

# Current Trends in Semiconductor Photoelectrochemistry

Photoelectrochemistry as an interdisciplinary research area has steadily grown since the early work of Heinz Gerischer during the late 1950s,<sup>1</sup> at the intersection of electrochemistry, solid-state physics, surface chemistry, and optics. Since the very beginning, the nonlinear development of the field was intimately linked to various aspects of energy (e.g., price of an oil barrel), and thus, different waves of interest can be identified upon the continuously changing energy landscape.<sup>2</sup> The most recent trigger of progress has been the urgent need for innovative technologies to store the intermittent energy of sunlight. This goal can be, in principle, achieved by either photoelectrochemical solar water splitting ( $\text{H}_2$  evolution) or via direct  $\text{CO}_2$  conversion.<sup>3</sup> Experts of this field gathered in Szeged, Hungary, from April 23 to 26, 2017 for the 21st Topical Meeting of the International Society of Electrochemistry. The aim of the meeting was to provide a common platform for researchers with interests in light-induced interactions at semiconductor interfaces, with a special focus on nanostructures. The topics covered the role of electrochemistry and photoelectrochemistry in the following for nanostructured semiconductor electrodes:

- (i) synthesis (e.g., both templated and templateless electrodeposition, light-assisted electrodeposition, electrophoretic deposition, etc.)
- (ii) characterization (e.g., electrochemical impedance spectroscopy (EIS), combined in situ electrochemical methods, surface photovoltage spectroscopy, intensity modulated photocurrent spectroscopy (IMPS))
- (iii) applications (all electrochemically operated applications ranging from solar fuel generation, through flow batteries, to electrochromics)

From a materials perspective, the meeting covered nanostructured electrodes made of the following:

- inorganic semiconductors (e.g., elements, oxides, chalcogenides)
- organic semiconductors (e.g., conducting polymers, covalent organic frameworks)
- hybrid organic/inorganic semiconductors (e.g., organic lead-halide perovskites, inorganic semiconductor/conducting polymer assemblies, graphene-based materials).

*Highlights of the 21st Topical Meeting of the International Society of Electrochemistry.* The conference hosted 4 keynote (see Figure 1), 7 invited, and 51 contributed talks, as well as 68 posters (with approximately 150 participants in total). Here we give a summary of the most relevant research topics discussed at the ISE topical meeting to set the stage for future research activities in this field.

In the opening lecture, Akira Fujishima (Tokyo University of Science, Japan) gave a firsthand historical overview on the early decades of the field,<sup>4</sup> mostly focusing on  $\text{TiO}_2$  and its myriad



Figure 1. Keynote speakers, the conference co-chair and secretary, together with some of the local organizing committee members at the conference banquet. Photo courtesy of B  orka B  hner.

practical applications. Examples of successful technology transfer from the laboratory to various markets were shown.

Prashant V. Kamat (University of Notre Dame, U.S.A.) discussed the most recent developments in lead halide perovskites for solar energy conversion,<sup>5</sup> specifically concentrating on intricate light-induced phase segregation in mixed bromide- and iodide-containing materials.<sup>6</sup> Additionally, the concept of an all-solution-processed tandem water splitting assembly composed of a  $\text{BiVO}_4$  photoanode and a single-junction  $\text{CH}_3\text{NH}_3\text{PbI}_3$  hybrid perovskite solar cell was shown.<sup>7</sup>

Nathan S. Lewis (California Institute of Technology, U.S.A.) summarized the latest achievements in sunlight-driven photoelectrochemical water splitting both in the Joint Center for Artificial Photosynthesis (supported by the U.S. Department of Energy) and, in particular, in his laboratory at Caltech.<sup>8</sup> He presented a modular, parallel development approach, in which the three distinct primary components of the cell (the photoanode, the photocathode, and the ion-conducting membrane) are fabricated and optimized separately before assembling them into a complete water-splitting system. The possibility of using bipolar membranes was specifically highlighted as a promising avenue to improve stability.<sup>9</sup>

Laurence M. Peter (University of Bath, U.K.) gave a comprehensive overview on the charge-carrier dynamics dictating light-driven water splitting. In addition, he showed the group's latest results on bare and CoPi-modified  $\text{BiVO}_4$ , where the main role of CoPi is to passivate the surface of

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BiVO<sub>4</sub>, and that, contrary to earlier assumptions, the photocurrent of BiVO<sub>4</sub> is limited by surface recombination instead of charge transfer.<sup>10</sup>

The seven invited speakers gave concise overviews of their recent research activities.

- Lionel Vayssieres (International Research Center for Renewable Energy, Xian Jiaotong University, China) presented an approach to develop novel purpose-built oxide heteronanostructures consisting of oriented arrays. Precise control over size, interfacial chemistry, and band structure was achieved, together with reasonable stability against photocorrosion.<sup>11</sup>
- Bunsho Ohtani (Hokkaido University, Japan) discussed the roles of electron traps in metal oxide particles by introducing the concept of energy-resolved distribution of electron traps (ERDT). This metric can be used as a fingerprint for particulate photocatalysts and was shown to be a decisive factor governing their photocatalytic activity.<sup>12</sup>
- The talk of Wojciech Macyk (Jagiellonian University, Poland) also dealt with the analysis and engineering of electronic states in semiconductor photocatalysts. He has shown that control over the density of states (DOS) distribution of a given semiconductor photocatalyst is feasible via chemical and structural modifications. This finding might also have practical implications in solar fuel generation.
- Hyunwoong Park (Kyungpook National University, Korea) reported on facile, environmentally benign synthesis of CuFeO<sub>2</sub>/CuO binary films via electrodeposition. He demonstrated that these binary films produce only liquid formate from aqueous CO<sub>2</sub> at energy efficiency exceeding natural photosynthesis while driving O<sub>2</sub> evolution from water on a wired Pt plate under continuous irradiation of simulated sunlight. An as-synthesized photocatalyst film with a three-dimensional, double-layer configuration showed the continued production of formate for over 17 days.<sup>13</sup>
- The presentation of Pawel Kulesza (University of Warsaw, Poland) concentrated on the group's recent achievements in developing hybrid materials for the photoelectrochemical reduction of carbon dioxide. Mixed metal oxide-based interfaces showed promising features toward improved long-term performance and selective production of small organic molecules (C1–C4). Metal oxides were also combined with conducting polymers, supramolecular complexes, submonolayers of metals (Cu, Au), and networks of noble metal nanoparticles (Au, Ag).
- Wolfram Jaegermann (TU Darmstadt, Germany) analyzed the physical boundary conditions and the materials science challenges related to photoelectrochemical solar fuel generation. According to their analysis, only buried junction devices will be able to fulfill appropriate band edge positions, metal Fermi level, and electrolyte density of states conditions. He also reported on their recent collaborative efforts with FZ Jülich, where a triple thin-film Si solar-cell-based device has been developed reaching 9.5% solar to H<sub>2</sub> conversion efficiency.
- Finally, Gerko Oskam (CINVESTAV-IPN, Mexico) showed how different photoelectrochemical characterization tools (EIS and IMPS/IMVS) could be used to

study metal oxides for solar water splitting. Specifically, he presented how the contribution of charge carrier transport and surface reactivity to photocurrent loss could be experimentally deconvoluted in *p*-CuBi<sub>2</sub>O<sub>4</sub>.

The contributed talks and posters were divided into five themed symposia:

- **Symposium 1.** Synthesis of semiconductor electrodes (keywords: electrodeposition, light-assisted electrodeposition, electrophoretic deposition, photodeposition, nanostructures, nanowires, nanotubes, nanosheets)
- **Symposium 2.** Novel characterization tools (keywords: combined in situ electrochemical methods, surface photovoltage spectroscopy, IMPS/IMVS, DOS plot determination)
- **Symposium 3.** Emerging applications (keywords: photoelectrochemical cells, photocatalysts, flow-batteries, electrochromics, sensors, photonics, plasmonics)
- **Symposium 4.** New materials (keywords: organic lead-halide perovskites, graphene based composites, 2D materials, organic semiconductors, MOFs)
- **Symposium 5.** Solar fuel generation (keywords: light absorber, hydrogen evolution, CO<sub>2</sub> reduction, co-catalyst, oxygen evolution, water splitting)

*Lively Discussions on Classic Problems and Innovative Concepts.* Here we mention only those few topics that were discussed by multiple speakers and for which a lively discussion emerged. The importance of the precise use of different terms related to light-triggered processes came up immediately at the beginning of the conference. There is a lot of confusion not only in the literature but even within the scientific community on the term “photocatalysis”. The use of photocatalysis is only appropriate when the reaction is thermodynamically downhill, and the light only accelerates the process that is kinetically sluggish in the dark.<sup>14</sup> On the other hand, when the energy input of the reaction is supplied by irradiation (the case of thermodynamically uphill reactions), the term photosynthetic (or photo-driven) is more appropriate. Notably, it was also highlighted by Frank Osterloh recently that the performances of photocatalytic and photosynthetic (or photodriven) systems show very different sensitivities to specific surface area, carrier mobility, and charge transfer kinetics.<sup>15</sup> Therefore, the two different scenarios should be treated differently.

Precise use of terminology and efficiency metrics are required to avoid confusion and hard-to-compare results.

An intense dialogue evolved on the importance of properly reporting the efficiency of photoelectrochemical cells. The correct definition of solar-to-hydrogen (or in general solar-to-fuel) efficiency was reviewed recently, together with other efficiency metrics, because a set of disparate methodologies has been used historically to evaluate the efficiency of systems using sunlight and/or electrical power as inputs to generate fuels.<sup>16</sup> Importantly, this topic is intimately linked to the use of sophisticated product detection methods, so that these calculations are supported with quantitative Faradaic efficiencies. This issue is specifically challenging for the CO<sub>2</sub> conversion scenario because there is no single analytical tool that could parallelly detect *all* typical CO<sub>2</sub> reduction products with rapid analysis time, at low concentration, both in gas and



liquid phases. This is clearly a challenge that can be solved in the future through collaborative efforts of the analytical and electrochemical communities.

A lively discussion emerged on the use and misuse of EIS and, specifically, the merits and limitations of Mott–Schottky analysis. It was evident that this latter is now routinely (mis)used, without considering the theory behind it and the physical limitations. For example, its use for nanoparticulate or nanostructured photoelectrodes was heavily debated as in these cases the particle size is much smaller than the typical thickness of a depletion layer; therefore, band bending does not occur in a way described for thick and flat electrodes. Tamás Pajkossy (Research Centre for Natural Sciences, Hungary) has demonstrated that charging–discharging of the electrical double layer is far from being immeasurably fast; in particular, in the case of ionic liquids, these processes are rather sluggish. Although the presented examples dealt with noble metal electrolyte systems, the basic idea—that the double-layer reorganization processes are governed not by electrostatics only—applies for semiconductor/electrolyte interfaces as well. These observations reiterated the conclusions that IMPS shall be more widely used in PEC laboratories, instead of simple EIS analysis. To further probe the kinetic aspects of photoelectrochemical processes, a new method was introduced by Damián Monllor-Satoca (Universitat Ramon Llull, Spain), where the photocurrent transients were recorded at different wavelength values (similarly to a regular IPCE measurement), and a wavelength-dependent kinetics model was developed.

Several talks described new synthetic tools to obtain semiconductor photoelectrodes. Anodization (electrochemical etching of metals) and electrodeposition were the most popular choices. Even more attention was paid to design and synthesize complex semiconductor electrode assemblies. Hybrid materials with complementary properties may offer a viable strategy to obtain photoelectrodes with enhanced performance. In this vein, Giovanni Valenti (University of Bologna, Italy) described synergetic effects among carbon nanotubes, transition metal oxide semiconductors, and noble metal particles, in a coaxial nanostructured morphology.<sup>17</sup> A similar rational design strategy

was presented by Balázs Endrődi (University of Szeged, Hungary), who demonstrated semiquantitative structure–property relationships for electrosynthesized semiconductor/nanocarbon hybrid photoelectrodes to achieve improved photoelectrochemical behavior.<sup>18</sup>

Finally, we note two novel research directions where we might see increased interest in the near future. Kristina Wedege (Aarhus University, Denmark) presented direct solar charging of a 0.74 V flow battery with a surface-modified hematite photoanode. This concept illustrated simultaneous photoelectrochemical harvesting and storage of solar energy using low-cost and environmentally benign materials with high stability.<sup>19</sup> Katharina Brinkert (TEC-SF, Netherlands) reported on the photoelectrochemical production of hydrogen in microgravity environments on p-type indium phosphide electrodes with deposited rhodium electrocatalysts. Their findings indicated that microgravity has a significant impact on the gas bubble evolution behavior and the mass transfer rate of the evolved hydrogen gas on the electrode surface. Even more interestingly, microgravity seemed to influence the current–voltage characteristics and the overall solar-to-hydrogen efficiency of the catalyst-functionalized semiconductor-based half-cell.

*New Insights Provided by New Techniques.* It was common in most of the talks that careful materials and system engineering is of prime importance to tailor the interfacial properties of the photoelectrodes. As another common theme, it was often

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claimed that novel in operando tools are indeed necessary to gain better understanding of the fundamental elementary steps of the photoelectrochemical processes. Thus, the special lecture given by Peter Dombi, head of the Scientific Applications



Figure 2. Selected pictures captured during the conference. Photos courtesy of Attila Kormányos.

Division within the Extreme Light Infrastructure – Attosecond Light Pulses (ELI-ALPS) facility, which is currently being implemented in Szeged, Hungary, took on particular relevance to future photoelectrochemical studies. The ELI-ALPS infrastructure will provide primary laser pulses in conjunction with an impressive array of synchronized secondary light and particle pulses to study light–matter interactions. The outstanding characteristics of the source parameters include:

- Few-cycle pulses, from the terahertz/infrared up to the petahertz/ultraviolet, with an impressive 10 Hz to 100 kHz repetition rate
- Attosecond extreme-ultraviolet, soft and hard X-ray mJ pulses with a 10 Hz–100 kHz repetition rate
- Subfemtosecond hard X-ray pulses up to 10 keV photon energy and controlled ultrarelativistic pulse shapes with ultrahigh contrast with a 1 Hz repetition rate
- Controlled ultrarelativistic pulse shapes with ultrahigh contrast at a few Hz repetition rate
- Precise synchronization of the above light sources

Two groups from the conference participants took a guided tour of the facility (Figure 2) and got first-hand information about ELI-ALPS.

Conference participants also had the chance to enjoy Szeged, a major university town located at the southern part of Hungary, also called the City of Sunshine. Szeged has been long renowned for its cultural and architectural heritage, as well as its gastronomic traditions and innovations. Fish restaurants with a unique atmosphere are perched on the bank of the River Tisza, serving the obligatory Szeged style fish soup, which was also served at the banquet (see also Figure 1).

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### Notes

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