Hybrid photovoltaic cells combine the light-harvesting and charge transport properties of semiconductor and metal oxide nanoparticles with polymer semiconductors. Cells based purely on semiconducting polymers suffer from poor harvestig of red light, poor long term stability, and fast charge recombination. In contrast, nanoparticles can have good photostability, long recombination lifetimes and an absorption edge that can be tuned, by control of their size, to optimise energy extraction from the solar spectrum. It has been suggested that multiple exciton generation (MEG) can occur in semiconductor nanoparticles [1]. When a photon with energy greater than the band gap is absorbed generally only one electron-hole pair is created, however, if MEG occurs then one high energy photon can produce multiple electron-hole pairs. If species which can undergo MEG were incorporated into a hybrid solar cell then the efficiency would be significantly improved.

Transient absorption spectroscopy is a sensitive technique which has been previously used to probe the properties of semiconductor quantum dots [2]. However, the many variables in such experiments make it hard to show the unequivocal existence of MEG. Results can be affected by not only the chemical composition of the nanoparticle itself, but also the choice of solvent, the identity of the nanoparticle capping groups, and the specific experimental set up used. The complex nature of these measurements means that there is some discussion within the community as to whether or not MEG occurs in semiconductor nanoparticles [3].

Experimental Design

We have recently completed construction of our transient absorption set-up represented schematically in figure 1. In brief, a laser system produces an intense 800 nm beam. This is split such that 95 % pumps an OPA, which can generate a wide range of wavelengths, this is known as the pump beam and is used to excite the sample. The remaining 5 % of the laser output, which is known as the probe beam, is used to generate a white light continuum in a sapphire plate, shown in figure 4, and is used to obtain the absorption spectra as a function of time. Absorption spectra are recorded at varying time delays from the excitation pulse and the results collected and analysed on a computer.

This system records the change in absorption as a function of pump-probe delay time. The spectra recorded are expected to be vastly different for single compared to multiple exciton generation. Single excitons have relatively long lifetimes, in the order of ns, whereas multiple excitons decay in the order of ps.

Both the wavelength and the intensity of the pump beam are known to affect the spectra. Short wavelength, high energy, photons should produce MEG signatures, but longer wavelength, lower energy, photons at a high enough intensity should produce similar spectra due to multiphoton absorption occurring. Thus it is important to study not only a range of pump wavelengths, but also a wide range of pump intensities.

The spectra recorded at various pump delays will also give information on state filling during relaxation of the excitions and coulomb interactions between excitons [4].

Initial Results & Future Work

We have previously carried out an investigation, using soft x-ray photoemission spectroscopy, XPS, of the valence band characteristics and lead 4f and sulphur 2p core levels of PbS in bulk form and as 6 nm 4-ethylpyridine capped PbS nanoparticles. These measurements were carried out at the STFC Synchrotron Radiation Source at the Daresbury Laboratory, UK, on a multipole wiggler beamline (MPW6.1).

The core level XPS spectra provide vital information about the oxidation states and local environment of the component elements. The spectra of the lead 4f core levels (figure 2) and sulphur 2p core levels (figure 3) show that both the bulk and nanoparticulate samples contained Pb$^{2+}$ and S$^{2-}$ as found in PbS, but the nanoparticulate sample also contained a large proportion of neutral Pb and S and the nanoparticle capping group significantly increased the binding energy of the sulphur 2p core levels.

The XPS spectra make it clear that the chemical composition of the nanoparticulate PbS is very much more complex than that of the bulk material and the nature of the capping group has a large impact on its chemical and electronic properties. The effect on MEG of the precise nature of the nanoparticle capping group, and configuration of core/shell layers has not been widely investigated.

By measuring transient absorption spectra for PbS and commercially available CdSe and InP quantum dots (Nanoco Ltd.) each with various capping groups, we hope to characterise the specific effects which surface composition has on the photochemistry of the quantum dots and unequivocally show the existence, or not, of MEG in semiconductor nanoparticles.

References