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Hybrid Inorganic/Organic Systems for Opto-Electronics (HIOS)

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This Special Issue of *physica status solidi (a)* showcases selected scientific highlights from the final funding period of the Collaborative Research Center 951 (CRC 951) "Hybrid Inorganic/Organic Systems for Opto-Electronics (HIOS)". Overall, the CRC 951 has received funding from the Deutsche Forschungsgemeinschaft (DFG, project no. 182087777) for 12 years, and recently ended in June 2023. By bringing together researchers from Humboldt-Universität zu Berlin (coordinating university), Freie Universität zu Berlin, Technische Universität Berlin, Universität Potsdam, the Fritz-Haber-Institut der Max-Planck-Gesellschaft, as well as the Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, the emerging research field of HIOS was initiated, cultivated, and expanded.

The ansatz of the CRC 951 was the combination of fairly dissimilar materials, i.e., inorganic semiconductors, metal nanostructures, and conjugated organic materials, to realize heterostructures with superior electronic and optoelectronic-functionality. The underlying rationale can be pictured in a straightforward way from the different chemical, electrical, and optical properties of the materials and their specific advantages and drawbacks. (i) Inorganic semiconductors are well established opto-electronic materials. Highest purity levels, thin film and crystal growth far from equilibrium, stability, structural control on the atomic scale, exceptionally high charge carrier mobility, and efficient electrical charge injection are prime merits of these materials. However, the absorption cross-section of inorganic semiconductors stays markedly behind those of conjugated organic molecules. (ii) Conjugated organic molecules and polymers (organic semiconductors) have also found their way into devices, defining the field of organic opto-electronics, including the vision of functional units reduced in size down to the single-molecule level. Conjugated organic materials stand out by their strong light-matter coupling and highly flexible tunability of the electrical and optical properties through their chemical structure. Moreover, they feature (self-)assembly from the molecular level up to macroscopic crystalline phases, and tremendous structural and morphological variability. However, charge carrier mobility in organic materials is notoriously low, thus seriously limiting the operation frequency and band-width of devices. Moreover, the efficient injection of charge carriers into organic materials and reaching high charge carrier densities has turned out to be comparably difficult. (iii) Metal nanostructures are a third material component ultimately involved when aiming at opto-electronic function on very small length scales. Such structures are capable of confining and guiding light at subwavelength dimensions via plasmonic excitations. In this way the electric field strength and thus the light-matter coupling is dramatically enhanced. Coupling processes – even to single molecules – are more efficient and occur on a much faster time-scale. Plasmonic nanoantennae and -cavities can be constructed that function as excellent local receivers or emitters of photons. For practical applications, these plasmonic elements must be coupled to other active building blocks, e.g., for processing the received energy or for efficient pumping of nanoemitters. Appropriate geometries and schemes ensuring strong and controllable interaction between plasmonic fields and the optical dipoles of suitable co-materials yet need to be developed and tested.

During the first funding period, the CRC 951 established a sound knowledge-base of HIOS formation and property characterization for a few model systems, focusing on ZnO as inorganic component and several well-established molecular materials. During the second funding period, the inorganic material base was expanded, now including Si, GaN, and other semiconductors. On the organic side new functionality was added by including molecular switches in the research portfolio. With respect to stimulated processes, new approaches were introduced. The insight obtained during the first two funding periods revealed that the ubiquitous surface and interface states of the traditional bulk semiconductors are bottlenecks for advanced HIOS functionality. Consequently, the research program for the third and final funding period considered two-dimensional (2D) semiconductors, specifically transition metal dichalcogenides (TMDCs), as the most promising emerging material class to mitigate the above problem. Specifically, semiconducting transition metal dichalcogenides thinned to the monolayer were included. The thin or even 2D character also allows for optimized interaction with tightly confined plasmonic excitations. Altogether, advanced HIOS could pave the way for unequalled nanoscale solid-state devices, not achievable with any of the individual material classes alone.

The articles featured in the current Special Issue exemplify highlights from experiment and theory obtained in the recent past by CRC 951 members, and also show how the field could move forward from today.

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A combined experimental and theoretical study by V. Bender et al. (pssa.202300113) unravels excitonic properties of mechanically exfoliated monolayer MoS_2 under multivariate physical and chemical stimuli. Midgap exciton states that originate from lattice defects are characterized and are compared to existing models. Through statistical data analyses of substrate-, temperature-, and laser-power-dependent measurements, a photoluminescence enhancement is revealed through physisorption of water molecules of the controversially discussed excited-state A biexciton. Furthermore, the impact of adsorbed water at defect sites on electron-phonon coupling is explained.

J. Krumland and C. Cocchi (pssa.202300089) assess the capability of semi-local and hybrid variants of density functional theory (DFT) to describe the energy level alignment at a HIOS interface, for the example of anthracene and monolayer MoS_2. While properly parametrized hybrid functionals can approximate with reasonable accuracy the quasiparticle properties of the individual components, they fail for the hybrid interface. Instead, they suggest that ab initio-parametrized effective models mimicking the environment offer a scalable alternative without compromising accuracy and predictivity, in comparison the computationally more expensive many-body simulations.

For a HIOS comprising ethyl-diaminodicyanoquinone molecules on a monolayer of MoS_2 on Au(111), S. Trishin et al. (pssa.202300105) find a linear-chain-like self-assembled structure of the dipolar molecules using scanning tunneling microscopy, in line with expected energy minimization structure of interacting dipoles. Because MoS_2 effectively decouples the molecules from the underlying metal, vibronic states of the molecules are resolved, and their intensity found to be depending on the molecular surrounding. The authors suggest that the molecular vibrations are strongly damped by electrostatic interactions with the environment.

For all HIOS, a detailed knowledge of the coupling among the different constituents is crucial. In their contribution, L. Greten et al. (pssa.202300102) present a unified description based on Maxwell Bloch equations to describe dipolar interactions among different types of heterostructures. Exemplary, Förster-type energy transfer from dye molecules to MoS_2 monolayers, strong coupling at $MoSe_2$-metal nanoparticle interfaces, Meitner-Auger-like interlayer coupling in WSe_2-graphene stacks, and relaxation processes of hot interlayer excitons in $MoSe_2$-WSe_2 heterobilayers are discussed.

Based on photoemission and optical absorption measurements, Ma et al. (pssa.202300106) suggest that a hybrid organic-inorganic interlayer exciton may exist at the interface of hexafluoro-tetracyano naphthoquinodimethane molecules and a WS_2 monolayer. However, the signature of that state is only found for strongly n-doped WS_2, going in hand with the presence of molecular anions. Therefore, the state is likely a hybrid excitation between the inorganic component and the organic anionic one, also highlighting the impact of structural defects of the WS_2 monolayer on the resulting HIOS properties.

A novel kind of device for simple optical (de-)multiplexing is introduced by S.-Y. Rhim et al. (pssa.202300177). They combine a polymeric electrochromic material with waveguides, where the utilized layout consisted of two layers of Y-branches that were connected in series enabling a split into four channels. Two electrodes deposited with the polymer on each arm of a Y-branch were paired up with an ion gel electrolyte. By controlling one of the paired electrodes, each channel could be addressed exclusively through coloring and bleaching. Thus, an advanced method of optical multiplexing was demonstrated in which each channel can be addressed with a binary 2-bit signal.

J. Müller et al. (pssa.202300148) demonstrate that 4D scanning transmission electron microscopy (4D-STEM) is a powerful method for characterizing electron-transparent samples with down to sub-Ångstrom spatial resolution. 4D-STEM can reveal local crystallinity, orientation, grain size, strain, and many more sample properties by scanning a convergent electron beam over a sample area and acquiring a transmission diffraction pattern (DP) at each scan position. The large field of view together with down to sub-nm spatial resolution, achieved by implementing this method in a scanning electron microscope (SEM), are ideal to map sample properties. As an example, they could reveal the single crystallinity of MoS_2 exfoliated with gold-mediation as well as the crystal orientation and coverage of both components of a HIOS comprising C_{60} and MoS_2.

Intensity-modulated photocurrent spectroscopy (IMPS) with steady-state background illumination was performed by M. Raoufi et al. (pssa.202300107) to investigate the photoresponse dynamics in a hybrid photodetector based on monolayer MoS_2 covered with an ultrathin layer of phthalocyanine (H_2Pc) molecules. The results demonstrate that adding the H_2Pc layer speeds up the photoresponse of the neat MoS_2 photodetector by almost two orders of magnitude without deteriorating its responsivity. Furthermore, the additional absorption of photons in the H_2Pc layer contributes to photocarrier generation, resulting in an enlarged responsivity of the hybrid device.

Defects are known to influence the electronic, optical, and mechanical properties of 2D materials, making defect stability under different thermodynamic conditions crucial for material–property engineering. A. Akkoush et al. (pssa.202300180) provide an account of the structural and electronic characteristics of point defects in monolayer MX_2 with M = Mo/W and X = S/Se through density functional theory using the hybrid HSE06 exchange-correlation functional including many-body dispersion corrections. The study relates the stability and the electronic structure of charged vacancy defects in monolayer MoS_2 to an explicit calculation of the S monovacancy in MoS_2 supported on Au(111), and finds convincing indication that the defect is negatively charged.

Singlet exciton fission (SF), the formation of two triplet excitons from one singlet exciton, involves electronic, nuclear, and spin degrees of freedom as well as their couplings. One important open question concerns the role of nuclear motion in SF. The Perspective article by A. Neef et al. (pssa.202300304) relates recent results on the exciton dynamics to the structural dynamics of single-crystal pentacene. To probe the electronic dynamics, orbital-resolved measurements of the electronic structure are carried out using time- and angle-resolved photoemission spectroscopy. With femtosecond electron diffraction and with *ab initio* computations, the complementary nuclear dynamics is tracked. Remaining open questions are outlined and potential routes are identified to tackle them, hopefully guiding future studies.

The Perspective article by I. Gonzalez Oliva et al. (pssa.202300170) explains the challenges of theoretical

investigations of HIOS interfaces; in addition to exhibiting large unit cells, they require highest-level theories to be described reliably. Consequently, hybrid materials pose a challenge for electronic structure theory, starting from density-functional theory to methods beyond, particularly many-body perturbation theory. In their article, the performance of state-of-the-art theoretical approaches applied to HIOS is summarized, mainly focusing on optoelectronic properties. To conclude, recent achievements, open challenges, and urgent needs are addressed.

Understanding and controlling interactions in HIOS is mandatory to achieve the desired functionality. The Review by N. Zorn Morales et al. (pssa.202300186) focuses on the charge and energy transfer processes and their dynamics in van der Waals heterostructures composed of semiconducting transition metal dichalcogenides and conjugated organic molecules. With the help of prototypical material combinations, the importance of a precise knowledge of the interfacial electronic structure is demonstrated as it governs the excited-state dynamics. The review also provides basic design guidelines to achieve functional 2D organic/inorganic van der Waals heterostructures.

H. Li et al. (pssa.202300302) investigate the effect of molecularly thin liquid layers on the optical spectra of MoS_2 and WS_2. Photoluminescence and differential reflectance spectra of the TMDCs on dry mica show dominant trion emission due to n-doping. Intercalation of water removes charge doping and results in purely neutral exciton emission, while an ethanol layer, which can be reversibly exchanged with water, does not completely suppress charge. The described charging/discharging of TMDCs by molecular thin liquid layers can provide important clues to better control the optical properties of TMDCs under environmental conditions.

The observation of hybrid optical transitions in the monolayer WS_2/terrylene hybrid is reported by B. T. Bonkano et al. (pssa.202300346). Based on a combination of first-principle calculations, linear optical, and transient absorption spectroscopy, the hybrid feature is assigned to a transition from the highest occupied molecular orbital of terrylene to the conduction band of WS_2 close to the Γ point. These results indicate that the conditions for strong electronic coupling are met in this hybrid system.

External control of directional transport of propagating surface plasmon polaritons (SPPs) would be highly interesting for applications. In their article, S. Qodratipour et al. (pssa.202300380), demonstrate the coupling of noble metal and magnetic nanoparticles to a silver nanowire acting as SPP waveguide using a hybrid self-assembly approach. Polarization-dependent directional excitation (spin-momentum locking) was achieved and magnetically controlled transport in such devices was investigated. Based on a heuristic numerical model the required improved parameters for future full magnetic control were estimated. One approach could be to enhance the magnetic response using a combination of metal and magnetic nanoparticles.

G. Kewes and O. Benson (pssa.202300366) propose a tunnel-current-driven plasmonic nanoantenna for the generation of single photons, based on small gold nanoparticles that feature Coulomb blockade already at room temperature combined with a self-similar nanorod arrangement. Calculations suggest high photon purities, repetition rates beyond, and efficiencies comparable to ordinary single-photon sources based on emitters like color centers or heralded single-photon sources. Given recent achievements in the field and the simplicity of the proposal, the device can be built with existing technology.

Overall, CRC 951 has provided comprehensive insights into HIOS and derived guidelines for the fabrication of advanced inorganic-organic structures for optoelectronics in the future. Particularly during the final funding period, the CRC 951 inspired and impacted the research field of functional combinations of organic molecules and 2D semiconductors, as can be observed from a steady increase in reports published on this topic and its presence at every recent major pertinent international conference. We are looking forward to exciting new science and applications of HIOS in the future.

Oliver Benson is Professor for Experimental Nano Optics at Humboldt-University Berlin. He received his PhD in 1995 at LMU München and the Max-Planck-Institute of Quantum Optics, Garching. He turned to solid-state quantum optics during his postdoctoral stay at Stanford University from 1997 to 1999. Then, he was a Junior Group leader (DFG Emmy-Noether program) at Konstanz University, before he accepted an offer from Humboldt-University in 2001. His research interest concerns fundamentals of light-matter interaction on the quantum level. More recently, he explores first steps towards photonic quantum processing. From 2015 until 2023 he was vice-spokesperson of the Collaborative Research Center 951.

Norbert Koch studied technical physics at the Technische Universität Graz, Austria, and received there a doctorate in solid state physics in 2000. After two years as postdoc at Princeton University, he started building his own group at Humboldt-Universität zu Berlin. In 2009 he was appointed as professor in the Department of Physics of Humboldt-Universität, and in 2010 his group at Helmholtz-Zentrum Berlin für Materialien und Energie was established. At present, doping of organic semiconductors, and interfacial phenomena with perovskites and 2D materials are in the focus of his research agenda. From 2015 until 2023 he was spokesperson of the Collaborative Research Center 951.