

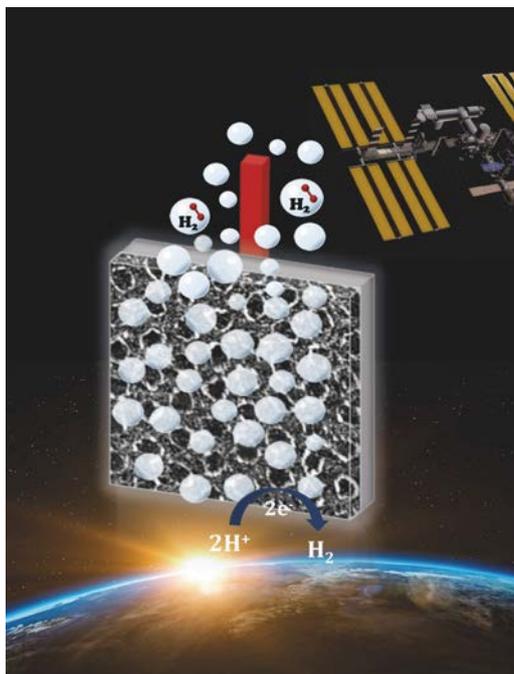
## Advancing Semiconductor-Electrocatalyst Systems: Application of Shadow Nanosphere Lithography for Efficient Solar Hydrogen Production in Terrestrial and Microgravity Environments

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Efficient artificial photosynthesis systems follow the concept of the Z-scheme of natural photosynthesis. They are realized as catalyst- and surface-functionalized photovoltaic tandem devices enabling photoelectrochemical water oxidation while simultaneously recycling CO<sub>2</sub> and generating hydrogen as a solar fuel for storable renewable energy. Inorganic systems have yielded the hitherto highest efficiencies and stabilities when combining surface modified photovoltaic tandem absorbers with high activity electrocatalysts [1, 2]. The introduction of corrosion-derived surface protection films has resulted in a substantial increase of the efficiency-stability product that determines the ultimate cell output. Several avenues of catalyst preparation have been followed such as sputtering, evaporation and e-beam lithography. A practical approach to obtain desired catalyst nanostructures of high fidelity is provided by shadow nanosphere lithography (SNL) [3].

We demonstrate that the method allows direct deposition of the catalyst on photoactive semiconductors and that SNL can be used as a tool to specifically modify and design electrocatalyst structures. Our approach allows tuning of the optical properties of the electrocatalysts, it alters the catalytic activity via the exchange current density and influences the genesis of gas formation. First results are demonstrated by means of the photoelectrochemical production of hydrogen on p-type InP photocathodes where standard photoelectrodeposition and SNL deposited Rh electrocatalysts are compared based on their I-V and spectroscopic behavior. Structural analyses include scanning probe microscopy, HRSEM and TEM and the surface chemistry is analyzed by photoelectron spectroscopy. The optical performance is compared to theoretical models on light scattering and propagation. Our findings indicate that the designed electrocatalyst nanostructures provide significant advantages for the photoelectrocatalytical half-cell performance, to the fore, for solar-assisted hydrogen production in microgravity environments, realized in an experimental series at the Bremen Drop Tower.

We demonstrate that shadow nanosphere lithography can be used as prosperous tool to precisely change the surface nano- and microtopography of the electrocatalyst on a lightabsorbing semiconductor surface and therefore, establish new routes for the further development of efficient prototypes for unassisted solar fuel generation.



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