Journal of Visualized Experiments

Efficient Solar Hydrogen Production in Microgravity Environment: Experimental Methods

--Manuscript Draft--

Article Type:	Invited Methods Article - JoVE Produced Video
Manuscript Number:	JoVE59122R3
Full Title:	Efficient Solar Hydrogen Production in Microgravity Environment: Experimental Methods
Keywords:	Solar Fuels, Photoelectrochemistry, Microgravity, Hydrogen, Photoelectrocatalysis, Shadow Nanosphere Lithography, Solar Energy Conversion in Space
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Additional Information:	
Question	**Response**
Please indicate whether this article will be Standard Access or Open Access.	Standard Access (US$2,400)
Please indicate the **city, state/province, and country** where this article will be **filmed**. Please do not use abbreviations.	Berlin, Germany and Bremen, Germany

TITLE

Experimental Methods for Efficient Solar Hydrogen Production in Microgravity Environment

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KEYWORDS

solar fuels, hydrogen, microgravity, photoelectrocatalysis, drop tower, shadow nanosphere lithography, semiconductor-electrocatalyst systems

SUMMARY

Efficient solar-hydrogen production has recently been realized on functionalized semiconductor-electrocatalyst systems in a photoelectrochemical half-cell in microgravity environment at the Bremen Drop Tower. Here, we report the experimental procedures for manufacturing the semiconductor-electrocatalyst device, details of the experimental set-up in the drop capsule and the experimental sequence during free fall.

ABSTRACT

Long-term space flights and cis-lunar research platforms require a sustainable and light life-support hardware which can be reliably employed outside the Earth's atmosphere. So-called 'solar fuel' devices, currently developed for terrestrial applications in the quest for realizing a sustainable energy economy on Earth, provide promising alternative systems to existing air-revitalization units employed on the International Space Station (ISS) through photoelectrochemical water-splitting and hydrogen production. One obstacle for water (photo-) electrolysis in reduced gravity environments is the absence of buoyancy and the consequential, hindered gas bubble release from the electrode surface. This causes the formation of gas bubble froth layers in proximity to the electrode surface, leading to an increase in ohmic resistance and cell-efficiency loss due to reduced mass transfer of substrates and products to and from the electrode. Recently, we have demonstrated efficient solar hydrogen production in microgravity environment, using an integrated semiconductor-electrocatalyst system with p-type indium phosphide as the light-absorber and a rhodium electrocatalyst. By nanostructuring the electrocatalyst using shadow nanosphere lithography and thereby creating catalytic 'hot spots' on the photoelectrode surface, we could overcome gas bubble coalescence and mass transfer limitations and demonstrated efficient hydrogen production at high current densities in reduced gravitation. Here, the experimental details are described for the preparations of these nanostructured devices and further on, the procedure for their testing in microgravity environment, realized at the Bremen Drop Tower during 9.3 s of free fall.

INTRODUCTION

Our atmosphere on Earth is formed through oxygenic photosynthesis, a 2.3-billion-year-old process converting solar energy into energy-rich hydrocarbons, releasing oxygen as a by-product and using water and CO_2 as substrates. Currently, artificial photosynthetic systems following the concept of the energetic Z-scheme of catalysis and charge transfer in natural photosynthesis are realized in semiconductor-electrocatalyst systems, showing hitherto a solar-to-hydrogen conversion efficiency of 19 %[1-3]. In these systems, semiconductor materials are employed as light absorbers which are coated with a thin, transparent layer of electrocatalysts[4]. Intense research in this field is promoted by the global quest for renewable energy systems with hydrogen and long-chain hydrocarbons making excellent candidates for an alternative fuel supply. Similar obstacles are also faced on long-term space missions, where a resupply of resources from Earth is not possible. A reliable life-support hardware is required, employing an efficient air revitalization unit providing about 310 kg of oxygen per crew member per year, not accounting for extravehicular activities[5]. An efficient solar water-splitting device, capable of producing oxygen and hydrogen or reduce carbon dioxide solar-assisted and in a monolithic system would provide an alternative, lighter route to currently employed technologies on the ISS: the air revitalization unit is comprised of a separated system with an alkaline electrolyzer, a solid amine carbon dioxide concentrator and a Sabatier reactor for the reduction of CO_2.

Unprecedentedly, we realized efficient solar-hydrogen production in microgravity environment, provided by a 9.3 s during free-fall at the Bremen Drop Tower (ZARM, Germany)[6]. Using p-type indium phosphide as a semiconducting light-absorber[7,8] coated with a nanostructured rhodium electrocatalyst, we overcame substrate and product mass transfer limitations to and from the photoelectrode surface, which is an obstacle in reduced gravity environments due to the absence of buoyancy[9,10]. The application of shadow nanosphere lithography[11,12] directly on the photoelectrode surface allowed the formation of rhodium catalytic 'hot spots', which prevented hydrogen gas bubble coalescence and the formation of a froth layer in proximity of the electrode surface.

Herein, we provide experimental details of the p-InP photoelectrode preparation including surface etching and conditioning, followed by the application of shadow nanosphere lithography on the electrode surface and the photoelectrodeposition of rhodium nanoparticles through the polystyrene spheres. Furthermore, the experimental set-up in the drop capsule at the Bremen Drop Tower is described and details of the experimental sequence during the 9.3 s of free fall are provided. Sample installment and handling before and after each drop are outlined as well as the preparation of the drop capsule and its equipment to operate illumination sources, potentiostats, shutter controls and video cameras upon command.

PROTOCOL

1. Preparation of p-InP photoelectrodes

1.1 Use single crystal p-InP (orientation (111 A), Zn doping concentration of 5×10^{17} cm^{-3}) as the photoabsorber. For the back contact preparation, evaporate 4 nm Au, 80 nm Zn and 150 nm Au on the backside of the wafer and heat it to 400 °C for 60 s.

1.2 Apply Ag paste to attach the ohmic contact to a thin-plated Cu wire. Thread the wire to a glass tube, encapsulate the sample and seal it to the glass tube using black, chemical resistant epoxy.

1.3 In order to remove native oxides, etch the 0.5 cm^2 polished indium face of p-InP for 30 s in 10 mL of bromine/methanol solution (0.05 % w/v), rinse the surface with ethanol and ultrapure water for 10 s each and dry the sample under nitrogen flux. Prepare the solutions from ultrapure water and analytical grade chemicals with an organic impurity level below 50 ppb.

CAUTION: Bromine causes acute toxicity upon inhalation, skin corrosion and acute aquatic toxicity. Wear protective equipment such as safety glasses, gloves and lab coat. Work under the fume hood. Methanol is flammable, causes acute toxicity (oral, dermal and inhalation) and is known to cause specific target organ toxicity. Wear protective equipment such as safety glasses, gloves and a lab coat. Work under the fume hood.

1.4 Subsequently, condition the p-InP electrode photoelectrochemically in a standard three-electrode potentiostatic arrangement. Use a borosilicate glass cell with a quartz window as a photoelectrochemical cell in order to illuminate the sample with a white-light tungsten halogen lamp (100 mW/cm^2) during the procedure.

1.5 Adjust the light intensity with a calibrated silicon reference photodiode.

1.6 Prepare a 0.5 M HCl solution and purge it in the photoelectrochemical cell with nitrogen of 5.0 purity for 15 min.

1.7 Use potentiodynamic cycling between -0.44 V und +0.31 V at a scan rate of 50 mV s^{-1} for 50 cycles to photoelectrochemically condition the sample under continuous illumination.

CAUTION: Hydrochloric acid causes serious eye damage, skin corrosion and it is corrosive to metals. Furthermore, it possesses specific target organ toxicity following single exposure. Wear protective equipment such as safety glasses, gloves and a lab coat. Work under the fume hood.

2. Fabrication of rhodium nanostructures

2.1 Employ shadow nanosphere lithography (SNL)[11,12] for the formation of rhodium nanostructures on the p-InP photoelectrode. In order to create the polystyrene masks on the p-InP electrode, obtain mono-dispersed beads of polystyrene (PS) sized 784 nm at a concentration of 5% (w/v) and dissolve them in ultrapure water.

2.2 To obtain the final volume of 600 µL, mix 300 µL of the polystyrene bead dispersion with 300 µL of ethanol containing 1% (w/v) styrene and 0.1% sulphuric acid (v/v).

2.3 Apply the solution onto the water surface using a Pasteur pipette with a curved tip. In order to increase the area of the monocrystalline structures, turn the Petri dish gently. Carefully distribute the solution to cover 50% of the air-water interface with a hcp monolayer. Leave place for stress relaxation and avoid forming cracks in the lattice during the next preparation steps.

2.4 Protect the Cu wire of the photoelectrochemically conditioned p-InP electrodes with parafilm. Place them delicately under the floating closed packed PS sphere mask by carefully taping them to a microscope slide, preventing the samples from rotating. Gently remove residual water with a pipette and by evaporation, causing the mask to be subsequently deposited onto the electrode surface.

2.5 Take the electrode out of the Petri dish and gently dry the surface with N_2. Store the electrode under nitrogen until rhodium photoelectrodeposition (e.g., in a desiccator).

NOTE: The protocol can be paused here for up to one week.

3. Photoelectrodeposition of rhodium nanoparticles

3.1 For the photoelectrochemical deposit of rhodium nanoparticles through the PS sphere mask, place the electrode in an electrolyte solution containing 5 mM $RhCl_3$, 0.5 M NaCl and 0.5% (v/v) 2-propanol and apply a constant potential of V_{dep} = +0.01 V for 5 s under simultaneous illumination with a W-I lamp (100 mW/cm^2). Electrochemical specifications such as the electrochemical cell, reference and counter electrode are the same as for the photoelectrochemical conditioning procedure.

3.2 Rinse the photoelectrode with ultrapure water and dry it under a gentle flow of N_2.

3.3 In order to remove the PS-spheres from the electrode surface, place the electrodes for 20 min under gentle stirring in a beaker with 10 mL of toluene (the electrode should be covered with toluene). Subsequently, rinse the electrode with acetone and ethanol for 20 s each.

3.4 Remove residual carbon from the surface by O_2-plasma cleaning for 6 min at a process pressure of 0.16 mbar, 65 W and gas inflows of O_2 and Ar of 2 sccm and 1 sccm, respectively.

3.5 Prepare the samples up to one week prior to tests in the drop tower and store them until the experiments under N_2 atmosphere in the dark (e.g., in a glove bag or desiccator).

NOTE: The protocol can be paused here for about 1-2 weeks.

4. Photoelectrochemical experiments in microgravity

4.1 For the experiments in microgravity environment, contact one of the major drop tower facilities, (e.g., the Centre of Applied Space Technology and Microgravity (ZARM), Bremen Germany).

NOTE: By employing a catapult system, 9.3 s of microgravity environment can be generated at ZARM with an approached minimum g-level of about $10^{-6}\ \mathrm{m \cdot s^{-2}}$[13]. A hydraulically controlled pneumatic piston-cylinder system is used to launch the drop capsule (**Figure 1A**) upwards from the bottom of the tower. The capsule is decelerated again in a container which is placed onto the cylinder system during the time of free fall.

4.2 Use a two-compartment photoelectrochemical cell (filling volume of each cell: 250 mL) for the photoelectrochemical experiments in order to carry out two experiments in microgravity environment in parallel. The front of each cell should consist of an optical quartz glass window (diameter: 16 mm) for illuminating the working electrode (see **Figure 1B**).

4.3 Employ a three-electrode arrangement in each cell for the photoelectrochemical measurements with a Pt counter electrode and an Ag/AgCl (3 M KCl) reference electrode in $HClO_4$ (1 M). Add 1% (v/v) isopropanol to the electrolyte in order to reduce the surface tension and enhance gas bubble release. Use a W-I white light source for illuminating each cell compartment through the optical windows.

CAUTION: Concentrated perchloric acid is a strong oxidizer. Organic, metallic and non-organic salts formed from oxidation are shock sensitive and pose a great fire and explosion hazard. Wear safety glasses, gloves and a protective lab coat. Work under the fume hood and minimize bench top storage time.

4.4 For gas bubble investigations, attach two cameras to each cell via optical mirrors and beamsplitters (e.g., a color camera at the front and a monochromatic camera at the side, see **Figure 1**) to record gas bubble evolution during free fall of the experiment. For each drop, store the recorded data on an integrated board computer in the drop capsule. Record single pictures at a frame rate of (e.g., 25 fps (color camera) and 60 fps (monochromatic camera)).

4.5 The drop capsule is equipped with several boards (**Figure 1**). Mount the photoelectrochemical set-up and the cameras onto an optical board and attach it to one of the middle boards in the capsule. Use the remaining boards for installment of additional equipment such as potentiostats, light sources, shutter controls and the board computer. Attach a battery supply at the bottom board of the capsule to power the set-up during free fall (**Figure 1**).

4.6 Set the capsule and the photoelectrochemical cell under Ar atmosphere prior to each drop. Maintain the Ar atmosphere during the evacuation time of the drop shaft (about 1.5 h), the experiment in free fall and during capsule recovery after the drop (about 45 min).

4.7 Write an automated drop sequence for the experimental steps which should be controlled and carried out in microgravity environment. The program should be started prior to each drop. Upon reaching microgravity environment, the sequence should automatically start cameras, illumination sources and the electrochemical experiment for the duration of 9.3 s while simultaneously immersing the working electrode into the electrolyte using a pneumatic system (see **Figure 1**, **Table 1**).

4.8 Investigation of light-assisted hydrogen production on the samples in photoelectrochemical measurements (e.g., cyclic voltammetry and chronoamperometry).

4.8.1 Control the electrochemical parameters by the two potentiostats in the capsule. For optimal resolutions in J - V measurements, use scan rates (dE/dt) of 218 mV/s to 235 mV/s in order to run 3 scan cycles in cycling voltammetry experiments, using voltage ranges of +0.25 V to -0.3 V *vs* Ag/AgCl (3 M KCl). Employ the initial potential, E_i = +0.2 V *vs* Ag/AgCl (3 M KCl) and the finishing potential, E_f = +0.2 V *vs* Ag/AgCl (3 M KCl). To compare the recorded J - V measurements, take the second scan cycle of each experiment for analysis.

4.8.2 In chronoamperometric measurements, use the time scale of generated microgravity environment, 9.3 s, to record the photocurrent produced by the sample. Apply potential ranges of -0.3 V to -0.6 V *vs* Ag/AgCl (3 M KCl) to compare produced photocurrents.

4.9 At the end of each drop, when the drop capsule is decelerated again to zero velocity, use the drop sequence to let the sample be removed from the electrolyte and cameras, potentiostats and illumination sources be switched off.

4.10 After retrieving the capsule from the deceleration container, remove the capsule protection shield. Remove the samples from the pneumatic stative, rinse them with ultrapure water and dry them under gentle nitrogen flux. Store them under N_2 atmosphere until optical and spectroscopic investigations are carried out.

4.11 Exchange the electrolyte in the two cells, ensure the function of all instruments before equipping the cells with new samples and prepare the capsule for another drop experiment.

REPRESENTATIVE RESULTS

Etching the p-InP surface in Br_2/ methanol for 30 s with consecutive photoelectrochemical conditioning of the sample by cycling polarization in HCl is well established in the literature and discussed (e.g., by Schulte & Lewerenz (2001)[14,15]). The etching procedure removes the native oxide remaining on the surface (**Figure 2**) and electrochemical cycling in HCl causes furthermore a considerable increase in the fill factor of the cell performance, accompanied by a flat band shift of the p-InP from +0.56 V to +0.69 V[15]. Furthermore, the passive layer formation during cyclic polarization in HCl photocathodically protects the InP surface from anodic corrosion. After the conditioning procedure, the self-assembly of 784 nm polystyrene latex nanospheres on the p-InP surface is employed for the formation of a colloidal particle monolayer which further on serves as a lithographic mask during the Rh deposition process (**Figure 3A, B**). **Figure 3B** shows an AFM image of the photoelectrode after removal of the PS spheres. The application of SNL results in a nanosized, two-dimensional periodic Rh structure with a homogenous array of holes in the metallic, transparent Rh film. The high-resolution AFM image (**Figure 3C**) illustrates the hexagonal unit cell structure with recognizable grains of Rh. Cross-section profiles in **Figure 3D** show that the rhodium mesh is homogenously distributed on the p-InP surface with a height of about 10 nm, forming a catalytic layer. Combined high-resolution TEM and FFT analysis were used to determine the lattice plane spacing, the distance of the diffraction points representing the reciprocal lattice space. Our calculations show that the lattice plane is in the order of 2.17 to 2.18 Å, validating the (111) cubic structure of the deposited rhodium (**Figure 4**). X-ray photoelectron spectroscopy reveals that the nanostructured p-InP-Rh electrode contains an InO_x/PO_x layer, with evidence being provided by the larger InP signal at 128.4 eV. This is not surprising due to the open InP areas resulting from the removal of the PS spheres; here, the InP is directly exposed to the environment (i.e., air and the electrolyte (**Figure 5**)).

The microgravity environment has been shown to have a significant impact on the electrolysis of water which has been known since the 1960s and the effect of reduced gravity on the motion of bubbles and drops is well-documented (see e.g., reference 16). Studies have been carried out especially within the frame of developing a life support system for space travel which includes a water-electrolyzing component.

Hitherto investigations of water electrolysis under microgravity environment in 'dark' experiments resulted in a stable gas bubble froth layer formation in proximity to the electrode surfaces and the accompanying ohmic resistance increased linearly to the froth layer thickness in both acidic and alkaline electrolytes[17-19]. Additionally, the diameter of the gas bubbles increased and the bubbles adhered to the membrane separating the two half-cells[20,21]. Furthermore, it was demonstrated that bubble-induced microconvection dominates the mass transfer in microgravity environments[8,21] and it has been suggested that mass transfer of the substrate water to the electrode surface controls the process of water electrolysis, which is controlled under normal gravity conditions by the electrode reaction[22].

The here employed nanostructured p-InP-Rh photoelectrodes manufactured via SNL could overcome this problem: the photocurrent-voltage measurements do not show significant differences between terrestrially tested samples in 1 M $HClO_4$ and samples tested in 9.3 s of microgravity environment at the Bremen Drop Tower (**Figure 6A, B**)[6]. J-V characteristics (**Figure 6A**), additionally, chronoamperometric measurements (**Figure 6B**) of the nanostructured samples are nearly identical in terrestrial and microgravity environment. The difference in the open circuit potential (V_{OC}) is attributed to performance differences of the photoelectrodes as shown earlier[6]. The introduced rhodium catalytic 'hot spots' on the p-InP surface by SNL allow the formation of gas bubbles to occur at distinct spots on the photoelectrode surface, preventing bubble coalescence and increasing the yield of gas bubble release. The addition of 1% (v/v) isopropanol to the electrolyte decreases the surface tension of the electrolyte furthermore, also leading toward favored gas bubble detachment from the electrode surface.

FIGURE AND TABLE LEGENDS

Figure 1: Scheme of the experimental set-up of the electrochemical experiments in microgravity environment. The images show the equipped drop capsule (**A**) and details of the photoelectrochemical set-up on the second platform of the drop capsule (**B**). The capsule contains batteries for power supply during free fall (platform 5), the capsule control system for experimental control (platform 4), two W-I light sources and a board computer (platform 3, see **Table of Materials**), the photoelectrochemical setup including four digital cameras (platform 2), and two potentiostats and two shutter control boxes (platform 1). The four digital cameras in the photoelectrochemical setup (platform 2) allows recording gas bubble formation on the photoelectrode from the front of each electrochemical cell through beam splitters and from the side through mirrors. The photoelectrodes were illuminated through the beam splitters in front of the cell. Via a pneumatic lifting ramp, the photoelectrodes are immersed in the electrolyte immediately before reaching microgravity conditions. This figure has been modified from Brinkert et al. (2018)[6].

Figure 2: Tapping-mode AFM topography images of the p-InP surface before and after the surface modifications steps. Panel **A** shows the p-InP surface before modification procedures, (**B**) after etching the surface in bromine/methanol solution and (**C**) after conditioning the sample in HCl. (**D**) Histogram analysis of the height distribution of terraces on the p-InP sample (blue line), after etching in bromine/ methanol (yellow line) and after conditioning in HCl (red line).

Figure 3: Tapping-mode AFM topography images (see Table of Materials) of the p-InP surface after application of shadow nanosphere lithography. (**A**) The deposited polystyrene particle monolayer on the p-InP substrate. (**B**, **C**) The surface after deposition of rhodium and removal of the polystyrene particles at two magnifications. (D) A height profile of three different spots on the electrode surface was generated to allow the further characterization of the deposited Rh mesh.

Figure 4: High-resolution TEM analysis of photoelectrodeposited rhodium grains on the p-InP electrode at different magnifications (see Table of Materials). The 2D-Fourier transformation images show the corresponding diffraction pattern with a lattice plane spacing of 2.2 Å (111), typical for cubic structures.

Figure 5: **X-ray photoelectron spectra of the nanostructured p-InP-Rh photoelectrodes.** (**A**) In 3d core levels; (**B**) P 2p core levels and (**C**) Rh 3d core levels. The color coding under the lines refers to the respective composition as illustrated in the legend. This figure has been modified from Brinkert et al. (2018)[6].

Figure 6: **Results of the photoelectrochemical experiments in microgravity environmen**t. (**A**) J-V measurements of nanostructured p-InP-Rh photoelectrodes in terrestrial (1 g, red) and microgravity environments (10^{-6} g, blue) in 1 M $HClO_4$ with the addition of 1% (v/v) isopropanol to the electrolyte at 70 mW/cm^2 illumination with a W-I lamp. Differences in the V_{OC} of the nanostructured samples in terrestrial and microgravity conditions are subject to performance differences of the photoelectrodes as shown earlier[6]. (**B**) Chronoamperometric measurements of the nanostructured p-InP-Rh photoelectrodes in terrestrial (red) and microgravity environment (10^{-6} g, blue) in 1 M $HClO_4$ with the addition of 1% (v/v) isopropanol to the electrolyte at 70 mW/cm^2 illumination with a W-I lamp. The applied potential was set to -0.09 V *vs* RHE. The increased signal-to-noise ratio at the end of the measurements is due to the deceleration of the drop capsule after 9.3 s.

Table 1: Detailed experimental sequence for photoelectrochemical hydrogen production hydrogen production in microgravity environment at the Bremen Drop Tower. This table has been modified from Brinkert et al. (2018)[6].

DISCUSSION

For the preparation of photoelectrodes, it is important to minimize oxygen exposure between the etching and conditioning procedure and to purge the 0.5 M HCl before usage for about 10 - 15 min with nitrogen. Once the samples are conditioned, they can be stored under nitrogen atmosphere in 15 mL conical tubes for a few hours to allow sample transport and/ or preparation time of the polystyrene particle masks. In order to achieve a homogenous arrangement of PS spheres on the electrode substrate, it is important to form a continuous mask of PS spheres on the water surface which can be observed as a continuous, reflective film. Once the mask is formed, the consecutive rhodium photoelectrodeposition step should follow in 2 - 3 h. The best results for a homogenous monolayer of PS spheres on the electrode are achieved by slow water evaporation instead of carefully removing water by pipetting. The mask is stable on the electrode surface for several days, however, direct photoelectrodeposition of rhodium is recommended. It is important that the electrode with the PS mask is placed in the aqueous $RhCl_3$ solution only shortly before and removed after the deposition to prevent dissolution of the PS spheres. In order to remove residual surface oxides from the photoelectrode which results from the application of SNL and the removal of PS spheres from the electrode surface, it is recommended to repeat the step of cycling polarization in HCl for about 10 cycles after removal of the polystyrene particles, following the same protocol as above.

For photoelectrochemical measurements during 9.3 s of free fall, some aspects have to be considered. Timing of the experiment is crucial and the programmed drop sequence has to be carefully tested in terrestrial conditions before the drop capsule with the experimental set-up is transferred to the drop tower. Prior to closing the capsule, a final equipment check is recommended, ensuring that potentiostats and light sources are turned on and additional screws and tools are removed from the capsule. Non-secured items in the capsule can easily destroy the experimental set-up during free fall.

An important parameter for the measurement of the photocurrent-voltage behaviour inside the drop tower is the light intensity which has to be adjusted to the camera lens: if gas bubble evolution behaviour is recorded simultaneously through the cameras which are attached to the cell, direct illumination at >70 mW/cm^2 excludes recording gas bubbles from the front of the photoelectrochemical cell; the incoming light blinds the lenses. Electrode images during free fall can therefore only be recorded and evaluated from the front of the cell at light intensities ≤ 70 mW/cm^2 without any further applications of lens protection. The experimental time of 9.3 s also has to be considered in the design of the photoelectrochemical measurements; for J - V measurements, scan rates (dE/dt) of 218 mV/s to 235 mV/s were used to allow for about 3 scan cycles in cycling voltammetry experiments. To compare the recorded J - V measurements, the second scan cycle of each experiment is recommended to be taken for analysis.

Given the excellent microgravity quality of 10^{-6} g at the Bremen Drop Tower, analysis of gas bubble formation in video recordings is possible which has been found to be more difficult in water electrolysis experiments in parabolic flights due to additional mechanical movements of the airplane (i.e., g-jitter)[21]. Using a board computer for data storage during free flight has been shown to be a sufficient alternative (see **Table of Materials**).

In conclusion, shadow nanosphere lithography is an easy and valuable tool for introducing an electrocatalyst nanostructure directly onto a semiconductor surface - various polystyrene particle sizes can be employed to vary the size of catalytically active sites on the light-absorber surface. Different electrocatalyst deposition procedures such as (photo-)electrodeposition and evaporation of the electrocatalyst allow the variation of catalytic shapes. The method allows the design of devices which efficiently produce light-assisted hydrogen in microgravity environment by forming electrocatalytically active ‘hot spots’ on the photoelectrode surface. Although long-term studies in microgravity environment are still required to investigate and optimize the devices’ stability for application in space environment, p-InP has already been shown to be a stable photocathode material in terrestrial conditions upon introduction of a TiO_2 protection layer, preventing photocorrosion of the material[23].

We have shown that drop tower facilities such as the Bremen Drop Tower at the Centre of Applied Space Technology and Microgravity (ZARM) are excellent microgravity facilities allowing the investigation of the photoelectrocatalytic performance of these devices during free-fall. They provide an easy-access, low-cost alternative to the *International Space Station* with a high microgravity quality over a time-range of 9.3 s. The here reported experimental set provides therefore an ideal starting point for the investigation of further photoelectrochemical half-cell reactions and devices for unassisted water-splitting and CO_2 reduction in reduced gravity environments to develop and optimize life support hardware for long-duration space travels and terrestrial applications.

ACKNOWLEDGMENTS

K.B. acknowledges funding from the fellowship program of the German National Academy of Sciences *Leopoldina*, grant LPDS 2016-06 and the *European Space Agency*. Furthermore, she would like to thank Dr. Leopold Summerer, the Advanced Concepts Team, Alan Dowson, Dr. Jack van Loon, Dr. Gabor Milassin and Dr. Robert Lindner (ESTEC), Robbert-Jan Noordam (Notese) and Prof. Harry B. Gray (Caltech) for their great support. M.H.R. is grateful for generous support from Prof. Nathan S. Lewis (Caltech). K.B. and M.H.R. acknowledge support from the Beckman Institute of the *California Institute of Technology* and the *Molecular Materials Research Center*. M.G. acknowledges funding from the *Guangdong Innovative and Entrepreneurial Team Program* titled "Plasmonic Nanomaterials and Quantum Dots for Light Management in Optoelectronic Devices" (No.2016ZT06C517). Furthermore, the author team greatly acknowledges the effort and support from the ZARM Team with Dr. Martin Castillo and Magdalena Thode at the Bremen Drop Tower. It is also thankful for enlightening discussions with Prof. Yasuhiro Fukunaka (Waseda University), Prof. Hisayoshi Matsushima (Hokkaido University) and Dr. Slobodan Mitrovic (Lam Research).

DISCLOSURES

The authors have nothing to disclose.

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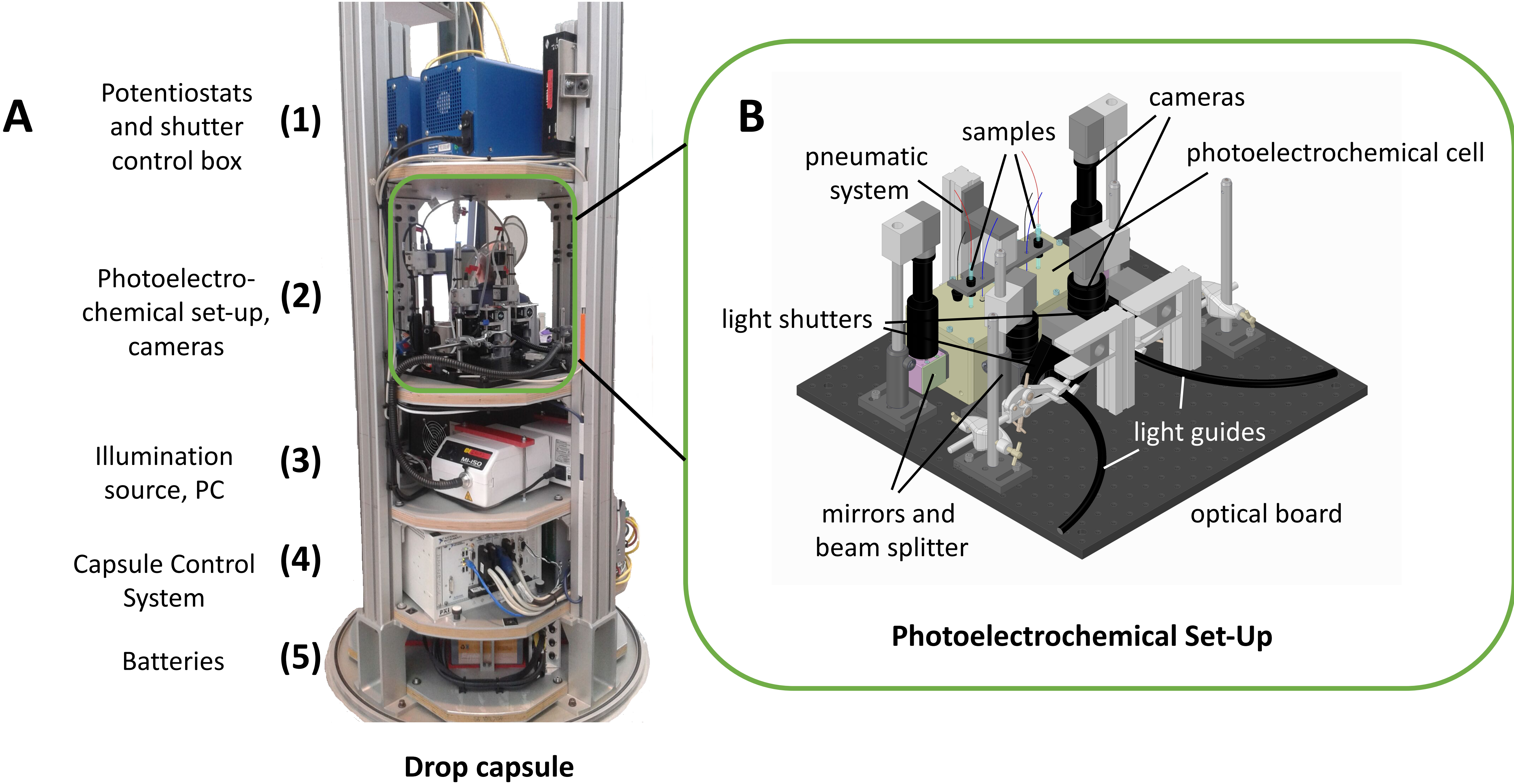
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Photoelectro-chemical set-up, cameras
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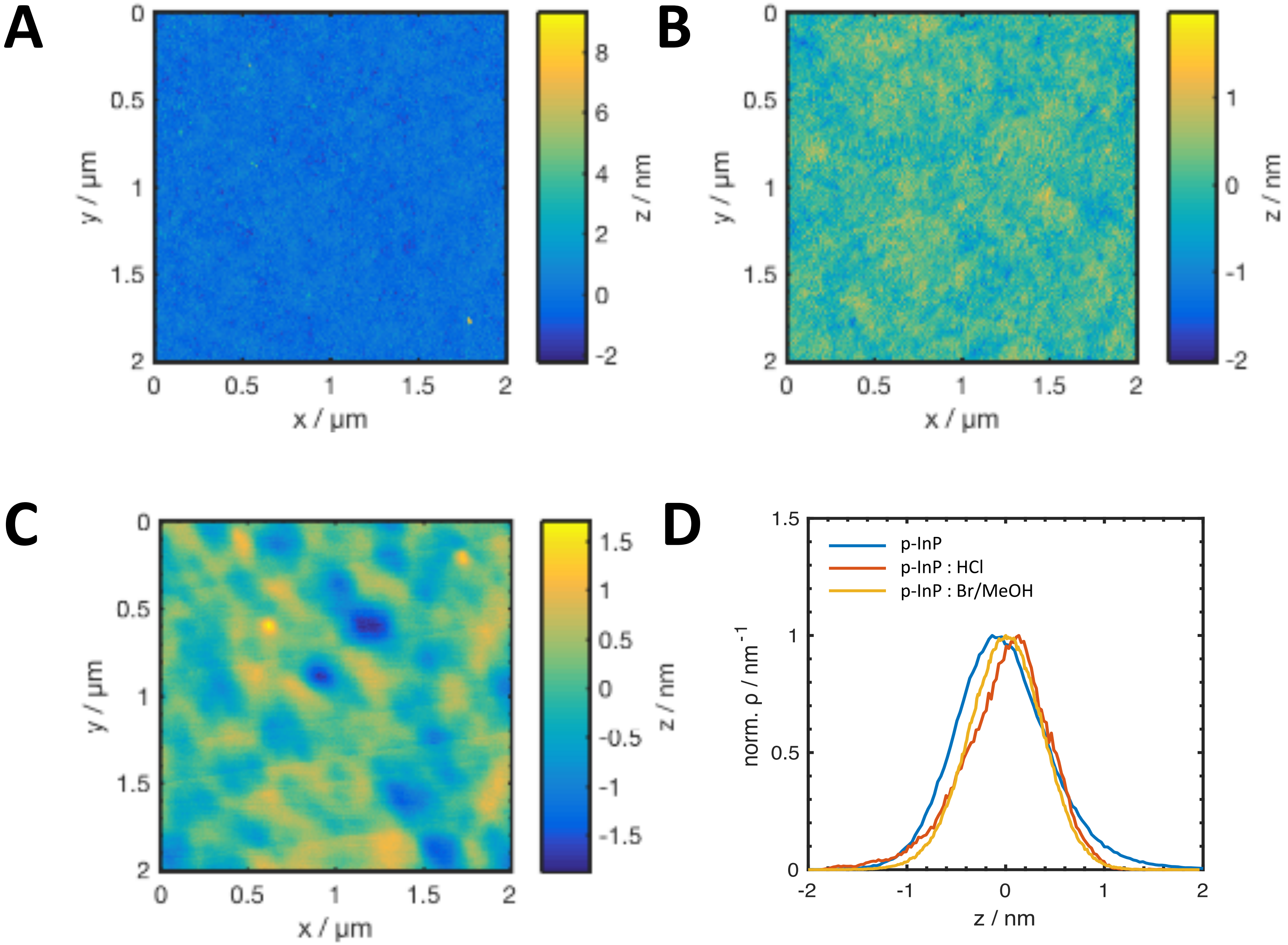
optical board
Photoelectrochemical Set-Up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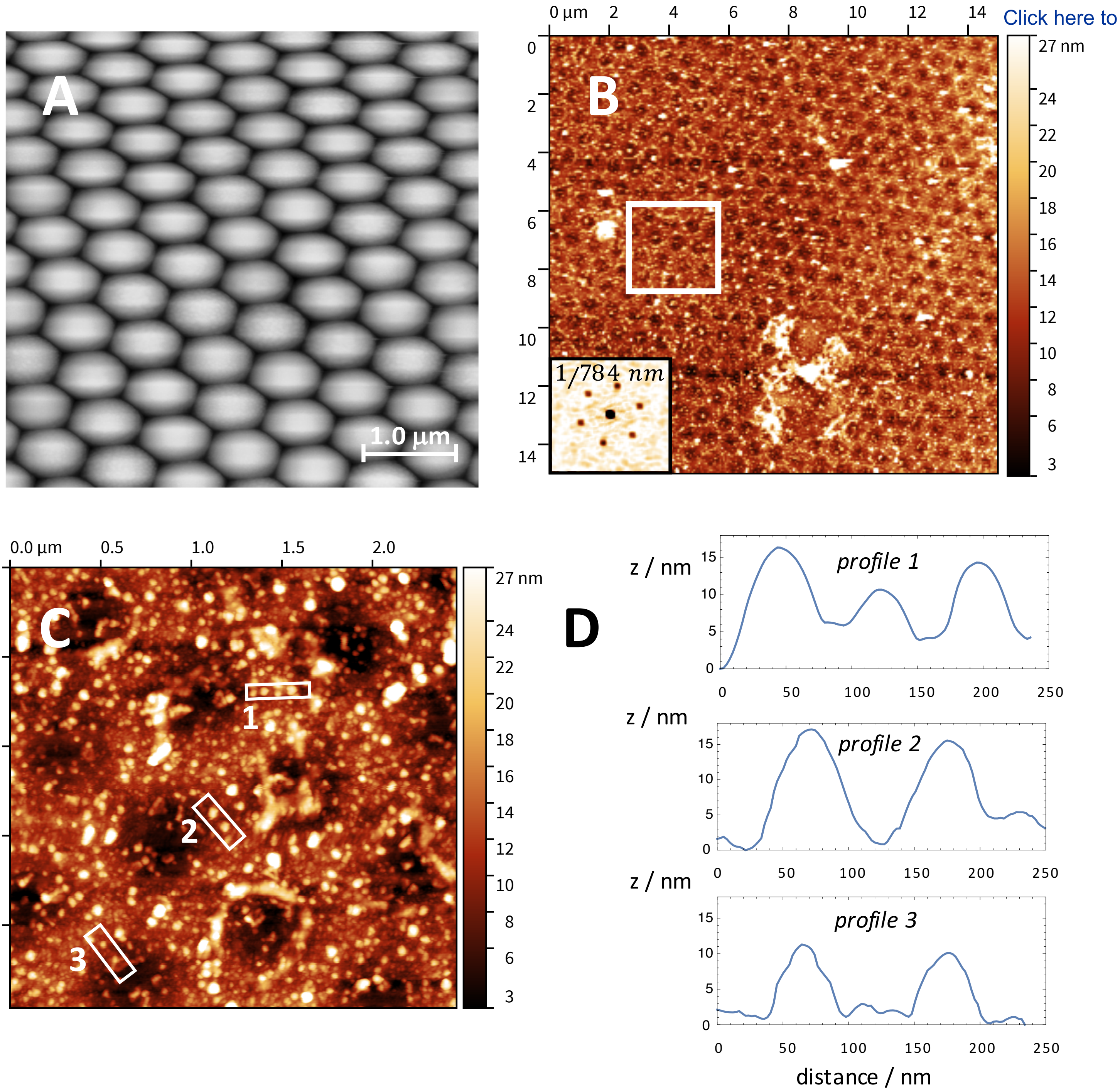
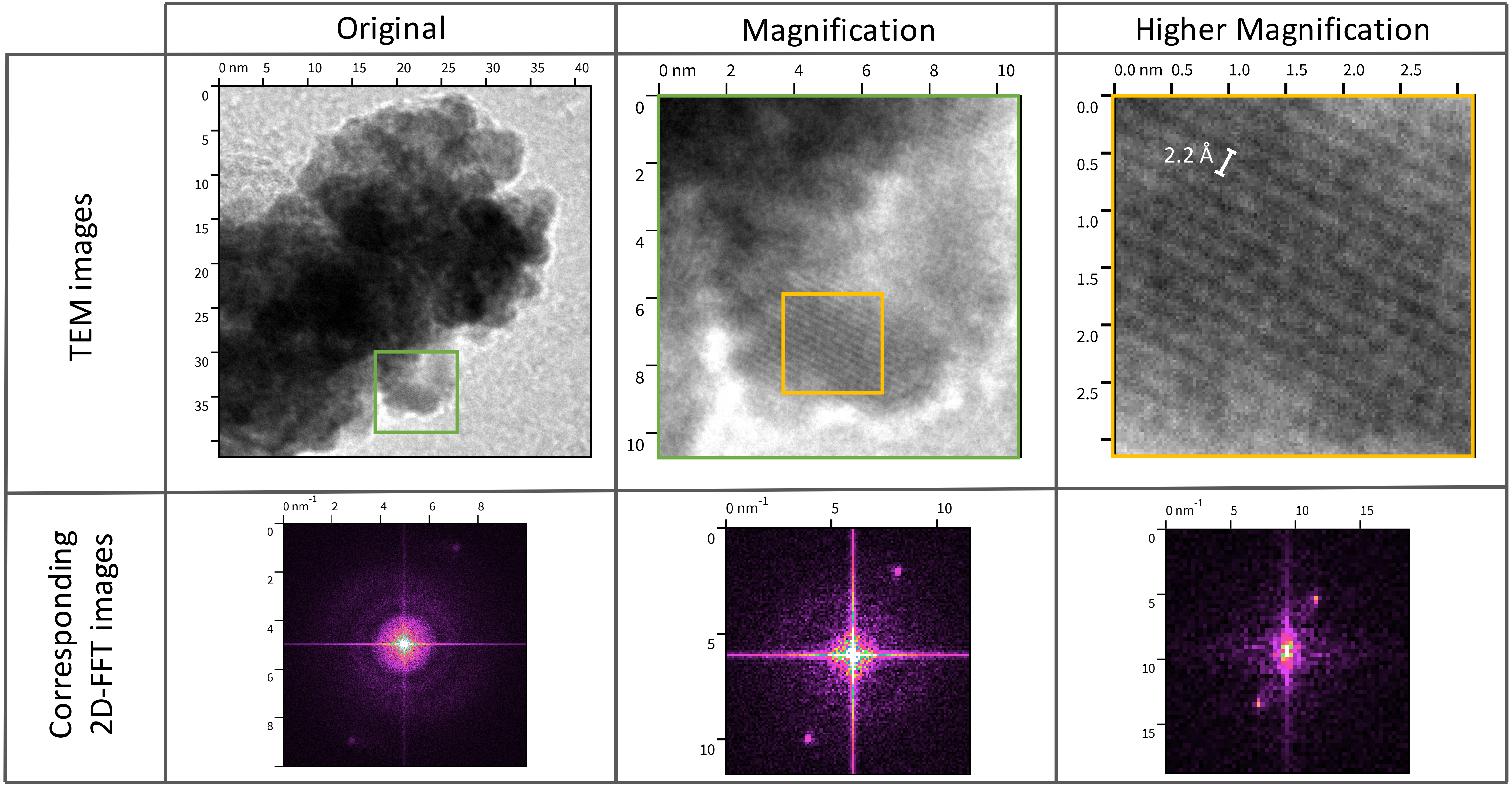


Figure_4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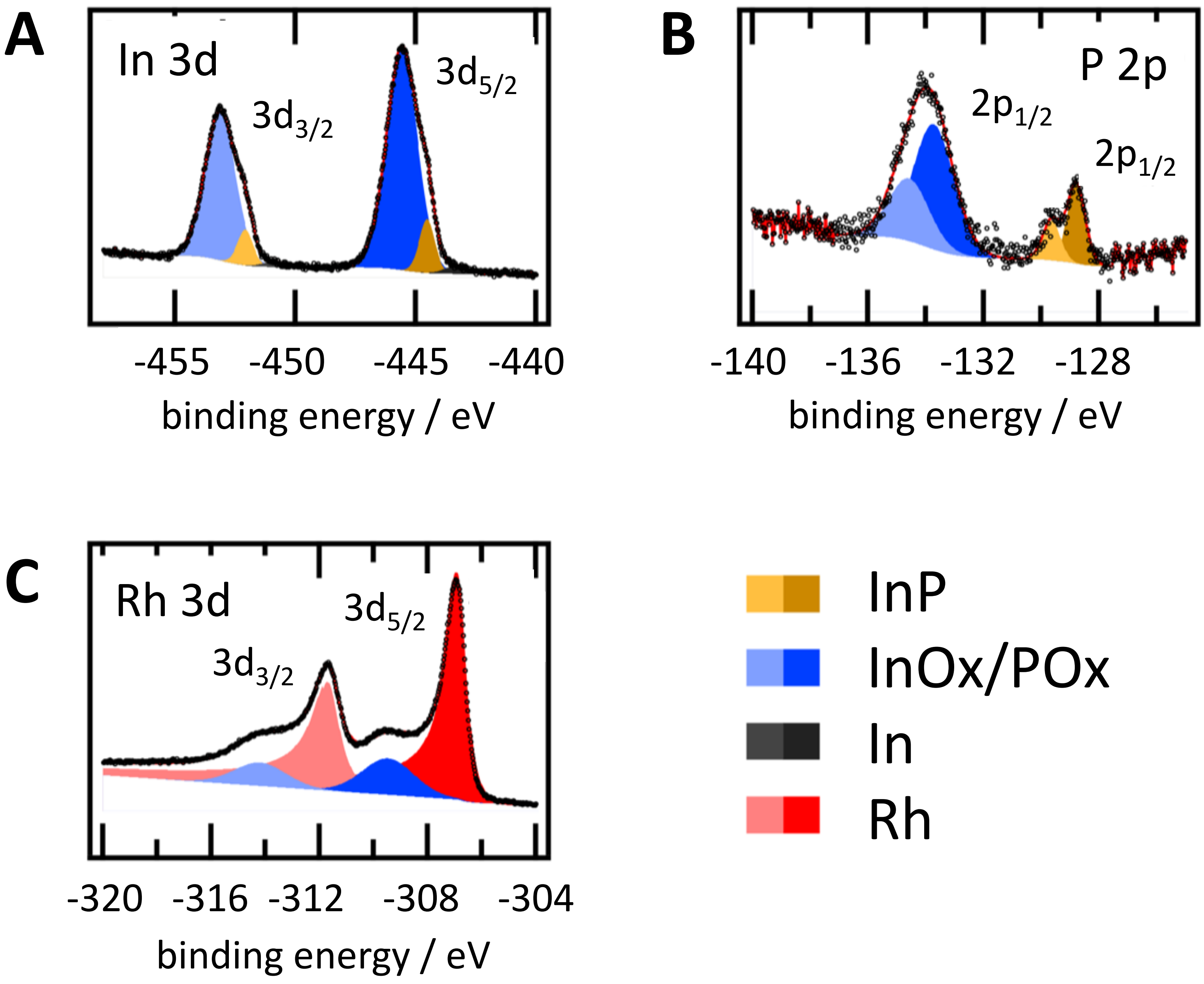
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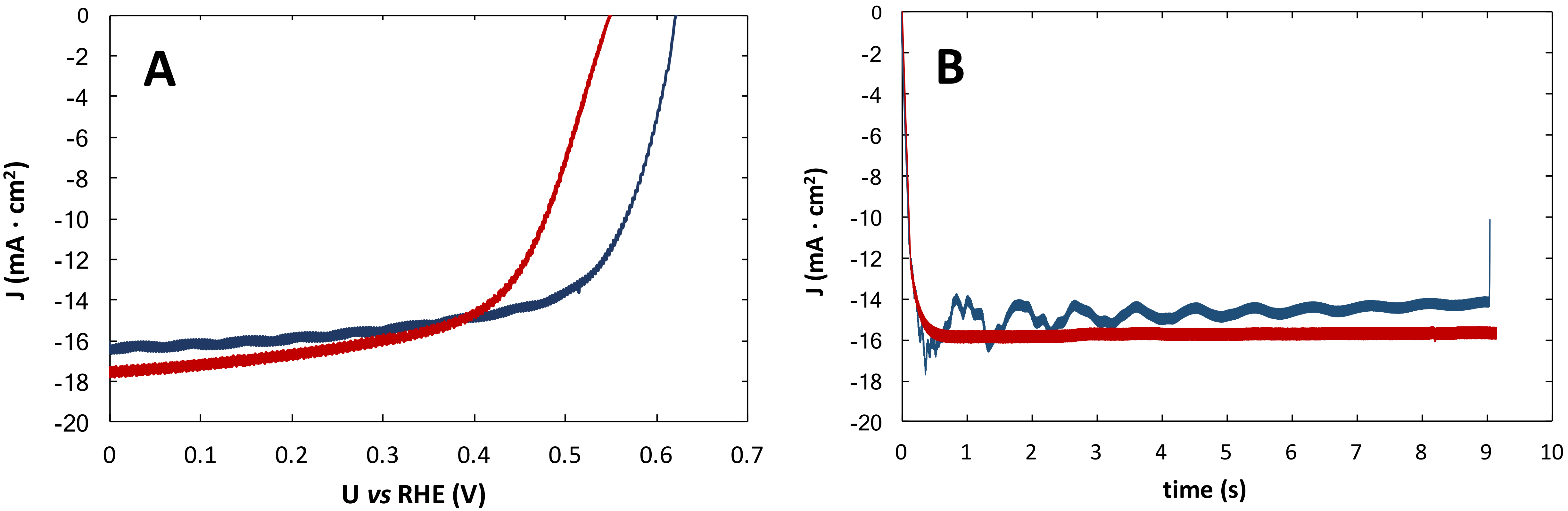
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time (s)

Figure_1

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Figure_5

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Figure_6

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Time	Experimental Sequence
-120 min	Photoelectrodes are placed in PEC cell set-up, capsule is closed with cover
-105 min	Capsule is transported into drop tower, attachment to catapult
-90 min	Start of drop tube evacuation; capsule is purged with argon
-12 min	Evacuation is stopped, removal of power supply to capsule, catapult pulls capsule onto start position
0	**Start programmed drop sequence**
-0.31 s	Cameras turn on, samples are immersed into electrolyte
-0.01 s	Lights turn on
0 s	Capsule is released from catapult, microgravity environment enabled
0.02 s	Potentiostats turn on
	Experiment starts
9.32 s	Capsule decelerates in container, microgravity environment disabled
11.32 s	Experiment stops; lights turn off
12.32 s	Samples are removed from electrolyte
19.32 s	Potentiostats and cameras turn off, **programmed drop sequence stops**
15 min	Capsule is lifted up from deceleration container
20 min	Capsule cover is removed, sample is no longer under argon; capsule is transported back to docking station where instruments are connected again to power supply
25 min	Samples are rinsed with MiliQ water, dried under nitrogen and transferred into the glove box for temporary storage

Name of Material/ Equipment
12.7 mm XZ Dovetail Translation Stage with Baseplate, M4 Taps (4 x)
Beam splitters (2 x)
Beamsplitters (2 x)
Ohmic back contact: 4 nm Au, 80 nm Zn, 150 nm Au
Glass tube, ca. 10 cm, inner diameter about 4 mm
p-InP wafers, orientation 111A, Zn doping concentration: 5 x 10^17 cm^-3
Photoelectrochemical cell for terrestrial experiments
Matrox 4Sight GPm (board computer)
2-propanol
35mm Kowa LM35HC 1" Sensor F1.4 C-mount (2 x)
Acetone
Ag/AgCl (3 M KCl) reference electrode
Aluminium breadboard, 450 mm x 450 mm x 12.7mm, M6 Taps (2 x)
Beaker, 100 mL
Black epoxy
Bromine
Colour camera (2 x)
Conductive silver epoxy
Copper wire
Ethanol
Falcon tubes, 15 mL
Glove bags
Hydrochloric acid (1 M)
Magnetic stirrer

Methanol
Microscope slides
MilliQ water
NIR camera (2 x)
Nitrogen, grade 5N
Ø 1" Stackable Lens Tubes (6 x)
O2 Plasma Facility
OEM Flange to SM Thread Adapters (4 x)
Parafilm
Pasteur pipette
Perchloric acid (1 M)
Petri dish

Photoelectrochemical cell for microgravity experiments
Polystyrene particles, 784 nm, 5 % (w/v)
Potentiostats (2 x)
Pt counter electrode
Rhodium (III) chlorid
Shutter control system (2 x)
Silicon reference photodiode
Sodium chlorid
Stands and rods to fix the cameras
Sulphuric acid (0.5 M)
Telecentric High Resolution Type WD110 series Type MML1-HR110
Toluene
Various spare beakers and containers for leftover perchloric acid etc for the drop tower
W-I lamp with light guides (2 x)
CM-12 electron microscope with a twin objective lens, CCD camera (Gatan) system and an energy dispersive spectroscopy of X- rays (EDS) s
Dimension Icon AFM, rotated symmetric ScanAsyst-Air tips (silicon nitride), nominal tip radius of 2 nm

Company	Catalog Number
Thorlabs	DT12XZ/M
Thorlabs	CM1-BS013
Thorlabs	CM1-BS014
Out e.V., Berlin, Germany	https://www.out-ev.de/english/index.html
E.g., Gaßner Glasstechnik	
AXT Inc. Geo Semiconductor Ltd. Switzerland	
E.g., glass/ materials workshop	
Matrox imaging	
Sigma Aldrich	I9516-500ML
Basler AG	
Sigma Aldrich	650501-1L
WPI	DRIREF-5
Thorlabs	MB4545/M
VWR	10754-948
Electrolube	ER2162
Sigma Aldrich	1.01945 EMD Millipore
Basler AG	acA2040-25gc
MG Chemicals	8331-14G
E.g., Sigma Aldrich	349224-150CM
Sigma Aldrich	459844-500ML
VWR	62406-200
Sigma Aldrich	Z530212
Sigma Aldrich	H9892
VWR	97042-626

Sigma Aldrich	34860-100ML-R
VWR	82003-414
Basler AG	acA1300-60gm
Airgas	NI UHP300
Thorlabs	SM1L03
Thorlabs	SM1F2
VWR	52858-000
VWR	14672-380
Sigma Aldrich	311421-50ML
VWR	75845-546
E.g., glass/ materials workshop	
Microparticles GmbH	0.1-0.99 µm size (50 mg/ml): 10 ml, 15 ml, 50 ml
Biologic	SP-200/300
ALS-Japan	12961
Sigma Aldrich	520772-1G
Thorlabs	FDS1010
Sigma Aldrich	567440-500GM
VWR	
Sigma Aldrich	339741-100ML
Basler AG	
Sigma Aldrich	244511-100ML
VWR	
Edmund Optics	Dolan-Jenner MI-150 Fiber Optic Illuminator
Philips	
Bruker	

Comments/Description
50:50 400-700nm
50:50 700-1100nm
Company provides custom made ohmic back contacts
Custom made
Custom made
Custom made
Ivy Bridge, 7 x Cable Ace power I/O HRS 6p, open 10m, Power Adapter for Matrox 4sight GPm, Samsung 850 Pro 2,5" 1 TB, Solid State Drive in exchange for the 250Gb hard drive

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Author(s):	Katharina Brinkert, Matthias H. Richter, Ömer Akay, Janine Liedtke, Michael Giersig, Katherine T. Fountaine, Thorben Könemann, Hans-Joachim Lewerenz

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January, 2nd 2019

Nandita Singh, Ph.D.
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We were very glad to hear that our manuscript finds consideration for publication in your journal and thank you very much for your support.

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4. *Please use standard SI unit symbols and prefixes such as µL, mL, L, g, m, etc.*

   We revised the manuscript using standard SI unit symbols.

5. *Step 4.7: For steps that are done using software, a step-wise description of software usage must be included in the step. Please mention what button is clicked on in the software, or which menu items need to be selected to perform the step.*

   As already indicated, we have indeed been using a software to program the drop sequence, but this step was carried out by engineers employed at the drop tower. Their installation support and help is part of the service the drop tower provides to each research team individually and the sequence is usually deleted when the experiments are finished. Therefore, we have unfortunately no detailed information on how the programming was carried out. Moreover, due to the fact that the drop sequence is programmed for each experimental setup individually, we would argue that the program details are not very beneficial to the reader - every team and experimental set-up will receive their own, individual drop sequence.

6. *4.8: Please add more details to your protocol steps. Please ensure you answer the "how" question, i.e., how is the step performed?*

   We have carefully revised protocol step 4.8 and added more information on the experimental procedure. It is important to notice that this step also depends on the experimentators explicit research question, therefore, we included an example procedure from our experiments.

7. *Figure 2: Please provide a title for the whole figure in Figure Legend.*

   We included a title for Figure 2.

8. *Figure 3: Please provide a title for the whole figure in Figure Legend.*

   We included a title for Figure 3.