and topographic images of chiral surfaces and to study the correlation between those factors, open up the possibility for very interesting research such as the optical properties of prochiral surfaces.

We thank Nanonics Imaging Ltd and Prof. Aaron Lewis from the Department of Applied Physics, Hebrew University of Jerusalem, for useful discussions and help with the NSOM measurements.

Notes and references

1 J. D. Horvath and A. J. Gellman, *Top. Catal.*, 2003, **25**, 9–15.
2 R. M. Hazen and D. S. Sholl, *Nat. Mater.*, 2003, **2**, 367–374.
3 A. J. Gellman, J. D. Horvath and M. T. Buelow, *J. Mol. Catal. A: Chem.*, 2001, **167**, 3–11.
4 K. H. Ernst, M. Bohringer, C. F. McFadden, P. Hug, U. Muller and U. Ellerbeck, *Nanotechnology*, 1999, **10**, 355–361.
5 B. Bhatia and D. S. Sholl, *Angew. Chem., Int. Ed.*, 2005, **44**, 7761–7764.
6 A. Baiker, *Catal. Today*, 2005, **100**, 159–170.
7 D. Avnir, E. Wellner and M. Ottolenghi, *J. Am. Chem. Soc.*, 1989, **111**, 2001–2003.
8 Q. Chena and N. V. Richardson, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.*, 2004, **100**, 313–347.
9 R. McKendry, M. E. Theoclitou, T. Rayment and C. Abell, *Nature*, 1998, **391**, 566–568.
10 G. P. Lopinski, D. J. Moffatt, D. D. Wayner and R. A. Wolkow, *Nature*, 1998, **392**, 909–911.
11 G. A. Attard, C. Harris, E. Herrero and J. Feliu, *Faraday Discuss.*, 2002, **121**, 253–266.
12 J. Kobayashi and Y. Uesu, *J. Appl. Crystallogr.*, 1983, **16**, 204–211.
13 J. Kobayashi, Y. Uesu and H. Takehara, *J. Appl. Crystallogr.*, 1983, **16**, 212–219.
14 M. O. Lorenzo, S. Haq, T. Bertrams, P. Murray, R. Raval and C. J. Baddeley, *J. Phys. Chem. B*, 1999, **103**, 10661–10669.
15 M. A. Kriech and J. C. Conboy, *J. Am. Chem. Soc.*, 2005, **127**, 2834–2835.
16 W. Kaminsky, K. Claborn and B. Kahr, *Chem. Soc. Rev.*, 2004, **33**, 514–525.
17 R. C. Dunn, *Chem. Rev.*, 1999, **99**, 2891.
18 E. Betzig, A. Lewis, A. Harootunian, M. Isaacson and E. Kratschmer, *Biophys. J.*, 1986, **49**, 269–279.
19 A. Lewis, A. Radko, N. Ben Ami, D. Palanker and K. Lieberman, *Trends Cell Biol.*, 1999, **9**, 70–73.
20 E. B. McDaniel, S. C. McClain and J. W. P. Hsu, *Appl. Opt.*, 1998, **37**, 84–92.
21 L. Ramoino, M. Labardi, N. Maghelli, L. Pardi, M. Allegrini and S. Patane, *Rev. Sci. Instrum.*, 2002, **73**, 2051–2056.
22 D. A. Higgins, D. A. VandenBout, J. Kerimo and P. F. Barbara, *J. Phys. Chem.*, 1996, **100**, 13794–13803.
23 D. M. Rampulla and A. J. Gellman, in *Dekker Encyclopedia of Nanoscience and Nanotechnology*, ed. J. A. Schwarz, C. I. Contescu and K. Putyera, Marcel Dekker Inc, New York, 2004.
24 J. J. Madden, N. C. Seeman and E. L. Mcgandy, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **28**, 2377.
25 P. J. Moyer, K. Walzer and M. Hietschold, *Appl. Phys. Lett.*, 1995, **67**, 2129–2131.