SUPPLEMENTARY INFORMATION

On the Unique Temperature Dependent Interplay of B-Exciton and Its Trion in Monolayer $MoSe_2$

Durgesh Banswar[1], Renu Raman Sahu[2], Rupali Srivatsava[1] Md Samim Hassan[3], Sahil Singh[3], Sameer Sapra[3], Tapajyoti Das Gupta[2], Ankur Goswami[1], Krishna Balasubramanian[1]*
[1]Department of Material Science and Engineering, Indian Institute of Technology Delhi
[2]Instrumentation and Applied Physics, Indian Institute of Science, Bangalore
[3]Chemistry Department, Indian Institute of Technology Delhi
Email: bkrishna@mse.iitd.ac.in

S1: SAMPLE PREPRATION

Prepared $MoSe_2$ nanosheets power (0.5 mg) were dissolved in 5 ml of toluene and further sonicated for 1 hour so that $MoSe_2$ nanosheets completely dissolved. As reported in our previous work the thickness of the single layer is 1.02 nm [19]. Obtained solution (gray colored) as shown in Fig. (S1) was deposited on GPNS substrate and on normal glass substrate by spin coater with drop casting method at 2400 rpm for 45 seconds. $MoSe_2$ coated samples were kept at room temperature for 24 hours so that solvent completely evaporates. Prepared samples were further characterized with FESEM and optical measurements.

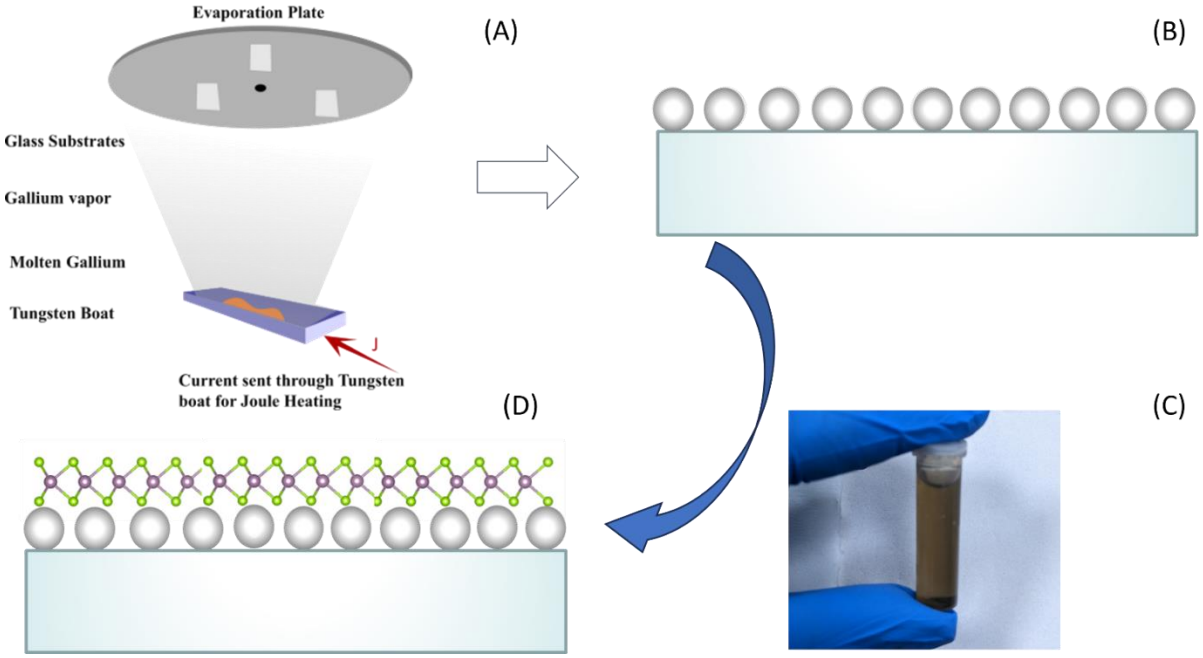

Figure S1: Process flow from fabricating GPNS substrate to deposition of $MoSe_2$ (A) Schematic of thermal evaporation method, (B) Gallium based plasmonic Nano-substrates (GPNS), (C) prepared $MoSe_2$ solution in toluene after sonication bath, (D) $MoSe_2$ on top of the GPNS substrate.

S2: OPTICAL CHARACTERIZATION

Optical properties of the prepared $MoSe_2$ with and without GPNS have been analysed, first Raman Spectroscopy measurements were conducted by Reinishaw-Raman Spectrometer with laser excitation wavelength of 785 nm, optical power of 1 mW at 100x objective lens and acquisition time remain to be 40 seconds with 10 accumulations.
Ultraviolet -visible (UV-vis) absorption and reflectance spectra were recorded with UV-Vis-NIR Spectrometer (UV-3600iPlus) with scan rate of 1 nm/sec. To measure the reflectance spectra of $MoSe_2$-GPNS, integrating sphere assembly was used as shown in Fig. S2(A) and first baseline was corrected by putting standard white plate in both exit window of reference and sample side, once baseline was corrected in measuring range of wavelength (here 350 nm to 850 nm), white standard plate at sample side was replaced with the prepared $MoSe_2$-GPNS sample and measurements were recorded in reflectance mode. Further as $MoSe_2$ on glass substrate is transparent in nature, therefore absorption measurement was performed to depict the positions of exciton transitions. Absorption measurement was performed by using Direct Detection Unit (DDU) in which film holder assembly (P/N 204-58909) was used to hold the samples shown in Fig. S2(B). First normal glass substrates were used in reference side and sample side for the baseline corrections. Once baseline corrected in specified wavelength range (here 400 nm to 800 nm), glass substrate in sample side was replaced with the prepared $MoSe_2$ coated glass substrate and further measurements were performed in absorption mode of the spectrometer.

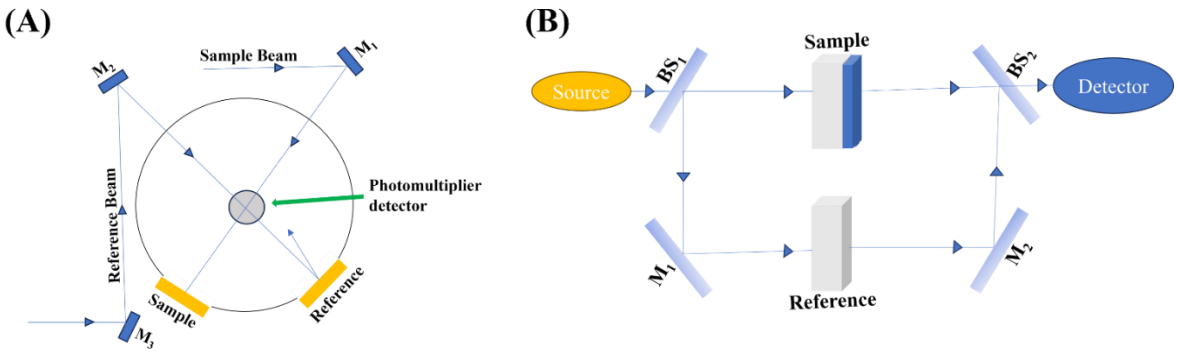

Figure S2: (A) Schematic for measurement of Reflectance of $MoSe_2$-GPNS in UV-vis with integrating sphere assembly, (B) Direct detection unit for absorption measurement of $MoSe_2$ over glass substrate (BS is beam splitter and M is denoted for Mirror).

photoluminescence measurements were performed with Edinburgh Instruments-FLS920 (Study State PL) at temperatures ranging from 100 K to 300 K. Liquid Nitrogen assembly was used to keep the sample at cryogenic temperatures. Measurements were carried out with excitation wavelength of 502 nm by Xenon lamp (300 Watt)-Study State PL with dwell time 0.20 sec and scan rate of 5 nm/sec.

S3: GPNS - TIME DEPENDENT MEASUREMENTS

Gallium based plasmonic nano-substrates were used here for 100 nm (GPNS-100) and for 150 nm (GPNS-150). $MoSe_2$ nanosheets were drop casted over GPNS-100 and GPNS-150 respectively and further details of sample preparation is given in S1. To make sure the presence of the $MoSe_2$ monolayer, Raman measurements were performed, and characteristic peaks were identified which shows the presence of monolayer as shown in Figure S3(A).

Figure S3(B) shows the LSPR coupling of B species to the plasmonic modes. As emission coupling to the plasmonic modes can be indicated by lifetime measurements. Thus, we conducted time dependent photoluminescence measurement at room temperature. Time dependence of the integrated emission at two different excitation wavelengths are shown in Figure S3(B). While the typical PL lifetimes in $MoSe_2$ is about 3 – 10 ns, an order of magnitude faster PL lifetime (τ_1 = 0.57 ns) was noted with the $MoSe_2$ on 100 nm Ga nanoparticles. Such fast excited carrier decay dynamics in comparison to similarly prepared

monolayer flakes at room temperature are clear evidence for strong emission coupling into the plasmonic nanoparticles.

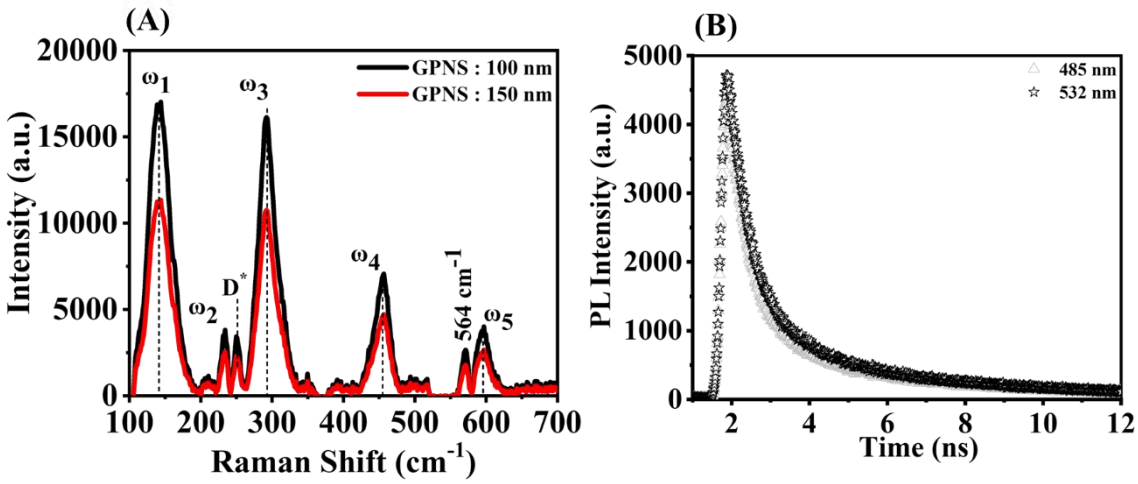

Figure S3: (A) Raman spectra of $MoSe_2$-GPNS with Gallium droplet radius of 100 nm and 150 nm, (B) time dependent PL spectra of $MoSe_2$-GPNS with excitation wavelengths of 485 nm and 532 nm.

S4: FEM CALCULATIONS

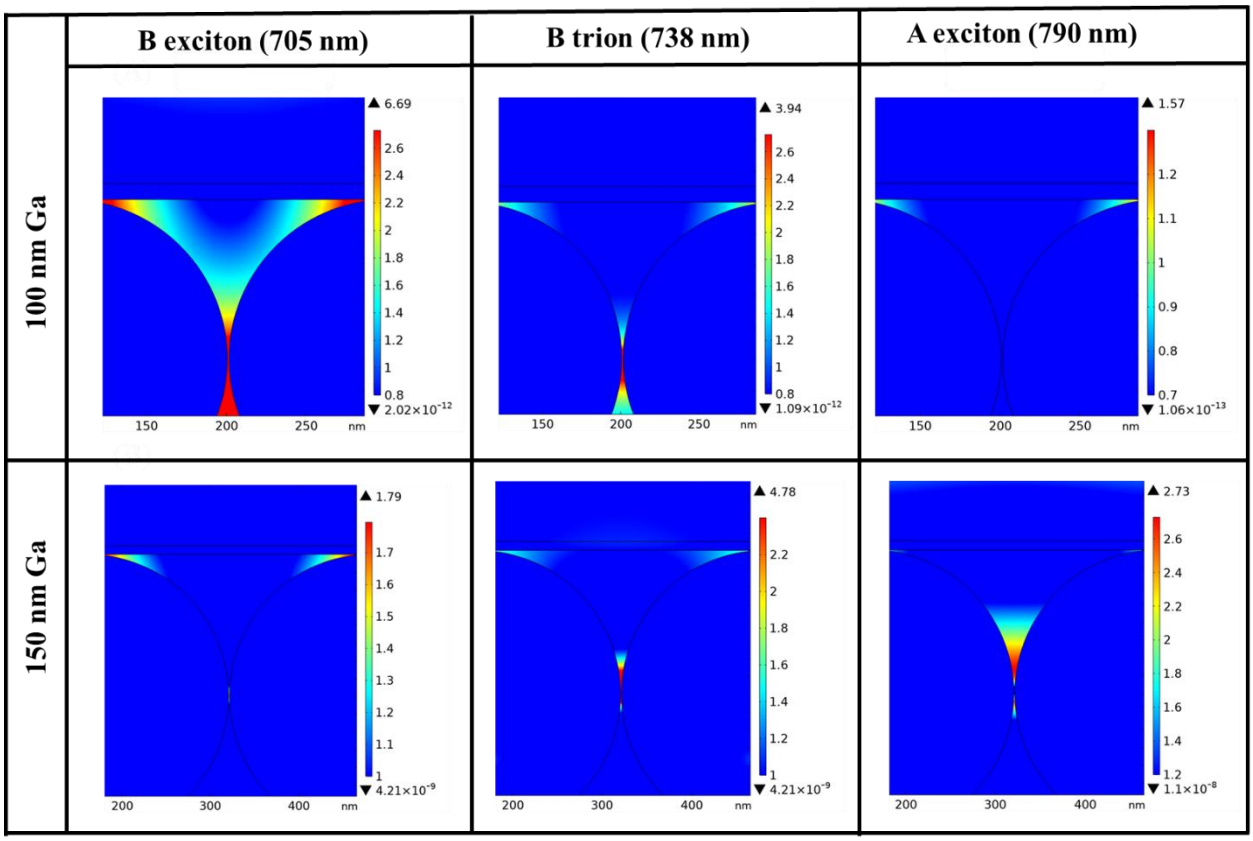

Figure S4: Light-matter Interaction between Gallium nanoparticles and $MoSe_2$ monolayer at B and A exciton positions for-radius of particle to be 100 nm and radius of Ga particles to be 150 nm.

Using Finite element method (FEM), Detailed electric field calculations at predetermined excitation wavelengths show the difference in the coupling field intensities between the Ga nanoparticle and $MoSe_2$ layer for different particle sizes. This is illustrated in Figure S4 for 100 nm and 150 nm gallium particles respectively. For the 100 nm Ga particle (GPNS-100), a strong confined electric field intensity

is visible for the B-exciton (705 nm) and the B-trions (738 nm) positions which is three orders of magnitude higher than the field at A exciton position (E_B = 6.69 V/m and E_A = 0.007 V/m). On the other hand, for the 150 nm particle, an emergence of inter-particle plasmonic field enhancement is noted at the A exciton position with a weaker field near the B-exciton. The field intensities are tabulated below:

Table 1: Parameters obtained from FEM calculations.

Size of Nanoparticle	**R = 100 nm**			**R = 150 nm**		
Species	B exciton	B trion	A exciton	B exciton	B trion	A exciton
Wavelength position (nm)	705	738	-	705	738	790
E_1 (V/m)	6.69	3.94	**0.007**	1.78	4.74	**2.78**
E_2 (V/m)	3.5	1.9	1	1.5	1.8	1.2

S5: FEM CALCULATIONS WITH VARIATION IN SIZE AND SEPERATION

Regulation of the A exciton species is identified using FEM calculations, here absorbance is calculated for the nanoparticles of radius 100 – 175 nm with fixed particle separation of 1 nm as shown in Figure S5. It can be observed that the plasmonic resonance red shifts and the full width half maximum broadens with increase in the particle size. For the case of the Ga nanoparticle interfacing with $MoSe_2$, it is observed that particles with diameter close to 100 nm selectively excites B exciton species. An emergence of A-exciton enhancement can be observed with particle sizes greater than 125 nm. However, the selectivity of a single exciton species is lost due to the widening of the plasmonic resonance. The B-exciton enhancement persists for particle sizes smaller than 175 nm. In contrast, for particles of size 175 nm, A-exciton and its trion is significantly promoted, with minimum overlap with the B-exciton position. Such dependence on the particle size is also widely observed in several other plasmonic systems [27]. This illustrates the strong influence of the particle size on the plasmonic resonance and that numerical calculations serve as an effective tool to design such experiments for selective enhancements.

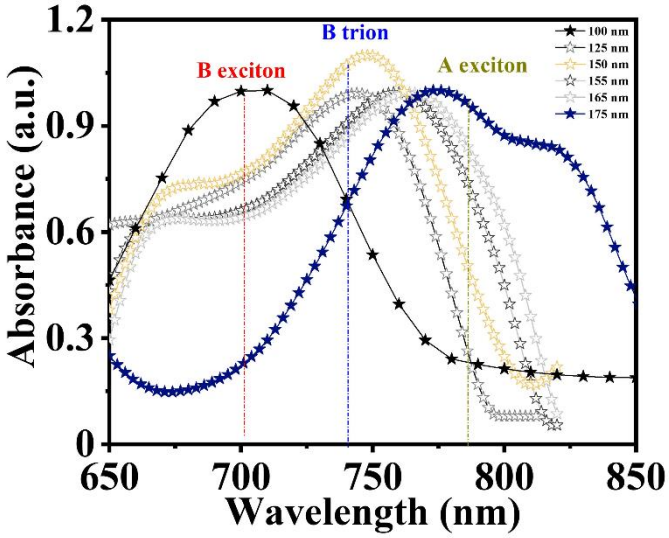

Figure S5: calculated absorbance spectra of Ga-$MoSe_2$ with radius of particles (100 – 175) nm.