

Toward Multifunctional Analytical Platforms: Progress in Combining Optical, Electrochemical, and Topographical Information

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Chemical sensor technology in the mid-infrared (MIR) spectral range (3-20 μm) is gaining importance in process monitoring, environmental analysis, security/surveillance applications, and the biomedical field, due to the increasing demand for robust sensor technology with inherent molecular specificity. Interfacing IR-transducers with continuous measurement situations in the gas and liquid phase becomes increasingly feasible with the advent of appropriate waveguide technology (e.g., MIR transparent optical fibers and planar waveguides), protective surface coatings (e.g. diamond-like carbon, sol-gels, polymers, etc.), and the availability of advanced light sources such as room-temperature operated quantum cascade lasers (QCLs) leading to miniaturized IR diagnostics. Selected examples will highlight recent advances in miniaturizing IR sensor technologies along with application examples including extreme environments (e.g., deep sea), and biomedical analysis (e.g., in-vivo surgical monitoring).

Recent developments in scanning probe microscopy (SPM) are focusing on the combination of individual SPM techniques, or on the combination with optical techniques to expand the information content accessible at the nanoscale. In particular, combined AFM-SECM (atomic force – scanning electrochemical microscopy) probes have gained considerable interest for simultaneously providing topographical and laterally resolved electrochemical information during AFM imaging. Combined SPM probes with an electroactive area integrated into the AFM probe enable applying a potential to the integrated electrode and recording Faradaic currents resulting from electroactive surface processes, such as e.g., corrosion or biological redox activity. These processes can be (electro)chemically detected with spatial resolution, and directly correlated to the topographical information obtained by the AFM measurement.

Consequently, the next-generation of multifunctional analytical platforms ideally combines the benefits of scanning probe techniques, electrochemistry, and IR spectroscopy into unique analytical tools. Molecular specific information of electrochemical processes can be obtained by combining IR spectroelectrochemistry using *in-situ* infrared attenuated total reflection spectroscopy (IR-ATR) with AFM as simultaneous spectroscopic access to surface processes during topographical imaging is provided. An overview on the state-of-the-art, current challenges, and the future potential of such hyphenated analytical surface techniques will be presented, and complemented by selected examples relevant to biomedical and material sciences.

Selected References:

- C. Kranz, G. Friedbacher, B. Mizaikoff, A. Lugstein, J. Smoliner, E. Bertagnolli, Integrating an Ultramicroelectrode in an AFM Cantilever: Combined Technology for Enhanced Information, *Anal. Chem.* 73, 2491-2500 (2001).
 - Martin Brucherseifer, C. Kranz, Boris Mizaikoff, Combined In-Situ AFM-IR-ATR, *Anal. Chem.* 79, 8803-8806 (2007).
 - Eifert, W. Smirnov, S. Frittmann, C. Nebel, B. Mizaikoff, C. Kranz*, Atomic Force Microscopy Probes with Integrated Boron Doped Diamond Electrodes: Fabrication and Application, *Electrochem. Commun.*, 25, 30-34 (2012).
 - B. Mizaikoff, Waveguide-Enhanced Mid-Infrared Chem/Bio Sensors, *Chemical Society Reviews*, 42, 8683-8699 (2013).
 - X. Wang, J. Antoszewski, G. Putrino, W. Lei, L. Faraone, B. Mizaikoff, Mercury-Cadmium-Telluride Waveguides – A Novel Strategy for On-Chip Mid-Infrared Sensors, *Analytical Chemistry*, 85, 10648–10652 (2013).
 - M. Sieger, F. Balluff, X. Wang, S.-S. Kim, L. Leidner, G. Gauglitz, B. Mizaikoff, On-Chip Integrated Mid-Infrared GaAs/AlGaAs Mach-Zehnder Interferometer, *Analytical Chemistry*, 85, 3050-3052 (2013).
 - R. Lu, G. Sheng, W. Li, H. Yu, Y. Raichlin, A. Katzir, B. Mizaikoff, IR-ATR Chemical Sensors Based on Ethylene/Propylene Copolymer Coated Planar Silver Halide Waveguides for In-Situ and Simultaneous Detection of Multiple Organic Contaminants in Water, *Angewandte Chemie Int. Ed.*, 52, 2265-2268 (2013).
 - D. Neubauer, J. Scharpf, A. Pasquarelli, B. Mizaikoff, C. Kranz, Combined In-Situ Atomic Force Microscopy and Infrared Attenuated Total Reflection Spectroelectrochemistry, *Analyst*, 138, 6746–6752 (2013).
 - P. Knittel, M. J. Higgins, C. Kranz, Nanoscopic polypyrrole AFM-SECM probes enabling force measurements under potential control, *Nanoscale*, 6, 2255-2260 (2014).
- Kranz, Recent advancements in nanoelectrodes and nanopipettes used in combined scanning electrochemical microscopy techniques, *Analyst* (invited critical review), 139, 336-352 (2014).

Short Biographies



Dr. Boris Mizaikoff received his Ph.D. in Analytical Chemistry at the Vienna University of Technology in 1996. Heading the Chemical Sensor Laboratory (CSL) he has been responsible for numerous research projects in the field of chemical IR sensors, including 4 multinational projects funded by the European Union. In 1997, he has been with the University of Texas, Austin/USA as a postdoctoral fellow. In October 2000 he finalized his Habilitation (Assoc. Prof. for Analytical Chemistry) at the Vienna University of Technology. Since Fall 2000 he was faculty member at the Georgia Institute of Technology, School of Chemistry and Biochemistry, heading the Applied Sensors Laboratory (ASL). Since 2004 he was Director of the Focused Ion Beam Center (FIB² Center) at Georgia Tech, and since 2005 member of the Center for Cell and Molecular Signaling at Emory University, School of Physiology. In Fall 2007, he has joined the faculty at the University of Ulm, Germany, as a Chaired Professor heading the Institute of Analytical and Bioanalytical Chemistry. Today, his research interests focus on optical sensors, biosensors, and biomimetic sensors operating in the mid-infrared spectral range, applications of novel IR light sources (e.g., quantum cascade lasers), system miniaturization and integration based on micro- and nanofabrication, multifunctional scanning nanoprobes (e.g., combination AFM-IR and AFM-SECM-IR), scanning probe tip integrated nano(bio)sensors, focused ion beam (FIB) microscopy, development of chemical recognition interfaces for separation and sensing applications (e.g., molecularly templated materials), chemometric data evaluation, advanced vibrational spectroscopic techniques (e.g., SEIRA), environmental analytical chemistry, process analytical chemistry, and biomedical diagnostics. Dr. Mizaikoff is author/co-author of over 190 peer-reviewed publications, 17 patents, and numerous invited contributions at scientific conferences; his current h-index is 31.



Dr. Christine Kranz received her M.S. and Ph.D. degrees in Chemistry from Ludwig-Maximilians University in Munich (1992) and Technical University of Munich (1996), Munich, Germany, respectively. After spending a year as a postdoctoral fellow at Vienna University of Technology, Institute of Analytical Chemistry (Austria), she accepted a position at the School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, where she is appointed to senior research scientist (until June 2008). In July 2008, she has accepted a permanent position at the University of Ulm, Institute of Analytical and Bioanalytical Chemistry (IABC), Ulm, Germany, where she is heading the surface sciences group and coordinates the biosensing research activities at the IABC. In addition, she is the Scientific Coordinator of the Focused Ion Beam Center UUlm, which was established at the IABC in 2008. Her main research focus is in the field of scanning probe microscopy in particular scanning electrochemical microscopy (SECM), multifunctional scanning probes (e.g. combination AFM- SECM, IR-SECM, IR-AFM), and miniaturized amperometric biosensor technology, integrated microsystems, biomimetic sensors, and (FIB)-based microfabrication. She has authored 9 Patents (2 national patents, Austria and 7 PCT Int. Appl.), more than 65 publications in internationally reviewed journals, and more than 100 lectures presented at international and national conferences (h-index: 23). Since January 2012, Dr. Kranz is member of the Editorial Board of *Frontiers in Renal and Epithelial Physiology*.