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Virtually free clean hydrogen generation by photoelectrochemical devices?

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This preview highlights a halide perovskite-based photoelectrochemical device that allows simultaneous generation of clean hydrogen and production of value-added product from polymeric waste materials with high selectivity. This concept provides an exciting new avenue for significant cost reduction of solar hydrogen.

The role of hydrogen in the future energy mix is becoming increasingly important worldwide as it plays a crucial part in most countries' strategy toward net zero emissions.[1,2] The high potential of hydrogen stems from the possibility of using it as an energy vector for long-term and large-scale energy storage to overcome the challenge of intermittent solar power generation. Currently, "blue hydrogen" by methane reforming is the cheapest ($1–2 kg^{-1}) form of hydrogen production, which is an unsustainable, carbon-intensive process. A promising solution is the generation of green hydrogen by direct water splitting using the most abundant energy resource on Earth: solar energy. This technology, "photoelectrochemical water splitting", is at a low technology readiness level and in order to become competitive the current estimated price of hydrogen (~$10 kg^{-1}) needs to be reduced.[3]

In photoelectrochemical water-splitting, due to the high overpotential of water oxidation (>+0.8 V without, and >+0.3 with the best catalysts), a significant amount of energy is lost producing oxygen, which is a low market value product. An exciting, alternative approach to reducing the cost of solar hydrogen is performing oxidation of polymeric waste at the photoanode (e.g., biomass, plastics), which can result in the production of a value-added product and reduced energy consumption at the same time. The lower energy consumption is due to the thermodynamically less demanding process of biomass oxidation, compared to water oxidation, which could also allow for bias-free operation even with a single photoactive layer.[4]

By changing the oxygen evolution reaction to the generation of a sufficiently high value product, one could envisage a system where hydrogen is produced as a virtually free by-product. An example is the oxidation of biomass-derived glucose into glucaric acid, which is a key intermediate for biodegradable polymer and detergent production, with its market size expected to reach $1.30 billion by 2025.[5] In reality hydrogen does have a market value, meaning that its price would only need to meet targets (e.g., the $2 kg^{-1} target of the US Department of Energy) allowing it to become economically favourable compared to blue hydrogen.[2] There are a few reports of photoelectrochemical devices producing hydrogen and a value-added product, but they either require high applied external bias or generate only relatively low photocurrent densities.[6]

Bhattacharjee et al. have recently achieved remarkable development by demonstrating a perovskite-based photoelectrochemical device capable of bias-free biomass reforming of real-world polymeric waste on the anode and hydrogen generation on the photocathode under 1 sun (AM 1.5G, 100 mW cm^{-2}) illumination with orders of magnitude (10^2-10^4) higher activity compared to conventional photoreforming systems.[7] The photocathode of the two-compartment device (Figure 1A) was based on an p–i–n structure solar cell with an ~1.6 eV bandgap mixed-cation perovskite photoactive layer, which was protected from the aqueous environment by a conductive graphite epoxy. The catalyst for the hydrogen production was platinum (perovskite|Pt photocathode), while for the oxidation a bimetallic $Cu_{30}Pd_{70}$ alloy was developed with flower-like microstructure on Ni foam (Ni|$Cu_{30}Pd_{70}$ anode).

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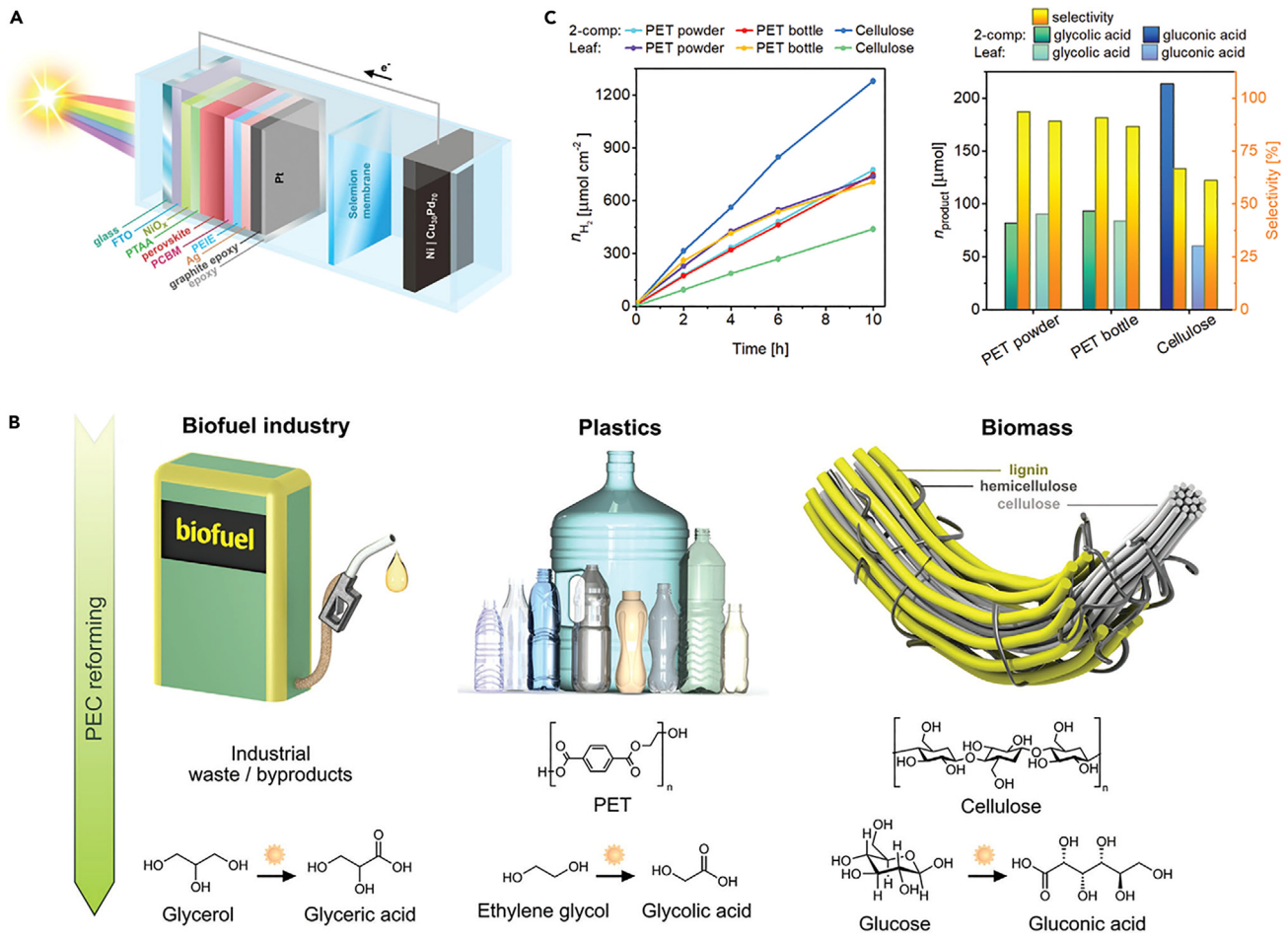

Figure 1. Perovskite-based photoelectrochemical device for simultaneous hydrogen and value-added product generation

Adapted from Bhattacharjee et al.[7]

(A) Schematic of the two-compartment photoelectrochemical device with perovskite|Pt photocathode and Ni|$Cu_{30}Pd_{70}$ anode.

(B) Illustration of waste materials and the value-added products that can be generated from them by reforming.

(C) The amount of hydrogen and value-added oxidation products produced during bias-free operation from real-world substrates of PET powder, PET bottle, and cellulose.

Importantly, the presented photoelectrochemical device was tested for the reforming of different waste materials (glycerol as waste feedstock, ethylene glycol derived from PET and glycol produced from biomass) into industrially relevant high value products (glyceric acid, glycolic acid and gluconic acid, respectively) as illustrated in Figure 1B. A significant achievement of the work is the high selectivity (91%) toward the aimed high value chemical of glycolic acid produced from a real-world PET bottle. The high selectivity resulting from the novel $Cu_{30}Pd_{70}$ micro-flower catalyst is essential for the future application of such devices. This was accomplished at a rate of 9.3 µmol cm^{-2}- h^{-1} for the oxidation product, in parallel with a hydrogen generation rate of 74.8 µmol cm^{-2}- h^{-1} with above 90% Faradaic efficiency (Figure 1C). The origin of such remarkable performance is in the combination of the perovskite photoelectrode generating sufficient photovoltage (>1 V), the high catalytic activity of $Cu_{30}Pd_{70}$ and the two-compartment device allowing for the separation of the oxidation and reduction reactions. The reported high rates of product formation are major improvements (at least 100 times) compared to the best conventional waste photoreforming.[8]

Further to the high rates and selectivity achieved with bias-free operation, the system presented by Bhattacharjee et al. has several other advantages including the need for only one photoactive layer to produce the necessary photovoltage due to the thermodynamically less demanding oxidation reaction (compared to water splitting) allowing for a less complex, single-junction device. This enables the use of non-transparent waste streams, while the two-compartment setup also allows

for separating in space the oxidation and reduction processes.

Even after such considerable leap forward, there is large space left for further development before photoelectrochemical devices for hydrogen and value-added product generation could be applied commercially. The long-term stability of these perovskite-based systems remains a challenge, as the presented continuously decreasing photocurrents during a few hours need significant improvement to reach closer to the required years-long operation. Bridging the gap between the model and real-world substrate reforming in terms of product yield as well as selectivity for biomass-derived glucose would increase economic viability. Finally, future research directions should also include up-scaling and importantly the application of catalyst consisting of Earth-abundant materials (i.e., replacement of the precious metal Pt and Pd).

The potential for reducing the cost of clean hydrogen production by biomass valorization is high, considering that ~10% of the world's energy need could be met if all available biomass waste was used for hydrogen generation.[9] The work highlighted here by Bhattacharjee et al. points toward a bright future for simultaneous hydrogen and value-added product generation by photoelectrochemical devices, which will be reached once the above-mentioned challenges are addressed.

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DECLARATION OF INTERESTS

The author declares no competing interests.

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