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Measuring transient phenomena in photoactive materials by FTIR

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PhD Seminar

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Developing of new, highly efficient, photocatalytic materials depends to large extent on better understanding of the physical and chemical phenomena occurring right after photon absorption. Over the years, three major techniques have been utilized for such studies, using pulsed lasers beams for excitation: Transient UV-vis absorption/reflection, transient photoluminescence, and Time Resolved Microwave Conductivity (TRMC). While these complementary methods provide important information on the life times of free carriers they are almost silent with respect to the chemical species involved in the process and with respect to specific loci at which the post-excitation processes occur.

Here we present a fourth method for studying the excitation of photoactive and, in particular, photocatalytic materials. The method is based on measuring time resolved ($5*10^{-9}$ sec in resolution) IR spectroscopy of the photocatalytic materials upon excitation with the third harmonic (355 nm) of a Nd:YAG pulsed laser. The time resolved FTIR spectra is obtained by using a "step-scan" configuration, i.e. by recording a temporal signal at a fixed location of the moving mirror in the Michelson interferometer, following by altering the position of the mirror and re-measuring the temporal signal upon re-excitation. At the end of the process, an array of data points in the time-distance is obtained, facilitating to perform Fourier Transformation of all data points gathered at the same specific time.

The technique is demonstrated here by measuring temporal changes in the FTIR spectrum of BiOCl, BiVO4 and g-C_3N_4. Six types of well-defined BiOCl particles were prepared and measured. The main results showed a negative correlation between the rate constant of photo-reduction of Cr(VI) and the time duration of changes in the Bi-O signal. These results have been explained by the presence of deep traps, which may be located at the un-faceted sidewalls.

The excitation of four different of $BiVO_4$ particles revealed a change in the 740 cm^{-1} peak (V-O) and the appearance of two dominating signals at 694 cm^{-1} and 802 cm^{-1}. These peaks show similarity to the Bi-O signal (680 cm^{-1}) and the symmetric V-O signal at 822 cm^{-1}. Here, again, the observations show a negative correlation between the photoreduction of Cr(VI) and the time duration of the transient signals, and a correlation between the photoreduction of Cr(VI) to the percentage of oxygen on the surface. The explanation for These results are explained based on accumulation of charge carriers at a deep level traps.