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MoS₂-capped Cu_xS nanocrystals: a new heterostructured geometry of transition metal dichalcogenides for broadband optoelectronics†

Yuan Li, Dabc Akshay A. Murthy, be Jennifer G. DiStefano, b Hee Joon Jung, bc Shiqiang Hao, b Cesar J. Villa, b Chris Wolverton, b Xinqi Chen*cd and Vinayak P. Dravid ** *bce

Heterostructuring of different transition metal dichalcogenides (TMDs) leads to interesting band alignment and performance improvement, and thus enables new routes for the development of materials for next-generation semiconductor electronics. Herein, we introduce a new strategy for the design and synthesis of functional TMD heterostructures. The representative product, molybdenum disulfide-capped copper sulfide (Cu_xS@MoS₂, 1.8 < x < 2.0), is typically obtained by chemical vapor deposition of cap-like MoS₂ layers on Cu_xS nanocrystals, yielding the formation of a sharp, clean heterojunction interface. The heterostructures exhibit strong light-matter interactions over a broadband range, with interesting band alignment for separating photocarriers and mediating charge transfer. A phototransistor made from Cu_xS@MoS₂ heterostructures shows particularly high photoresponse for near infrared light, which is enabled by the heterojunction of MoS₂ with a small band gap semiconductor as well as the plasmonic enhancement from the Cu_xS nanocrystals. Our study paves a way for the development of new TMD heterostructures towards achieving functional electronics and optoelectronics.

1. Introduction

Semiconductor heterostructures are essential components in modern high-speed electronics and optoelectronic devices.¹ With the need for continued device scaling to achieve faster

Conceptual insights

Conventional TMD heterostructures, aligned in lateral or vertical geometries (e.g., MoS2/WS2, MoSe2/WSe2, WSe2/MoS2, etc.), exhibit new chemical, structural and electronic properties for various applications in transistors, diodes and photovoltaic/photodetection devices. However, the main protocols, mechanical transfer and chemical vapor deposition, for preparing such heterostructures, are limited by their inevitable interface contamination and lack of massive and constant yields. Beyond the scope of such traditional heterostructures, our study reports a critical scientific step forward for bringing the concept of a new heterostructural geometry (namely MoS2-capped CurS nanocrystals) into the family of TMD heterostructures. Using a direct chemical vapor deposition approach, we are able to create an atomically clean interface between the CuxS core and MoS2 cap, which, as compared with conventional TMD heterostructures, effectively maximized the interfacial area and would be very facile to realize large-scale production. Our structural design and synthesis strategy of the MoS2-capped CuxS nanocrystals can be generalized to abundant TMD materials and thus allow for a wide range of explorations across diverse disciplines and the originality of the approach.

and miniaturized electronic components, new semiconductor systems such as two-dimensional (2D) transition metal dichalcogenides (TMDs) have attracted wide attention due to their unique layer-dependent electronic and optical properties.²⁻⁴ When these TMD semiconductors are combined in tandem, exciting new chemical, structural and electronic properties for various applications, such as transistors, diodes and photovoltaic/photodetection devices, are observed.5-10 For instance, heterostructures of layered TMDs (e.g., MoS₂/WS₂, MoSe₂/ WSe₂, WSe₂/MoS₂, 9,10 etc.) have been demonstrated to form p-n junctions, which serve as the basis for these optoelectronic devices. The main function of these heterostructures is the ability to mediate optical transitions and charge transfer across the junction of two materials, 11-13 and thus, maintaining a largearea, clean, and high-quality interface is of great importance. Unfortunately, to date most reported 2D heterostructures have been fabricated through mechanical transfer methods or multi-step chemical vapor deposition. While the former are troublesome

^a School of Materials Science and Engineering, Center of Advanced Lubrication and Seal Materials, Northwestern Polytechnical University, Xi'an, Shaanxi, 10072, China

^b Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, USA

^c Northwestern University Atomic and Nanoscale Characterization Experimental (NUANCE) Center, Northwestern University, Evanston, Illinois 60208, USA. E-mail: x-chen@northwestern.edu

^d Department of Mechanical Engineering, Northwestern University, Evanston, Illinois 60208, USA

^e International Institute for Nanotechnology (IIN), Northwestern University, Evanston, Illinois 60208, USA. E-mail: v-dravid@northwestern.edu

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due to the interfacial contamination commonly introduced via the polymer-based transfer process, the latter is problematic due to challenges related to the lack of spatial control over the synthesized products, more limited heterojunction interface, and lack of consistent yields.⁷

Toward this end, exploring new geometries of TMD heterostructures beyond the existing library of 2D materials is of great interest for interface engineering and scalable production. Recently, surface decoration of TMD monolayers with nanocrystals¹⁴⁻¹⁶ or quantum dots^{17,18} of other chalcogenides has been studied as a typical approach to create heterojunctions. The resultant nanocomposites can effectively overcome the low optical cross-section of MoS2 and thus lead to enhanced absorption¹⁴ and improved photodetectivity.¹⁸ For instance, chalcocite copper sulfide (Cu_rS) nanocrystals are one of the most interesting materials due to their natural abundance, p-type semiconductor nature, and relatively small band gap leading to strong light absorption from the visible to near infrared region. 19,20 When combined with MoS2, the resultant band alignment at the interfaces can potentially enable superior interfacial charge transfer. 21,22 However, the reported preparation of the TMD heterostructures mostly relies on mechanical transfer^{14,15} or solution-based chemical synthesis 16,17 and thus has been difficult to realize an uncontaminated and atomically-contacted sharp interface.

Herein, we introduce a new geometry design for the family of TMD heterostructures by encapsulating Cu_xS (1.8 < x < 2) nanocrystals with cap-like MoS2 layered structures, namely CuxS@ MoS₂ heterostructures. An atomically clean interface between the CuxS core and MoS2 cap is created via direct chemical vapor deposition, which effectively maximizes the interfacial area and thus facilitates photoemission and charge transfer between the two materials. Using discrete dipole approximation (DDA), we examined the optical properties of these heterostructures, and density functional theory (DFT) calculations were carried out to better understand the band alignment and charge transfer dynamics at the heterojunction interface. The viability of these heterostructures for photodetection applications was evaluated as well. The results indicate that our Cu_xS@MoS₂ heterostructures exhibit highly improved light-matter interactions over a broad wavelength range compared to bare MoS2, and thus lead to a strong photoresponse from violet to near-infrared light.

2. Results and discussion

The synthesis of Cu_xS@MoS₂ heterostructures is illustrated in Fig. 1a. Briefly, a 4 nm Cu film was first deposited on a Si/SiO₂ substrate by thermal evaporation and then annealed at 600 °C

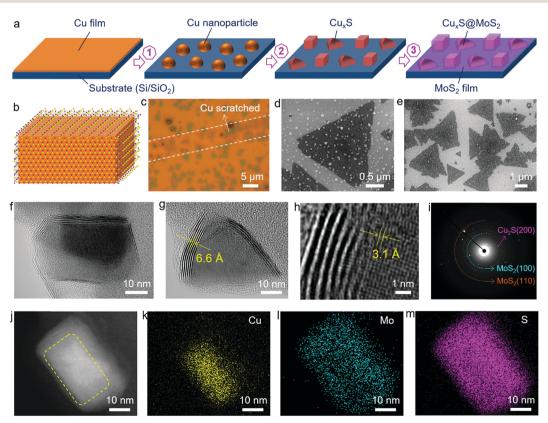


Fig. 1 Synthesis of Cu_x S@MoS₂ heterostructures. (a) Schematic illustrating the synthesis steps, including (1) annealing, (2) sulfurization, and (3) CVD. (b) Schematic of a single $Cu_xS@MoS_2$ heterostructure, illustrating the cap-like MoS_2 layers encapsulating a Cu_xS nanocrystal. (c) Optical view and (d and e) SEM images of the product after CVD. The substrate was left unexposed to the copper film in the dotted line region in (c). (f and g) TEM images of individual Cu_xS@MoS₂ heterostructures. (h) High-resolution TEM image indicating the atomic contact at the Cu_xS-MoS₂ interface and (i) the resultant diffraction pattern. (j) STEM image of a single heterostructure and (k-m) the corresponding EDS maps.

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in a N₂ environment (step 1). The samples were then sulfurized at 600 °C (step 2) for 30 min. The encapsulation of MoS₂ caps was finally accomplished via a chemical vapor deposition process utilizing MoO₃ and S powders as precursors (step 3). The resultant product, Cu_xS@MoS₂ heterostructures, is schematically illustrated in Fig. 1b. An optical image of the resultant sample surface is shown in Fig. 1c. The Cu film within the dotted lines was removed by scratching prior to MoS₂ deposition. Thus, in this region, which exhibits a lighter optical contrast, we observed the growth of MoS2 monolayers with no CuxS. The flakes outside the dotted region exhibit a relatively darker color due to the formation of CuxS@MoS2 heterostructures, as indicated by the SEM images in Fig. 1d and e. One can also observe that the Cu_xS@MoS₂ nanocrystals are distributed uniformly throughout the substrate. It is worth noting that the size and distribution of the nanocrystals can be effectively modulated by varying the thickness of the preliminary Cu film and the ramp rate of the subsequent annealing process, similar to that we have otherwise demonstrated previously.²³ XRD patterns obtained over the entire substrate (Fig. S1, ESI†) indicate that the Cu_xS nanocrystals have a chalcocite structure with x varying from 1.8 to 2.0.

The TEM images in Fig. 1f and g confirm that the MoS₂ layers, with a layer-to-layer spacing of 6.6 Å and thickness of $\sim 3-5$ nm, cap the faceted Cu_xS nanocrystals. The highresolution image (Fig. 1h) further indicates the direct atomic connection of CurS and MoS2 at the interface. CurS exhibits a lattice spacing of 3.1 Å, corresponding to the (200) plane, which is also found to be the dominant facet of CurS from the diffraction pattern (Fig. 1i). EDS maps obtained for a typical Cu_xS@MoS₂ heterostructure (Fig. 1j) demonstrate the elemental composition of Cu, Mo and S (Fig. 1k-m). The distribution of Cu is mostly concentrated inside the heterostructure as

outlined in Fig. 1j, indicating effective MoS₂ encapsulation of the Cu_rS nanocrystals.

XPS spectra are further displayed in Fig. 2a-c. The spectra for the Cu_xS@MoS₂ heterostructures are compared to a control sample prepared by transferring a pre-grown MoS2 monolayer onto Cu_rS nanocrystals (represented as Cu_rS/MoS₂ hereafter). Details about the MoS₂ transfer can be found in Fig. S2 (ESI†). The Mo and S spectra are generally consistent for both samples. The Mo 3d peaks at 233.11 eV and 229.92 eV correspond to the 3d_{5/2} and 3d_{3/2} doublets (Fig. 2a), while the S 2p peak can be deconvoluted into two peaks at 163.91 eV and 162.73 eV (Fig. 2b), which can be assigned to the $2p_{1/2}$ and $2p_{3/2}$ orbitals, respectively. 24,25 The peaks for metallic Mo or MoO_r are insignificant, suggesting high quality MoS₂ layers on both products. The Cu_xS(a) MoS₂ heterostructures present Cu 2p peaks at 952.32 eV (2p_{1/2}) and 932.45 eV (2p_{3/2}), which are consistent with the peak location of copper sulfides.²⁶ However, the intensities of the Cu peaks are weaker compared with the Mo and S peaks, due to the encapsulation of the MoS₂ layers. It is worth noting that peaks representing CuSO₄ are also observed on the transferred samples, probably due to the inevitable surface oxidation of Cu_xS in air, which indicates that MoS₂ encapsulation leads to improved air stability of the nanocrystals and serves as an additional highlight of this geometry.

Raman spectroscopy is used to assess the crystallinity and layer thickness of the MoS2 layers through the two characteristic MoS_2 vibrational modes, E^1_{2g} and $A_{1g}^{25,27}$ The E^1_{2g} mode is attributed to the in-plane vibration of Mo and S atoms, while the A_{1g} mode is related to the out-of-plane vibration of S atoms.²⁷ Fig. 2d shows the Raman spectra of monolayer MoS₂ (spectrum 1, obtained inside the dotted lines in Fig. 1b), Cu_xS/MoS₂ (spectrum 2) and Cu_xS@MoS₂ (spectrum 3). The Cu_xS@MoS₂ heterostructures exhibit two vibrational modes centered at 381.10 cm⁻¹ and

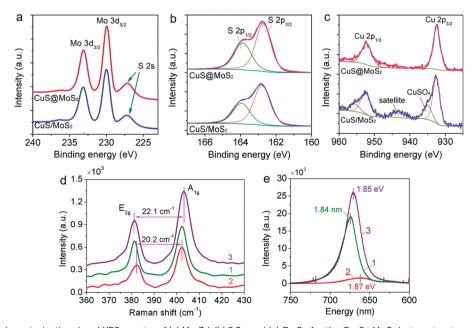


Fig. 2 Spectroscopic characterization. (a-c) XPS spectra of (a) Mo 3d, (b) S 2p and (c) Cu 2p for the Cu_xS@MoS₂ heterostructures and conventional MoS₂ monolayer transferred onto Cu_xS nanocrystals. (d) Raman and (e) photoluminescence spectra of (1) monolayer MoS₂ inside the dotted lines in Fig. 1c, (2) conventional MoS₂ monolayer transferred onto Cu_xS nanocrystals and (3) Cu_xS@MoS₂ heterostructures

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403.23 cm⁻¹ with a E_{2g}^1 -to- A_{1g} frequency difference of ~ 22.13 cm⁻¹. This value is smaller than that of bulk MoS₂, but larger than that of the pristine and transferred monolayer MoS2, probably due to the multilayer nature of the MoS₂ caps.²⁸ The corresponding photoluminescence spectra are also collected at ambient temperature with a small laser power of 1 μ W to avoid heating the sample. As shown in Fig. 2e, the pristine MoS2 exhibits photoluminescence emission near ~ 674 nm and another insignificant emission peak around ~623 nm. The former is attributed to the A exciton emission due to the interband transition at the Brillouin zone K point in MoS₂, while the latter arises from the higher energy B exciton emission from another direct transition between the conduction band and a lower-lying valence band. 29,30 The CuxSa MoS₂ heterostructures exhibit equivalent photoluminescence emission peaks, with a slight blue-shift (670 nm) probably originating from the change in local strain because of the presence of Cu_xS cores.³¹ It is worth noting that a remarkable quenching effect and more significant blue-shift (to 663 nm) of the photoluminescence were observed for the transferred MoS₂ sample, probably due to the inevitable contamination and released local strain from the original SiO2 substrate after the transfer process.³² This again proves the necessity of building a clean interface as demonstrated in our heterostructures.

The optical properties of the Cu_rS@MoS₂ heterostructures are further understood using the discrete dipole approximation (DDA) method. The simulation was carried out for a 50 \times 25 \times 25 nm³ rectangular Cu_xS target and the same Cu_xS capped with 6-layer MoS₂ as shown in Fig. 3a and b, respectively. The details regarding the DDA method can be found in the Experimental section (ESI†). 33,34 The simulated absorption spectra are shown in Fig. 3c. The Cu_xS nanocrystal shows high absorption in the visible region (400 nm to 600 nm) as well as in the near infrared region (700 nm to 1000 nm), which is consistent with a previous experimental report. 35 The Cu_xS@MoS₂ heterostructure exhibits overall increased absorption in the visible region, with the emergence of two peaks at 673.1 nm and at 628.0 nm due to the presence of A and B exciton absorption pathways indicated in Fig. 3e.

The DDA calculations also model the interaction of the refractive index with the geometry and incident light to evaluate the electric field distribution, 33 which is an indicator of the magnitude of the light-matter interaction present. Fig. 3d-i display the front view (arrow direction in Fig. 3a) of the obtained electric field maps of both targets at different incident wavelengths (400 nm, 610 nm and 900 nm). The electric field strength $(|E/E_0|^2)$ can be correlated with the absorption efficiency at various locations of the sample in Fig. 3c. Overall, one can observe that the CuxS nanocrystal shows a weak electric field response (Fig. 3d-f), while the electric field distribution of the Cu_xS@MoS₂ heterostructure is confined to the MoS₂ cap, with significantly enhanced strength (Fig. 3g-i), suggesting the significant improvement of the light-matter interactions due to the formation of a heterojunction. This aspect is particularly clear under an incident radiation of 900 nm, where even though coupling of light with the localized surface plasmon resonance (LSPR) of CuxS leads to an enhanced electric field in the bare nanocrystal. 36,37

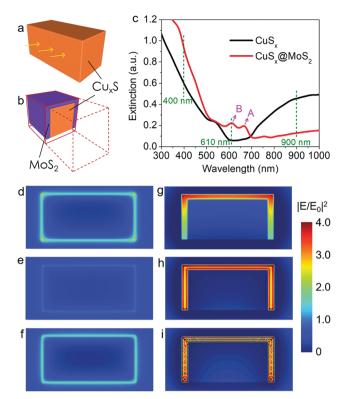


Fig. 3 Simulation of light-matter interactions. (a and b) 3D models for the Cu_xS (a) and Cu_xS@MoS₂ (b) targets used for DDA modeling. The arrows indicate the direction of incident light applied for all simulated targets unless otherwise noted. (c) Calculated extinction (absorption + scattering) efficiency as a function of incident wavelength. The A and B labels correspond to the A and B excitons observed in the photoluminescence spectra (Fig. 2e). (d-i) Calculated electric field distributions on Cu₂S (d-f) and Cu_xS@MoS₂ (g-i) nanocrystals under various incident wavelengths: (d and g) 400 nm, (e and h) 610 nm, and (f and i) 900 nm.

By contrast, the Cu_xS@MoS₂ heterostructure exhibits a stronger response, due to the possible plasmonic coupling enabled by the clean Cu_xS-MoS₂ interface.³¹ These simulations suggest that our Cu_xS@MoS₂ heterostructure is a promising optoelectronic material particularly for applications where a near infrared source is required.

The DDA results theoretically suggest interesting light-matter interactions in our Cu_xS@MoS₂ heterostructures, allowing us to further explore their potential application in broadband optoelectronics. A field-effect phototransistor made from the Cu_xS@ MoS₂ heterostructures was constructed with the schematic provided in Fig. 4a. In this device geometry, Cu_xS@MoS₂ heterostructures act as the light sensitizers, while the underlying MoS₂ monolayers act as the channel material (Fig. 4b). A similar transistor made from the transferred CuxS/MoS2 is also studied for comparison. All measurements were carried out at room temperature. As shown in Fig. 4c, the transferred Cu_xS/MoS₂ device exhibits a typical n-type channel behavior, which is consistent with the n-type nature of monolayer MoS₂.³⁰ The Cu_xS@MoS₂ device also shows an n-type electronic behavior; however, a gate-dependent drain current was only observed for small positive gate voltages before immediately saturating.

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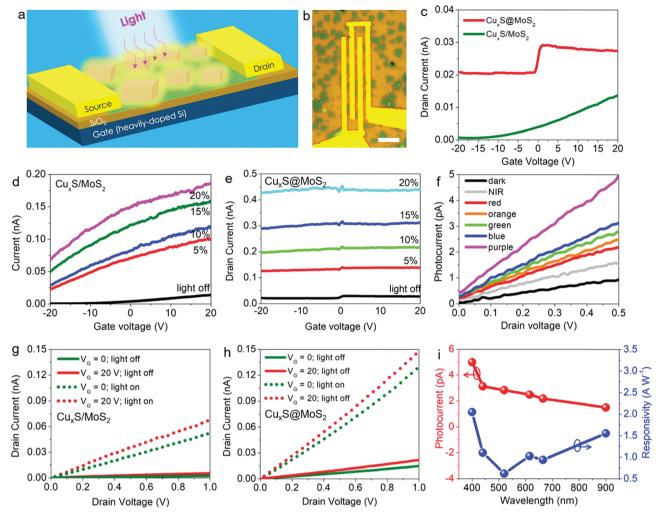


Fig. 4 Optoelectronic device application. (a) Device design and (b) optical view of the phototransistor. Scale bar in (b): 5 µm. (c) Transfer characteristics of the Cu_xS/MoS₂ and Cu_xS@MoS₂ devices. (d and e) Transfer curves of Cu_xS/MoS₂ (d) and Cu_xS@MoS₂ (e) transistors under illumination with varying power. (f and g) Output curves of Cu_xS/MoS_2 (f) and $Cu_xS@MoS_2$ (g) transistors with and without illumination. (h) Output curve of the $Cu_xS@MoS_2$ device with illuminations of different wavelengths. (i) Photocurrent and photoresponsivity of the Cu_xS@MoS₂ device as a function of illumination wavelength.

This is possibly due to the Fermi level of MoS2 being aligned with that of p-type Cu_rS after the formation of the heterojunction. A further increase of the gate voltage in the positive direction can lead to misalignment in these bands, which would induce a decrease in the current.³⁸ From the transfer curves, we obtain a carrier mobility of 1.76 \times 10^{-4} cm 2 V $^{-1}$ s $^{-1}$ for the $Cu_rS@MoS_2$ device and 0.11×10^{-4} cm² V⁻¹ s⁻¹ for the $Cu_rS/$ MoS₂ device. It is also worth noting that both devices show a relatively weak gate dependence with ON/OFF ratios of 1.2-1.5, 39 which is probably due to the electric field screening provided by the underlying Cu_xS nanocrystals. The dependence of transfer curves on the illumination power for the Cu_xS/MoS₂ and Cu_xS@MoS₂ transistors is demonstrated in Fig. 4d and e, respectively. Both devices show a photocurrent generation ability over the entire gate voltage range, which is also consistent with the results previously reported for monolayer MoS₂ transistors. 40 However, the photoresponse of the Cu_xS@MoS₂ device is more significant, with a negligible gate dependence, and exhibits a linear relationship with the increase of illumination power, which is usually more desirable for practical optoelectronics.

The output curves in the dark and light states for both devices are further shown in Fig. 4f and g. It is worth mentioning that the linear relationship between the drain current and drain voltage indicates good ohmic contact of the channel materials and contact electrodes. One can again observe that the Cu_rS@ MoS₂ device exhibits a more substantial photoresponse compared to the Cu_xS/MoS₂ device. The output curves of the Cu_xS@ MoS₂ device at various illumination wavelengths are shown in Fig. 4h. The device shows remarkable response for wavelengths ranging from the violet to near infrared region due to the presence of small-band gap CuxS, which is one of the key advantages of the heterostructure compared to MoS2 devices. The corresponding photocurrent and the calculated photoresponsivity are further displayed in Fig. 4i. The trend of photoresponsivity variation according to the incident wavelength is consistent with the absorption curve of Cu_xS@MoS₂ in Fig. 3c. It is worth noting that the photoresponsivity under near infrared

MoS₂

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а b С Energy (eV) Energy (eV) 0.55 eV 0.56 eV 0.5 ORCC path: -0.5 Х M R XR Х R Α XR -X-S-R-A-Z-Γ-Y-X₁-A₁-T-Y|Z-T е 4.85 eV! 4.70 eV 4.78 eV

Fig. 5 Electronic structure calculations. (a) High symmetry points in the Brillouin zone of Cu_xS. The inset shows the corresponding atomic structure. (b and c) Band structures calculated for Cu₂S (b) and Cu_{1.8}S (c). (d) Calculated energy band diagram for Cu₂S, Cu_{1.8}S, and MoS₂. (e and f) Schematics showing the possible formation of a type-II heterojunction between $Cu_{1.8}S$ and MoS_2 (e) and a type-I heterojunction between Cu_2S and MoS_2 (f) under

Cu_{1.8}S

incident radiation is significantly pronounced compared to the absorption spectra (consistent with the near field distribution in Fig. 3i). This should be enabled by (1) the band bending and electric fields present at the heterojunction interface between MoS₂ and a small-band gap material and (2) possibly the strong light-matter interaction due to the LSPR effect as theoretically predicted in Fig. 3i and experimentally demonstrated in our previous report,41 further suggesting the potential of our TMD heterostructures in broadband optoelectronics.

Cu_{1.8}S

MoS₂

Cu₂S

Finally, we performed density functional theory (DFT) calculations to understand and corroborate our experimental findings and conclusions regarding the optoelectronic properties of this heterostructure. Fig. 5a shows high symmetry points in the Brillouin zone of Cu_rS (inset atomic structure) used for the calculation. The obtained electronic band structures for Cu2S and Cu_{1.8}S are shown in Fig. 5b and c, respectively. We find that the ideal chalcocite Cu₂S has an indirect band gap of 0.56 eV; however, the band structure can be effectively modulated by introducing Cu vacancies in the system. For instance, the chalcocite Cu_{1.8}S is found to exhibit a direct band gap of 0.55 eV (Fig. 5c). This suggests that the incorporation of Cu_xS can not only supplement the low IR absorption for MoS₂ (Fig. 3c), but also significantly improve the photoelectronic effect since the photon-related excitation and emission in the slightly deficient Cu_xS are significantly improved.

The DFT calculations also reveal the work function of the components, which allows us to predict the alignment of the band structure at the interface. Fig. 5d shows the band energy diagram of the Cu2S, Cu1.8S and MoS2 systems before heterojunction formation. Again, this directly indicates the modulation of the band structure of CuxS with slight variations in the stoichiometry (see more details in Fig. S3, ESI†), and accordingly

we are able to predict possible charge transfer pathways following heterojunction formation. As shown in Fig. 5e and f, Cu_xS-MoS₂ is expected to exhibit better photocarrier separation efficiency due to the formation of a type-II band alignment (Fig. 5e), as compared with the possible type-I heterojunction formed in the Cu₂S-MoS₂ system (Fig. 5f). Thus, combined with evidence from our optical results, we can surmise that the noteworthy optoelectronic performance of our Cu_xS@MoS₂ phototransistor is probably attributed to a comprehensive contribution from (1) the improved interfacial charge transfer that originated from the clean, atomically-connected interface, (2) the formation of a type-II heterojunction structure between CuxS and MoS2, and (3) the potentially enhanced light-matter interactions due to the LSPR of Cu_rS.

3. Conclusions

Depletion layer

MoS₂

In summary, we explored a new route for the geometry design and synthesis of TMD heterostructures beyond traditional lateral/ vertical heterostructures. The heterojunction formation was accomplished via a single-step direct chemical vapor deposition of MoS₂ on nanocrystals of another transition metal sulfide. The resultant product, e.g., Cu_xS@MoS₂ heterostructures, has an appreciable atomically-sharp interface area and is found to exhibit strongly improved light-matter interactions over a broad wavelength range. The formation of this heterojunction also leads to useful band alignment and can potentially facilitate the charge separation and transfer in an optoelectronic process. The field-effect phototransistor based on the Cu_xS@MoS₂ heterostructures represents interesting transfer characteristics, and

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importantly, a constant photoresponse is observed throughout the entire positive and negative gate voltage regions. The photocurrent generation was observed over a broadband range, particularly for the near infrared photodetection enabled by the band alignment at the heterojunction as well as the surface plasmon effect from Cu_rS. As such, this geometry potentially serves as a new scalable material system for future optoelectronic semiconductor devices.

Conflicts of interest

There are no conflicts to declare.

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