Engineering Active and Stable Semiconductor Photoelectrodes by Atomic Layer Deposition

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The capture of solar energy and its direct conversion to chemical fuel in artificial photosystems provides a promising route to sustainably meet global energy demands and to overcome our current reliance on fossil fuels. However, development of practical photosystems has been impeded by a lack of semiconductor light absorbers that are simultaneously efficient and stable under the reactive conditions required for driving desired chemical transformations. To address this issue, new strategies based on atomic layer deposition (ALD) of conformal corrosion protection layers onto photoelectrode surfaces have recently been developed and yield highly robust systems. Here, we provide an overview of such approaches, discuss outstanding challenges that must be addressed, and highlight a multi-functional water splitting catalyst that is specifically engineered to be interfaced with semiconductor light absorbers. In particular, plasma-enhanced ALD is used to create biphasic cobalt oxide composites that strike a careful balance of necessary chemical, optical, and electrical properties [1]. This coating consists of nanocrystalline Co_3O_4 spinel that is physically robust and provides a stable interface with the chemically sensitive light absorber. This is combined with a chemically labile and disordered $Co(OH)_2$ surface layer that can be easily activated to provide high catalytic activity (Fig. 1). Functional characteristics of the working interface are probed by advanced *in situ* electrochemical X-ray photoelectron spectroscopy, which reveals how the interface transforms from the resting to the active state [2]. Application of the protective catalyst to Si photoanodes results in long-term stable operation with high photochemical activity. These results demonstrate that PE-ALD is a powerful method for synthesizing multi-functional catalysts that support desired chemical transformations, permit efficient interfacial charge transport, and minimize parasitic light absorption due to their conformal nature even at very low thicknesses.

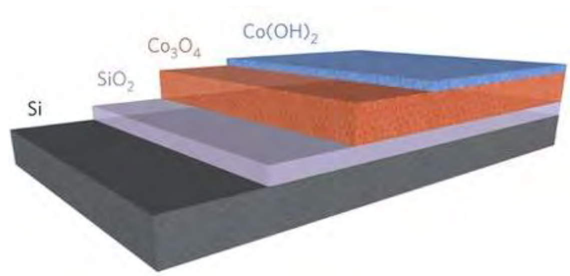

Figure 1: Schematic illustration of the biphasic $Co_3O_4/Co(OH)_2$ coating formed by PE-ALD that provides high stability and catalytic activity when coupled to a Si photoanode.

[1] J. Yang, et al., Nature Mater. **16**, 335 (2017).

[2] M. Favaro, *et al.*, J. Am. Chem. Soc. **139**, 8960 (2017).

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