Enhanced absorption with quantum dots, metal nanoparticles, and 2D materials

Ergun Simsek* and Bablu Mukherjee
Department of Electrical and Computer Engineering, The George Washington University, Washington, D.C. 20052, USA

Asim Guchhait and Yin Thai Chan
Department of Chemistry, National University of Singapore (Singapore)
Singapore 117543, Singapore

ABSTRACT

We fabricate and characterize mono- and few- layers of MoS_2 and WSe_2 on glass and SiO_2/Si substrates. PbS quantum dots and/or Au nanoparticles are deposited on the fabricated thin metal dichalcogenide films by controlled drop casting and electron beam evaporation techniques. The reflection spectra of the fabricated structures are measured with a spatially resolved reflectometry setup. Both experimental and numerical results show that surface functionalization with metal nanoparticles can enhance atomically thin transition metal dichalcogenides' absorption and scattering capabilities, however semiconducting quantum dots do not create such effect.

Keywords: 2D Layered Materials, Quantum dots, Nanoparticles, Optical properties

1. INTRODUCTION

Being in the family of two-dimensional (2D) layered transition metal dichalcogenides (TMD), mono- and a few- layer of molybdenum disulfide (MoS_2) and tungsten diselenide (WSe_2) show fine absorption and emission features, which change as a function of TMD thickness and excitation wavelength [1-9]. Their absorption spectra show three major peaks in the visible part of the electromagnetic spectrum, which correspond to their bandgap and excitons A and B [1, 2, 6-9]. The strength and the width of these absorption peaks change with Fermi energy, in other words with temperature, doping level, and voltage (if applied).

Metal nanoparticles and quantum dots also exhibit absorption resonances in the visible and near infrared regions. In fact, we can control where this resonance occurs by changing their dimensions, composition, and density [10]. In this work, we are primarily interested in how these different resonance mechanisms affect each other when we illuminate complex structures composed of TMDs, metal nanoparticles, and quantum dots.

The interactions between TMD excitons and surface plasmons that are excited on the surface of metal nanoparticles are not completely understood. When we illuminate a TMD film decorated with metal nanoparticles, three additional interactions happen compared to illuminating a bare TMD film: (i) since metal nanoparticles absorb some of the incident energy, TMDs receive less light; (ii) induced dipole moment of metal nanoparticles make them act like local antennas and create secondary fields; and (iii) this secondary field gets reflected back from the substrate to the metal nanoparticle. If we neglect the third interaction for the sake of simplicity, we can expect having no enhanced field if the metal nanoparticles are so small compared to the wavelength and their density is low to have a localized plasmonic resonance. And if we think about the opposite scenario (i.e. metal nano-particles are not so small and the inter-particle distance is equal to or less than their diameter), we might observe an enhancement or a weakening. The question is under what condition(s) field enhancement occurs?

* E-mail: simsek@gwu.edu

Quantum Dots and Nanostructures: Growth, Characterization, and Modeling XIII, edited by Diana L. Huffaker, Holger Eisele, Kimberly A. Dick, Proc. of SPIE Vol. 9758, 97580G · © 2016 SPIE
CCC code: 0277-786X/16/$18 · doi: 10.1117/12.2213054

For the case with metal nanoparticles, the enhancement comes from the plasmonic resonance. This fact leads us to two different outcomes. First, when the opto-electronic properties of the TMD film change, the strength and the frequency of plasmonic resonance are very likely to change as well. In other words, we can tune plasmonic resonance by changing exciton dynamics of TMDs. Second, if we replace metal nanoparticles with semiconducting quantum dots, there should not be any enhancement (however, having both metal nanoparticles and quantum dots can create enhancement).

In order to answer our question (What are the requirements to enhance the absorptance within TMDs?) and verify our claims (i.e. semiconducting quantum dots should not be able to enhance the absorption), we conducted a series of experiments with thin TMD films, gold (Au) metal nanoparticles, and lead sulfide (PbS) quantum dots.

We synthesize thin MoS_2 and WSe_2 films (mono-, bi-, tri-layer, etc.) via both mechanical exfoliation and chemical vapor decomposition. Their number of layers and crystalline quality are determined via atomic force microscopy (AFM), Raman spectroscopy, and photoluminescence (PL) measurements. Quantum dots are prepared via wet chemical reaction techniques. Reflection and transmission spectroscopy experiments are conducted on TMD coated opaque (silicon) and transparent (glass) substrates, respectively, decorated with metal nanoparticles and quantum dots. The accuracy of our measured data is verified via numerical simulations. Our experimental results show that

i. Quantum dots do not enhance the absorption of TMD films

ii. Metal nanoparticles can enhance the absorption of TMD films where the amount of enhancement depends on the size, shape, material composition, uniformity, and density of metal nanoparticles.

2. METHODS

Preparation of Thin TMD Films

Chemical Vapor Deposition (CVD): High temperature (~950° C) tube furnace set-up is used to synthesize WSe_2 film under controlled gaseous environments (mixture of 5% H_2 with Ar gas) and optimized conditions on sapphire and SiO_2/Si substrates, as shown in Figure 1 (a) and (b) respectively. Nearly triangular WSe_2 crystals show quite good color contrast especially when it is on SiO_2/Si substrate. Details of the procedure can be found in [7].

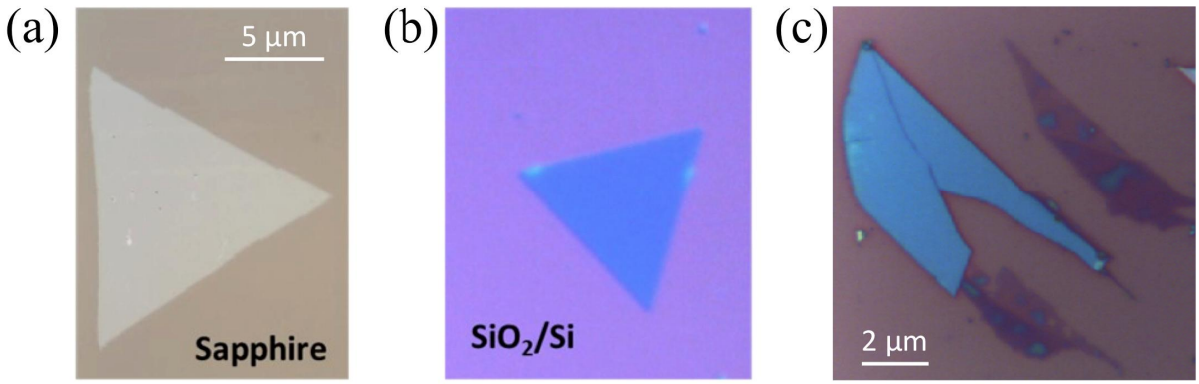

Figure 1. Optical images of CVD grown bilayer WSe_2 on top of (a) sapphire and (b) SiO_2/Si substrate and mechanically exfoliated (c) MoS_2 flakes.

Mechanically Exfoliation: Single- and few- layer MoS_2 films are deposited on 285-300 nm thick SiO_2/Si substrates via mechanical exfoliation as follows. First, a small piece of bulk MoS_2 is placed in the sticky side of a piece of scotch tape. Then repeated folding and unfolding of the tape containing MoS_2 flake is performed to produce thin flakes at different parts of the tape. At the final step, the tape with different thickness of the flakes is gently pressed onto a cleaned substrate. After few times mild rubbing with cotton tipped wood sticks, we remove the tape from the substrate leaving behind MoS_2 flakes with different thickness.

The number of the layers and crystalline quality of the prepared TMD flakes are determined through three different techniques: AFM, Raman spectroscopy, and PL measurements. For example, Fig. 2 (a) shows the PL spectrum of one of the grown WSe_2 films. It is reported that monolayer and bilayers of WSe_2 have peaks at the 752 and 773 nm,

respectively, corresponding to the exciton A. Based on our measurement; we can say that this sample is tri-layer. Raman spectroscopy is another very powerful tool of 2D material research. In Fig. 2 (b), Raman spectrum collected over a MoS_2 coated silicon wafer shows two prominent peaks at ~384.5 cm^{-1} and ~403.5 cm^{-1}, which are reported to be E^1_{2g} and A^1_g vibrational modes, respectively, of monolayer MoS_2 prepared by micromechanical exfoliation.

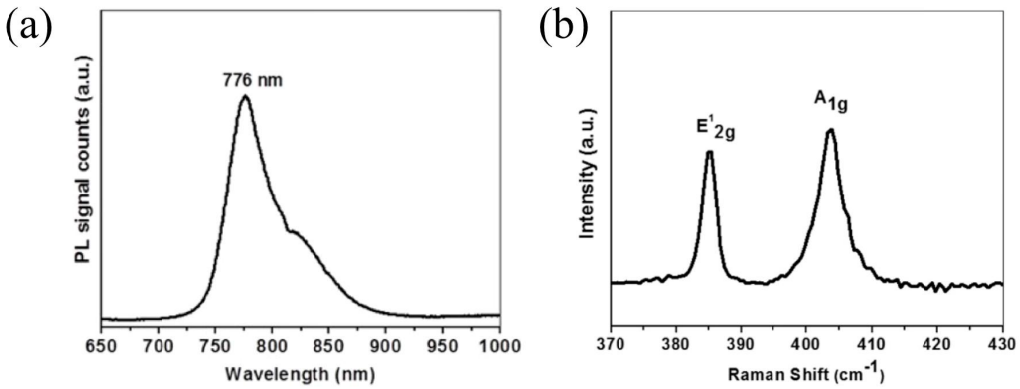

Figure 2. (a) Photoluminescence PL spectra of the WSe_2 film and (b) Raman spectra of monolayer MoS_2 flake under excitation of 532 nm laser.

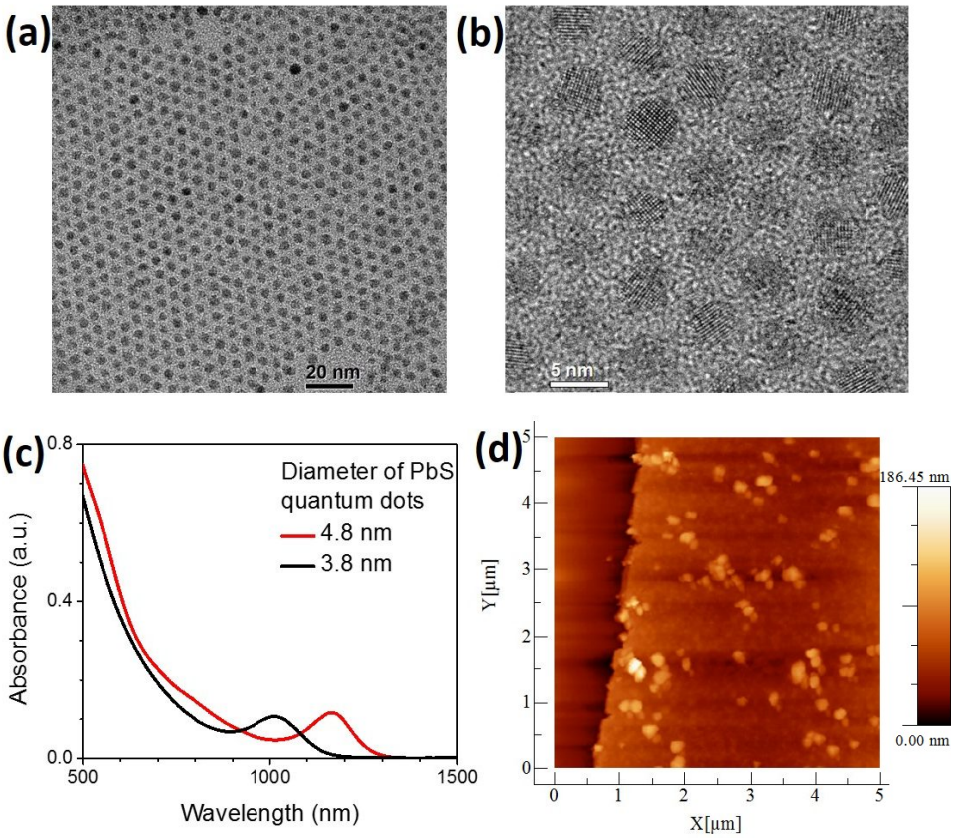

Figure 3. TEM images of PbS quantum dots with (a) low and (b) high magnification. (c) Absorption spectra of quantum dots solutions with two different size dots. (d) TEM image of quantum dot thin film formation.

Preparation of Quantum Dots

PbS nanocrystalline quantum dots are prepared via wet chemical reaction techniques; as synthesized quantum dots are shown by the Transmission Electron Microscopy (TEM) images in Figure 3 (a, b). Especially in the high resolution image, we can clearly see the crystalline planes of quantum dots. In Fig. 3 (c), we plot the absorption spectra of nanocrystalline quantum dots solutions with two different particles sizes (3.8 nm and 4.8 nm) measured using a Shimadzu UV-VISNIR UV-3600 spectrophotometer. PbS quantum dot sample has band edge absorption at infrared (IR) range however it also possesses good absorption at visible wavelength range.

For the transfer of these quantum dots on to substrates, we use the layer-by-layer sequential spin coating technique. Ligand exchange process is performed with mercaptopropionic acid (MPA) for each layer. First, the touluene solution of PbS nanocrystals is spin coated on the substrate with a speed of 3000 rpm for 10 seconds. Subsequently few drops of MPA solution in methanol is added to the film on the substrate and wait for 20 seconds then spin with same speed and time. Finally, the film is washed by methanol and toluene. The process is repeated for 8 layers which results the thickness around 50-60 nm. Figure 3 (d) is an AFM image that shows the quantum dots on top of the substrate.

Digital micropipet is used to drop cast metal nanoparticle solutions.

Spectroscopy Experiments

We measure the intensity of the light reflected from and transmitted through (if substrate is transparent) using a home-made spectroscopy setup that consists of a halogen lamp, spectrometer, optical fibers, objective lenses, and irises. For details, please see [8].

3. RESULTS

TMDs and Quantum Dots

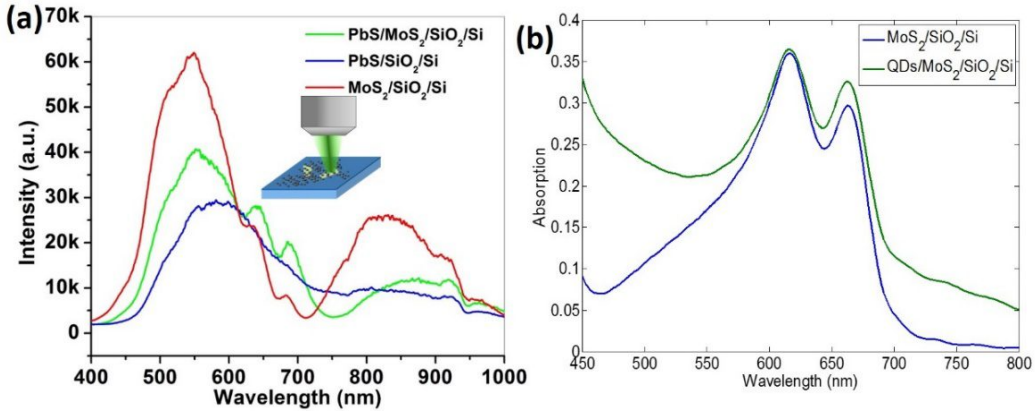

Figure 4. (a) Reflection spectra measured on (red) MoS_2-only, (blue) PbS quantum decorated only, and (green) PbS quantum dot decorated over MoS_2 coated substrate. (b) Simulated absorption spectra of trilayer MoS_2 with and without PbS quantum dots.

First, we investigate the interaction between TMDs and quantum dots. Unlike metal nanoparticles of moderate size (i.e. diameter is 0.1 λ or bigger), the quantum dots we deal with are so small compared to the wavelength and their semiconducting nature prevents them to act like good tiny antennas. This is why here we do not expect any field enhancement. In order to verify this claim, we measure the reflectance from 3 different spots on the same silicon wafer: where there is only MoS_2 film, only quantum dot decoration, and quantum dot decorated MoS_2 film. Measurement results are shown by red, blue, and green lines in Fig. 4 (a), respectively. Our aim is to determine how much loss is experienced in TMD and/or quantum dot region but the lossy nature of silicon wafer prevents us to determine this directly from reflectance measurements. This is why in [9], we first show the excellent agreement between experimental and numerical results that we produce with Lumerical FDTD (www.lumerical.com) for the reflectance; then we calculate the absorptance within the TMD and quantum dot region based on the numerical solution only, as shown in Fig. 4 (b). Our simulation results infer that the average absorption of PbS/MoS_2 film is equal to addition of quantum dots film into

MoS_2 film absorption in wavelength range of 450-800 nm. From the physical point of view, this result suggests two things. First, the method we decorate our PbS quantum dots indeed removes the un-reactants; otherwise, we would not observe such a linear response in average absorption from the hybrid material. Second, the polarizability of PbS quantum dots in the wavelength range we conduct experiments is weak so that the secondary field (created by the induced PbS quantum dots) is almost negligible compared to field scattered from quantum dots.

The thickness dependent direct-to-indirect bandgap transition of MoS_2 has strong consequences in the optical absorption results in the hybrid material. The direct bandgap nature of single-layer MoS_2 is very fragile as the interlayer coupling between just two to three MoS_2 layers is strong enough to produce indirect bandgap related higher absorption. Thus overcoming the main limitation of monolayer MoS_2 of the low absorption due to reduced thickness, our results [9] demonstrate the potential of using few layer i.e. trilayer MoS_2 as optically active material with high optical absorption. For the fact that thicker MoS_2 layer absorb more excitation light, we use trilayer thick MoS_2 (potentially much higher than that of monolayer MoS_2) coated with another optical absorb material with 0D nanocrystalline structures. Our calculations [9] show that absorbance cross-section (σ_{abs}) of PbS quantum dots is always much higher than scattering cross-section (σ_{sca}). For example at the wavelength of 600 nm, $\sigma_{abs} \approx 20000 \times \sigma_{sca}$. This means that scattered field is 4 orders of magnitude smaller than the absorbed field. Considering how fast electric field decays with distance, there is no doubt that quantum dots, which are made of very lossy material and extremely small compared to wavelength, cannot create an enhancement in the overall absorption of the hybrid structure.

TMDs and Metal Nanoparticles

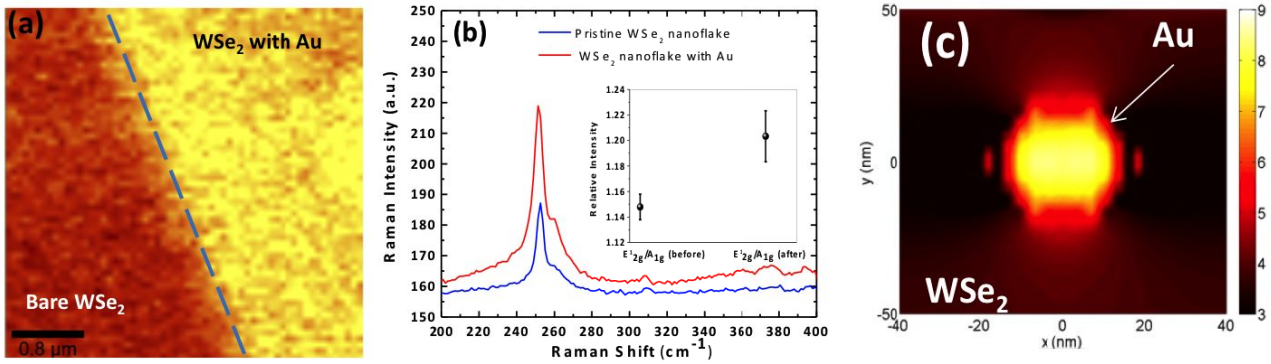

Figure 5. (a) High resolution Raman intensity map of the E^1_{2g} band of a typical WSe_2 film that was half-decorated by Au nanoparticles. (b) Raman spectra of both Au-decorated and bare WSe_2 films and its inset shows their relative intensity difference in E^1_{2g}/A_{1g}. (c) Electric field intensity distribution on the interface between WSe_2 film and Au NP.

In the second part of our study, we focus on the interaction of TMD films with metal nanoparticles. In this direction, we decorate MoS_2 and WSe_2 films with gold nanoparticles and measure their Raman spectra and absorptance. For example, Fig 5 (a) shows a high resolution Raman intensity map in which bare WSe_2 and gold decorated WSe_2 regions can be distinguished easily. Figure 5 (b) compares the Raman intensity taken on these two regions and clearly the Raman signal is enhanced by the gold nanoparticles while maintaining TMD behavior. At the conference, we will discuss how we can predict the enhancement ratio using the coupled dipole approximation theory extended to multilayered backgrounds [10].

We carry a similar study with monolayers of MoS_2. In this case, we use a gold metal nanoparticle solution to be decorated on top of monolayer MoS_2 coated quartz substrates. Figure 6 (a) shows our analysis of nanoparticle size distribution of the solution sample. This information is important for the accurate simulation of the geometry. Our experiment results show that the monolayer MoS_2 absorbs ~11.2 % in the wavelength range of 500-900 nm; whereas Au nanoparticles deposited monolayer MoS_2 absorb ~21.6 % and Au nanoparticles deposited bare glass absorb 18 %. Unlike the lossy silicon substrate case, here we can safely claim that the absorptance is increased due to plasmonic resonance. The dependence of this enhancement ratio to the size, shape, material composition, uniformity, and density of metal nanoparticles will be discussed at the conference under the light of experiment and simulation results.

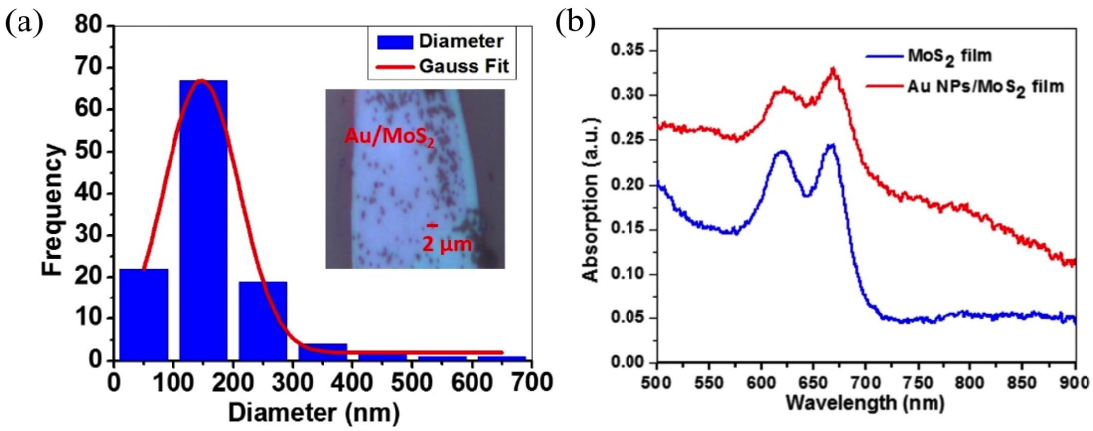

Figure 6. (a) Spherical Au nanoparticles size distribution on surface of MoS2 flake. Inset shows the optical image of spherical Au nanoparticles deposited on top of MoS2 flake. (b) Measured absorption spectra of monolayer MoS2 film dispersion with and without Au nanoparticles on top.

4. CONCLUSION

To sum up, we do not observe any enhancement in the absorptance when we decorate thin transition metal dichalcogenide films with semiconducting quantum dots. However, metal nanoparticles can crate enhancement in the absorptance, Raman, and PL spectra thanks to their plasmonic resonance. This enhancement changes as a function metal nanoparticle's material composition, size, shape, uniformity, and density.

REFERENCES

[1] Zhao W., Ghorannevis Z., Chu L., Toh M., Kloc C., Tan P-H., Eda G., "Evolution of Electronic Structure in Atomically Thin Sheets of WS_2 and WSe_2," ACS Nano 7(1), 791-797 (2013).

[2] Tonndorf P., Schmidt R., Böttger P., Zhang X., Börner J., Liebig A., Albrecht M., Kloc C., Gordan O., Zahn D. R. T., de Vasconcellos S. M., Bratschitsch R., "Photoluminescence emission and Raman response of monolayer MoS_2, $MoSe_2$, and WSe_2," Opt. Expr. 21(4), 4908-4916 (2013).

[3] Li H., Wu J., Yin Z., Zhang H., "Preparation and Applications of Mechanically Exfoliated Single-Layer and Multilayer MoS_2 and WSe_2 Nanosheets," Acc. Chem. Res. 47, 1067-1075 (2014).

[4] Xia F., Wang H., Xiao D., Dubey M., Ramasubramaniam A., "Two-dimensional material nanophotonics," Nature Photonics 8, 899-907 (2014).

[5] Sahin H., Tongay S., Horzum S., Fan W., Zhou J., Li J., Wu J., Peeters F. M., "Anomalous Raman spectra and thickness-dependent electronic properties of WSe_2," Phys. Rev. B 87, 165409-165415 (2013).

[6] Mukherjee B., Tseng F., Gunlycke D., Amara K. K., Eda G., Simsek E., "Complex Electrical Permittivity of the Monolayer Molybdenum Disulfide (MoS_2) in Near UV and Visible," Opt. Mat. Exp. 5(2), 447-455 (2015).

[7] Mukherjee B., Leong W. S., Li Y., Gong H., Sun L., Shen Z. X., Simsek E., Thong J. T. L., "Raman analysis of gold on WSe_2 single crystal film," Materials Research Express 2(6), 065009 (2015).

[8] Mukherjee B., Simsek E., "Plasmonics Enhanced Average Broadband Absorption of Monolayer MoS_2," Plasmonics 11(1), 285-289 (2016).

[9] Mukherjee B., Guchhait A., Chan Y. T., Simsek E., "Absorptance of PbS Quantum Dots Thin Film Deposited On Trilayer MoS_2," Advanced Materials Letters 6(11), 936-940 (2015).

[10] Simsek E., "Full Analytical Model for Obtaining Surface Plasmon Resonance Modes of Metal Nanoparticle Structures Embedded in Layered Media," Optics Express 18(2), 1722-1733 (2010).