

BNL-112026-2016-JA

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Dots to Single-Layer and Few-Layer Tin Disulfide

Mircea Cotlet

Huidong Zang, ¹, Prahlad K. Routh, ^{1,2}, Yuan Huang¹, Jia-Shiang Chen, ^{1,2} Eli Sutter,³ Peter Sutter⁴, and Mircea Cotlet^{1,2}

¹Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton NY

²Materials Science Department, Stony Brook University, Stony Brook, NY

³Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln,

Lincoln NE

⁴Department of Electrical and Computer Engineering Department, University of

Nebraska-Lincoln, Lincoln NE

Submitted to the Journal of ACS Nano

Center for Functional Nanomaterials

Brookhaven National Laboratory

U.S. Department of Energy Office of Science Basic Energy Sciences

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Nonradiative Energy Transfer from Individual CdSe/ZnS Quantum Dots to Single-Layer and Few-Layer Tin Disulfide

Huidong Zang,^{1,†} Prahlad K. Routh,^{1,2,†} Yuan Huang^{1,†}, Jia-Shiang Chen,^{1,2} Eli Sutter,³ Peter Sutter^{4,*} and Mircea Cotlet^{1,2,*}

¹Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton NY 11973,

USA; ²Materials Science Department, Stony Brook University, Stony Brook, NY 11794, USA;

³Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, Lincoln NE 68588, USA; and ⁴Department of Electrical and Computer Engineering Department,

University of Nebraska-Lincoln, Lincoln NE 68588, USA

[†]These authors contributed equally to this work

*Correspondence: cotlet@bnl.gov and psutter@unl.edu

Abstract. The combination of zero dimensional (0D) colloidal CdSe/ZnS quantum dots with Tin Disulfide (SnS₂), a two-dimensional (2D) layered metal dichalcogenide, results in 0D-2D hybrids with enhanced light absorption properties. These 0D-2D hybrids, when exposed to light, exhibit intra-hybrid nonradiative energy transfer from photoexcited CdSe/ZnS quantum dots to SnS₂. Using single nanocrystal spectroscopy, we find that the rate for energy transfer in 0D-2D hybrids increases with added number of SnS₂ layers, a positive manifestation towards the potential functionality of such 2D-based hybrids in applications such as photovoltaics and photon sensing.

Keywords: layered metal dichalcogenides, quantum dots, hybrid nanomaterial, energy transfer, single nanocrystal spectroscopy.

Layered metal dichalcogenides (LMDs) including transition metal dichalcogenides have emerged as exciting 2D semiconductors for energy harvesting, photocatalysis and photon detector applications, partly due to the strong dependence of their band structure on the thickness or number of layers.^{1,2} For example, layered transition metal dichalcogenides like MoS₂, WS₂ and WSe₂ show a transition from an indirect bandgap in multilayer films to a direct bandgap in monolayers,²⁻⁴ and this bandgap inversion provides enhanced photoluminescence (PL) for monolayer LMDs, making them appealing light harvesting materials for photovoltaics $(PV)^2$ or photon detection. Tin disulfide (SnS₂) was recently introduced and characterized as an emerging LMD for potential optoelectronic and photon detection applications and it was found to remain an indirect bandgap semiconductor down to the monolayer limit, with the emitted PL intensity decreasing with the decrease in number of layers.^{5, 6} Despite generally strong light-matter interactions, LMDs exhibit weak photon absorption due to their ultrathin thickness and this can limit potential applications in optoelectronic devices, especially those functioning on the principle of photon harvesting and excitonic generation. One way to increase photon absorption is to combine LMDs with other semiconducting nanomaterials, used as sensitizers from which photogenerated excitons can be transferred onto the LMD, for example by non-radiative energy transfer. One such class of excitonic nanomaterials is colloidal quantum dots (Qdots), 0D nanosystems with typical sizes of 3-10 nm. Qdots exhibit large absorption cross sections spanning from UV-Vis to the NIR spectral range, a size dependent bandgap which can be matched in terms of energy transfer with that of the LMD, and large PL emission quantum yields that promise efficient exciton generation.^{7, 8} Thus, a hybrid combination (0D-2D) of the type $Qdot-SnS_2$ can provide the advantage of increased photon absorption/exciton generation obtained by the Qdot and high charge mobility by the 2D LMD, two properties which are very useful in the development of LMD-based optoelectronic devices.

Generally, there are two possible interaction mechanisms between 0D Qdots and 2D LMD semiconductor materials undergoing photoexcitation: non-radiative energy transfer and/or photoinduced charge transfer. Brus *et al.* reported energy transfer between CdSe/ZnS Qdots and single- and few-layer graphene, with the observation of increased rates for energy transfer with increasing number of graphene layers.⁹ Prins *et al.* reported energy transfer from CdSe/ZnS Qdots to single- and few layers of MoS₂, where they observed increased rates of energy transfer with decreasing number of MoS₂ layers, a behavior they attributed to a reduced dielectric screening effect from few layers to single-layer MoS₂.¹⁰ Recently Raja *et al.* reported similar behavior of energy transfer rate vs number of LMD layers for Qdots transferring to MoS₂.¹¹ Koppens *et al.* recently studied PbS/MoS₂ hybrid devices in which they identified the interaction between nanocomponents as photoinduced charge transfer.¹²

Here, we combine CdSe/ZnS Qdots and layered SnS_2 to demonstrate hybrids with improved light harvesting properties *via* non-radiative energy transfer from Qdots to SnS_2 . We show that single nanocrystal PL spectroscopy can uniquely assess the interaction between CdSe/ZnS Qdots and single and few-layers of SnS_2 LMD as being energy transfer by comparing PL blinking dynamics of isolated Qdots on glass substrates and on SnS_2 LMDs. We find the rate for non-radiative energy transfer from individual Qdots to SnS_2 to increase with increasing number of SnS_2 layers, and we provide a theoretical understanding for the observed non-radiative energy transfer characteristics.

RESULTS AND DISCUSSIONS

 SnS_2 flakes with varying thickness containing single- and few-layer areas were obtained by mechanical exfoliation from large layered, bulk crystals⁵ and transfer to SiO₂/Si substrates. An optical bright field microscopy image of a typical SnS_2 flake is shown in Figure 1a, where single, three- and six layer segments are identified through optical contrast and confirmed by atomic force microscopy (AFM) measurements (Figure 1b). Single-layer SnS_2 is known to have a



Figure 1. (a) Optical bright field microscopy image of a mechanically exfoliated SnS_2 flake with varying thickness (number of layers) and supported on 300 nm SiO₂/Si; (b) atomic force microscopy height profile of single- and six-layer SnS_2 LMD; (c) confocal FLIM image of SnS_2 LMD, and (d) of a CdSe/ZnS Qdot-SnS₂ hybrid.

thickness of 0.6 nm, but our height measurements by AFM indicated a thickness of around (1.1 ± 0.2) nm (Figure 1b). Such a discrepancy is usually the result of trapping of adsorbed molecules

(*e.g.*, water) in between SnS_2 flake (monolayer) and SiO_2/Si substrate. We further confirmed that this is a single SnS_2 layer by confocal Raman microscopy⁵.

An optical absorption spectrum of an SnS_2 crystal from which flakes were isolated is shown in Figure 2. The absorption increases sharply below 600 nm and has an intercept at around 2.01 eV, somewhat lower than the previously reported values of the band gap⁵. A confocal fluorescence lifetime image (FLIM) of the SnS_2 flake from Figure 1a is shown in Figure 1c and a micro-PL spectrum from the same flake is shown in Figure 2. The micro-PL spectrum was observed with optical pumping at 440 nm at high power (10 μ W average power @10 MHz repetition rate and 90 ps pulse width), about 100 times stronger than the powers we used in the single nanocrystal experiments reported herein. The weak PL emission from the SnS₂ flake has a single peak at 650 nm (1.9 eV, Fig. 2), whereas previous PL measurements on doped SnS₂ showed two emission bands at 650 nm and 565 nm⁵. The weak emission results from a rather low absorption cross-section and a low PL quantum yield of the flake.



Figure 2. Optical absorption spectrum of an SnS_2 crystal (black, left side), micro-photoluminescence spectrum of an exfoliated SnS_2 flake shown in Figure 1a (black, right side) and micro-PL spectrum of CdSe/ZnS Qdots in toluene (red).

CdSe/ZnS Qdots used for assembling 0D-2D hybrids were selected such that their PL emission (peak at 535 nm) overlaps strongly with the optical absorption of layered SnS₂ so that energy transfer from photoexcited Qdots to SnS₂ is enabled (Figure 2). 0D-2D hybrids were assembled by drop casting highly diluted CdSe/ZnS Qdots in a mixed-solvent solution on a SnS₂ flake with varying thickness (# of layers). Figure 1d depicts a confocal FLIM image of the same flake shown in Figs.1a-c, now landed with Qdots. This FLIM image and the single nanoparticle measurements reported herein have been recorded with 100x lower average power than the FLIM image of the bare SnS₂ flake shown in Figure 1d we learn that Qdots on the SnS₂ flake experience PL quenching when compared to Qdots supported on Si/SiO₂, for example those on the substrate near the flake, and that the thicker the SnS₂ flake, the stronger the Qdot PL quenching becomes.

PL intensity time trajectories, photon count histograms, PL decays and correlograms of PL intensity vs. PL lifetime are shown in Figure 3 for individual CdSe/ZnS Qdots on SiO₂/Si substrate (Fig. 3a) and on single layer SnS₂ (Fig. 3b), 3-layer SnS₂ (Fig. 3c) and 6-layer SnS₂ (Fig. 3d). When under laser illumination, a Qdot on SiO₂/Si substrate features the typical two-state, on-off blinking (Fig. 3a) with clearly separated on- and off-states (see associated histogram in Fig. 3a) and with a radiative exciton recombination lifetime of about 25 ns and an average photon count rate of 6 kHz (Fig. 3a). Qdots supported on a SnS₂ flake (*i.e.*, Qdot-SnS₂ hybrids) feature PL quenching in both the intensity and lifetime (Figure 3b-d) and this quenching increases with added number of layers of SnS₂. From single layer to 3-layers and to 6-layers of SnS₂, both the PL intensity and PL lifetime of the Qdots decrease (Figure 3b-d, average PL lifetimes of 18 ns, 11 ns and 7.5 ns, respectively). Correlograms of PL intensity vs. PL lifetimes

shown in Figure 3 (rightmost panels) further support the observation of enhanced PL quenching in both intensity and lifetime with added number of SnS_2 layers, thus strongly suggesting that the presence of SnS_2 opens additional non-radiative decay channels competing with exciton radiative recombination in the photoexcited Qdots. This behavior in Qdot PL quenching shown in Figure 3b-d has been observed for many individual Qdots and is demonstrated by the PL lifetime histograms shown in Figure 4, each incorporating data from around 10-15 individual Qdots.



intensity vs. PL lifetimes for CdSe/ZnS Qdots on (a_1-a_4) SiO₂/Si, (b_1-b_4) monolayer SnS₂, (c_1-c_4) 3-layer SnS₂ and (d_1-d_4) 6-layer SnS₂.

For these distributions, although each contributing Qdot was probed for 60 seconds, single nanocrystal PL decays were constructed from the detected photon count stream, so that each contains an equal (2000) total number of photons spread over 128 channels. These single nanocrystal PL decays were then fit with a single exponent function using a Maximum Likelihood Estimator approach.¹³ Gauss fits of the PL lifetime histograms from Figs.4a-d render mean values (τ_{PL}) of τ_{PL} (SiO₂/Si) = 27 ns for Qdots on SiO₂/Si, of τ_{PL} (1L-SnS₂) = 17 ns for



Figure 4. Single nanocrystal PL lifetime histograms for Qdots on (a) SiO_2/Si , (b) monolayer SnS_2 , (c) 3layer SnS_2 and (d) 6-layer SnS_2 . Blue curves are Gauss fits. (e) Mean PL lifetime (black and square) and full width at half maximum (FWHM, red and triangles) vs layer numbers of SnS_2 on Si/SiO_2 as obtained from the Gauss fits of the histograms in panels a-d. Inset shows the heterogeneity in PL lifetime vs number of SnS_2 layers estimated according to¹³ (see SI for details).

Qdot-single-layer SnS₂ hybrids, of $\tau_{PL}(3L-SnS_2) = 11.6$ ns for Qdot-3-layer SnS₂ hybrids and of $\tau_{PL}(6L-SnS_2) = 9.4$ ns for Qdot-6-layer SnS₂ hybrids. The expected standard deviations σ (τ_{PL}) calculated for these distributions (Fig.4a-d) according to¹³ and following MLE fits of PL decays of 2000 total counts spread over 128 channels are given in Table S1, SI (see details on

calculations S.I.) and is in the sub-ns range. However, full widths at half-maximum (FWHM, $\Delta \tau_{PL}$) values for the same distributions have large values, $\Delta \tau_{PL}(SiO2/Si) = 17.8$ ns for Qdots on SiO₂/Si, $\Delta \tau_{PL}(1L-SnS_2) = 10.2$ ns for Qdot-1-layer SnS₂ hybrids, $\Delta \tau_{PL}(3L-SnS_2) = 8.7$ ns for Qdot-3-layer SnS₂ hybrids and $\Delta \tau_{PL}(6L-SnS_2) = 5.9$ ns for Qdot-6-layer SnS₂ hybrids. We also noticed that these FWHM values decrease with added number of layers of SnS₂. (Fig. 4e). Subtracting the standard deviation of PL lifetime from each of the FWHM we obtain a measure of the static heterogeneity in PL lifetime with added numbers of SnS₂, H(τ_{PL}) = FWHM (τ_{PL})- $\sigma(\tau_{PL})$ (Fig. 4e, inset), which decreases with added number of SnS₂ layers and therefore increased PL quenching. Below we provide an explanation of why such a trend occurs in Qdot-SnS₂ hybrids.

According to Figures 3a-d, right most panels, correlograms of PL intensity vs PL lifetime of isolated Qdot-SnS₂ hybrids show synchronous quenching independent of the number of existing SnS₂ layers. Whether this synchronous PL quenching in Qdot-SnS₂ hybrids is the result of energy transfer or charge transfer from the photoexcited Qdot to the layered SnS₂ or due to both processes, this is difficult to assess from PL data as those presented in Figures 3&4 since both processes can reduce both the PL lifetime and PL intensity of an isolated Qdot. However, one indication data in Figures 3 provide, in particular the PL intensity trajectories of the Qdot-SnS₂ hybrids which does not change with added number of SnS₂ layers and which also remains similar to that of Qdots on Si/SiO₂ (assumed to be non-interacting, unquenched Qdots). The photon counting histograms derived from the PL intensity traces shown in Figures 3a-d in right panels, next to PL intensity trajectories are all bimodal, further supporting our initial visual observation of unchanged PL blinking dynamics from Qdots on SiO₂/Si substrate to Qdot-SnS₂ hybrids. We

obtained further evidence of unaltered dynamics in PL blinking for Qdot-SnS₂ hybrids vs QDs on SiO₂/Si from the analysis of the on/off-periods associated with PL blinking from populations of individual Qdots deposited on SiO₂/Si, monolayer SnS₂, 3-layer SnS₂, and 6-layer SnS₂ (on average, 10-15 Qdots per group). For each group, we built $P(t_{on})$ and $P(t_{off})$ probability distributions which incorporate blinking events from all Qdots associated with a group. On- and off-times were selected from PL intensity traces as those shown in Figure 3a-d by using a conventional threshold method^{14, 15,16-18} (Fig.3, see details on calculation in SI). The $P(t_{on})$ distributions in Figure 5, left, were fit with a power law model function^{14, 19}

$$P_{on}(t) = b \times t^{-m_{on}} \tag{1}$$



Figure 5. Probability distributions $P(t_{on})$ (left panel), and $P(t_{off})$ (right panel) for CdSe/ZnS Qdots on SiO₂/Si (black squares) and Qdot-SnS₂ hybrids with Qdots on monolayer SnS₂ (red circles), 3-layer SnS₂ (green triangles), and 6-layer SnS₂ (blue crosses). Solid lines are fits according to eqs.1 and 2. Parameters of the fits are given in Table 1.

with m_{on} power law exponent and b a constant. For Qdot-SnS₂ hybrids, P(t_{on}) distributions corresponding to Qdots on monolayer, 3-layer and 6-layer SnS₂ do not differ significantly in the

values of the power low exponent ($m_{on} \sim 1.5$ -1.6, see Table 1), and they are also similar to the value obtained for the P(t_{on}) distribution of Qdots on SiO₂/Si. P(t_{off}) distributions shown in Figure 5, right, are more complex and require for all substrates, including SiO₂/Si, modelling with a modified power law function^{15, 19, 20}

$$P_{off}(t) = b \times t^{-m_{off}} \exp\left(-\frac{t}{T_{off}}\right)$$
(2)

with T_{off} a cross-over time constant from power law behaviour to exponential behaviour. Still, we could not observe a clear trend in power law exponent with added number of SnS₂ layers; instead we observed a large scatter in the values of the power law exponent (m_{off} ~ 1.40-1.64) which we believe that it might reflect the rather poor statistics of these off-time distributions due to the limited number of off-events and the limited number of Qdots associated with each distribution, here imposed by the small area size of the layers of a given thickness making up the SnS₂ flake (Fig. 1a).

The observation of similar on/off blinking dynamics among Qdot-SnS₂ hybrids with varying number of layers, in particular the lack of change in the $P(t_{on})$ distributions from SiO₂/Si support to SnS₂ supports with different number of layers is a strong indication that Qdots and SnS₂ interact by non-radiative energy transfer.²¹ Below we discuss why this is the case for Qdot-SnS₂ hybrids and we show the utility of PL blinking analysis as a single nanocrystal method capable to discriminate between energy and charge transfer in coupled 0D-2D hybrid materials such as the Qdot-SnS₂ hybrids investigated here.

PL blinking of isolated Qdots, or the switching of emitted light between bright (on-) and dark (off-) states under continuous laser illumination (Fig. 3a-d), initially discovered by Nirmal *et al.*²² is usually associated with charge accumulation at the Qdot core surface or photoinduced

ionization,^{22, 23} with the Qdot core becoming charged and undergoing efficient non-radiative Auger recombination (dark state). Since the work of Nirmal et al.²², modified models based on Auger recombination and invoking the presence of charge traps distributed outside the Qdot core have been proposed in order to explain the power law and modified power law behavior of the PL blinking data.²⁴⁻²⁷ In such a model, a photoexcited Qdot can become positively charged and non-emissive (off-state) following the ejection of a photogenerated electron to a charge trap at the core/shell interface followed by efficient non-radiative Auger recombination. The emissive (on-) state will resume when the trapped electron recombines with the hole in the QD core, providing the core becomes neutral again (see cartoon in Fig. 6b, Qdot only). The role of charge traps in blinking has been further demonstrated with the use of external electron acceptors whose presence dramatically affected the blinking of Qdots,^{19, 28, 29} with the observation of an enhanced decrease in on-time distributions (increase in m_{on}, values) with the increase in electron transfer rate. For example, by tuning the electron transfer rate through either donor/acceptor separation distance or through donor/acceptor energy band offset, we have previously shown that an external electron transfer process introduces a bias (increase in mon) Qdot's P(ton) probability, with the bias (increase) being proportional with the efficiency of electron transfer and with the PL intensity and PL lifetimes being always synchronously quenched (correlated).^{19, 28, 30} A bias introduced to Qdot's P(ton) probability by the external acceptor occurs because this acceptor, if strong in electron affinity, it can defeat "internal" charge traps located at the core/shell interface, thus itself becoming a (external) charge trap. For Qdots on SnS₂, the PL intensity and PL lifetime are synchronously quenched when compared to Qdots on SiO₂/Si and this is observed independent of the number of SnS₂, layers. Yet P(ton) distributions do not change, even for the strongest quenching observed (6-layer SnS₂, Figs.3&5, and Table 1), suggesting PL blinking is

dictated by the "internal" trap states located at the core/shell interface (Fig. 6b) and no charges are exchanged between donor (Qdot) and acceptor (SnS₂). Rather non-radiative energy transfer is the interaction mechanism on which a transfer of excitons occurs form the photoexcited Qdot onto layered SnS₂, case in which PL blinking remains similar to that observed for isolated Qdots on SiO₂/Si support.²¹ Two additional experimental facts support our hypothesis of non-radiative energy transfer: (i) the complete overlap of the Qdot's PL emission (535 nm) and SnS₂ absorption (Fig. 2) and (ii) the rather large (\geq 2.38nm) donor-acceptor separation distance which is unfavorable for the occurrence of electron transfer. Indeed, a rough estimation of this separation distance can be done using the transmission electron microscope (TEM) data measured for the present Qdots (Fig.S2, SI) which indicate an average core/shell size of 3.36 nm for a known core size of 2.6 nm.³⁰ By factoring in the length of the Qdot ligands (octadecylamine, ~2 nm), we obtain a donor-acceptor separation distance \geq 2.38nm at which both the electron transfer and exchange energy transfer can be excluded as potential mechanisms responsible for quenching.

We can therefore treat the energy transfer interaction in $Qdot-SnS_2$ hybrids as a system with dipole-dipole interaction, equivalent to the removal of an exciton from the photoexcited Qdot core onto the SnS_2 layer (see Figure 6b).

The rate of energy transfer in $Qdot-SnS_2$ hybrids can be estimated from the mean PL lifetimes obtained from the single nanocrystal histograms in Figure 4 by,

$$k_{ET} = \frac{1}{\tau_{Qdot-SnS2}} - \frac{1}{\tau_{Qdot}}$$
(3)

where k_{ET} is the rate for energy transfer from photoexcited Qdot to SnS₂, and τ_{Qdot} and $\tau_{Qdot-SnS2}$ are mean values of the single nanocrystal PL lifetimes of Qdots on SiO₂/Si and on SnS₂ substrates, respectively (Fig. 4), presented in Figure 6a as a function of the number of SnS₂ layers. To calculate the expected rate for energy transfer we used the theoretical model of resonant energy transfer previously developed for an excited molecule transferring to graphene as a 2D material^{9, 31-34}

$$k_{ET}(z) = \frac{1}{192\pi\hbar^5 \nu_F^4} \left(\frac{\mu_{eg}e}{\varepsilon_0 \varepsilon_{eff}}\right)^2 \Delta E^2 \sum_{i=0}^n \int_0^1 dt e^{-\frac{2\Delta E z_i t}{\hbar \nu_F}} \frac{t^3}{\sqrt{1-t^2}}$$
(4)

with k_{ET} the energy transfer rate, \hbar the reduced Planck constant, ν_F the Fermi velocity for SnS₂, μ_{eg} the transition dipole moment for the photoexcited Qdot, ΔE the energy of the photons emitted by a Qdot, z_i the distance from the center of the Qdot to the i^{th} layer of SnS₂, and ε_0 and ε_{eff} the vacuum permittivity and effective dielectric constant, respectively (see SI for details and values of named constants). In the assumption of decoupled (non-interacting) SnS_2 layers, we can treat the energy transfer from the photoexcited Qdot to the (i-1)th layer and the ith layer of SnS₂ as independent processes so that the final rate for energy transfer from the Qdot to multiple layers of SnS₂ becomes a sum of the rate of energy transfer from the Qdot to each SnS₂ layer composing the multilayer (eq. 4). Based on the dimensions estimated for the Qdot by TEM (Fig.S2, SI), we obtained calculated rates vs. number of SnS₂ layers as shown in Figure 6a which are in agreement with those calculated experimentally using the mean values obtained from the distributions shown in Figures 4a-d and eq.(3) are in good agreement with the values determined experimentally. This close correspondence further supports our argument that non-radiative energy transfer is the mechanism of PL quenching for CdSe/ZnS Qdot-SnS₂ hybrids. Here, both the theoretical and the measured rates for energy transfer show increase with added layers of SnS_2 a behavior opposite to the one found for similar Qdots transferring to single and few layers of MoS_2 .¹⁰ Bulk time-resolved confocal PL experiments on concentrated Qdot- SnS_2 samples reveal similar trend for the experimental rates for energy transfer with added number of SnS_2 layers (Fig.S3, SI), with the rate of energy transfer increasing with added number of SnS_2 layers, and with the rate following a stretch exponential dependency vs number of SnS_2 layers (see Fig.S3, SI and Fig.6, left).



Figure 6. Left panel: single nanocrystal experimental rates for energy transfer (black squares and line) and calculated rates for energy transfer according to eq.4 (red triangles and line) for CdSe/ZnS Qdots transferring to single- and few-layer SnS₂. Standard deviations are also shown (see SI for estimations). Right: Cartoon representation of the mechanism of interaction by non-radiative energy transfer between a CdSe/ZnS Qdot and a single layer of SnS₂. k_r : radiative rate, k_{ct} : electron transfer rate with internal charge trap, k_{nr} : non radiative rate, k_{ET} .: energy transfer rate to SnS₂.

Rates for energy transfer estimated here for Qdot-SnS₂ hybrids are in the 10^7 /s order which is two orders of magnitude smaller than those reported in^{10, 11, 35} for Qdot-MoS₂ hybrids (10^9 /s) for Qdots of similar type, composition and for similar donor-acceptor separation distances. We believe such difference in rates for energy transfer originate from differences in the two acceptor materials, SnS₂ being an indirect bandgap material down to monolayer, while MoS₂ has a unique behavior exhibiting bandgap inversion from indirect to direct bandgap semiconductor at monolayer. In this sense, SnS₂ is comparable to bulk Si which is a well-known indirect bandgap semiconductor for which optical transitions are dictated by phonon-exciton interaction. Several recent studies dealt with energy transfer from direct bandgap CdSe/ZnS Qdots to bulk Si and reported similar slow rates for energy transfer as those observed by us for Qdot-SnS₂ hybrids.³⁶⁻³⁸ Off these studies, it is reference³⁷ which proposes to treat bulk Si as an indirect (weakly luminescent) acceptor in which phonons are heavily involved in optical transitions, thus suggesting the occurrence of a phonon-assisted exciton transfer which is not as performing as an energy transfer of a Qdot with a direct bandgap acceptor material, and this is supposedly due to a weaker dipole-dipole coupling in the former case. As such, Qdots may couple stronger with a direct bandgap (luminescent) monolayer MoS₂ which in turn delivers a by far more performant energy transfer process. Therefore our study can be classified as the first report of energy transfer between 0D nanomaterials (Qdots) and a 2D indirect band gap layered material.

Table 1. PL blinking parameters estimated from the on-/off-time probabilities from Figure 5 for CdSe/ZnS Qdots deposited on SiO₂/Si substrate and on SnS₂ substrates with varying number of layers.

CdSe/ZnS Qdot	m _{on}	m _{off}	$ au_{ m off}$
on-substrate			
SiO ₂ /Si	1.62±0.02	1.32±0.02	1250±175
1-layer SnS ₂	1.57±0.02	1.58±0.02	1157±237
3-layer SnS ₂	1.53±0.02	1.41±0.01	1300±167
6-layer SnS ₂	1.61±0.01	1.64±0.01	1869±317

CONCLUSIONS

Summarizing our present study, we demonstrated, by single nanocrystal spectroscopy, the occurrence of energy transfer between photoexcited CdSe/ZnS Qdots and single-layer and few-layer SnS₂, and we found that the rate for energy transfer increases with increasing number of SnS₂ layers. An analysis of the photoluminescence blinking in Qdot-SnS₂ hybrids has allowed us to unambiguously identify energy transfer as the mechanism responsible for PL quenching of isolated Qdots by nearby SnS₂ thus providing a straight forward method to discriminate between energy transfer and charge transfer in 0D-2D hybrid semiconducting materials.

METHODS

CdSe/ZnS Qdots with emission at 525 nm (in toluene) were purchased from Ocean NanoTech Inc. High-quality bulk crystals of layered SnS₂, grown by the vertical Bridgman method⁵ were used as a starting material for isolating single- and few-layer SnS₂ flakes, which were deposited onto clean SiO₂ (300nm)/Si substrates by mechanical exfoliation. Qdots were diluted by a hexane/octane (9:1) solvent mixture, transferred to SnS₂ flakes *via* drop casting and examined by single nanoparticle microscopy. For AFM experiments used to confirm the SnS₂ thickness (number of layers) we used a Veeco Multimode V AFM instrument. Confocal FLIM, including single nanocrystal studies, was performed with a home-built scanning confocal inverted microscope with optical excitation delivered by a pulsed diode laser (440 nm, pulse width 90 ps, 10 MHz repetition rate, PicoQuant Germany). For single nanocrystal studies we used an average power at the sample of 100 nW. Experiments were performed with an Olympus IX81 inverted microscope equipped with a scanning piezo stage (Physik Instrumente) using a 100x, 0.95 NA air lens (Olympus), with the PL optically filtered through a dichroic mirror (Di440, Semrock) and a combination of long pass (488LP Semrock) and bandpass (525/50, Semrock) filters, spatially filtered by a pinhole (75 μ m) and finally detected by a single-photon counting avalanche photodiode (MPD, PicoQuant) combined with a time analyzer (Picoharp 300, PicoQuant). Data acquisition and analysis were performed with the Symphotime software (v5.32, PicoQuant) and with the BIFL Data Analyzer software (Scientific Software Technologies Center).

Supporting Information. Supporting information includes calculation of energy transfer rates, details on single nanocrystal PL microscopy data acquisition, analysis and error estimations, measurements of bulk energy transfer rates between CdSe/ZnS QDs and layered SnS₂.

Acknowledgement. Research carried out at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012704.

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Table of Contents Figure and Text

Nonradiative Energy Transfer from Individual CdSe/ZnS Quantum Dots to Single-Layer and Few-Layer Tin Disulfide

Huidong Zang,¹ Prahlad K. Routh,^{1,2} Yuan Huang¹, Jia-Shiang Chen,^{1,2} Eli Sutter,³ Peter Sutter^{4,*}

and Mircea Cotlet^{1,2,*}

¹Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton NY 11973,

USA; ²Materials Science Department, Stony Brook University, Stony Brook, NY 11794, USA;

³Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, Lincoln

NE 68588, USA; and ⁴Department of Electrical and Computer Engineering Department,

University of Nebraska-Lincoln, Lincoln NE 68588, USA



Single nanocrystal spectroscopy identifies the interaction between 0-dimensional CdSe/ZnS nanocrystals and 2-dimensional SnS_2 as a non-radiative energy transfer, whose rate increases with increasing number of SnS_2 layers.