BIOINSPIRED PHOTOELECTROCHEMISTRY

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The topic of this talk is inspired by Prof. Adam Heller, whose pioneering contributions, especially during the post-Bell Labs years, spanned both the fields of photoelectrochemistry/photocatalysis and bioelectrochemistry. A recurring theme in his studies was the virtue of nanostructured architectures on electrode surfaces for driving targeted multi-electron processes. Of course Nature has evolved such intricate self-assembled architectures over millions of years, and remarkably enough, none of these structures rely on precious metals such as Pt for the catalytic function. The second feature of these assemblies is that all the components are designed for complementarity in that they perform specific functions that as a whole contribute toward achieving the net goal of moving electrons and protons toward a targeted reaction site. In this talk, I shall outline how we can learn from Nature in designing multi-component photoelectrochemical assemblies for solar splitting of water and CO_2.

The talk will begin with a history-tinged perspective on what has been accomplished in photoelectrochemistry and photocatalysis over a 35-year timeframe from 1975 through 2010 [1]. Progress in this field was aided by the infusion of new concepts and contributions from the materials chemistry and physics communities. A related aspect of discussion is how the active semiconductor material has evolved both chemically and morphologically in these applications. It is shown that despite impressive research advances, only a handful of the above concepts (e.g., dye-sensitized solar photon conversion, self-cleaning and anti-fogging surfaces) have made the successful transition from the laboratory to the marketplace.

Oxide semiconductors are eminently attractive candidates as the active material in solar photovoltaic or photocatalysis systems both from inherent cost and photochemical stability considerations. The prototype oxide is TiO_2; however, it has too large an energy band gap, E_g (3.0-3.2 eV), for efficiently harnessing solar energy. Yet, the photocatalysis community has largely continued to focus on this oxide material in spite of its many handicaps. Strategies for getting out of the "titania rut" will be outlined. In this regard another lesson to be learnt from Nature is that it is extremely unlikely that single-component systems will be successful in being able to efficiently drive multi-electron photoprocesses of interest such as water and CO_2 splitting

In this regard, electro- and photoelectrosynthetic methods for preparing complex photoelectrode architectures (including organic-inorganic hybrids) will be discussed. Strategies for electrodeposition of inorganic semiconductors that incorporate galvanic displacement as an integral step will be presented using CdSe-ZnO [2] and Au-ZnO [3] as test systems. The utility of substrate photoexcitation as a synthetic tool will be illustrated using polypyrrole- and polyaniline-impregnated oxide semiconductor nanostructures [4] as examples.

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This paper is dedicated to Prof. Adam Heller who inspired so many of us with his insights into the importance of surface chemistry on photoelectrochemical activity, on chemical effects in semiconductor/metal electronic barriers, conjugate reaction kinetics in photocatalytic processes, and so many other aspects of semiconductor-solution interfaces. Equally important he taught at least one of us (KR) that human qualities are as important as intellectual stature; I am forever indebted to him as a mentor and teacher.

References

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