Università degli Studi di Padova

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Venerdì **28 febbraio 2025** alle ore **12:30 presso l'aula C** del DiSC

il Dr. Marco Favaro

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terrà il seminario dal titolo:

Charge Separation Mechanisms and Electrolyte Effects in Photoelectrochemistry:

From Chemical Potential Gradients to Enhanced Performance

The most common explanation for photocurrent generation in photoelectrodes assumes that electron-hole pair separation occurs near the surface due to the internal built-in electric field created by band-bending at the solid/liquid interface in equilibrium (i.e. dark conditions, no bias applied). This interpretation suggests that the built-in electric field independently drives positive and negative charges toward their respective contacts. However, this view leads to the several discrepancies that will be described in the talk. As it will be discussed, it is the gradient of the charge carrier's chemical potential (i.e. their QFLs under non-equilibrium conditions) that actually drives the charge separation, via the establishment of selective contacts for electrons and holes [1, 2]. The usual FTO/semiconducting photoanode interface is likely acting as a "good enough" electron selective contact, thus imposing enough gradient to the QFLs to drive the charge separation under illumination conditions. It will be discussed how the so-far lack of optimized selective contacts for semiconducting oxides (together with defect trap states and polaron-type of transport) could explain why the observed photovoltage for this class of materials is consistently well below their detailed balance (Schottky-Queisser) limit [3]. In the second part of the talk, the influence of various acidic electrolytes (KPi, K_2SO_4, Na_2SO_4, $NaClO_4$, and $NaNO_3$; pH = 2) on the PEC glycerol oxidation over $BiVO_4$ will be discussed. We observed that $BiVO_4$ exhibited the following GOR performance trend: $NaClO_4$, $NaNO_3$ > Na_2SO_4 > K_2SO_4 > KPi, with the photocurrent in NaClO4 ~3-fold of that in KPi [4]. Although our $BiVO_4$ photoanodes exhibited the highest photocurrent in $NaClO_4$, the low production rate of GOR products, due to the poor stability of BiVO4 in this electrolyte solution, made it less promising than $NaNO_3$. $NaNO_3$ emerged as the preferred electrolyte for PEC glycerol oxidation on $BiVO_4$, offering superior performance in terms of photocurrent, stability, and selectivity towards value-added GOR products [4, 5]. Glycolaldehyde was identified as the most dominant GOR product in our study, achieving a selectivity of more than 50% in $NaNO_3$.

[1] M. Schleuning et al., Sust. Energy Fuels 2022, 6, 3701-3716
[2] T. Hannappel et al., Solar RRL 2024, 8, 2301047
[3] J. Garcia-Navarro, et al. Global Challenges, 2023, 2300073
[4] H. Kong et al., Chem. Sci. 2024, 15, 10425-10435
[5] A. F. Pérez-Torres et al., Chem. Commun. 2025, 61, 2083-2086

La presenza della S. V. sarà molto gradita

Il Direttore del Dipartimento

Stefano Agnoli

Stefano Mammi