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Dyes are key elements of dye sensitized solar cells (DSSC). Understanding their chemical properties at the molecular level and their adsorption mechanism on TiO₂ is of paramount importance for DSSC characterization and further developments. The crystal structure of a polyene aniline based dye, named D5 [1], was solved from synchrotron high resolution powder patterns, while that of its precursor without linking moiety was solved by standard single crystal XRD. The two molecules show remarkable differences in their intermolecular interactions and in crystal packing. In the precursor a T-like interaction is observed between pairs of molecules, while in D5 π - π interactions, together with intermolecular H-bonds between carboxyl groups, impose a planar stacking. However in both structures the packing is driven by the hydrophobic interactions between the phenyl moieties in adjacent molecules. This structural information sheds light on the features of D5 when bonded to TiO₂ (P25) in the working DSSC devices and can help explaining the limited (8%) conversion efficiency. Indeed the strong hydrophobic interactions can interfere with the dye grafting process. After grafting, intermolecular H bonds can not play a role, since the COO⁻ is involved in the bond with TiO₂, but strong lateral interactions between adjacently bonded D5 molecules may facilitate the charge recombination processes that lower the yield of electron injection into the P25 conduction band, with an overall smaller efficiency of DSSC cells.

The adsorption mechanism of D5 on the TiO₂ surface has been characterized by UV-Vis spectroscopy, Grazing Incidence-XRPD and Scanning Electron Microscopy together with elemental analysis by Energy Dispersive Spectrometry (EDS). UV-Vis spectra on the D5 solutions after contact with TiO₂ allowed to determine, by difference, the quantity of adsorbed dye. The experiments were carried out on both P25 powders and on commercial Dyesol glasses, and, using an optimized analytical procedure, the number of adsorbed molecules was determined under different conditions: D5 concentration, contact time and presence of CDCA anti-aggregation agent. Dyesol glasses were also analyzed by GI-XRPD to verify the size of TiO₂ crystallites, while the thickness of the TiO₂ layer was determined by SEM. The elemental analysis by EDS showed that the sulfur signal, only due to D5, is uniformly distributed along the TiO₂ thickness. The results of all these crystallographic and spectroscopic analyses and their relevance for the characterization of TiO₂-D5 interactions will be presented.

[1] D.P. Hagberg, T. Marinado, K.M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt, L. Sun, *Journal of Organic Chemistry* **2007**, 72(25), 9550-9556.

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The cation distribution in off stoichiometric CuInSe₂ and CuGaSe₂

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Chalcopyrite type compound semiconductors with Cu(In,Ga)Se₂ composition are successfully implemented as absorber layers in

thin film solar cells. The stoichiometric compound Cu(In,Ga)Se₂ crystallizes in the tetragonal chalcopyrite type crystal structure with space group *I42d*. Within this crystal structure the monovalent cations (Cu⁺) occupy the 4a site (0 0 0), the trivalent cations (In³⁺ and Ga³⁺) are situated on the 4b position (0 0 ½) and the selenium anions are on the 8d site ($x \frac{1}{4} \frac{1}{8}$). The cations are tetrahedrally coordinated by the anions and vice versa.

In general Cu(In,Ga)Se₂ absorber layers exhibit a copper-poor composition (Cu/(In+Ga) < 1), whereby the chalcopyrite type crystal structure still persists but the occupation of the Wyckoff sites may change and various kinds of intrinsic point defects are present within the material. The kind and concentration of these defects strongly correlate with the electronic and optical properties of the final device and the knowledge about them is crucial to tailor high efficient photovoltaic devices made of such compounds.

Distinguishing between isoelectronic species like Cu⁺ and Ga³⁺ by conventional diffraction techniques, like laboratory X-ray powder diffraction, is almost impossible. Therefore, at first neutron powder diffraction with subsequent Rietveld refinement was applied to evaluate possible cation distribution models for copper – poor CuInSe₂ and CuGaSe₂, by the method of average neutron scattering length [1]. To decide if Cu⁺ and Ga³⁺ in Cu-poor CuGaSe₂ are ordered or partially disordered distributed within the structure, anomalous X-ray diffraction experiments were performed complementary to the neutron diffraction experiments.

For the anomalous diffraction experiments synchrotron X-rays with two different wavelengths, close to and far off the Ga-K-absorption edge (10367 eV), were used. This complementary diffraction technique made a differentiation between an ordered and a partially disordered distribution of the cations in copper-poor CuGaSe₂ possible.

The dominant native point defects in copper-poor CuInSe₂ were specified to be copper vacancies (V_{Cu}) and In_{Cu} anti-site defects. Moreover, the type and density of these isolated native defects is dependent on the Cu/In ratio [2]. The dominating native point defects in copper – poor CuGaSe₂ are copper vacancies and gallium on interstitial position (Ga_i).

The study presented here identified, by the use of advanced diffraction techniques, possible cationic point defects in off stoichiometric chalcopyrite type compound semiconductors. This knowledge leads to a further understanding of the complex electronic properties of Cu(In,Ga)Se₂ absorber layers in thin film solar cells, which is indispensable to aim in highly efficient photovoltaic devices based on such compounds.

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Pressure-induced phase transitions in Na-Au intermetallic compounds

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Sodium and gold are found to react at room temperature under high pressure. We have compressed a mixture of sodium and a fine powder of gold in a diamond anvil cell (DAC), and taken powder x-ray diffraction