Fifty years of semiconducting electrodes

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The field of semiconductor electrochemistry began once good control of impurities in semiconducting materials was achieved. The electronic industry first tried to use electrochemistry to polish the surface of monocrystalline silicon when Uhlir and Turner ended up producing porous silicon (without knowing it) which remained a curiosity until its room temperature visible photoluminescence was discovered ten years ago by Canham. For the past forty years Gerischer, working on monocrystalline III-V semiconductors, set down the fundamentals of the semiconductor/electrolyte interface. Thirty years ago, photoelectrolysis of water using monocrystalline TiO_2, published by Fujishima and Honda, was the trigger for the new field of "photoelectrochemistry" which became a very popular field of research. New materials like lamellar semiconductors were introduced by Tributsch which exhibited high efficiency photoelectrochemical properties when defect-free, van der Waals surface were used. Semiconductors commonly used in photovoltaics such as silicon, II-VI alloys and III-VI alloys exhibited excellent photoelectrochemical properties but suffered photocorrosion problems which were partly solved. The dye-sensitized, nanocrystalline TiO_2 liquid device proposed by Grätzel gave a major thrust to the field of photoelectrochemistry of nanostructured semiconductors. Shortly afterward, the concept of kinetic control of photoelectrochemical cells in nano-crystalline semiconductors in which no space charge layer was expected was demonstrated by Hodes and others. Fujishima's work has led to widespread application of photoelectrochemistry in an extraordinarily wide-ranging project based primarily on self-cleaning, nanostructured TiO_2 substrates. The corrosion process of semiconductors, which is so deleterious for photoelectrochemical-to-electricity conversion, turned out to be a powerful technique to produce porous semiconductors, including porous silicon. Numerous studies have been undertaken to understand the mechanism of formation of porous semiconductors leading to excellent control of the size and shape of the pores and to numerous application in the fields of sensors, photonic bandgap materials and photovoltaics. The science of manipulating atoms at the surface of semiconductors in an electrolyte using STM has emerged and is still in its infancy. Electrochemical deposition has been successful in producing 1D and 2D nanoparticles and nanostructured semiconductors. For probing the photoelectrochemical reactivity and kinetics of charge transport at nanostructured semiconductor or quantum dots/electrolyte interfaces, new characterization tools such as intensity modulated photocurrent (IMPS) and photovoltage (IMVS) spectroscopies and microwave-based techniques have been developed by Peter, Vanmelkerberg, Tributsch, Frank and others, while most recently, the promising in situ XPS surface characterization at electrode surfaces in solution has been developed by Jägermann at the German synchrotron (BESSY).