Ultrafast quasiparticle dynamics in ZnO and at its interface with an organic chromophore

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Due to its wide band gap and high carrier mobility, ZnO is an attractive material for light-harvesting and optoelectronic applications. Its functional efficiency, however, is strongly affected by defect-related in-gap states that open up extrinsic decay channels and modify relaxation timescales. As a consequence, almost every sample behaves differently, leading to irreproducible or even contradicting observations.

Using a complementary set of time-resolved spectroscopies that we applied to two ZnO samples of different defect density, we are able to disentangle the competing contributions of charge carriers, excitons, and defects to the non-equilibrium dynamics after photoexcitation. We find that defects affect the transient optical properties of ZnO across more than eight orders of magnitude in time, starting with photodepletion of normally occupied defect states on femtosecond timescales, followed by the competition of free exciton emission and exciton trapping at defect sites within picoseconds, photoluminescence of defect-bound and free excitons on nanosecond timescales, and deeply trapped holes with microsecond lifetimes. These findings do not only provide the first comprehensive picture of charge and exciton relaxation pathways in ZnO, but also uncover the microscopic origin of previous conflicting observations in this challenging material and thereby offer means of overcoming its difficulties.

We also characterize the ultrafast dynamics of electrons and excitons at a model organic/inorganic interface (5-phenyl-pyridine/ZnO(10-10)). In particular, we populate the LUMO of the organic molecules by two different pathways: (i) Via photoexcitation from an interfacial hybrid state just below E_F and (ii) by optical excitation of the organic dye. We thereby disentangle the two main contributions to interfacial charge separation, electronic coupling to the ZnO conduction band and electron-hole interaction in the organic molecule.