Enhancing the Electrical Properties of MoS_2 through Nonradiative Energy Transfer

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***Abstract* – In this study highly efficient nonradiative energy transfer from semiconductor quantum dots to monolayer MoS_2 with an efficiency of ~99% is demonstrated. Although the energy transfer efficiency is close to unity, there is little enhancement of the MoS_2 photoluminescence intensity. MoS_2 samples of varying layer thickness were electrically contacted and the optoelectronic performance of the devices was studied before and after adding quantum dots in a sensitizing layer. We find photocurrent enhancements as large ~12 fold for monolayer MoS_2 devices and enhancements as high as ~4 fold for few layer devices with no change in the photocurrent with the MoS_2 devices of bulk-like thicknesses after adding the QDs.**

I. INTRODUCTION

Two-dimensional (2D) materials have attracted substantial attention in recent years due to their promising optical and electrical properties. The transition metal dichalcogenide (TMDC) family have come to the forefront due to the presence of a direct optical bandgap once the materials becomes atomically thin [1]. Exploitation of this direct bandgap in TMDC materials paves the way for novel 2D devices such as photodetectors, solar cells and phototransistors. A drawback of these 2D materials is that the atomic thickness of the active regions in these devices limits the performance and thus the efficiency of the device due to low absorption of incoming light. However, the absorption of incoming light can be improved *via* the addition of a sensitizing layer on top of the 2D active region. An ideal candidate for the sensitizing layer should have a high extinction coefficient and broadband light absorption across the spectral region. Semiconductor nanocrystal quantum dots (QDs) fulfill both these criteria. QDs are also polymer soluble and the polymer/QD blend can be used to create a thin sensitizing film on top of the 2D device.

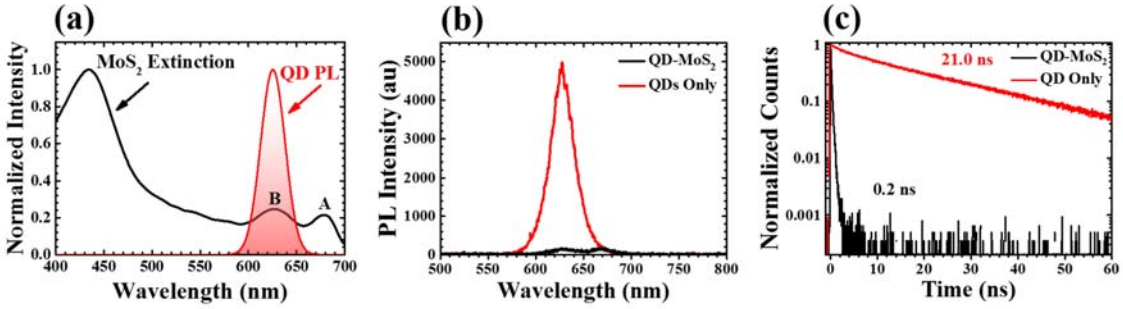
The 2D TMDC chosen for this study was MoS_2 primarily due to its optical bandgap at the low energy end (~1.8 eV) of the visible spectrum thus maximizing spectral coverage at visible wavelengths. The sensitizing layer utilized for this hybrid device increases the absorption of incident light, and allows for efficient transfer of energy from the QDs to the MoS_2 through nonradiative pathways when there is close proximity between the QDs (~ 6nm diameter) and the MoS_2 [2]-[3]. This nonradiative energy transfer (NRET) occurs through dipole-dipole coupling and not direct charge transfer. The devices studied in this work consist of monolayer, few layer and polycrystalline/bulk-like thicknesses of MoS_2. The MoS_2 layer number was varied to examine if the thickness of the active region affected the overall performance of the device after the sensitizing layer had been applied.

II. RESULTS

The MoS_2 samples were grown on Si/SiO_2 substrates using a chemical vapour deposition technique. The number of layers was determined using Raman spectroscopy. The sensitizing layer was applied using a spin-coating technique. Dilute solutions of QDs in 0.1% wt. PMMA (12.5 µL QDs in 500 µL PMMA) were prepared, which resulted in a monolayer of QDs in a PMMA film having a thickness of ~ 7 nm, verified using atomic force microscopy (AFM). The QDs were alloyed core/shell CdSeS/ZnS QDs, with peak emission wavelength of 630 nm which overlaps spectrally with the B exciton of the monolayer MoS_2, see Fig. 1(a). The interaction between the QDs and the MoS_2 was examined using steady-state and time-resolved photoluminescence (PL) measurements. These measurements were performed using excitation with a 405 nm pulsed diode laser with 90 ps pulses at a repetition rate of 10 MHz. Steady-state PL measurements show that the QD emission is significantly quenched on

the monolayer MoS_2, as can be seen in Fig. 1(b). The fluorescence decay curves extracted from the time-resolved PL data also show that the fluorescence lifetime of the QDs is substantially reduced on the monolayer MoS_2, see Fig. 1(c). In this hybrid system the QD and MoS_2 can be considered as a donor-acceptor pair where the QD is the donor and the MoS_2 is the acceptor. Two of the trademark signatures of NRET are a reduction in the donor fluorescence intensity and a reduction in the donor lifetime.

Fig. 1: (a) Normalized extinction spectra of MoS_2 and QD PL spectra, (b) PL spectra of QDs only (red) and QDs



on monolayer MoS_2 (black) and (c) fluorescence decay curves of QDs only (red) and QDs on MoS_2 (black).

The NRET efficiency (η) can be calculated directly from the fluorescence lifetimes and is given by

$$\eta = 1-(\tau_{DA}/\tau_D) \quad (1)$$

where τ_D is the lifetime of the QDs only (donor) and τ_{DA} is the lifetime of the QDs on the MoS_2 (acceptor). The NRET efficiency, η, for the QDs on monolayer MoS_2 is found to be 99 ± 1%. This NRET efficiency represents an average from measurements performed over 5 monolayer MoS_2 flakes. Similarly, an NRET efficiency can be obtained from the integrated PL spectrum. Replacing the lifetimes (τ_D and τ_{DA}) in Eqn. 1 with the integrated PL values of the QDs alone (I_D) and the QDs on MoS_2 (I_{DA}) gives an NRET efficiency, η = 98 ± 1%. These large efficiencies clearly demonstrate the strong interaction between the QDs and the MoS_2. However, while the NRET efficiency is high there is very little enhancement of the MoS_2 PL intensity. This lack of enhancement of the MoS_2 PL is attributed to nonradiative recombination of excitons at defect sites at the surface of the MoS_2.

To examine the changes in the optoelectronic performance of the MoS_2 due to NRET from the QDs, electrical contacts were fabricated on the MoS_2 samples using electron beam lithography (EBL). The contact pads have dimensions of 80 µm x 80 µm with a channel length of 5 µm between the contacts. The contacts and pads consisted of a 5 nm Ti adhesion layer and 35 nm Au for the contacts. MoS_2 regions of various layer thicknesses were electrically contacted to investigate how the NRET from the QDs affected the performance of the devices as a function of MoS_2 layer thickness. Optical images of monolayer, few layer and bulk-like MoS_2 devices can be seen in Fig. 2(a, b, c), respectively. The optoelectronic performance of the devices was studied as a function of optical excitation power and measured under excitation from a 405 nm continuous wave laser at excitation powers ranging from ~1 – 100 µW. The graphs in Fig. 2(d, e, f) show the photocurrent as a function of excitation power for the monolayer, few layer and bulk-like devices, respectively. These measurements were performed on the MoS_2 devices with (red) and without (black) the QD sensitizing layer. The largest enhancement in the photocurrent due to the QD sensitizing layer is seen for the monolayer MoS_2 device. The monolayer device shows ~12 fold enhancement of the photocurrent due to NRET from the QDs in the sensitizing layer as compared to the MoS_2 device alone. The few layer device in Fig. 2(e) shows a smaller enhancement in the photocurrent with the QD sensitizing layer, ranging from 2-4 fold across the excitation power range. This fall off in the enhancement indicates that NRET from the QDs to the MoS_2 is weaker in the few layer case. Interestingly Fig. 2(f) demonstrates that there is little to no difference in the photocurrent when the QD sensitizing layer has been applied to the bulk-like device. It has been proposed that dielectric screening can cause the NRET efficiency to decrease as the number of layers of MoS_2 increases [2, 3]. Similar effects have been also been predicted for superlattices of monolayer MoS_2, due modification of the mode distribution as the number of layers increases [4].

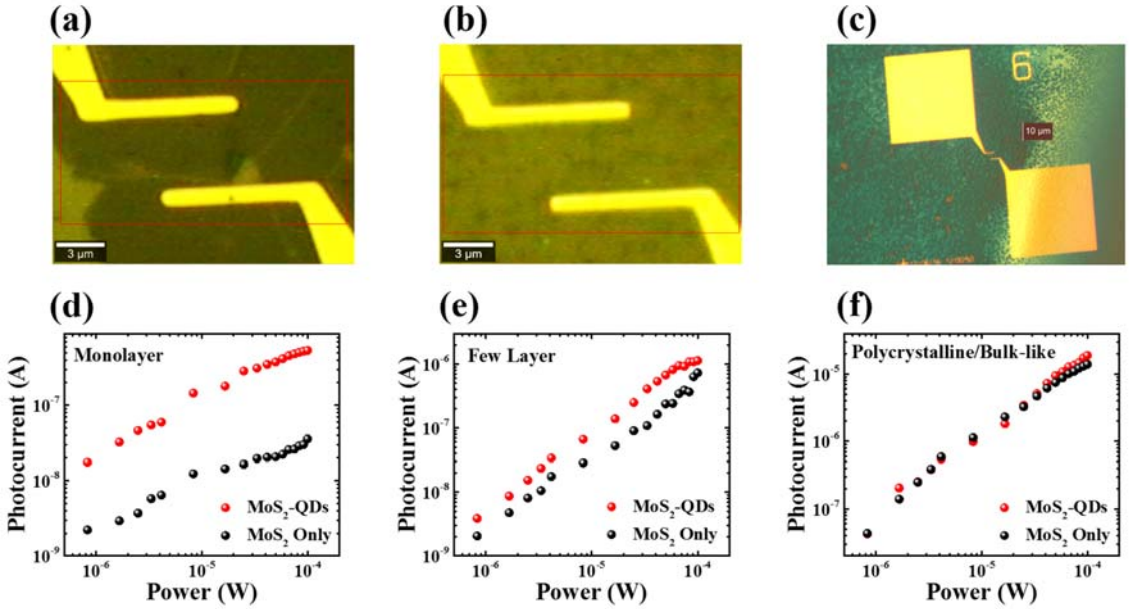


Fig. 2: Optical images of (a) monolayer, (b) few layer and (c) bulk-like MoS_2 devices. Plots of photocurrent as a function of excitation power for (d) monolayer, (e) few layer and (f) bulk-like MoS_2 devices.

III. Conclusion

This work has demonstrated highly efficient NRET from QDs to monolayer MoS_2. The NRET efficiency was found to be 99 ± 1% when calculated from the fluorescence lifetimes and 98 ± 1% when calculated from the integrated PL spectrum. Despite the large NRET efficiency no significant enhancement in the MoS_2 PL intensity was observed. The lack of PL enhancement for the MoS_2 is attributed to nonradiative recombination at defect sites. However, by studying the optoelectronic performance of the MoS_2 samples, with and without the QD sensitizing layer, it was found that the energy transferred to the MoS_2 from the QDs through NRET could be extracted as electrical current. Photocurrent enhancements as high as ~12 fold for monolayer MoS_2 devices and up to ~4 fold enhancements in few layer devices have been observed. For the polycrystalline/bulk-like MoS_2 devices no change in the optoelectronic performance after the addition of the QD sensitizing layer has been observed. This combined optical-electrical study shows that while energy transferred from QDs to MoS_2 *via* NRET may not be optically observed it can be extracted electrically, and that photocurrent enhancements are also limited by the number of MoS_2 layers.

Acknowledgement

This work was supported by the Irish Research Council (IRC), Grant No. GOIPG/2013/680 and Science Foundation Ireland (SFI), Grant No. 10/IN.1/12975.

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