Abstract

Understanding the efficiency of a material in its optoelectronic application requires a thorough investigation of its excited carrier dynamics. Ultrafast broadband transient absorption (TA) spectroscopy is a very mature technique to unravel excited carrier dynamics of any optoelectronic material. Excited state carrier dynamics includes information about carrier generation, thermalization, cooling, relaxation, and recombination. TA spectroscopy can also measure transport properties of carriers. This thesis presents a systematic study on the characterizing ultrafast dynamics of photo-excited carriers in two emerging optoelectronic materials- bulk mixed halide perovskite (MHP) and two dimensional (2D) Selenium (Se) using TA spectroscopy. In the first work, I have modified bulk MHP with copper-based chalcogenide, Cu_2ZnSnS_4 (CZTS) nanocrystal (NC) due to their uniquely combined favorable optoelectronic properties. I have extensively studied ultrafast hot carrier cooling and recombination dynamics of CZTS NC modified bulk MHP using femtosecond TA spectroscopy. The results show modification increases the light absorption of the bulk MHP. Although hot carrier cooling dynamics remains unperturbed, the modification causes drastic changes in the recombination dynamics of bulk MHP. Results show nearly one order reduction of recombination rate constant for trap state (k_1), band to band (k_2) and auger recombination (k_3) from $5.5 \times 10^8 s^{-1}, 8 \times 10^{-14} cm^3 s^{-1}$ and $1.2 \times 10^{-32} cm^6 s^{-1}$ to $8 \times 10^7 s^{-1}, 8 \times 10^{-15} cm^3 s^{-1}$ and $3 \times 10^{-34} cm^6 s^{-1}$ respectively, after the modification. Passivation and charge transfer play a significant role to reduce the recombination rate with longer diffusion length (from 0.34 μm to 1 μm), which signifies bright prospects in optoelectronic device application. In my second work, I have investigated the effect of Au@CZTS core-shell NC on the hot carrier cooling and recombination dynamics of bulk MHP. Core-shell modification increases the absorption as well as excited carrier density. This study reveals the presence of enhanced hot phonon bottleneck effect and reduced recombination rate constants in Au@CZTS core-shell NC modified perovskite ((i) Auger (from $1.2x10^{-32}$ cm^6s^{-1} to $1.7x10^{-34}$ cm^6s^{-1}), (ii) band to band (from 8 x 10^{-14} cm^3s^{-1} to 8 x 10^{-15} cm^3s^{-1}), and (iii) trap state (from $5.5x10^8$ s^{-1} to $5x10^7s^{-1}$). The diffusion length also increases nearly one order from 0.34 μm to 1.3 μm after the modification that paves the way for the development of highly efficient perovskite based solar cell. The final work focuses on thorough ultrafast carrier dynamics of 2D Se in one- and multi-photon absorption regime. This study shows presence of large two-photon absorption cross-section (2.9×10^5 GM where $1GM = 10^{-50} cm^4 s/\text{photon}$) in 2D Se. The carrier recombination process is dominated by surface and sub-surface defect states in one- and multi-photon absorption regime respectively, resulting nearly one order increased carrier lifetime in case of three-photon-absorption compared to one-photon-absorption. Reflection Z scan measurement shows saturable absorption coefficients of ~ $10^3 cm/GW$ and two photon absorption coefficients around 30-70 cm/GW for 2D Se. We theoretically predicted photo-responsivity of $7.78\,\mu$A/W for two-terminal photo-detector based on 2D Se. The study highlights the potential of 2D Se as a versatile material for various linear and non-linear optoelectronic applications. The systematic investigation of ultrafast carrier dynamics in bulk MHP and 2D Se demonstrates the immense potential of these materials for advancing optoelectronic applications and lays the foundation for the development of highly efficient and versatile optoelectronic devices.

Keywords: Transient absorption spectroscopy, Hot carrier cooling, Recombination dynamics, Multi-photon absorption, Perovskite, Nanocrystal modification, 2D Selenium