Investigations of exciton-trion and exciton-biexciton coupling in van der Waals hBN/WS₂/hBN heterostructures by upconversion photoluminescence excitation measurements

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The monolayer transition metal dichalcogenides (TMDCs) are unique systems to study electronic and phononic interactions as well as intra- and intervalley excitons and trions. These excitonic complexes are optically either active or inactive due to selection rules from spin or momentum conservation. In W-based materials the inverted order of the optically allowed and optically forbidden states in the K⁻/K⁺-valley results in a dark exciton band lying at lower energy than the bright band. Hence, their optical properties are determined by a manifold of bright and dark exciton states. The involved transitions positioned energetically below the bright direct exciton (X) have been identified as bright singlet and triplet trions, neutral and charged bright biexcitons, spin-forbidden dark excitons, dark trions and momentum-indirect dark excitons activated by scattering with defects or phonons. Recent works have demonstrated that upconversion (UPC) photoluminescence (PL) where, in contrast to the conventional PL, emission is detected at energies above the excitation energy, is an alternative route to address the different excitonic species in TMDC monolayers [1, 2]. The excess energy required for the UPC process can be taken from either phonons or resident electrons in the monolayer hence; the UPC PL provides information on both the energy spectra of the TMDC as well as the scattering mechanism related to exciton-electron, or exciton-phonon interaction. Here, we excite resonantly the UPC PL in hBN/WS₂/hBN heterostructures by tuning the laser energy between the T₅ peak and the high-energy flank of the XX₀ peak, marked by the red arrows. (Fig.1a). The UPC PLE spectra are depicted in the Fig. 1b by a color map which gives the X emission line as a function of the excitation energy E_{exc} detuned from E_X. The integration across the UPC PL energy range yields the dependence shown in the Fig.3. It clearly exhibits three resonances at energy gains of 18, 29.5, and 36.0 meV. The first resonance matches the spectral positions of the biexciton XX₀ and further two correspond to the spin-triplet T₃ and spin-singlet trion Tₛ, respectively. The revealing of the fine trion structure in the UPC PL sheds a new light on exciton-trion coupling in monolayer WS₂.