

# Photophysics in photoactive oxides probed using infrared reflection absorption spectroscopy: Polarons in TiO<sub>2</sub> and ZnO

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TiO<sub>2</sub> and ZnO are wide-band gap metal oxides exhibiting various desirable physico-chemical properties, e.g. high photocatalytic activity. In the context of photo-excitations, in previous work primarily excitons have been studied including their very recently reported ultrafast formation dynamics.<sup>[1]</sup> It is important to note that charge carriers generated from dissociation of excitons – a crucial step in photovoltaics and photocatalysis – may be trapped in polaronic states. Consequently, the polaron binding energy becomes crucial for the photocatalytic activity, as this energy is not available to drive the desired reaction. Yet, so far only very little work has been devoted to these polaronic trap states.

Here, we report a novel approach to study polarons in metal oxide single crystals by populating these trap states via UV-light irradiation and probe them using infrared reflection absorption spectroscopy (IRRAS). We will present results for TiO<sub>2</sub> (cf. <sup>[2]</sup>) and ZnO, where a number of previously unobserved bands ascribed to polaronic states appear in the IR-spectra upon irradiation and compare them to theoretical work. Exploiting time-resolved IRRAS, we were able to deduce lifetimes and binding energies of these states experimentally for ZnO. We will conclude the talk by discussing the potential of IR-Spectroscopy for studying charge transfer at oxide-molecule interfaces and present first data for TCNQ deposited on ZnO(10-10).

- [1] J.-C. Deinert, D. Wegkamp, M. Meyer, C. Richter, M. Wolf, J. Stähler, *Phys Rev Lett* **2014**, *113*, 057602.
- [2] H. Sezen, M. Buchholz, A. Nefedov, C. Natzeck, S. Heissler, C. Di Valentin, C. Wöll, *Sci Rep* **2014**, *4*, 3808.

# **Nano-composite materials and their application in energy harvesting and sensing**

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We will report on novel nano-patterned composite materials for sensing and energy harvesting. We rely on a wealth of nano-composites composed of silicon (Si) as well as GaN nanowires (NWs) from chemical vapor deposition (CVD) based processing including NW shaping based on reactive ion etching, plasmonic nano-structures realized by thin metal layer (silver, gold) patterning with focused ion beam microscopes as well as few layer graphene from CVD processing. The NWs show large surface areas that can chemically be functionalized to account for sensing functionality. The graphene requires proper chemical treatment to permit attachment of functional groups. The chemical routes to nano-materials functionalization will be reported. Sensing mechanisms with functional nano-materials can be e.g. of electrical, optical or mechanical nature. Examples will be given for selected cases. Emphasis will reside on optical detection based on the surface-enhanced Raman scattering (SERS) effect.

We will report SERS of graphene layers transferred on arrays of split ring resonators (SRRs). Raman enhancement factors per area up to 75 demonstrate the strong plasmonic coupling between graphene and the metamaterial resonances. The SRR/graphene material offers a perspective to control SERS and may pave the way towards advanced SERS substrates that could lead to the detection of single molecules attached to graphene for bio-chemical sensing. For energy harvesting applications we develop Si and GaN nanowires with which Mie modes can be controlled and efficient absorption of solar light can be tuned. The integration of NWs in thin film solarcell concepts with efficiency potential  $\gg 15\%$  will be demonstrated. The same type of Si NWs and their applicability to solarfuels generation will be shown.