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Surface charge transfer induced p-CdS nanoribbon/n-Si heterojunctions as fast-speed self-driven photodetectors[†]

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Heterojunctions composed of single p-type CdS nanoribbons (NRs) and n-type silicon (Si) were successfully fabricated. The p-type CdS NRs were realized through a facile surface charge transfer doping approach. A typical as-fabricated p-n heterojuction exhibits excellent rectifying behavior with a rectification ratio up to $\sim 2 \times 10^3$ within ± 1.5 V, a low turn-on voltage of ~ 0.5 V and a small ideality factor of 1.29. Furthermore, due to the strong photovoltaic effect, the heterojunction is found to be highly sensitive to visible light irradiation at zero bias voltage with a large $I_{\text{light}}/I_{\text{dark}}$ ratio (2×10^3), fast response speed ($t_r = 26 \,\mu\text{s}$ and $t_f = 112 \,\mu\text{s}$), good reproducibility and long-term stability. The present work suggests great potential of such a heterojunction for future high-speed photodetector applications, and more importantly, signifying the feasibility of applying the surface charge transfer doping technique for constructing novel nano-optoelectronic devices.

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Introduction

One dimensional semiconductor nanostructures such as nanowires (NWs),¹ nanoribbons (NRs),^{2,3} nanotubes (NTs),⁴ etc. have attracted a great deal of attention in the application as novel electronic and optoelectronic devices due to their unique optical, physical and electrical properties relative to their thin films or bulk counterparts. As an important II–VI semiconductor, cadmium sulfide (CdS) with a wide direct band-gap of 2.42 eV at room temperature has long been considered as a promising material for constructing nano-electronic and nano-optoelectronic devices.^{5,6} To date, many efforts have been made to prepare CdS nanostructures,^{7,8} and a variety of nano-electronic and nano-optoelectronic devices including field-effect transistors (FETs),⁹ logic circuits,¹⁰ optoelectronic switches,¹¹ solar cells,^{12,13} lightemitting diodes (LEDs),¹⁴ and lasers,¹⁵ etc. have been explored based on CdS nanostructures.

P-n junctions are of great importance in modern microelectronics applications, as they are fundamental elements for devices and circuits.¹⁶ The rapid advances in the development of nanotechnology open up the successful fabrication of p-n junctions based on semiconductor nanostructures with various architectures, including core-shell, axial, crossed and branched p-n junctions.^{17,18} To construct a p-n junction with designed properties, controlled doping of semiconductor nanostructures is crucial. The electrical conduction properties of the semiconductor nanostructures can be efficiently tuned through appropriate n- and p-type doping. Thus far, efficient n-type doping of CdS nanostructures has been achieved through introducing impurity elements including indium (In), nitrogen (N), phosphorus (P), chlorine (Cl) and gallium (Ga), etc.^{19,20} as dopants during the nanostructures growth stages. However due to the strong selfcompensation effect, namely, doping of the acceptors will inevitably introduce one or more donor defects in the lattice, p-type doping of CdS nanostructures has been extraordinarily difficult.²¹ Recently, through a facile surface charge transfer doping technique, we successfully illustrated efficient p-type doping of CdS NWs.²² As a result of spontaneous electron exchange, the MoO₃-coated CdS NWs exhibit a striking hole mobility as high as 2035 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Furthermore, by selective coating of a MoO₃ layer on half part of a single nanowire, a CdS NW p-n homojunction with pronounced photovoltaic behavior was realized. However in spite of the progress, using p-type CdS nanostructures as building blocks for constructing high-performance nano-optoelectronic devices is still less explored. Because of the huge difference between the

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surface charge transfer doping with traditional doping approaches,^{23,24} constructing p-type CdS nanostructures based optoelectronic devices with designed performance remains a challenge. On the other hand, homojunction based optoelectronic devices usually suffer from weak absorption of incident light due to the narrow light absorption region, which may greatly restrict the promotion of their device performance.²⁵ In light of this, the utilization of p-n heterojunctions consisting of two or more semiconductor materials with different bandgaps is supposed to be one of the most efficient routes.²⁶ As a matter of fact, due to different absorption wavelength coverage, it is found that such novel structures could enable more effective light absorption, thus greatly increasing the device performance.^{27,28}

In this work, we present the construction and investigation of p-CdS NR/n-Si heterojunctions, based on successful p-type doping of CdS NRs *via* a surface charge transfer approach. The as-fabricated heterojunction exhibits a well-defined rectifying effect with a large rectification ratio, a low turn-on voltage and a small ideality factor. Further photoresponse analysis reveals that such heterojunction devices could work as high sensitivity, fast speed self-driven visible photodetectors in a wide range of switching frequencies with prominent reproducibility and air stability. The generality of the above results suggests that the p-CdS nanostructures and the present heterojunction devices will have potential application in future nano-optoelectronic devices.

Experimental

Materials synthesis and characterization

The undoped CdS (u-CdS) NRs used in this work were synthesized by using CdS powder as a source material in a horizontal quartz tube furnace at 850 °C *via* a chemical vapor deposition (CVD) method. Detailed description of the synthesis was reported in a previous work.²⁹ The p-CdS NRs were obtained by coating a thin layer of MoO₃ (~100 nm) onto the surface of u-CdS NRs.²² The morphologies and structures of as-prepared u-CdS NRs were characterized using a field-emission scanning electron microscope (FESEM, Philips XL 30 FEG) equipped with an X-ray energy dispersive spectrometer (EDS), a highresolution transmission electron microscope (HRTEM, JEOL JEM-2010) and an X-ray diffractometer (XRD, Rigaku D/Max-rB). Room-temperature photoluminescence (PL) measurement was conducted by using a 325 nm He–Cd laser as an excitation source (LABRAM-HR).

Device fabrication and characterization

In order to assess the electrical transport properties of both the u-CdS NRs and the p-CdS NRs, back-gate field effect transistors (FETs) based on individual NRs were constructed. The as-synthesized u-CdS NRs were first dispersed on a SiO₂ (300 nm)/p⁺-Si substrate using a contact printing technique, and then Cu/Au (4/80 nm) double-layer electrodes were defined on the two end of the NRs by photolithography and a lift-off process, followed by electron beam evaporation. The degenerately doped Si substrate serves as the global

back-gate in the FETs. Back-gate FETs based on individual p-CdS NRs were achieved by directly coating a thin MoO₃ layer $(\sim 100 \text{ nm})$ using a pulsed laser deposition (PLD) system onto the surface of back-gate FETs based on u-CdS NRs, followed by annealing at 200 °C for 10 min with Ar gas protection. To fabricate the p-CdS NR/n-Si heterojunction, the SiO₂ (300 nm)/ n-Si (0.02 Ω cm) substrate was used in this process. SiO₂ insulating pads (200 μ m \times 200 μ m) were first defined by using a photolithography process and subsequently wet etching with a buffered oxide etch (BOE) solution at room temperature. After that, the u-CdS NRs were dispersed on the substrate, and Cu/Au (4/80 nm) double-layer electrodes were defined by additional photolithography and a lift-off process, followed by electron beam evaporation. Finally, the substrate was directly coated with a thin MoO₃ layer (\sim 100 nm) and annealed at 200 °C for 10 min with Ar gas protection. The p-n heterojunction were formed at the regions where some NRs would cross the edges of the SiO₂ pads and partially contact with the underlying n-Si substrate.

Characterization of the electrical properties was performed by using a semiconductor parameter analyzer system (Keithley 4200-SCS) on a probe station at room temperature. To measure the optoelectrical properties of the heterojunction, a homebuilt system combing monochromatic light sources, an oscilloscope (Tektronix, TDS2012B) and an optical chopper (LE-oc120) was used.

Results and discussion

Fig. 1(a) shows a typical SEM image of as-synthesized u-CdS NRs with length of several hundred μ m, width in the range of 2–6 μ m, and a thickness of 50–100 nm. The corresponding EDS profile (Inset in Fig. 1(a)) reveals that the atomic ratio of Cd:S is about 50.4:49.6, which is very close to the stoichiometric



Fig. 1 (a) SEM image of the as-prepared u-CdS NRs. Inset shows the corresponding EDS spectrum. (b) HRTEM image of a u-CdS NR and the corresponding FFT pattern. (c) XRD pattern of the u-CdS NRs. (d) Room-temperature PL spectrum of the p-CdS NR.

ratio of CdS. Fig. 1(b) depicts the HRTEM image and the corresponding selected-area electron diffraction (SEAD) pattern recorded on the tip of a single NR, revealing that the u-CdS NRs have a single crystal wurtzite structure with a lattice spacing of 0.67 nm and a growth orientation of [001]. In the XRD patterns (Fig. 1(c)), all the diffraction peaks can be readily assigned to wurtzite CdS (JCPDS 41-1049) and no impurity phases are observed, suggesting a high phase purity of the product. Fig. 1(d) depicts the room-temperature PL spectrum of the p-CdS NRs. A dominant emission peak corresponding to the near-band-edge (NBE) emission of CdS at 515.5 eV is observed. We note that the emission peak exhibits no obvious shift compared with those observed from u-CdS NRs, which indicates that the crystalline quality and structural integrity of the p-CdS NRs are not significantly degraded by the MoO₃ coating.^{2,29}

The influence of MoO₃ coating on the transport properties of CdS NRs was first assessed by electrical measurements on an individual NR before and after coating with a MoO₃ thin layer. Fig. 2(a) compares the electrical conduction of a pure MoO_3 thin film (~100 nm), an individual u-CdS NR with and without MoO_3 coating (~100 nm). From the typical current-voltage (I-V) curves, it can be seen that the u-CdS NR exhibits an extremely low conduction current ($\sim 10^{-12}$ A). Its conductivity is estimated to be as low as 10^{-6} S cm⁻¹. In contrast, a substantial enhancement in the conduction current was observed after MoO₃ coating ($\sim 10^{-4}$ A). The conductivity increases dramatically by more than 7 orders of magnitude, to 50 S cm^{-1} . The pronounced enhancement in the conductivity can be attributed to the efficient charge transfer between the MoO3 and u-CdS NR interface due to their Fermi level difference,²² in light of that the poor conductivity of a MoO₃ coating layer $(10^{-7} \text{ S cm}^{-1})$ can hardly be responsible for this phenomenon. Fig. 2(b) depicts the source-drain current (I_{DS}) *versus* source-drain voltage (V_{DS}) of a representative single u-CdS NR FET coated with a MoO₃ layer at varied gate voltage (V_G) ranging from -40 V to 40 V at room temperature, revealing typical p-type electrical conduction behavior. The hole mobility and concentration are estimated to be 1850 $\mbox{cm}^2\ \mbox{V}^{-1}\ \mbox{s}^{-1}$ and $6.62 \times 10^{17} \text{ cm}^{-3}$, respectively, according to the transfer characteristic curve (inset in Fig. 2(b)), which is in distinct contrast with the weak n-type conductance of u-CdS NRs (electron mobility: 7.8 \times 10⁻³ cm² V⁻¹ s⁻¹ and electron concentration:



Fig. 2 (a) I-V curves of a MoO₃ layer and a single u-CdS NR before and after MoO₃ coating. Inset shows a SEM image of the FET with a channel length of 12 μ m. (b) $I_{DS}-V_{DS}$ characteristics of the FET measured at varied V_G ranging from -40 V to 40 V at a step of 20 V after coating with a MoO₃ layer. Inset shows the transfer characteristics of the FET (V_{DS} = 0.2 V) after coating with a MoO₃ layer.

 2.11×10^{15} cm⁻³ at room temperature, respectively, see Fig. S1 and detailed calculation in the ESI†). The high crystallinity, high purity and clean surface of the u-CdS NR are responsible for the high hole mobility, while the high hole concentration can be ascribed to the effective surface charge transfer doping effect, that is a large number of electrons in NRs are spontaneously transferred to MoO₃ because of their distinct difference in Fermi levels.²² The above results demonstrate that coating with a MoO₃ layer is an efficient way to convert u-CdS NRs from a weak n-type to an effective p-type.

By taking advantage of this surface charge transfer doping phenomenon, we are capable of fabricating p-CdS NR/n-Si heterojunctions by coating u-CdS NRs with a MoO₃ layer. In our study, a positive voltage applied at the Cu/Au electrode was defined as forward bias. Fig. 3(a) plots a representative I-V curve recorded from the u-CdS NR/n-Si heterojunction without MoO_3 coating in dark at room temperature. Clearly, the device exhibits a poor "reverse" rectifying behavior, that is a small current at forward bias while a large current at reverse bias, with a rectification ratio of ~ 20 within ± 4 V. The rectifying behavior can be ascribed to the formation of a n-n heterojunction between u-CdS NR and n-Si, considering that u-CdS NRs exhibit weak n-type electrical conduction behavior. The detailed working mechanism will be discussed later in the energy band diagram analysis. Interestingly, an obvious "positive" rectifying behavior with a rectification ratio as high as $\sim 2 \times 10^3$ within ± 1.5 V was observed for the device upon coating with a MoO₃ layer, as illustrated in Fig. 3(b and c). This phenomenon results from the formation of a p-n heterojunction between p-CdS NR and n-Si. From the rectification curve, a low turn-on voltage of ~ 0.5 V can be deduced at the forward bias direction. Based on the p-n junction theory, the ideality factor (n) for the heterojunction can be estimated to be 1.29 based on the lnI-V



Fig. 3 Dark I-V curves of the u-CdS NR/n-Si heterojunction (a) before and (b) after MoO₃ coating. Insets in (a) and (b) show the schematic illustration of the heterojunction devices, respectively. (c) Dark I-V curve of the heterojunction after MoO₃ coating on the semi-logarithmic scale. Inset shows the SEM image of the heterojunction device. (d) The lnJ-Vcurve of the heterojunction after MoO₃ coating. Inset: plot of the ln/-Vshows the ideality factor of the heterojunction after MoO₃ coating.

curve in the dark (inset in Fig. 3(d)), according to the following relation: 28

$$n = \frac{q}{k_{\rm B}T} \frac{\mathrm{d}V}{\mathrm{d}\ln I} \tag{1}$$

This value is superior to those of previously reported n-CdS NR/ p-Si,³⁰ p-ZnS NR/n-Si,³¹ p-ZnTe NR/n-Si³² and p-CdTe NR/n-Si nanowire array (SiNW)³³ heterojunctions, revealing the formation of a high-quality heterojunction between p-CdS NR and n-Si. To further assess the quality of the p-CdS NR/n-Si heterojunction, we calculated the barrier height (Φ) of the heterojunction. The diode characteristics of the heterojunction could be described by thermionic emission theory of majority charge carriers over a potential zero bias barrier, Φ , from the n-Si to the p-CdS NR:²⁸

$$J(T, V) = J_{\rm S}(T) \left[\exp\left(\frac{eV}{nk_{\rm B}T}\right) - 1 \right]$$
(2)

where J(T,V) is the current density across the p-CdS NR/n-Si interface, *V* the applied voltage, *e* the elementary charge, $k_{\rm B}$ the Boltzmann constant, *T* the temperature, and *n* the ideality factor. The saturation current density $J_{\rm S}(T)$ is defined by

$$J_{\rm S}(T) = A^* T^2 \exp\left(-\frac{e\Phi}{k_{\rm B}T}\right)$$
(3)

where A^* is the effective Richardson constant, which is 252A/ (cm² K²) for n-Si.¹⁶ $J_{\rm S}(T) = 1.66 \times 10^{-2}$ mA cm⁻² could be deduced from the ln/-V curve in Fig. 3(d). Therefore, based on eqn (3), the barrier height of the p-CdS NR/n-Si heterojunction can be estimated to be 0.557 eV, which is large than that of both graphene/n-Si (0.41 eV) and graphene/p-Si (0.45 eV) junctions.³⁴

The forming mechanism of the heterojunction could be understood from the energy band diagrams, as displayed in Fig. 4. The energy band diagrams of the u-CdS NR and the n-Si are depicted in Fig. 4(a), revealing a small difference in Fermi energy levels between the two materials. Therefore the barrier height of the u-CdS NR/n-Si homojunction is quite low, which results in a poor rectifying behavior of the junction, as mentioned above. However upon coating with a MoO₃ layer, the Fermi energy level of the CdS NR will shift towards its valance band as a result of the electron transfer from the CdS NR to MoO₃, converting the u-CdS NR to the p-CdS NR (Fig. 4(a)). Thus, the difference in the Fermi energy levels between the p-CdS NR and the n-Si becomes larger, leading to an increased barrier height and consequently a pronounced rectifying behavior of the junction.

We further studied the optoelectrical properties of the as-fabricated p-CdS NR/n-Si heterojunction. The *I–V* curves of the heterojunction in dark and exposed to 510 nm light illumination with an intensity of ~1.1 mW cm⁻² are depicted in Fig. 5(a), from which a typical photovoltaic effect with an open-circuit voltage (V_{OC}) of ~120 mV and a short-circuit current (I_{SC}) of ~1.33 nA is observed. The remarkable photocurrent is associated with photo-generated carriers in the heterojunction under light illumination, which could be understood from the energy band diagram in Fig. 4(b). Upon light irradiation, photo-generated electrons and holes within the space charge region can be driven towards the n-Si and the



Fig. 4 Energy band diagrams of (a) p-CdS NR, u-CdS NR, n-Si, and (b) p-CdS NR/n-Si heterojunction at zero bias under light irradiation.



Fig. 5 (a) *I–V* characteristics of the p-CdS NR/n-Si heterojunction in dark and under illumination of 510 nm. (b) Photoresponse of the heterojunction device at zero bias. (c) Photoresponse of the heterojunction device under varied light intensities at zero bias. (d) Normalized responsivity of the heterojunction device as a function of incident light wavelength. Inset shows the fitting curve of relationship between the photocurrent and light intensity.

p-CdS NR, respectively, by the built-in electric field. Besides, photo-generated electron-hole pairs in both n-Si and p-CdS NR sides within one minority carrier diffuse length from the edge of the space charge region can diffuse to the space charge region and subsequently be extracted by the built-in electric field. Both processes result in the generation of photocurrent when p-CdS NR and n-Si are connected through a load.

Photoresponse properties of the p-CdS NR/n-Si heterojunction device were measured at zero bias (under short-circuit conditions). Fig. 5(b) displays the time response of the heterojunction when light illumination is turned on and off alternately. Clearly, it can be found that the electrical current increases sharply and is stabilized

Paper

at a high-conduction 'on' state upon light irradiation, while it decreases quickly to a low-conduction 'off' state after light illumination is turned off, giving rise to a high $I_{\text{light}}/I_{\text{dark}}$ ratio of more than 2×10^3 , with excellent stability and reproducibility. To further quantify the performance of the heterojunction photodetector, we calculated the responsivity (*R*), a critical metric of the device. The *R* is defined as the photocurrent per unit of incident power on a photodetector and can be estimated by using the following equation:³⁵

$$R(AW^{-1}) = \frac{I_{\rm p} - I_{\rm d}}{P_{\rm opt}} = \eta \left(\frac{q\lambda}{hc}\right)G \tag{4}$$

where $I_{\rm P}$ is the photocurrent, $I_{\rm d}$ the dark current, $P_{\rm opt}$ the incident light power, η the quantum efficiency, q the charge of an electron, λ the incident light wavelength, h Planck's constant, c the light speed and G the photoconductive gain of the photodetector, which means the number of electrons detected per incident photon.¹⁶ Based on these values, R and G are estimated to be 0.545 A W⁻¹ and 0.74, respectively. Besides R and G, specific detectivity (D^*) is another key figure of merit for a photodetector, which indicates the smallest detectable signal and is usually given by:³⁶

$$D^* = S^{1/2} R / (2qI_d)^{1/2}$$
(5)

where *S* is the area of the heterojunction device ($\sim 221 \ \mu\text{m}^2$). According to the above equation, *D** is estimated to be 2.07 × 10¹² cm Hz^{1/2} W⁻¹. Note that the *R* and *D** achieved here are comparable to traditional Si and InGaAs photodiodes.³⁷ We also estimated the external quantum efficiency (EQE) of the p-CdS NR/n-Si heterojunction photodetector, which means the number of photo-generated electron–hole pairs detected per incident photon.¹⁶ For a heterojunction photodetector working under short-circuit conditions, all the electrons detected should originate from photo-generated electrons. Therefore, the EQE value of the heterojunction photodetector studied herein equals to its *G* value. This value can be further improved by applying working voltage upon the photodetector.³⁸

To further reveal the response properties of the p-CdS NR/n-Si heterojunction, we studied the incident light intensity dependent photoresponse of the device. Fig. 5(c) shows the time response of the device exposed to light illumination with different intensities (from $P = 5 \mu W \text{ cm}^{-2}$ to 1.1 mW cm⁻²) at zero bias. Obviously, it is found that the currents in dark are constant without normalization processing, indicating that the device performed excellent stability and reproducibility. Meanwhile, the photocurrents of the device increase gradually with increased light intensities. This dependence of photocurrent on light intensity can be fitted by a simple power law: $I_{\text{light}} = AP^{\theta}$, where A is a constant for a certain wavelength, and the exponent θ (0.5 < θ < 1) determines the response of photocurrent to light intensity.³⁹ Fitting the curve leads to θ = 0.92 (inset in Fig. 5(d)), in other words, the photocurrent is nearly proportional to the incident light intensity.⁴⁰ This nearly integer exponent suggests that a low number of trap states exist in our photodetector, which is highly beneficial to the photosensing ability.41

The photoresponse of the p-CdS NR/n-Si heterojunction photodetector can extend to a wide visible spectrum range. Fig. 5(d) depicts the normalized responsivity of the heterojunction device as a function of incident light wavelength. Clearly, one can see that the highest responsivity is located at around 510 nm (corresponding to the energy band gap of CdS NRs). This spectral selectivity is understandably associated with the photocarrier generation mechanism in the heterojunction. For wavelength longer than 510 nm, photo-induced electron-hole pairs can only be generated within n-Si and contribute to the photocurrent. As for short wavelength, the reduction in responsivity can mainly be associated with the large absorption coefficient of the CdS NR and Si in this region.¹⁶ Photons of short wavelength tend to be absorbed by the p-CdS NR and n-Si near their surface regions. The severe surface carrier recombination due to surface defects such as dangling bonds and impurities may lead to low conversion of incident light into photocurrent.⁴² The I-V curves of the heterojunction device in dark and exposed to 450 nm and 630 nm light and corresponding time responses are shown in Fig. S2 (see ESI[†]), which also reveals excellently stable and reproducible photoresponses.

On the other hand, given that the response speed of a photodetector, which reflects its capability to follow a fast-varying optical signal, is particularly important for its practical application in light-wave communication and optical switches. In this work, the photoresponse of the p-CdS NR/n-Si hetero-junction was further studied under zero bias by modulating the incident light with a mechanical chopper to generate pulsed light with varied frequencies from 0 to 2000 Hz (Fig. 6(a)). It is clear that for all switching frequencies, the response is very fast and exhibits long-term stability and reproducibility, as depicted in Fig. 6(b). In particular, even at 2000 Hz, the relative balance ($I_{max} - I_{min}$)/ I_{max} only decreases by ~ 10% (Fig. 6(c)), indicating that our device is capable of monitoring pulsed light with higher frequency. Fig. 6(d) shows a single normalized modulation cycle



Fig. 6 (a) Schematic illustration of the measurement configuration for photoresponse detection. (b) Response of the heterojunction to pulsed light irradiation at frequencies of 400 Hz, 1200 Hz and 2000 Hz. (c) Relative balance $(I_{max} - I_{min})/I_{max}$ versus switching frequency. (d) Enlarged rising and falling edge for estimating rise time and fall time.

Table 1 Summary of the performance of heterojunction and Schottky junction based photodetectors

Device structure	Working voltage (V)	Light intensity (mW cm ⁻²)	I _{dark} /I _{light} ratio	Responsivity $(A W^{-1})$	Rise/fall time (μs)	Ref.
p-CdS NR/n-Si	0	1.1	$2 imes 10^3$	0.545	26/112	This work
n-CdS NR/p-Si	_	5.3	_	_	300/740	30
p-ZnS NR/n-Si	-0.5	100	36	$2 imes 10^2$	48/180	31
p-ZnTe NR/n-Si	-2	5.3	_	$1.8 imes 10^3$	790/960	32
p-CdTe NR/n-SiNWs	0	0.4	$\sim 10^4$	_	1200/1508	33
Si/CdS nanowire heterojunction	-2	0.2	_	1.37	10.2	38
n-CdSe NR/graphene	0	2.7	$3.5 imes10^5$	10.2	82/179	44



Fig. 7 Reproducibility of (a) the rectifying characteristics and (b) the photoresponse properties of the heterojunction device when stored in air after a month.

measured at 2000 Hz. The rise time (t_r) and fall time (t_f) of a photodetector are defined as the time required for its photocurrent to increase from 10% to 90% of the peak value and to decrease from 90% to 10% of the peak value.⁴³ Further analysis reveals a small t_r of 26 µs and a small t_f of 112 µs. It should be noted that our heterojunction photodetector exhibits much faster response speed than the previously reported heterojuctions and Schottky junctions based photodetectors (Table 1). We attribute the fast response speed to the extraordinary high carrier mobility of the p-CdS NR with hardly any carrier trap centres due to the unique surface charge transfer doping method and fast separation of photogenerated electron–hole pairs by high quality built-in electric field formed between p-CdS NR and n-Si.

The air stability of a photodetector is crucial for its practical applications. We further investigated the air stability of the rectifying characteristics and photoresponse properties of the p-CdS NR/n-Si heterojunction by storing it under air ambient conditions for a month without any encapsulation. As depicted in Fig. 7, it is obvious that the heterojunction exhibits an excellent stable device performance with negligible degradation after a month, revealing the great potential of such a surface charge transfer doping technique applying for long-term, air stable nano-optoelectronic devices.

Conclusions

In summary, p-CdS NR/n-Si heterojunctions were successfully fabricated and their electrical/optoelectrical properties were investigated. The p-CdS NRs with a high hole mobility were achieved by a facile surface charge transfer doping technique. Electrical measurements reveal that the resultant heterojunction exhibits pronounced rectifying characteristics in terms of a large rectification ratio, a low turn-on voltage and a small ideality factor. Further photoresponse analysis discloses that such heterojunction devices could serve as self-driven visible photodetectors with a large $I_{\rm light}/I_{\rm dark}$ ratio (2 × 10³), a fast response speed ($t_{\rm r}$ = 26 µs and $t_{\rm f}$ = 112 µs), an excellent reproducibility and stability. It is expected that this new heterojunction architecture and the novel surface charge transfer doping scheme will find great applications in future nanooptoelectronic devices.

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Notes and references

- 1 Y. Cui, Z. Zhong, D. Wang, W. U. Wang and C. M. Lieber, *Nano Lett.*, 2003, **3**, 149–152.
- 2 J. S. Jie, W. J. Zhang, Y. Jiang, X. M. Meng, Y. Q. Li and S. T. Lee, *Nano Lett.*, 2006, **6**, 1887–1892.
- 3 L. Li, P. C. Wu, X. S. Fang, T. Y. Zhai, L. Dai, M. Y. Liao, Y. Koide, H. Q. Wang, Y. Bando and D. Golberg, *Adv. Mater.*, 2010, 22, 3161–3165.
- 4 L. Yang, S. Wang, Q. Zeng, Z. Zhang and L. M. Peng, *Small*, 2013, 9, 1225–1236.
- 5 T. Zhai, X. Fang, L. Li, Y. Bando and D. Golberg, *Nanoscale*, 2010, **2**, 168–187.
- 6 H. Li, X. Wang, J. Xu, Q. Zhang, Y. Bando, D. Golberg, Y. Ma and T. Zhai, *Adv. Mater.*, 2013, 25, 3017–3037.
- 7 P. Wu, Y. Ye, T. Sun, R. Peng, X. Wen, W. Xu, C. Liu and L. Dai, ACS Nano, 2009, 3, 3138–3142.
- 8 G. Shen and C. J. Lee, Cryst. Growth Des., 2005, 5, 1085–1089.
- 9 J. S. Jie, W. J. Zhang, Y. Jiang and S. T. Lee, *Appl. Phys. Lett.*, 2006, **89**, 223117.
- 10 R. M. Ma, L. Dai, H. B. Huo, W. J. Xu and G. G. Qin, *Nano Lett.*, 2007, 7, 3300–3304.
- 11 K. M. Deng and L. Li, Adv. Mater., 2014, 26, 2619-2635.
- 12 Z. Fan, H. Razavi, J. W. Do, A. Moriwaki, O. Ergen, Y. L. Chueh and A. Javey, *Nat. Mater.*, 2009, **8**, 648–653.
- 13 Y. Ye, L. Dai, P. C. Wu, C. Liu, T. Sun, R. M. Ma and G. G. Qin, *Nanotechnology*, 2009, **20**, 375202.

- 14 J. Zhao, J. A. Bardecker, A. M. Munro, M. S. Liu, Y. Niu, I. K. Ding, J. D. Luo, B. Q. Chen, A. K. Y. Jem and D. S. Ginger, *Nano Lett.*, 2006, 6, 463–467.
- 15 B. L. Cao, Y. Jiang, C. Wang, W. H. Wang, L. Z. Wang, M. Niu, W. J. Zhang, Y. Q. Li and S. T. Lee, *Adv. Funct. Mater.*, 2007, **17**, 1501–1506.
- 16 S. M. Sze and K. K. Ng, *Physics of Semiconductor Devices*, John Wiley & Sons, Hoboken, NJ, 2007.
- 17 B. Z. Tian, X. L. Zheng, T. J. Kempa, Y. Fang, N. F. Yu, G. H. Yu, J. L. Huang and C. M. Lieber, *Nature*, 2007, 449, 885–889.
- 18 Y. Huang, X. Duan, Y. Cui, L. J. Lauhon, K. H. Kim and C. M. Lieber, *Science*, 2001, **294**, 1313–1317.
- 19 J. S. Jie, W. J. Zhang, I. Bello, C. S. Lee and S. T. Lee, *Nano Today*, 2010, 5, 313–336.
- 20 K. Deng and L. Li, Adv. Mater., 2014, 26, 2619-2635.
- 21 T. Dietl, H. Ohno, F. Matsukura, J. Cibert and D. Ferrand, *Science*, 2000, **287**, 1019–1022.
- 22 F. Z. Li, L. B. Luo, Q. D. Yang, D. Wu, C. Xie, B. Nie, J. S. Jie, C. Y. Wu, L. Wang and S. H. Yu, *Adv. Energy Mater.*, 2013, 3, 579–583.
- 23 L. B. Luo, F. X. Liang, X. L. Huang, T. X. Yan, J. G. Hu, Y. Q. Yu, C. Y. Wu, L. Wang, Z. F. Zhu, Q. Li and J. S. Jie, *J. Nanopart. Res.*, 2012, 14, 1–9.
- 24 L. B. Luo, T. W. Ng, H. Tang, F. X. Liang, Y. C. Dong, J. S. Jie, C. Y. Wu, L. Wang, Z. F. Zhu, Y. Q. Yu and Q. Li, *RSC Adv.*, 2012, 2, 3361–3366.
- 25 D. A. Neamen and B. Pevzner, *Semiconductor Physics and Devices: Basic Principles*, McGraw-Hill, New York, 2003.
- 26 W. Wei, X. Y. Bao, C. Soci, Y. Ding, Z. L. Wang and D. L. Wang, *Nano Lett.*, 2009, 9, 2926–2934.
- 27 F. T. Zhang, B. Q. Sun, T. Song, X. L. Zhu and S. T. Lee, *Chem. Mater.*, 2011, 23, 2084–2090.
- 28 C. Xie, B. Nie, L. H. Zeng, F. X. Liang, M. Z. Wang, L. B. Luo, M. Feng, Y. Q. Yu, C. Y. Wu, Y. C. Wu and S. H. Yu, ACS Nano, 2014, 8, 4015–4022.
- 29 J. J. Cai, J. S. Jie, P. Jiang, D. Wu, C. Xie, C. Y. Wu, Z. Wang, Y. Q. Yu, L. Wang, X. W. Zhang, Q. Peng and Y. Jiang, *Phys. Chem. Chem. Phys.*, 2011, 13, 14663–14667.

- 30 D. Wu, Y. Jiang, S. Y. Li, F. Z. Li, J. W. Li, X. Z. Lan, Y. G. Zhang, C. Y. Wu, L. B. Luo and J. S. Jie, *Nanotechnology*, 2011, 22, 405201.
- 31 Y. Q. Yu, L. B. Luo, Z. F. Zhu, B. Nie, Y. G. Zhang, L. H. Zeng, Y. Zhang, C. Y. Wu, L. Wang and Y. Jiang, *CrystEngComm*, 2013, **15**, 1635–1642.
- 32 D. Wu, Y. Jiang, Y. G. Zhang, J. W. Li, Y. Q. Yu, Y. P. Zhang, Z. F. Zhu, L. Wang, C. Y. Wu, L. B. Luo and J. S. Jie, *J. Mater. Chem.*, 2012, **22**, 6206–6212.
- 33 C. Xie, L. B. Luo, L. H. Zeng, L. Zhu, J. J. Chen, B. Nie, J. G. Hu, Q. Li, C. Y. Wu, L. Wang and J. S. Jie, *CrystEngComm*, 2012, 14, 7222–7228.
- 34 C. C. Chen, M. Aykol, C. C. Chang, A. F. J. Levi and S. B. Cronin, *Nano Lett.*, 2011, **11**, 1863–1867.
- 35 J. Li, L. Niu, Z. Zheng and F. Yan, *Adv. Mater.*, 2014, 26, 5239–5273.
- 36 X. Liu, L. L. Gu, Q. P. Zhang, J. Y. Wu, Y. Z. Long and Z. Y. Fan, *Nat. Commun.*, 2014, 5, 4007.
- 37 X. Gong, M. Tong, Y. Xia, W. Cai, J. S. Moon, Y. Cao, G. Yu, C.-L. Shieh, B. Nilsson and A. J. Heeger, *Science*, 2009, 325, 1665–1667.
- 38 S. Manna, S. Das, S. P. Mondal, R. Singha and S. K. Ray, J. Phys. Chem. C, 2012, 116, 7126–7133.
- 39 X. F. Wang, W. F. Song, B. Liu, G. Chen, D. Chen, C. W. Zhou and G. Z. Shen, *Adv. Funct. Mater.*, 2013, 23, 1202–1209.
- 40 S. C. Kung, W. E. Van der Veer, F. Yang, K. C. Donavan and R. M. Penner, *Nano Lett.*, 2010, 10, 1481–1485.
- 41 H. Kind, H. Yan, B. Messer, M. Law and P. Yang, *Adv. Mater.*, 2002, 14, 158–160.
- 42 S. L. Chuang, *Physics of Photonic Devices*, John Wiley & Sons, New York, 2012.
- 43 W. Tian, T. Y. Zhai, C. Zhang, S. L. Li, X. Wang, F. Liu, D. Q. Liu, X. K. Cai, K. Tsukagoshi, D. Golberg and Y. Bando, *Adv. Mater.*, 2013, **25**, 4625–4630.
- 44 W. Jin, Y. Ye, L. Gan, B. Yu, P. Wu, Y. Dai and L. Dai, J. Mater. Chem., 2012, 22, 2863-2867.