Nanoscale charge transport in water splitting photoanodes

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Photoelectrochemical (PEC) water splitting is a promising approach to provide carbon neutral power and renewable fuels. In this context, a highly interesting semiconductor light absorber is bismuth vanadate ($BiVO_4$). $BiVO_4$ has a moderate bandgap, favorable band alignment for water oxidation, relatively long charge-carrier diffusion length, and it can yield high quantum efficiencies under water oxidation conditions.[1-3] However, its PEC performance is limited by poor majority carrier transport, stoichiometry deviations, and structural defects leading to interfacial charge trapping and non-uniform energy landscapes. To unravel the performance limitations in energy materials, accurate characterization of the charge transport mechanism is necessary which will enable design and development of new functional systems.

We used photoconductive AFM in carefully controlled environments (*in-situ*) to characterize nanoscale charge transport in $BiVO_4$ photoelectrodes. Specifically, we revealed the critical impact of (i) contact formation between the nanoscale probe and semiconductor [4] and of (ii) chemical environment and surface/adsorbate interactions on nanoscale transport measurements of PEC devices [5]. We revealed the impact of contact formation between probe and surface on image contrast, which allowed detecting morphology-dependent variations in the optoelectronic properties. We showed that the local current voltage characteristics can be modeled as a space-charge-limited current in the presence of trap states, which in turn allowed us to quantify the impact of shallow defect states on charge transport in $BiVO_4$ films. The overall charge transport properties are impacted by both bulk and surface states, whereby the latter are strongly modified by surface adsorbates. Therefore, we elucidated the influence of chemical interactions of adsorbed oxygen and water on charge transport and interfacial charge transfer of photogenerated charge carriers by combining *in-situ* Kelvin probe spectroscopy and photoconductive atomic force microscopy. The research revealed that surface-adsorbed oxygen acts as a shallow trap state limiting electronic performance of $BiVO_4$ thin films, and it contributes as much as 40% to the total trap state density.

References

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