Graphite-protected organic photoactive layer for direct solar hydrogen generation

Performance issues have limited the use of organic photoactive materials in direct solar water-splitting devices. Now, anodes containing a single-junction organic bulk heterojunction solar cell protected by a graphite sheet functionalized with an Earth-abundant electrocatalyst achieve a high water oxidation photocurrent density and days-long operational stability. Moreover, tandem devices achieve unassisted solar water splitting.

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The mission

Organic photoactive materials have been developed for high-performance solar cells with photocurrent densities of >25 mA cm^{-2}. Owing to their tuneable optical and electronic properties and large-scale solution processability, organic photoactive materials are also of interest for applications in photoelectrochemical cells to produce solar fuels, such as hydrogen, and chemicals[1]. However, the most efficient organic photoactive materials are typically not stable in an aqueous environment, limiting their application in devices for direct solar water splitting[2]. Moreover, their direct application is hampered by recombination losses at the interface with catalysts. Thus, to date, the high photocurrents and stability achievable with organic solar cells have not been translated to photoelectrodes.

If these challenges were addressed, then organic photoactive materials could be applied in integrated photoelectrochemical systems to generate solar fuels without the need to wire photovoltaic devices to electrolysers. The integrated design is simpler and, thus, more cost effective, and allows for beneficial photothermal effects on the catalytic activity[3–5].

The discovery

We fabricated single-junction organic solar cells protected with self-adhesive graphite sheets functionalized with an Earth-abundant nickel–iron oxyhydroxide (NiFeOOH) electrocatalyst and used them as anodes for solar water oxidation. We refer to these devices as integrated photovoltaic (IPV)-anodes (Fig. 1a). The multifunctional graphite sheet provides protection from water, electrical contact for the extraction of charge carriers from the photoactive layer to the electrocatalyst, and a highly active NiFeOOH electrocatalyst at the electrolyte interface.

Each IPV-anode comprises a SnO_2 electron transport layer, an organic photoactive layer consisting of a ternary bulk heterojunction blend of PM6 and D18 donor polymers and the non-fullerene accepter L8-BO, a MoO_3 hole transport layer, a thin gold layer and the graphite sheet functionalized with the NiFeOOH catalyst (Fig. 1a). The direct electrical connection between the different layers eliminates almost all electrical losses between the photoactive layer and the electrocatalyst. IPV-anodes based on the PM6:D18:L8-BO photoactive layer with optimized transport layers and layer thicknesses achieved a photocurrent density of 26 mA cm^{-2} at an applied potential of +1.23 V versus the reversible hydrogen electrode (Fig. 1b), matching the short-circuit current density of the best-performing organic solar cells.

The organic IPV-anodes also achieved days-long operational water oxidation stability (maintaining 70% of their initial photocurrent after 40 h) when using an ultraviolet filter, compared with less than 1 h stability without the graphite sheet (Fig. 1c). The loss of electrocatalyst owing to the generated oxygen bubbles was detrimental to photocurrent stability; however, this issue can be overcome by electrodepositing a thicker, more robust layer of NiFeOOH and by replacing the graphite sheet upon signs of deterioration. Spectroscopic analyses revealed that the primary factor limiting the operational stability of the single-junction IPV-anodes was the morphological instability of the organic photoactive layer.

The days-long stability enabled us to compare the light-intensity dependence of IPV-anode performance as solar cells and in photoelectrochemical cells. Unlike the solar cells, at light intensities of <30 mW cm^{-2}, there is increased charge recombination in the IPV-anode, probably due to insufficient energetic driving force at the IPV-anode–electrolyte interface. This issue might be avoidable by using photoactive materials with deeper energy levels.

Building on the single-junction IPV-anodes, we fabricated tandem IPV-anodes containing two organic bulk heterojunction photoactive layers with complementary light absorption. The tandem devices generated a high photovoltage of >2 V, enabling unassisted (that is, bias-free) direct solar water splitting with 5% solar-to-hydrogen efficiency.

The implications

With current densities close to those of the best organic solar cells and days-long stability, our IPV-anodes open an avenue for further research into integrated photoelectrochemical devices for water oxidation and reduction, as well as other chemical reactions.

The next challenge is to increase the operational stability of organic IPV-anodes to weeks, months and, eventually, years. Importantly, this goal needs to be achieved with tandem devices operating without external bias. Our findings indicate that advancing the stability and performance of tandem IPV-anodes for direct solar water splitting will require targeted efforts in the application of organic bulk heterojunction layers with enhanced morphological stability, the development of more effective electrocatalysts, and the optimization of local pH control and bubble management.

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EXPERT OPINION

"The outstanding and customizable optoelectronic properties of organic semiconductors make them ideal-to-manufacture electrodes for solar water splitting, but their rapid degradation and poor response under operation, especially for solar water oxidation, are major challenges. This study demonstrates that a graphite coating can extend their lifespan and maximize their performance, rivalling photovoltaic counterparts. Overall, this pioneering work is a significant step towards competitive solar water splitting devices." **Néstor Guijarro, University of Alicante, Alicante, Spain.**

FIGURE

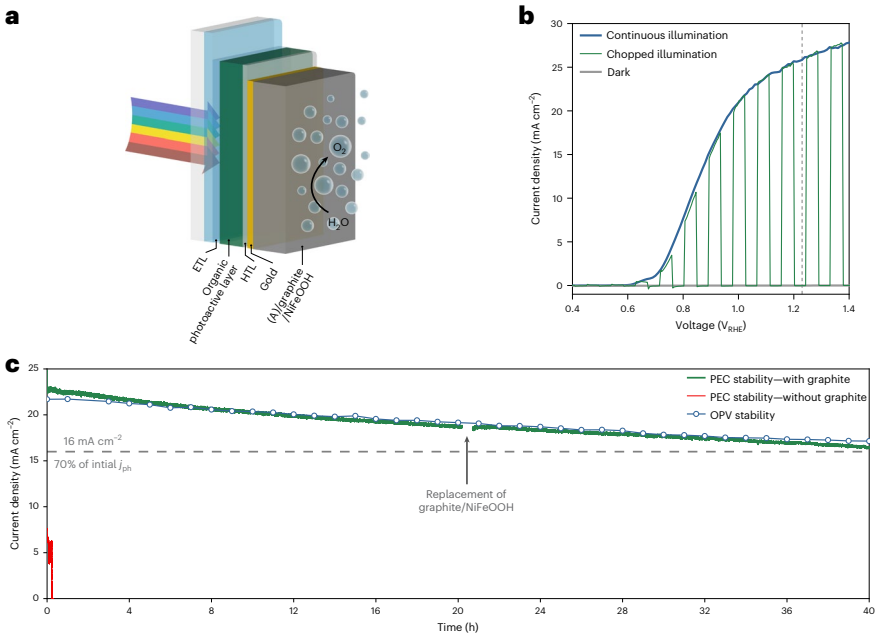

Fig. 1 | Organic bulk heterojunction IPV-anode for solar water oxidation. a, The organic IPV-anode for water oxidation consists of an organic PM6:D18:L8-BO photoactive layer between the electron and hole transport layers (ETL and HTL, respectively) and a self-adhesive (A) graphite sheet functionalized with NiFeOOH that serves as a conductive protective layer. **b**, Typical current–voltage scans of an organic IPV-anode under continuous and chopped 1 sun illumination and in the dark. The dashed vertical line at +1.23 V_{RHE} indicates the standard oxidation potential of water to oxygen. **c**, Operational photoelectrochemical (PEC) stability of an organic IPV-anode with and without the graphite layer under continuous 1 sun illumination with an ultraviolet filter at +1.23 V_{RHE}, compared with that of an organic photovoltaic (OPV) device with the same composition at 0.2 V. A 1 M aqueous NaOH electrolyte was used. j_{ph}, photocurrent density.

BEHIND THE PAPER

This work comes from years of exploring materials for photoelectrochemical applications. In our search for materials for solar water splitting, we started with inorganic oxides, which were valuable for studying the charge transfer dynamics but did not deliver high photocurrents and photovoltages. We then transitioned to halide perovskites, which helped to increase the photocurrent and challenged us to develop effective protection strategies. Finally, we focused on organic bulk heterojunctions, which enabled us to simultaneously achieve high photocurrents and stability after elucidation of the role and limitations of each layer in the performance of the IPV-anodes.

'Eureka!' moments were when we hit a photocurrent of 26 mA cm^{-2} with our IPV-anodes and achieved unassisted solar water splitting with the tandem devices. These breakthroughs were made possible by the collaborative environment fostered by the Centre for Processable Electronics and the Seeds for Success programme at Imperial College London. **M.D. & S.E.**

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FROM THE EDITOR

"Few solar hydrogen devices based on organic photoactive layers are able to achieve both promising efficiency and stability, but this work does just that. My hope is that devices with even higher performance will follow in the future based on design aspects discussed here." **James Gallagher, Senior Editor, *Nature Energy*.**