Light-Matter Interactions in Complex Media with 2D Materials, Metamaterials, and Quantum Dots

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***Abstract*—We discuss our recent theoretical, numerical, and experimental studies investigating the light-matter interaction occurring in complex structures composed of atomically thin layered materials, periodic and randomly distributed metal nano-structures, and quantum dots.**

I. Introduction

In parallel to the recent developments in our abilities to fabricate structures at the nano scale and obtain one atom thick materials, the number of possibilities to make a given type of opto-electronic component is increasing every day. Now we can use nano-particles [1], [2], quantum dots [3], 2D materials including graphene [4], [5] and a few layers of transition metal dichalcogenides (TMDs) [2], [6], [7] to control the light-matter interaction. With the help of both macroscopic theoretical models and robust computational methods, now we can easily design ultra-sensitive and tunable surface plasmon sensors [4], ultra broadband and extremely efficient absorbers [6], [8], ultra-fast and low energy consuming electro-optic modulators [5], etc.

In all of these applications, each component has some certain responsibilities. For example, when metal nanoparticles are excited with light, their free electrons start to oscillate in the direction of the applied electric field. From the material perspective, these oscillations are controlled by three factors. First, the speed of electrons (c) is not equal to light's phase velocity. Second, in each tour of the oscillation, the maximum distance they can cover is approximately equal to the diameter (D) of the nanoparticle. Third, nearby metal nanoparticles influence each other. If we neglect the third constraint for the sake of simplicity, we can say that the frequency of their oscillation is $f = c/2D$ and whenever the frequency of the excitation is equal to the oscillation frequency, we obtain surface plasmon resonance. If we increase the particle size, resonance frequency decreases, resonant wavelength increases, so that we see the famous "red shift" in spectroscopy experiments. Similar to this, 2D TMDs exhibit excitonic resonances in which electron-hole pairs' oscillation is controlled by TMD's atomic structure, lattice constant, and band gap. Quantum dots stay in between these groups such that their optoelectronic properties can be controlled by changing their particle size, shape, and concentration (same as metal nanoparticles) and band gap (same as 2D TMDs).

The question we are trying to answer here is what happens when we put these different materials next to each other. In this direction, we present a series of experiments conducted with monolayer and a few layers of TMDs, metal nano-particles, and quantum dots and compare our experiment results with simulation results. The good agreement for the broadband excitations confirm that the interactions are linear and such structures can be analyzed using full-wave Maxwell's equations solvers. However, for weak and non-linear interactions such as the ones we observe in Raman spectra, such electromagnetics solvers should be hybridized with molecular dynamics solvers.

II. Methods

Mono- and few-layers of transition metal dichalcogenides (MoS_2 and WS_2) are obtained with mechanical exfoliation and deposited on SiO_2/Si substrates where the oxide is 285 nm thick. Figure 1 (a) shows one of these samples' optical image. The number of layers and crystalline quality are determined through atomic force microscopy (AFM) and Raman spectroscopy, as shown in Fig. 1 (b) and (c).

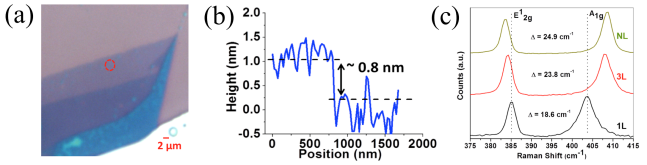

Fig. 1. (a) A TMD flake obtained with mechanical exfoliation, where the region marked with a red circle is monolayer. (b) Determination of the height via AFM. (c) Raman spectra taken at mono, tri, and N-layer regions.

Following the determination of layer numbers, we decorate our samples with gold nano-particles and PbS quantum dots, as shown in FIg. 2 (a) and (b), respectively, using a digital micropipet. Since the solutions do not have perfectly uniform metal nanoparticles or quantum dots, we can do a simple histogram analysis of our samples as shown in Fig. 2 (c) to determine the size of the particles we are dealing with.

At the end, we conduct two sets of experiments (i) regular reflection spectroscopy to measure the linear response of the hybrid structure using the setup shown in Fig. 2 (d) and (ii) Raman spectroscopy to observe vibrational, rotational, and other

low-frequency modes of the samples using a Horiba Jobin-Yvon LabRam microscopic system. We take measurements at three different spots (one on the bare substrate, one on the TMD coated substrate, and another one on the nanoparticle or quantum dot decorated TMD coated substrate) to observe the true enhancement in average absorption.

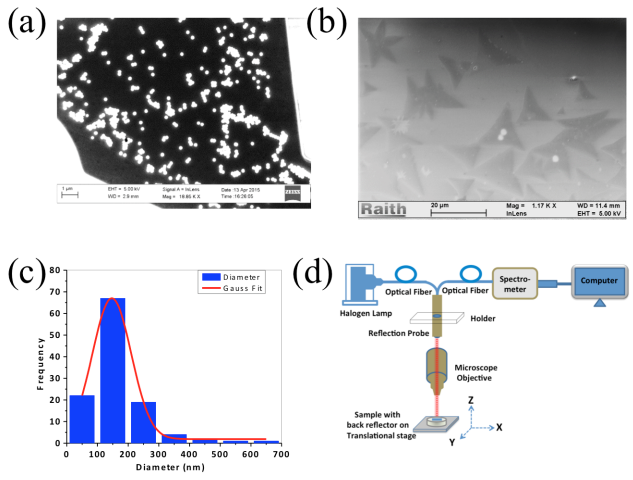

Fig. 2. (a) Gold metal nano-particles and (b) PbS quantum dots decorated MoS_2 flakes. (c) Number of particles vs. diameter analysis. (d) Schematic of the normal incident reflection spectroscopy setup used to probe sample.

III. Results

In Fig. 3 (a), Raman signal strength is plotted as measured on bare MoS_2 (Position A) and gold nanoparticle decorated MoS_2 flakes (Position B). The peaks observed at 385 and 409 cm^{-1} confirms the existence of thin MoS_2 flakes in the excited regions. Clearly, Au nanoparticles act like local antennas and enhance the local electric field strength almost 3 times. However, the enhancement at those characteristic peaks is not that strong, which is almost 1.4 times.

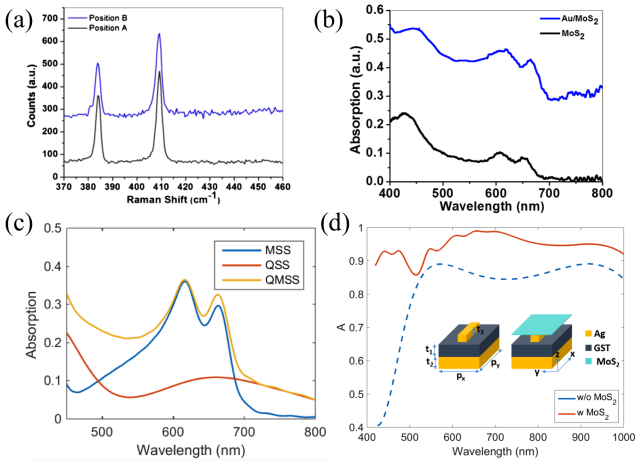

Fig. 3. (a) Enhanced Raman signal and (b) absorption of Au decorated monolayer MoS_2 samples; (c) absorptance of MoS_2 with (QMSS) and without (MSS) quantum dots; (d) enhanced absorptance (A) of excito-metamaterials.

In Fig. 3 (b), we compare the absorptance of bare (A_1) and gold decorated MoS_2 flakes. Once again, we observe a much stronger average absorption for the latter. However, this picture does not reflect true enhancement by the plasmonic resonance in average absorption. In order to do that, the absorptance of Au nanoparticle decorated SiO_2/Si should be subtracted from the A_1. Once we do that, we realize that the enhancement is strong at lower wavelength region.

A similar outcome is observed for PbS quantum dots (QD): the average absorptance of PbS QD/MoS_2 film is almost equal to the linear summation of individual average absorptances of PbS QD film and thin MoS_2 film in wavelength range of 450 to 800 nm as shown in In Fig. 3 (c). We do not observe any enhancement in optical absorptance of the hybrid material.

For the final study, we try to improve the performance of the metamaterial absorber proposed in [8] with thin TMD films. Their design has an absorptance of 92 % or even more over a broad wavelength range from 640 to 1290 nm and a wide field-of-view up to incident angle of $\pm$ 40°. However, the performance of their design significantly drops when $\lambda < 640$ nm. Since some TMDs (for example MoS_2) is very lossy in that region, they might be helpful to increase the bandwidth of this metamaterial absorber. As shown in Fig. 3 (d), monolayer MoS_2 indeed helps to increase the absorptance around 400 nm region. To be more precise, the average absorption increases from 75.4 % to 91.5 % after placing monolayer MoS_2 into the metamaterial structure for the wavelength range of 400-1000 nm.

IV. Conclusions

The interaction among excitons, plasmons, and quantum dots might be strong at the atomic level but at the macroscopic level, the structures composed of 2D materials, metal nanoparticles, and quantum dots show a linear character of those components.

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