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Multiple Exciton Harvesting at Zero-Dimensional/Two-Dimensional Heterostructures

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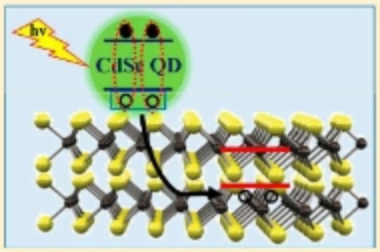
Supporting Information

ABSTRACT: Heterostructures of zero-dimensional/two-dimensional (0D/2D) materials, especially quantum dots (QDs)/nanosheets (NSs), have attracted significant attention for extracting photogenerated electrons and holes. Herein, we report the dissociation of excitons at the heterojunction of CdSe (cadmium selenide) QDs and MoS_2 (molybdenum disulfide) nanosheet utilizing steady-state and time-resolved spectroscopic techniques. Quasi type II semiconductor-like band energy alignment of the 0D/2D heterojunction facilitates exciton breaking via hole transfer from the QD to MoS_2. Furthermore, we demonstrate the extraction of two holes from doubly excited QDs (created via high-power excitation) following the dissociation of a biexciton at the 0D/2D interface. This work is expected to provide a new approach of exploiting multiple exciton generation in quantum dot-sensitized solar cells by harvesting multiple carriers.



Colloidal semiconducting quantum dots (0D-QDs) is a class of materials that exhibit high absorption cross sections, broad tunability of band gaps, and high quantum efficiencies.[1,2] These unique electronic properties make them ideal materials for photovoltaics,[3−6] photodetectors,[7−9] and light-emitting (LEDs) devices.[10,11] Multiple exciton generation (MEG) or carrier multiplication (CM) is a process where several excitons are generated as a result of the absorption of a high-energy photon, typically higher than double the band gap, in QDs.[12,13] Efficient MEG was observed in many QDs (PbSe,[14,15] PbS,[14,16,17] Si,[17,18] CdSe,[18−20] and InAs[21]) by many groups using different techniques. Successful exploitation of CM could improve the efficiency of quantum dot-sensitized solar cells (QDSSCs).[12] Klimov[22] has theoretically shown that an ideal CM yield in QDSSC can produce a power conversion efficiency exceeding 44%, which is much higher than the Shockley−Queisser limit (~33%) for a single-junction photovoltaic.[23] In fact, successful utilization of MEG using metal oxides (MOs) in QDSSCs has been demonstrated in several studies.[24,25]

Two-dimensional (2D) materials, on the other hand, have attracted incredible interest due to their intriguing electrical, optical, and mechanical properties[26−30] since the exfoliation of graphene in 2004. 2D transition-metal dichalcogenides (2D TMDCs) having chemical formula MX_2, where the transition-metal atom (M) is sandwiched between two chalcogen (X) atoms, show unique optoelectronic properties including a nonzero direct or indirect band gap.[31,32] Among all TMDCs, MoS_2 has particular importance in solar cells as n-type material because of large absorption coefficient[33−36] and direct nature of the band gap in monolayer.[37−39] Layered MoS_2 sheets find applications in photovoltaic and photodetector devices due to high carrier mobility.[40−42] In fact, Coulomb interaction in these materials is significantly enhanced[43] because of charge carrier confinement within the 2D plane.[44]

Recently, van der Waals heterojunctions of 2D TMDCs have been shown to be useful for the dissociation of excitons via fast interfacial charge transfer.[45−47] In the heterojunction between WS_2 and MoS_2, hole transfer was observed to occur in an ultrafast time scale from MoS_2 to WS_2.[45] The dissociation of excitons was reported to take place in the heterostructures of WSe_2/MoS_2 via ultrafast electron transfer from monolayer WSe_2 to MoS_2.[47] It was also noticed that both electron and hole transfers can occur at the $MoS_2/MoSe_2$ interface in opposite directions.[45] The type II semiconductor-like band energy alignment in these 2D/2D heterostructures facilitates the formation of an indirect exciton (IX), where the electron is located in one 2D material and the hole in another 2D material.[45,46] Nowadays, researchers are looking to combine 0D and 2D materials into one nanoheterostructure, which may provide additional benefits. Prins et al.[48] reported the enhancement of the efficiency of the Förster resonance energy transfer (FRET) at the 0D/2D heterojunction of cadmium selenide/cadmium zinc sulfide (CdSe/CdZnS) core/shell QD and MoS_2 with the decrease in layer number of MoS_2. In the recent past, Boulesbaa et al.[1] reported both electron and hole

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