Anisotropic growth of non-layered CdS on MoS$_2$ monolayer for functional vertical heterostructures

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Two dimensional (2D) semiconductors have emerged as a crucial material for use in next generation optotelectronics. Similar to micro-electronic devices, 2D vertical heterostructures would most likely be the elemental components for future nanoscale electronics and optotelectronics. To date, the components of mostly reported 2D van der Waals heterostructures are restricted to layer crystals. In this communication, we demonstrate that non-layered semiconductors of CdS can be epitaxially grown on to 2D layered MoS$_2$ substrate to form a new quasi vertical heterostructure with clean interface by chemical vapor deposition.

Photodetectors based on this CdS/MoS$_2$ heterostructure show broader wavelength response and ~50 fold improvement in photoresponsivity, compared to the devices fabricated from MoS$_2$ monolayer only. This research opens up a way to fabricate a variety of functional quasi heterostructures from non-layer semiconductors.

1. Introduction

Semiconductor heterostructures play a crucial role in modern microelectronics and optoelectronics[1]. Heterostructures, combining different materials, show bandgap offset and tunable electrical and optoelectrical properties. Conventional heterostructures are primarily based on group IV, III-V, or II-VI semiconductors, with covalent bonding between atoms at the hetero-interface.[1, 2] The usage of material components for conventional heterostructures is strongly dictated by lattice mismatch which determines the interface quality and thus, the heterostructure performance. Beyond the traditional group IV, III-V, or II-VI semiconductors, two-dimensional layered crystals (*e.g.* graphene[3], transition metal dichalcogenides (TMDs)[4], hexagonal boron nitride (*h*-BN)[5], phosphorene[6]*etc*) have emerged as promising candidates for next generation electronics and optoeelectronics due to their unique properties. These 2D layered materials can be artificially combined to fabricate various van der Waals (vdW) heterostructures without the lattice match limitation. Novel physical properties of these vdW heterostructures have been investigated theoretically and experimentally, and devices based on those new heterostructures such as tunnel transistors and sensors have already been demonstrated[7-11].

Thus far, these vdW heterostructures have mainly been fabricated by a top-down process of manual transfer or a bottom up method of chemical vapor deposition (CVD) growth. The first

demonstration of vdW heterostructures were realised by vertically stacking different 2D materials (grapnene/h-BN[8, 12], MoS$_2$/Graphene[10], Graphene/WS$_2$[9]etc) using conventional PMMA-mediated transfer method[7]. The physical properties of these heterostructures are significantly influenced by the relative orientation of the layers and interfacial quality between them. However, the stacking style and crystal orientation cannot be easily controlled by mechanical transfer method. In addition, such strategies cannot ensure good interfacial quality. Compared to manual transfer, CVD epitaxial growth is a powerful approach for fabricating 2D vdW heterostructures with controlled stacking style, crystal orientation and clean interface. Indeed, using this strategy, some vertical heterostructures have already been successfully grown, including graphene/h-BN[13], MoS$_2$/h-BN[14], MoSe$_2$/graphene[15], MoS$_2$/graphene[16], WS$_2$/MoS$_2$[17] and MoS$_2$/SnS$_2$[18].

Thus far, the components of the reported 2D-vertical vdW heterostructures have been restricted to layered materials with planar crystal structures. However, many non-layered materials such as cadmium sulfide (CdS) also exhibit attractive optoelectronic properties[19]. Combination of such non-layered functional semicomiductors with layered materials (e.g. MoS$_2$) could create a new type of vdW heterostructure to provide novel platform for applications in nanoscale electronics and optoelectronics. These non-layered materials typically incline to stack into three dimensional (3D) nanostructures due to their chain-like structure and the lack of driving force for 2D anisotropic growth. We note that some non-layered materials such as noble metals, metal oxides and metal chalcogenides can be confined to 2D anisotropic growth to form sheet-like nanomaterials through the assistance of organic surfactants via wet chemical synthesis[20]. However, these soluble sheet-like ultrathin

nanomaterials cannot be used for device applications as they become easily folded, crumpled or aggregated when they are transferred onto substrates during device fabrication. In addition, these surface-ligand protected nanosheets are not suitable for the fabrication of clean interfaces. To realize these novel vdW heterostructures with high quality interface, direct anisotropic growth of non-layered semiconductors on layered 2D materials through a CVD process is the most realistic approach. However, such a process is yet to be demonstrated.

In this work, we demonstrate epitaxial growth of non-layered CdS nanosheet on ultrathin MoS_2, creating a new vdW vertical heterostructure. We find that anisotropic growth of CdS on MoS_2 is driven by kinetics within a certain reaction temperature range influenced by the substrates, without forming energetically favored 3D structures. Photodetectors based on this CdS/MoS_2 heterostructure show broader wavelength response and significantly improved photoresponsivity compared to the devices fabricated from monolayer MoS_2 only.

2. Results and Discussion

Figure 1 shows the schematic representation of epitaxial growth of two-dimensional CdS/MoS_2 vertical heterostructures (further information in Figure S1). In the first stage, the left zone and MoO_3 zone in the furnace are heated to 250 ^{o}C and 670 ^{o}C, respectively. Subsequently, sulfur is pushed into the left zone quickly and kept for 25~30 mins. This stage is used to grow MoS_2. In the second stage, the zone of substrate containing as-grown MoS_2 cools down to 500~600 ^{o}C, meanwhile CdS zone is heated to 950 ^{o}C. Finally the CdS stream is submitted using Ar gas to the surface of MoS_2 to form the vertical heteostructure.

The as-grown triangular MoS_2 nanoflakes with sizes of up to 30 μm lateral dimension are uniformly distributed over the substrate. Such a typical MoS_2 flake is shown in Figure 2a. Figure 2b shows a scanning electron microscope (SEM) image of the vertical heterostructures, in which the dark part of the image represents a MoS_2 nanocrystal and the bright triangles or hexagons are epitaxial CdS nanosheets. The CdS/MoS_2 herterostructures are further characterized using atomic force microscopy (AFM), (Figure 2c, 2d, S2). The thickness of the eptaxial CdS on MoS_2 is in the range of 10~60 nm. Figure 2c shows an AFM image of a hexagonal CdS crystal, with ~50 nm uniform thickness. In Figure 2d, MoS_2 and CdS nanosheets with corresponding thicknesses of 1 nm and 30 nm can be observed on SiO_2/Si. Since CdS has two different crystal structures,[21] it is necessary to determine their crystallographic phase using X-ray diffration (XRD). In Figure 2e, the blue plot represents the XRD result of MoS_2, the red plot shows CdS powder XRD patterns from the database (PDF#41-1049), while the black plot is that of the CdS/MoS_2 heterostructure. The diffraction pattern of the heterostructure can be perfectly indexed on the database of a hexagonally phased CdS and MoS_2.

To explore the effects of MoS_2 on the growth of CdS, the CdS/MoS_2 heterostructure is studied by transmission electron microscopy (TEM) (shown in Figure 3a and Figure S3). Under TEM observation, the CdS sheets exhibit a deeper color while the MoS_2 films are almost transparent. A typical selected area electron diffraction (SAED) pattern (Figure 3b) is taken from the area of CdS/MoS_2 heterostructure (circle in Figure 3a). In this SAED pattern, two sets of six-fold symmetric diffraction spots are observed, in which the brighter and inner spots correspond to CdS (a=4.14Å) while the weaker set belongs to MoS_2 (a=3.14 Å). By

correlating the SAED pattern with the morphology (Figure 3a), the planes of the hexagonal CdS can be identified (Figure 3a), indicating that every plane of CdS is parallel to the corresponding MoS_2 plane, *e.g.* CdS (100) || MoS_2 (100) and CdS (110) || MoS_2 (110). Figure 3c and 3d show the Fourier transform high-resolution TEM of CdS and MoS_2 which were measured from the red and blue squares in Figure 3a, respectively. Both CdS and MoS_2 exhibit high quality crystallinity. The results indicate that the spacings of (100) and (110) planes of CdS are 0.36 nm and 0.21 nm, while the planes of MoS_2 are 0.27 nm and 0.16 nm respectively. These TEM characterization further demonstrate the good epitaxy of CdS on MoS_2 without any mis-orientation. Lattice mismatch between hexagonal CdS and MoS_2 is calculated to be 32% using the relationship f = $[d_{Cds}(100)-d_{MoS2}(100)]$/ $d_{MoS2}(100)$,[22] where $d_{Cds}(100)$= 0.359 nm, $d_{MoS2}(100)$= 0.272 nm. This lattice mismatch is larger compared to traditional group IV, III-V, or II-VI semiconductor heterostructures[23]. vdW epitaxy allows formation of high quality herostructure consisting of two crystals with such large lattice mismatch because of the weak vdW interation at the interface. We note that this is also applicable to manually stacked crystals. The cross-sectional electron microscope images with the clean interfaces without significant interlayer atomic mixing is shown in Figure 3e, guranteeing the heteropitaxial stacking. In addition, as shown in the SEM image in Figure S4, the CdS nanosheets show parallel edges, as indicated by the blue and red lines. This crystal orientation alignment (CdS (100) || MoS_2 (100) and CdS (110) || MoS_2 (110)) is attributed to vdW epitaxy. Based on the above discussio, we present a scheme of epitaxially grown CdS on MoS_2 in Figure 3f. This shows that hexagonal CdS is grown parallel to the (001) plane

surface of MoS_2 in the six equivalent directions (such as 110), rather than the preferential direction of (001). We propose that this growth kinetics is induced by the MoS_2 substrate.

To further investigate our proposal on the anisotropic growth of CdS by substrate induced kinetics, a controlled experiment is performed on the growth of CdS nanocrystals on SiO_2/Si under identical reaction parameters. This produces rod-like CdS nanocrystals, clearly showing an energetically favorable growth direction of (001) of hexagonal crystals (Figure S5). This substrate dependent growth can be well-understood by its surface energy E_s or its attachment energy E_a. A smaller value of E_s ensures higher stability while a larger $|E_a|$ indicates a faster growth process. The value of E_s and $|E_a|$ of $(001)_{CdS}$, calculated by Ref[21] are much higher than any other CdS plane. This indicates that the surface of $(001)_{CdS}$ is more active, with much faster growth rate than any other face under normal condition. This is why compared to the growth of CdS on MoS_2 (Figure 2b). CdS tripod nanocrystal is predominantly grown on SiO_2/Si (Figure S5a). Indeed the growth rate of the legs along the (001) crystallographic orientation on SiO_2/Si is much higher than that along the other surfaces. (The model of tripod nanocrystal is shown in Figure S6). On the other hand, the shapes grown on MoS_2 are different due to the substrate lattice structure and the energy barrier for nucleation (ΔG^*) at the growth temperature. Reference[24] has recently discussed growth kinetics on layered crystals that explains our observation. According to classical nucleation kinetics, the free energy change for nucleation at heterostructures can be written as follows: $\Delta G_{r,\gamma}=\pi r^2 t \Delta G_v + \pi r^2 (\gamma_c + \gamma_{sc} - \gamma_s) + 2\pi r t \gamma_{c,edge}$.[24] Here r and t are radius and thickness of nucleus of CdS. γ_s, γ_c, γ_{sc} and $\gamma_{c,edge}$ represent the E_s of the substrate (MoS_2 or SiO_2 in our case), E_s of the nucleus of the CdS crystals, interfacial energy between the nucleus and the substrate and the

E_s of nucleus edge of CdS crystals, respectively. The difference in free energy per unit volume during nucleation is expressed as ΔG_v. The maximum point $\Delta G_{r,\gamma}$ in the total Gibbs free energy corresponds to the critical free energy barrier for nucleation $\Delta G^* = \pi r(\gamma_{c,edge})^2/[\Delta G_v - (\gamma_c + \gamma_{sc} - \gamma_s)/t]$.[24] The term $(\gamma_c + \gamma_{sc} - \gamma_s)$ represents the effective change in E_s during the nucleation and is largely dependent on the growth substrate. The surface energy of MoS_2 is ~70-75 mJ/m^2.[25] On the other hand, CdS grown on SiO_2 forms tripod structures due to the significantly larger E_s of the substrate (γ_{SiO2}~300-400 mJ/m^2).[26] This indicates that a larger free energy barrier must be overcome for CdS growth on SiO_2/Si compared to the epitaxial growth of CdS on MoS_2 surface. We also note that, the CdS growth is further impacted by the reaction temperature. Above 1000 ^{o}C, CdS nanocrystals always grow in energically favorable (001) direction on both the SiO_2 and MoS_2 substrates, forming rod-like nanocrystals (Figure S5b). This is mainly attributed to the high concentration of precursor and the enhanced activity of CdS is at such high temperature (>1000 ^{o}C). Due to the grow rate increases faster along the (001) plane compared to that of the (100) plane under high temperature, the CdS nanocrystals tend to develop a rod-like morphology. Therefore, tripod-like structures (Figure S5b) rather than nanosheets (Figure 2b) of CdS nanocrystals are observed on MoS_2 surface for high temperature growth.

Raman and photoluminescence (PL) are effective ways to characterize the crystal quality and band gap these materials. The CdS/MoS_2 heterostructures (A hexagonal CdS on MoS_2 in Figure 4a and triangular CdS on MoS_2 in Figure S7) are characterized by Raman and PL with a 488 nm laser. The Raman mapping of CdS 1LO mode at 300 cm^{-1} is shown in Figure 4b. The blue hexagon in the centre is the CdS hexagon while the red zone represents MoS_2.

Figure 4c shows the Raman mapping at A_{1g} mode of MoS_2. Raman signal of MoS_2 can be obtained from the entire area oft he sample. However, the Raman signal of the central area where CdS is grown is much weaker. This Raman mapping further demonstrates the epitaxial nature of the structure. The Raman spectra of the heterostructures are shown in Figure 4d. The peaks of E_{2g} mode at 383 cm^{-1} and A_{1g} mode at 402 cm^{-1} are the characteristic peaks of MoS_2. On the other hand, the peaks at 212 cm^{-1}, 254 cm^{-1}, 300 cm^{-1} and 601 cm^{-1} are the characteristic peaks of CdS[19]. The PL spectra of the herterostructures are shown in Figure 4e. We identified PL peak of MoS_2 at 1.81 eV. However, this peak disappeared after the formation of CdS/MoS_2 heterostructure, accompanied by the appearance of a new peak at ~1.70 eV (Details on PL measurements using a 532 nm laser is presentend in Figure S8, Supporting Information). The peak at 1.70 eV can be attributed to the interlayer excitonic transition of MoS_2 conduction band maxima to the CdS valence band minima.[17] The three peaks in red line at 2.477 eV, 2.491 eV and 2.493 eV indicate the Raman peaks of Si, A_{1g} mode and E_{2g} mode of MoS_2, respectively.The peak at 2.45 eV indicates the existence of CdS. Because CdS has a strong visible optical absorption, it is an attractive material for enhancement of light absorption and photoresponse of the heterostructure. UV-Vis-NIR absorption spectrums of MoS_2 and CdS/MoS_2 heterostructures are measured by transferring 0.5 cm $\times$ 0.5 cm MoS_2 and CdS/MoS_2 films on to glass substrates; Figure 4f. The coverage of CdS on MoS_2 is ~20%, estimated from a series of SEM images. The plots indicate that the single layer MoS_2 has a weak light absorption and a small response scope (wavelength < 680 nm). Compared to MoS_2, the CdS/MoS_2 heterostructures have a much higher absorption and wider light response (wavelength < 1000 nm). The higher absorption and stronger response

can be explained by the band structure oft he heterostructure; Figure 4g.[27] Due to lower

conduction band edge of MoS_2, electrons located in the conduction band of CdS tend to

transfer to the conduction band of MoS_2, which leads to effective separation of electron-hole

pairs and prevents the electron-hole recombination. Therefore, the number of carriers

increases in the circuit, leading to the enhancement of photocurrent. We note that the

broadening of response wavelength of the heterostructure is expected to reach to up to 730 nm

after the formation oft he vertical heterostructure. However, the UV-Vis-NIR spectra of the

CdS/MoS_2 heterostructures indicates absorbance above 730 nm. This is likely due to the

variation in shape, size and thickness of the CdS nanocrystals.

The single-layer MoS_2 and CdS/MoS_2 heterostructure-based photodetectors are fabricated

using Ti/Au contacts on silicon substrates covered with 300 nm silicon oxide (SiO_2/Si).

Figure 5a presents a schematic diagram of a single-layer MoS_2 photodetector with epitaxially

grown CdS. The inset shows an optical microscope image of the actual device. The

photoelectrical characterizations are measured at room temperature in ambient condition. As

shown in Figure 5b, the photocurrent as a function of time is measured under alternative dark

and illumination condition at 0.266 mW/cm^2, with a bias voltage V_{ds} =1V and a gate voltage

V_g = 0V. At 610 nm (other wavelengths are shown in supporting information) ON and OFF

illumination, both the single-layer MoS_2 and CdS/MoS_2 heterostructure-based photodetectors

exhibit repeatable and stable response to the light. The response (light ON) and recovery

(light OFF) time is calculated by averaging the device response and considering the time it

take to reach 80% of the final values. The measured rise time is 100 ms, much faster than that

of the devices based on CVD grown single-layer MoS_2 (rise time >10 s). Compared to the

MoS_2 photodetector, the CdS/MoS_2 devices exhibit strong photocurrent enhancement under this illumination. Here, photocurrent (ΔI) is defined as the defference between I_{ON} and I_{OFF} with a voltage bias of 1V. Figure 5c shows the photocurrents of the MoS_2 and CdS/MoS_2 photodetectors under light with a series of wavelengths (365 nm, 490 nm, 550 nm, 610 nm and 700 nm). The photocurrent from MoS_2-based device gradually drops with the increase in wavelength, while that of the CdS/MoS_2-based device rises fast and reaches the maximum at 700 nm. Note that there is no significant response to light when the illumination wavelength is longer than the optical band gap of the single layer MoS_2 (1.82 eV, λ =681 nm). This is because only the incident photons with energies exceeding 1.82 eV excite electrons from the valence band into the conduction band of MoS_2. CdS has a band gap of 2.45 eV. Thus the CdS photodetector is not expected to respond to >506 nm. However, we observe photoresponse of the CdS/MoS_2 detector at >680 nm. We propose that the photoresponse in this forbidden optical absorption region for pristine MoS_2 arises from the photoinduced electron transfer from the valence band of CdS to the bottom of conduction band of MoS_2.

Responsivity (R_λ) is another critical parameter to evaluate the performance of a photodetector. R_λ is defined as the photocurrent generated per unit power of the incident light on the effective device area. The value of R_λ can be calculated using the relation: $R_\lambda = \Delta I / P_\lambda S$. Here, ΔI is the generated photocurrent, P_λ is the incident light intensity, S is the effective illuminated area (In the present study S ~1mm×20 μm). The photo-responsivity under different wavelengths of MoS_2 and CdS/MoS_2 photodetectors is measured and the results is shown in Figure 5d. The results demonstrate that the epitaxial CdS plays an important role to enhance the photoresponsivity, with over 50 times increase in responsivity (70.8 mA/W Vs

3.91 A/W) under 610 nm illumination. Such a strong enhancement in photoresponsivity and simple device configuration underscores the potential application of this CdS/MoS$_2$ heterostructure.

3. Conclusions

In summary, we have demonstrated successful epitaxial growth of non-layered CdS on to MoS$_2$ to fabricate their vertical heterostructures using a one-step CVD method. We propose that the substrate surface energy plays an important role in the growth of CdS. We further demonstrate CdS/MoS$_2$ heterostructure-based photodetectors. The photocurrent and photo-responsivity of CdS/MoS$_2$ heterostructure-based photodetectors are greatly enhanced, compared to their MoS$_2$ counterparts, making our strategy very attractive for high-performance optelectronic devices.

4. Experimental Section

Characterizations: The as–grown CdS/MoS$_2$ heterostructures are characterized by scanning electron microscopy (SEM, Hitachi S–4200), AFM (Nanoscope IIIa Vecco), UV-Vis-NIR absorption (Hitachi U-4100), transmission electron microscopy (TEM, Tacnai–G2 F30, accelerating voltage of 300 kV) and Raman spectroscopy (LabRAM XploRA, power 0.15 mW, excitation wavelength 488 nm and 532 nm). The detectors are annealed at 200 $^{\circ}$C for 30 min with 100 sccm Ar : H$_2$ (V/V=9/1) to reduce the resistance and improve the contact for the devices.

Electrical measurements: These devices are characterised using a semiconductor analyzer (Keithley 4200 SCS) combined with a Lakeshore probe station. Photoelectric data are obtained by using a 500 W xenon lamp as the light source. Mono-chromatic lights of 254-850 nm are obtained using optical filters. The intensities of the incident light source are measured by a power and energy meter (Model 372, Scienteck). The photocurrent measurements are performed using the Lakeshore probe station and an HP 4140B Semiconductor Parameter Analyzer.

Supporting Information Supporting Information is available from the Wiley Online Library or from the author.

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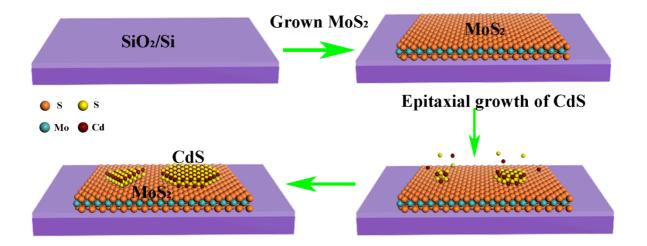
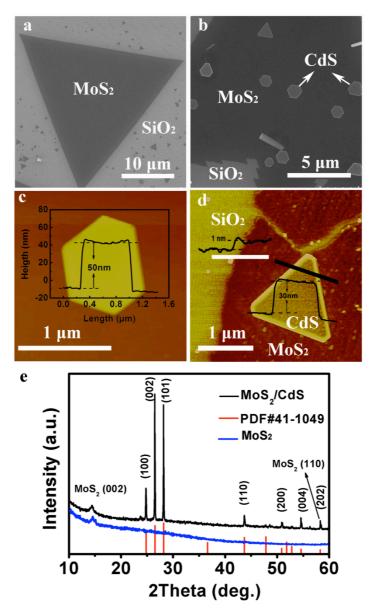Figure 1. Schematic illustration of one-step epitaxial growth of CdS/MoS$_2$ heterostructures.

Figure 2. Characterization of vdW epitaxial CdS/MoS$_2$. (a, b) SEM images of CVD grown triangle MoS$_2$ and CdS/MoS$_2$ heterostructures, respectively. (c) AFM image and associated height profile of a hexagonal CdS. (d) AFM phase image of the heterostructure with associated height profiles. (e) XRD characterization of MoS$_2$ and CdS/MoS$_2$.
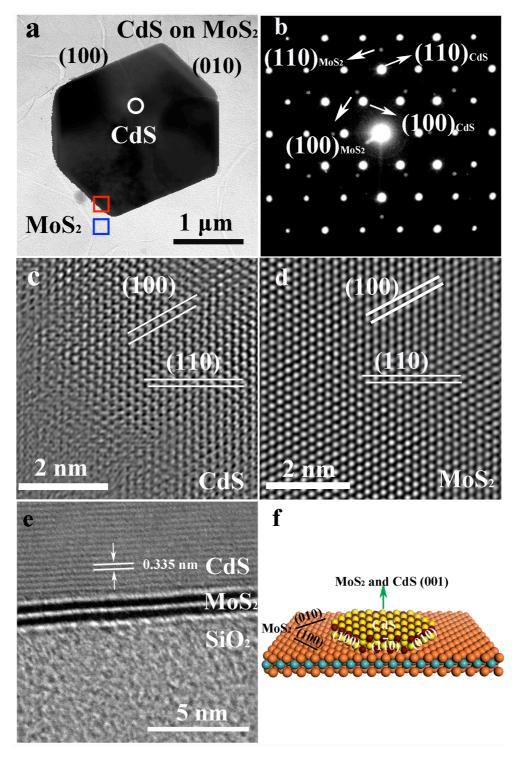
Figure 3. TEM characterization of the heterostructures. (a) Low-magnification TEM images of CdS/MoS$_2$ heterostructures. (b) Selected area electron diffraction (SEAD) of heterostructures. (c, d) Fast Fourier transform images of CdS and MoS$_2$, respectively. (e) Cross-sectional TEM images of the CdS/MoS$_2$ heterostructure. (f) Schematic model of the CdS/MoS$_2$ heterostructures.
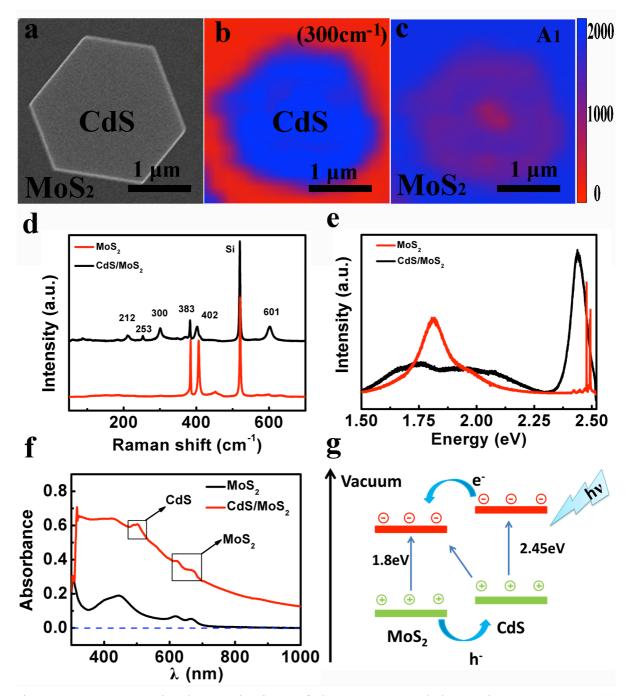
Figure 4. Spectroscopic characterizations of the as-grown CdS/MoS$_2$ heterostructures. (a) SEM image of hexagonal CdS on MoS$_2$. (b) Raman mapping of CdS at 300 cm^{-1}. (c) Raman mapping of MoS$_2$ at 402.1 cm^{-1} (d, e) Raman and PL spectrum of the CdS/MoS$_2$ heterostructures. (f) UV-Vis-NIR spectrum of the CdS/MoS$_2$ heterostructures and single-layer MoS$_2$. (g) Band gap schematic of CdS/MoS$_2$ heterostructure photodetector under illumination.
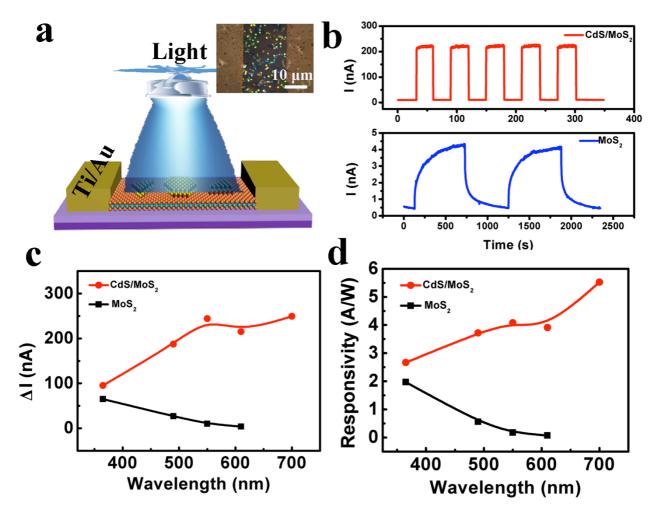
Figure 5. Characterizations of the photodetectors. (a) Schematic of CdS/MoS$_2$ heterostructure photodetector; inset shows an optical microscope image of the device. (b) Time-dependent photoresponse of CdS/MoS$_2$ heterostructure and single-layer MoS$_2$ photodetectors under 610 nm illumination, with a 1 V bias. (c, d) Photocurrent and photo-responsivity under 365, 490, 550, 610 and 700 nm wavelength of the same devices.

A new van der Waals heterostructure consisting of CdS nanosheet and MoS$_2$ via CVD process is presented. This is the first demonstration where a non-layered semiconductor has been epitaxially grown on to 2D layered crystal to fabricate a new type of van der Waals heterostructure. Compared to MoS$_2$ photodetectors, the photocurrent and photo-responsivity of CdS/MoS$_2$ heterostructure photodetector show significant enhancement.

Keywords: epitaxial growth, CdS/MoS$_2$ heterostructure, photodetector, responsivity

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Anisotropic growth of non-layered CdS on MoS$_2$ monolayer for functional vertical heterostructures

ToC figure