Department of Chemistry
Kolthoff Lectureship in Chemistry

University of Minnesota
Driven to Discover℠

February 6-8, 2012
Professor Michael Graetzel

Laboratory of Photonics and Interfaces
École Polytechnique Fédérale de Lausanne

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Faculty Hosts:Philippe Buhlmann & Aaron Massari

Professor Michael Graetzel pioneered research on energy and electron transfer reactions in mesoscopic-materials and their application in solar energy conversion systems, optoelectronic devices and lithium ion batteries. He discovered a new type of solar cell based on dye sensitized nanocrystalline semiconductor oxide particles.

He is the author of more than 800 peer-reviewed publications and two books, and is the inventor of more than 50 patents. He has received prestigious awards, including the Balzan Prize, the Galvani Medal, the Faraday Medal, the Harvey Prize, the Gerischer Award, the Dutch Havinga Award and Medal, the International Prize of the Japanese Society of Coordination Chemistry, the ENI-Italgas Energy-Prize and the year 2000 European Grand Prix of Innovation. He was selected by the Scientific American as one of the 50 top researchers in the world.

He received a doctor's degree in natural science from the Technical University Berlin and honorary doctors degrees from the Universities of Hasselt, Delft, Uppsala and Turin. He has been the Mary Upton Visiting Professor at Cornell University and a Distinguished Visiting Professor at the National University of Singapore. He was an invited professor at the University of Berkeley, the Ecole Nationale de Chachan (Paris) and Delft University of Technology. In 2009, he was named Distinguished Honorary Professor by the Chinese Academy of Science (Changchun) and the Huazhong University of Science and Technology. He is a member of the Swiss Chemical Society as well as of the European Academy of Science, a Fellow of the Royal Society of Chemistry and was elected honorary member of the Société Vaudoise des Sciences Naturelles.

Lecture 3: *Photo Meets Electrocatalysis: United we Split (. . .Water)*
4:15 p.m. Wednesday, February 8, 331 Smith Hall

The cleavage of water into hydrogen and oxygen by visible light remains the Holy Grail of current photochemical research. In contrast to the "brute-force" approach using photovoltaic panels to electrolyze water, these systems employ semiconductor films or particles, which are able to perform the multi-electron transfer reactions involved in the water oxidation and reduction process. Iron oxide (α-Fe_2O_3, or hematite) is especially attractive as a photo-anode due to its abundance, stability and environmental compatibility, as well as suitable band gap and valence band edge position. However, the reported efficiencies of water oxidation at illuminated hematite electrodes are notoriously low. We have deposited silicon doped mesoscopic α-Fe_2O_3 (hematite) films on F-doped SnO_2 glass substrates by chemical vapor deposition at atmospheric pressure (APCVD). Apart from rendering the films conductive the silicon doping strongly influences the mesoscopic film morphology. The silicon-doped α-Fe_2O_3 exhibits a cauliflower-type nanostructure as shown in Figure 1 below. When used in conjunction with surface adsorbed Co(II) ions to promote water oxidation to oxygen a photocurrent of 3.5 mA/cm2 was obtained. This corresponds to an overall solar to chemical conversion efficiency of about 5% in a tandem device using a dye sensitized solar cell (DSC) as a bottom electrode. The role of the DSC is to boost the potential of the cathode to enable evolution of hydrogen. A mechanistic model for water photooxidation is presented, involving stepwise accumulation of four holes by two vicinal iron or cobalt surface sites. Recent research on efficient photogeneration of hydrogen on mesoscopic Cu_2O electrodes will also be presented.

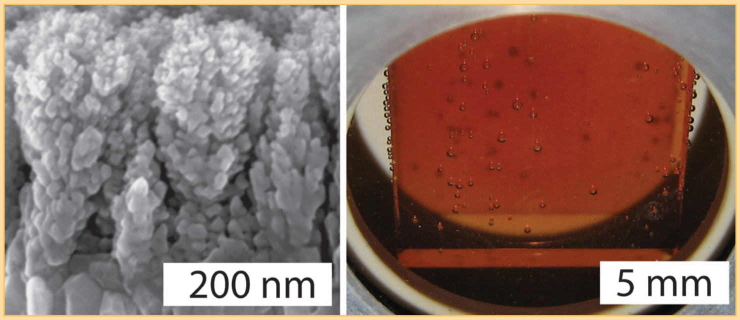

Figure 1. Scanning electron microscopy picture of a silicon doped hematite film supported on fluorine doped tin dioxide(FTO) conducting glass. Note the cauliflower-type nanostructure obtained by APCVD. Visible light induced oxygen evolution on such nanostructured hematite films.

Izaak Maurits Kolthoff was born on February 11, 1894, in Almelo, Holland. He died on March 4, 1993, in St. Paul, Minnesota. In 1911, he entered the University of Utrecht, Holland. He published his first paper on acid titrations in 1915. On the basis of his world-renowned reputation, he was invited to join the faculty of the University of Minnesota's Department of Chemistry in 1927. By the time of his retirement from the University in 1962, he had published approximately 800 papers. He continued to publish approximately 150 more papers until his health failed. His research, covering approximately a dozen areas of chemistry, was recognized by many medals and memberships in learned societies throughout the world, including the National Academy of Sciences and the Nichols Medal of the American Chemical Society. Best known to the general public is his work on synthetic rubber. During World War II, the government established a comprehensive research program at major industrial companies and several universities, including Minnesota. Kolthoff quickly assembled a large research group and made major contributions to the program. Many of Kolthoff's graduate students went on to successful careers in industry and academic life and, in turn, trained many more. In 1982, it was estimated that approximately 1,100 Ph.D. holders could trace their scientific roots to Kolthoff. When the American Chemical Society inaugurated an award for excellence in 1983, he was the first recipient.