Title:	Spectroscopic Investigation of Ultrafast Photo-physical Processes in Chalcogenide Based Two - Dimensional Material
Authors:	Tanmay, Goswami
Keywords:	Spectroscopic Investigation Ultrafast Photo-physical Processes Chalcogenide Based Two - Dimensional Material
Issue Date:	Mar-2023
Publisher:	IISER Mohali
Abstract:	Since the discovery of monolayer graphene in 2004, there have been growing interest on two dimensional (2D) layered materials, motivated by their outstanding optical, electrical, and mechanical properties. These materials are blessed with many unique characteristics like, high charge carrier mobility, large surface area, strong light-matter interactions, tunable electronic band structure, large quasiparticle binding energy etc. The evolution of these layered entities has revolutionized the condensed matter opto-electronic field, owing to their potential in many exquisite applications like lasers, light emitting diodes (LED), photodetectors, displays, optical sensors, as well as in energy harvesting devices. The efficiencies of these optical devices would be primarily dependent on the material itself. Following the absorption of an electromagnetic radiation, the material gets excited and follow many radiative and non-radiative pathways to relax back to the ground state. So, in order to utilize the material better in an optical device, we need to study those excited state photophysical processes inside the material. These processes are ultrafast in nature and to monitor them we need a technique which can probe very short time scale processes. Transient absorption spectroscopy (TAS) is one such technique; it can study ultrashort processes occurring in picosecond (ps), femtosecond (fs) or even attosecond (as) time scales. In my thesis work, we have employed Femtosecond Transient Absorption Spectroscopy (FTAS) to study the excited state charge carrier dynamics in different 2D metal chalcogenides and their doped or heterostructured counterparts. The first work deals with the formation and relaxation dynamics of exciton and trionic features in CVD synthesized monolayer MoS 2 flakes. Steady state photoluminescence (PL) measurements confirmed the presence of Characteristic A and B exciton of MoS 2 , as well as negatively charged A - trion in the system. Large exciton and trion binding energy made it possible, to observe these features even at room temperature. From the FTAS measurements, the exciton and trion formation time was calculated to be ~ 0.5 ps and ~ 1.2 ps, respectively. Subsequently, these quasiparticles decay with exciton-exciton annihilation or auger recombination processes. Further, we drop-casted Au nanoparticles (NPs) on top ofmonolayer MoS 2 in order to fabricate a metal-semiconductor (Au-MoS 2) heterojunction, where Au NPs act as a sink of electrons. With the illumination of pump, photoexcited electrons migrate from MoS 2 to Au with ~ 0.6 ps time scale, dissociating both the exciton and trions. In the next work, we have studied four different excitonic features in a few layer WS 2 . The WS 2 nanosheets were synthesized using liquid exfoliation technique, which were having 5-6 layers. Steady state absorption spectroscopy and FTAS study revealed the formation of A, B, C and D excitons in this layered material, irrespective of the excitation energy. Among which, A, B originate at the K/K' region and C, D form at the Λ-Γ region of the electronic band structure. This decides their formation and relaxation dynamics and influence the optical properties of this material. C, D excitons decay in a much slower manner than that of A, B, mainly because of Pauli blocking effect at the K valley and subsequent Λ-Γ indirect recombination channel. This slower decay of high energy excitons provides us a unique opportunity to extract these hot charge carriers for the betterment of an opto-electronic device. My next project is based on a ternary chalcogenide system, Cu 2 MoS 4 (CMS), which showed great potential towards photovoltaic as well as photocatalytic applications lately. However, optical properties of this material are almost unexplored. Raman spectroscopy unveils the presence of very strong electron-phonon (e-ph) coupling in this material. The PL spectrum is comprised of two broad peaks, originated from the radiative recombinations associated with the band edge and near band edge trap states, respectively. In FTAS, we probed the band edge excitons and found that they are strongly influenced by both the trap mediated recombination and the Auger recombination. The saturation density of the material lies in the range of 5.3 ± 0.7 x 10 14 photons/cm 2 , beyond which Auger like processes dominate. The e-ph coupling strength reaches maximum at around 100K, which was emphasized in faster decay dynamics of the CMS exciton in this temperature region. The band gap as well becomes larger as we approach lower temperatures. This detailed spectroscopic investigation would be helpful in implementing CMS like ternary chalcogenides in diverse photonic applications. Finally, we have employed FTAS in studying two modified 2D systems, a CdS/MoS 2 heterojunction and non-metal doped ZnIn 2 S 4 (ZIS) nanosheets. CdS/MoS 2 is a unique heterojunction, where 1D CdS nanorods are in close contact with 2D MoS 2 sheets. Here, MoS 2 works as a hot electron extractor. Upon photoexcitation, CdS hot charge carriers preferentially move towards the MoS 2 region. The hot carrier transfer rate was found to be much higher than the band edge transfer. This high probability of hot carrier transfer is a great sign for any opto-electronic device. In the other system, thin ZIS nanosheets are separately doped with 'O' and 'N' and their H 2 evolutionefficiencies were correlated with the modulated charge carrier dynamics. The doped nanosheets proved to be better photocatalysts, owing to their modified energy band structure and enhanced charge carrier separation. FTAS unveiled that, the H 2 evolution reaction in ZIS takes place in the near band edge trap states, not in the conduction band. This study will help in comprehending the H 2 evolution process and designing more photocatalytic materials like ZIS. In summary, we have explored the intrinsic photo-physical behaviours in some very important metal chalcogenide systems, which will be beneficiary in the study of these kind of materials and would guide the growing field of two-dimensional optical devices.
URI:	http://hdl.handle.net/123456789/5340
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