

Photoelectrode Architectures for Hybrid Organic/Inorganic Photoelectrochemical Water Splitting

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Hydrogen production through renewable sources, rather than fossil fuels, represents the missing element towards a carbon neutral energetic cycle. One of the most promising approaches is the direct conversion of solar energy into chemical fuels at a low cost semiconductor/water junction. Despite the theoretical simplicity of such a device, different limitations on suitable semiconductor materials' characteristics have hindered its development. In the last years, the capability of semiconductive polymers/fullerene-based acceptors compounds to steadily drive photo-generated electrons towards an electrocatalyst in a water environment was demonstrated.

We present a study of different architectures of hybrid organic-inorganic H₂ evolving photocathodes based on semiconducting polymeric absorbers. The relevance of this study can be summarized in few key points: (i) high performances with photocurrents up to 8 mA/cm² at 0V_{RHE}; (ii) optimal process stability with 100% faradaic efficiency along electrode's lifetime; (iii) excellent energetics with onset potential as high as +0.7V_{RHE}; (iv) promising operational activity of more than 10 hours and (vi) by-design compatibility for implementation in a tandem architecture. Collectively, this set of features establishes hybrid architectures employing organic semiconductors and organic photoelectrochemical systems as promising candidates for efficient solar fuel production.

Suitable materials were first investigated. Different PVD or solution processed inorganic interfacial layers (MoO₃, WO₃, CuI, TiO₂/Pt) and their influence on performances have been assessed, enlightening the working principles and limiting factors of actual implementations. We show the photocatalytic activity and long-term stability of a catalysed bulk heterojunction and the effect of selective contacts on performances is investigated separately. Introduction of an electron selective layer increases the photocurrent response while hole blocking layers shift the onset potential towards positive voltages allowing operation with a tandem photoanode and/or a PV cell.

Secondly the influence of system nanostructuring was assessed, the development of multi-layer systems based on structured absorbers in a host/guest architecture allowed us to orthogonalize light absorption and photogenerated carrier collection.

Finally, seeking the realization of an efficient and cost-competitive photocathode we combined PVD and solution-processed techniques realizing a 2"x2" photoelectrode in order to show the potential of cheap, large-scale production of organic photoelectrochemical systems. Such a system exhibits 0.8 mA/cm² at 0V_{RHE}, an onset potential of +0.7V_{RHE} and stability of over 1hr.

This work opens the way to the exploitation in photoelectrochemistry of organic semiconductors developed for OPVs and to the realization of a new generation of water splitting devices for renewable and low cost direct conversion of sunlight into H₂.