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Au@Hg_xCd_{1-x}Te Core@Shell Nanorods by Sequential Aqueous Cation Exchange for Near-Infrared Photodetectors

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Abstract: We have explored the synthesis of Au@Hg_xCd_{1-x}Te core@shell nanorods by sequential aqueous cation exchange (ACE) for near-infrared photodetector application. A number of related Au@telluride core/shell nanorod structures were put forwarded, taking advantage of multi-step transformations through a binary and then a ternary phase for the telluride shells. The latter have a high degree of crystallinity thanks to the step-wise ACE method. The use of only trace amounts of Cd²⁺ coordinated with tri-n-butylphosphine, assisted the phase transformation from an

amorphous Ag_2Te shell to a highly crystalline Ag_3AuTe_2 shell in the first stage; this was followed by a further cation exchange (CE) step with far higher Cd^{2+} levels to fabricate a highly crystalline CdTe shell, and with an additional CE with Hg^{2+} to convert it to a $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ shell. The composition of the shell components and the well-controlled thickness of the shells enabled tunable surface plasmon resonance properties of the Au@telluride nanorods in the NIR region. Utilizing the enhanced NIR absorption, a hybrid photodetector structure of $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ nanorods on graphene was fabricated, showing visible to NIR (vis-NIR) broadband detection with high photoresponsivity ($\sim 10^6$ A/W).

1. Introduction

Metal@semiconductor core/shell hybrid nanostructures with well-defined morphology and a hetero-interface are important both from the point of view of fundamental property investigations and device applications.[1-4] Cation exchange (CE) reactions have been widely utilized as an effective strategy to produce hybrid colloidal semiconductor nanocrystals (NCs) with well-controlled composition and morphologies.[5-16] Morphology retention, a precisely defined interface and regioselectivity are important points in the synthesis of hybrid nanostructures.[10-11, 17-18] Many previously published CE approaches utilized organic solution phase reactions to produce alloy/doped NCs,[9, 13] core/shell[1, 14-15] and Janus-like heterostructures.[4, 10-11, 16] Based on the mentioned advantages, CE has been widely applied on the synthesis of NCs for photodetector applications. [8-10]

Alongside organic CE methods, aqueous solution-based CE reactions, form an equally important strategy for NC synthesis, and have also been widely reported.[19-21] Aqueous cation exchange (ACE) reactions can be more environmentally friendly and cost effective compared with some organic routes and are of course more suited to cases involving hydrophilic NC surfaces and interfaces.[22-25]

Telluride based NCs have attracted a great deal of attention for their potential applications in quantum devices,[26-29] sensing[30-31] and thermoelectric devices.[32-33] In particular, CdTe, HgTe as well as $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ NCs with narrow band gaps are considered as promising candidates for optoelectronic and particularly infrared photodetector materials.[13, 34-38] Compared to well-studied application of isotropic semiconductor QDs or NCs on optoelectronic devices, rod-like structure materials may exhibit extraordinary optical properties due to the polarized properties.[39-40] Au nanorods (NRs), due to their tailorable surface plasmon resonances (SPR) in the near-infrared (NIR) spectral region,[23, 41-42] offer favorable enhancement of the optical performance when coupled with semiconductor NCs as hybrid structures.[15, 43-44] The rod-like core-shell NCs with telluride semiconductor shells homogeneously coated on plasmonic Au NRs may exhibit enhanced NIR optoelectronic properties due to their potential coupling of plasmons and excitons. In this work, we demonstrate the ACE approach to synthesize a sequence of Au@telluride core/shell NRs at low temperature and characterize their optoelectronic properties at vis-NIR region by fabricating Au@ $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs on graphene device. For the synthesis part, in the first reaction, using only a trace of

coordinated Cd^{2+} a phase transformation was induced in an amorphous Ag_2Te shell on Au NRs to yield a crystalline Ag_3AuTe_2 shell. In the next step, CE with higher Cd^{2+} concentrations facilitated the formation of a crystalline CdTe shell which was further transformed by Hg^{2+} treatment to a $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ shell, covering the Au NRs uniformly. For photodetector application part, a plasmonic enhanced $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs for NIR photodetector applications is demonstrated. Hybrid graphene/ $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs device displayed broadband vis-NIR detection and high photoresponsivity, arising from a photogating effect at the NR/graphene interface.[45-49]

2. Experimental Section

2.1. Chemicals

Te powder (99.999%), hydrazine hydrate (85%) and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ were purchased from Sinopharm Chemical Reagent Co., Ltd. $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.99%) and hexadecyl trimethyl ammonium chloride (CTAC) were purchased from Aladdin Reagent. Other chemicals were purchased from Beijing Chemical works. All reagents were used directly without further purification.

2.2. Synthesis of $\text{Au@Ag}_2\text{Te}$ NRs

Au@Ag NRs were prepared following our previous work.[15] 10 mL of the Au@Ag NRs were mixed with 1.2 mL of Te precursor (prepared by taking 30 mg Te powder dissolved in 15 mL hydrazine hydrate and heating it in an autoclave for 4 h to form an homogenous solution) drop by drop upon vigorous stirring for 2 min. The resulting solution was aged at 30 °C in a water bath for 30 min. The resulting product

was purified by centrifugation at 8000 r/min for 10 min, and re-dispersed in deionized water.

2.3. Synthesis of Au@Ag₃AuTe₂ NRs

1 mL of 0.2 M hexadecyl trimethyl ammonium bromide (CTAB) solution was added to the Au@Ag₂Te NRs followed by heating the solution to 45 °C and keeping it at this temperature for 2 min. 0.05 mL of Cd(NO₃)₂ solution (30 mg/mL) was added, followed by stirring for 2 min. 30 µl of tri-n-butylphosphine (TBP) was added under vigorous shaking, and the solution was aged at 45 °C for 30 min. The resulting product was collected by centrifugation at 8000 r/min for 10 min, and re-dispersed in deionized water.

2.4. Synthesis of Au@CdTe NRs

1 mL CTAB solution (0.2 M) was added to the Au@Ag₃AuTe₂ NRs upon stirring, and the solution was pre-heated in a 60 °C water bath for 5min. 1 mL of 30 mg/mL Cd(NO₃)₂ solution was added and gently stirred for 2 min. 60 µl of TBP was added under vigorous shaking for 2 min. The solution was aged in a 60 °C water bath for 2 h. The resulting product was washed with deionized water, centrifuged at 8000 r/min for 10 min, and re-dispersed in deionized water. The CdTe NRs were synthesized by similar methods as Au@CdTe NRs except for CE temperature increased to 120 °C in autoclave for 4 hours.[50-51]

2.5. Synthesis of Au@Hg_xCd_{1-x}Te NRs

0.5 mL CTAC solution (0.2 M) was added to the Au@CdTe NRs upon gentle stirring for 1 min, and HgCl₂ (5 mg/mL) solution was added under vigorous shaking.

The solution was aged at 25 °C for 0.5 h, followed by washing with deionized water. The resulting product was collected by centrifugation at 8000 r/min for 10 min, and re-dispersed in deionized water.

2.6. ^{31}P NMR characterization

The chosen transition metal salts were dissolved in deuterated methanol (CD_3OD) with phosphine. As an example, 0.2 mmol AgNO_3 was dissolved in 5 mL of CD_3OD . After several seconds sonication to ensure complete dissolution, 550 μl of the solution were pipetted out, placed into a NMR tube, and mixed with 20 μl of TBP.

2.7. Device Fabrication

Graphite (Kish) was bought from Covalent Material Corp., Japan. The graphene flakes were mechanically exfoliated onto a silicon substrate with a 300 nm SiO_2 layer. A copper TEM grid was used as the shadow mask. Electrodes were sputtered with Au (80nm)/Ti (10nm). $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs were deposited on the graphene by a spray deposition method.[28, 52-53] Briefly, the substrate (cleaned with water) was fixed on a 50 °C hotplate. An airbrush with adjustable nozzle (0.2-0.3 mm) was fixed at 10 cm height over the substrate. The $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs were loaded in the airbrush and the flow rate was controlled by varying the propellant gas pressure. A ligand exchange process was performed after each 5 passes.[45-46] Specifically, the substrate was soaked in 0.2 % vol EDT/acetonitrile solution for 1 min, followed by washing with ethanol. After 30 passes, the $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs covered the graphene without gaps.

2.8. Photocurrent Measurements

All the measurements were conducted at room temperature in ambient atmosphere using a Keithley 4200-SCS semiconductor parameter analyzer. A pulsed laser (EXR-4, NKT, Denmark, output wavelength from 540 to 2400 nm) was used as the light source with a light spot radius of about 2 mm. Laser wavelength and power attenuation was controlled by series of various filters such as bandpass filters from 550 to 1300 nm (FKB-VIS-10 and FKB-IR-10, Thorlabs Inc., USA), neutral density filters (GCC-301041, GCC-301061, and GCC-301071, Daheng Optics, China; NENIR10A, NENIR20A, and NENIR30A, Thorlabs Inc., USA). A power meter (PM100A, Thorlabs Inc., USA) was used to measure laser power by selecting a suitable sensor according to the wavelength ranges.

2.9. Structural Characterization

XRD patterns were collected using a Bruker D8 X-ray diffractometer (scan rate $6^\circ/\text{min}$). TEM images were collected using a HITACHI H-7650 transmission electron microscope operating at 80 kV. HRTEM images were collected using a FEI Tecnai G2 F20 S-Twin microscope operating at 200 kV. Elemental maps shown in Figures 4c, 5b, d and S8 were collected using a FEI Talos 200kV scanning transmission electron microscope, which was equipped with an X-FEG high brightness source and a Super-X EDS detector consisting of four silicon drift detectors (SDDs) with a total collection solid angle of approximately 0.9 sr. A convergence angle of 21 mrad and an acceptance inner angle of 55 mrad were used for the annular dark field (ADF) image acquisition. EDS spectrum shown in Figure S4 were collected on a FEI Tecnai G2 F20 S-Twin microscope operating at 200 kV, and equipped with an energy dispersive

X-ray spectroscopy (EDS) detector. UV-vis-NIR spectra were measured on a Shimadzu UV-3600 spectrophotometer. Nuclear Magnetic Resonance (NMR) spectra were measured on a Bruker AVANCE IIIITM (400 MHz) NMR spectrometer.

3. Results and Discussion

Metal-semiconductor hybrid structures, especially metal-semiconductor core-shell materials, have been well reported their enhanced performance on optical devices due to the plamonic enhancement from metal NCs.[3, 54-55] Besides, NCs with anisotropic structures such as NRs may exhibit extraordinary optical properties due to their arrangements.[39-40] Hence, the metal-semiconductor core-shell NRs with controlled morphology and components may exhibit enhanced optical properties, which could be attractive for photoelectronic device applications. Based on this, we put forwarded a sequential ACE method to synthesis $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs for such applications. The schematic diagram of the multi-step shell transformations from Au@Ag NRs to the final product, $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs, is shown in Figure 1. It is worth mentioning that in the case of Au@CdTe and $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NCs, a standard CE procedure between Ag_2Te and Cd^{2+} in water resulted in poorly crystallized products. To overcome this issue, we employed low concentrations of Cd^{2+} in an aqueous solution containing a trace of TBP to initialize the phase transformation of the amorphous Ag_2Te ($\text{a-Ag}_2\text{Te}$) shell into a highly crystalline Ag_3AuTe_2 layer. The fabrication of the Ag_3AuTe_2 intermediate, which has a similar crystal structure to cubic phase CdTe (as shown in the X-ray diffraction (XRD) patterns and transmission

electron microscopy (TEM) images of Figure 2(II-IV) and Figure S1), made it possible to accomplish further ACE between the Ag_3AuTe_2 shell and TBP coordinated Cd^{2+} , which resulted in a highly crystalline CdTe shell and then onward to the $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ shell by exchange with Hg^{2+} .

The aqueous synthesis of $\text{Au@Ag}_2\text{Te}$ NRs is achieved by the reaction of Au@Ag NRs with a Te precursor, which was obtained by the hydrothermal treatment of Te powder in hydrazine hydrate aqueous solution. The Au@Ag NRs and $\text{Au@Ag}_2\text{Te}$ NRs were characterized by XRD and TEM (Figure 2(I-II)). The TEM image of $\text{Au@Ag}_2\text{Te}$ NRs (Figure 2(II)) indicates that the Ag_2Te shell is relatively uniform and maintains the original shape of the Au@Ag NR (Figure 2(I) and S2). The XRD patterns of Au@Ag and $\text{Au@Ag}_2\text{Te}$ NRs both exhibit four sharp peaks fitting well with the cubic phase Au (JCPDS No. 65-2870), which indicates the stability of the Au core in the telluridation reaction. In addition to the Au peaks, there is no other extensive peak (Figure 2(II)), which indicates the majority of amorphous Ag_2Te in the shell. The very low peaks around Au peaks indicate trace amount of monoclinic phase Ag_2Te (JCPDS No. 65-1104) within the amorphous Ag_2Te shell (Figure S3).

It was previously reported that amorphous Ag_2Te NPs (~5 nm) could be successfully converted into CdTe by a phosphine-induced CE reaction in the organic phase.[1] When using TBP coordinated Cd^{2+} ions in the aqueous phase to react directly with $\text{Au@Ag}_2\text{Te}$ NRs at 60 °C, energy dispersive X-ray spectroscopy (EDS) (Figure S4a) demonstrated that some Cd ($K\alpha=23.1$ keV) was present in the resulting NRs. However, a large proportion of Ag ($K\alpha=22.2$ keV) remained in the shell. The

large amount of the residual Ag means that the Ag^+ ions in Ag_2Te NCs are only partially replaced by Cd^{2+} ; this leads to poor shell crystallinity, as confirmed by TEM and high resolution TEM (HRTEM) images presented in Figures S5a-b, respectively. In support of this observation, the XRD (Figure S5c) shows none of the characteristic peaks for CdTe. Even using a higher reaction temperature of 80 °C, the XRD (Figure S5c) indicates a mixture of cubic Ag_3AuTe_2 and hexagonal CdTe with poor crystallinity.

We then mediated the CE kinetics by using TBP coordinated Cd^{2+} . When using a trace amount of Cd^{2+} ions to react with $\text{Au@Ag}_2\text{Te}$ NRs at 45 °C for 30 min, the amorphous Ag_2Te shell was transferred to crystalline cubic Ag_3AuTe_2 . Normally, the phosphine-induced CE reaction happened with a large excess of cations (Cd^{2+} in our system) and reasonable amount of phosphines.[1, 5, 7] The large amount of Cd^{2+} coordinated with TBP induced the driving force of CE reactions between Ag^+ and Cd^{2+} . However, there was only trace amount of Cd-TBP introducing to the reaction system. The trace amount of Cd-TBP provided the driving force for CE reaction, however fully CE reaction cannot happen due to the lack of reactants. What's more, it has been reported that ion exchange could enable the miscibility of Au in Ag-X (X=S, Se, Te) system, which is mainly due to the strong affinity and higher bond energy between Au and X.[56-57] As a result, due to the driving force of CE, the localized CE reaction at the shell surface breaks the balance of Ag^+ and Te^{2-} , which causes Au atoms from the core to diffuse into the shell; this leads to formation of a highly

crystalline Ag_3AuTe_2 shell (Figure 3a). For our system, this phenomenon couldn't be initiated without the introduction of trace amount of Cd^{2+} (Figure S6).

We tested some other transition metal ions, such as Zn^{2+} and Pb^{2+} , for their ability to perform the same kind of process, and found out that these two cations cannot perform as efficiently as Cd^{2+} , which may be related to the different coordination ability of Cd^{2+} -phosphines and Ag^+ -phosphines.[1,7] To support this assumption, and to make comparison to other cations, nuclear magnetic resonance (NMR) was applied to study the coordination abilities of TBP to different cations. The ^{31}P NMR spectra for pure TBP, Ag-TBP, Cd-TBP, Zn-TBP and Pb-TBP are shown in Figure 3b. Compared to pure TBP, the Ag-TBP and Cd-TBP coordination shows nearly no shift from 0 to 100 ppm. However, Zn-TBP and Pb-TBP show an obvious shift, which means stronger coordination of TBP to Zn^{2+} and Pb^{2+} . Therefore, when introduced trace amount of these two cations to the system, they would rather coordinate with TBP than participate in the CE reaction. Hence, Zn^{2+} and Pb^{2+} cannot induced the transformation from Ag_2Te to Ag_3AuTe_2 in the aqueous system.

The $\text{Au@Ag}_3\text{AuTe}_2$ NRs were characterized by XRD, HRTEM and STEM-EDS analysis. The XRD pattern (Figure 2(III)) matches well with the cubic phase Ag_3AuTe_2 (JCPDS No. 65-0444) and Au (JCPDS No. 65-2870), which indicates the high crystallinity of the shell and the maintained majority of the Au core. During the transformation from Ag_2Te to Ag_3AuTe_2 , some of the Au core atoms were outside diffused and the sizes of Au cores were decreased after formation of crystalline Ag_3AuTe_2 shell (Figure 3a and S7). The HRTEM images for amorphous $\text{Au@Ag}_2\text{Te}$

(Figure 4a) and crystalline Au@Ag₃AuTe₂ NRs (Figure 4b and S8a) confirm the induced crystallization during the Cd²⁺ initialization process. The associated fast Fourier transformation (FFT) data presented in Figure 4b further confirm the presence of Ag₃AuTe₂ through identification of (321) and (220) lattice planes. EDS elemental mapping performed in the scanning transmission electron microscope (STEM) (Figure 4c) indicate that Au, Ag and Te elements are homogeneously distributed in the shell. Further XPS analysis (Figure S9) indicates the very low percent of Cd²⁺ located at the surface of Au@Ag₃AuTe₂ NRs, which means that Cd²⁺ ions are present in only trace amounts in the localized CE process. The cubic phase of the Ag₃AuTe₂ shell has rather similar (body-centered cubic) crystal structure to the face-centered cubic structure of CdTe (or HgTe), which is beneficial for the next step of the CE conversion.[5, 10]

After the trace TBP-Cd²⁺ addition step, the repeated CE between Au@Ag₃AuTe₂ NRs and TBP coordinated Cd²⁺ leads to high quality Au@CdTe NRs. The XRD of the latter (Figure 2(IV)) shows no characteristic peak of Ag₃AuTe₂ but pure cubic phase CdTe (JCPDS No. 75-2086). Compared to the XRD spectrum of Au@Ag₂Te synthesized by direct CE (Figure S5c), a higher crystallization of the CdTe shell is clearly obtained. The TEM image in Figure 2(IV) shows the monodispersity of as-prepared Au@CdTe NRs, and the HRTEM (Figure 5a and S8b) show the high crystallinity of the CdTe shell, where the measured lattice spacing of 0.372 nm is assigned to the (111) lattice planes of cubic phase CdTe. The STEM-EDS elemental mapping and line profile results (Figure 5b and S10) further confirm the high quality

of the CdTe shell. The TEM EDS spectrum (Figure S4b) indicates that a small proportion of Ag remains (Cd: Ag=35:1) after the CE reaction, which may suggest that Ag remains in the structure as a dopant.[7, 9]

Cubic bulk CdTe and HgTe have nearly identical lattice constants ($a_{\text{CdTe}}=6.481 \text{ \AA}$, $a_{\text{HgTe}}=6.461 \text{ \AA}$) but distinctly different band gaps ($E_{\text{g,CdTe}}=1.490 \text{ eV}$, $E_{\text{g,HgTe}}=-0.261 \text{ eV}$).[34] As a result, the $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ alloy is relatively easy to prepare, and has a composition-tunable band gap covering a wide IR spectral range. Aspects of the CE reaction between CdTe and $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ quantum dots, particularly concerning the CE depth from the particle surface and the resulting energy levels, have been reported by many groups.[13, 36, 58] In order to achieve efficient plasmon-exciton coupling further into the NIR region, we carried out the CE reaction between the CdTe shell and Hg^{2+} to realize highly crystalline $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs where the shell bandgap was reduced compared to the CdTe shells. The $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NR XRD spectrum (Figure 2(V)) shows almost no difference in comparison to the XRD spectrum of Au@CdTe , which is due to the almost identical lattice constants of HgTe (JCPDS No. 75-1553) and CdTe.[10, 34] HRTEM images (Figure 5c and S8c) indicate the high crystallinity of the $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs; the measured lattice spacings of 0.374 nm and 0.227 nm are assigned to (111) and (220) planes of cubic $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ respectively by considering the STEM-EDS elemental mapping results (Figure 5d).

It has been widely studied that the morphologies and components of NCs will deeply influence their optical properties. As to analyze the optical properties of NRs with different components, the normalized absorption spectra of the Au@telluride

NRs at each stage in the series of transformation processes are presented in Figure 6a. With the shell transformation from Ag_2Te to Ag_3AuTe_2 and subsequently to CdTe , the extinction peaks experience an obvious red shift. Au@CdTe NRs have an extinction peak at 1240 nm, while with the addition of Hg^{2+} , the $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs extinction peak red-shifts to wavelengths between 1563 nm ($\text{Au@Hg}_{0.19}\text{Cd}_{0.81}\text{Te}$ NRs) and 1817 nm ($\text{Au@Hg}_{0.73}\text{Cd}_{0.27}\text{Te}$ NRs). Compared to Au NRs, the absorption spectrum peaks of the as-prepared $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ core-shell NRs exhibited obvious red shift, which is mainly due to the higher dielectric constants of shell materials.[3, 15, 20-21] With the increase of Hg ratio, $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ exhibited lower bandgap than pure CdTe , which featured NIR wavelength absorption such as reported QDs or NCs.[13, 27, 58] When coupling with Au NRs, the as-prepared $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs exhibited enhanced absorption in NIR region compared to decoupled $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs with Au cores over etched (Figure S11). The enhancement is mainly due to the coupling of plasmons from Au cores and excitons from semiconductor shells. Besides, both the shell thickness and the aspect ratio of Au@CdTe NRs can be controlled independently to allow highly tailorable NIR SPR properties of the resulting structures. The extinction spectra of Au@CdTe NRs (shell thickness ranging from 5 nm to 17 nm, as determined from TEM images shown in Figure S12) are presented in Figure 6b. The absorption peaks of Au@CdTe NRs show an obvious red shift (921 nm to 1299 nm) with an increase in shell thickness.

To demonstrate the application potential of $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs which absorb photons in the IR spectral range, a hybrid structure of $\text{Au@Hg}_x\text{Cd}_{1-x}\text{Te}$ NRs on

graphene was fabricated (Figure S13). Schematics of the device and the charge transfer mechanism between NRs and graphene are presented in Figure 7. The vis-to-NIR absorption of Au@Hg_xCd_{1-x}Te NRs generates charge carriers (electrons and holes); the holes from NRs are transferred to graphene while the electrons are trapped for a time in the NRs.[59-60] Before the eventual electron-hole recombination, the holes in graphene can circle through the device and the external circuit for many times, yielding a high photogain.[45-49] The source–drain current (I_{sd}) in the dark and under light illumination (1200 nm wavelength) at different source–drain voltages (V_{sd}) for the hybrid graphene/Au@Hg_xCd_{1-x}Te device is depicted in Figure 7c. The device shows a photocurrent of ~13 μ A without any gating voltage. By applying a gate voltage of -40 V, the device features a higher photocurrent (~26 μ A). Gate-dependent photocurrents of the device at different wavelengths are given in Figure S14b. The light intensity-dependent photocurrent is plotted in Figure 7d (wavelength at 1200 nm and $V_{gs}=-40$ V). Under a low power (49 nW) illumination, the device shows a high photoresponsivity of $\sim 3.4 \times 10^4$ A/W at 1200 nm. Light intensity-dependent photoresponsivity at wavelengths of 1000 and 1100 nm are calculated and shown in Figure S14c-e. Responsivities up to $\sim 3.3 \times 10^5$ A/W (at 1000 nm) and $\sim 5.3 \times 10^5$ A/W (at 1100 nm) are observed.

Wavelength-dependent photoresponsivity of the graphene/Au@Hg_xCd_{1-x}Te NRs device is shown in Figure 7e. It features a broadband high photoresponse at wavelengths from 550 to 1300 nm. Photoresponsivity (R) and external quantum efficiency (EQE) are critical performance parameters of photodetectors.[61-62] The R

and EQE of the graphene/Au@Hg_xCd_{1-x}Te NRs photodetector versus the illumination wavelength are shown in Figure 7f and S15a. The R is as high as 10⁶ A/W, and the corresponding EQE exceeds 10⁷% (Figure S15a). The response time test was also applied on the graphene/Au@Hg_xCd_{1-x}Te NRs photodetector, which exhibited 7.3 ms. (Figure S15b)

To further evaluate the photodetector performance, graphene/Hg_xCd_{1-x}Te NRs and graphene/Au@Ag₃AuTe₂ NRs hybrid devices were also fabricated as comparable devices. Compared to graphene/Au@Hg_xCd_{1-x}Te NRs photodetector, the graphene/Hg_xCd_{1-x}Te NRs photodetector exhibited similar broadband response but with a lower responsivity in 550-1300 nm (Figure 7f and S17), which indicated the absence of SPR enhancement. Besides, graphene/Au@Ag₃AuTe₂ NRs photodetector exhibited lower photoresponsivity and narrower response wavelength range (cut off at 1200 nm) (Figure 7f and S18). Compared to reported photodetectors (Table S2), the graphene/Au@Hg_xCd_{1-x}Te NRs photodetector exhibited high responsivity and fast response time. Moreover, after the device process, the Au@Hg_xCd_{1-x}Te NRs nearly maintained the original morphology and components, which is examined by SEM, XRD and XPS (Figure S19).

4. Conclusions

In summary, we put forward the synthesis of Au@Hg_xCd_{1-x}Te NRs by sequential ACE for further application of NIR photodetector. We have demonstrated an ACE approach enabling a serial materials transformation (the robust multiple *in situ*

transformations from binary to ternary phase) resulting in the production of high quality Au@telluride NRs. We found that use of the traces of TBP coordinated Cd^{2+} led to efficient conversion of Au@Ag₂Te (amorphous shell) to Au@Ag₃AuTe₂ (cubic phase crystalline shell) as a prelude to the further shell transformations. Repeating the CE between Au@Ag₃AuTe₂ NRs and TBP-coordinated Cd^{2+} ions, highly crystalline Au@CdTe NRs were produced. As the next step, the ACE between Au@CdTe NRs and Hg^{2+} enabled highly crystalline Au@Hg_xCd_{1-x}Te NRs with precisely controlled shell compositions. Benefiting from the tunable optical absorption of the Au@Hg_xCd_{1-x}Te NRs in the vis-NIR region (550-1300 nm) combined with the surface plasmon resonance of the Au NR cores, the hybrid structure of Au@Hg_xCd_{1-x}Te NRs on graphene showed a broadband and high photoresponsivity ranging from 10^3 - 10^7 A/W.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen>.

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Figure 1. Scheme of aqueous cation-exchange reactions to realize multi-step Au@telluride NR transformations.

Figure 2. TEM images and X-ray diffraction patterns of (I) Au@Ag NRs, (II) Au@Ag₂Te NRs, (III) Au@Ag₃AuTe₂ NRs, (IV) Au@CdTe NRs and (V) Au@Hg_xCd_{1-x}Te NRs. Scale bars are 50 nm on all TEM images.

Figure 3. a) Scheme of the cation induced phase transformation process, from the amorphous Ag_2Te ($a\text{-Ag}_2\text{Te}$) to cubic Ag_3AuTe_2 ($\text{c-Ag}_3\text{AuTe}_2$). b) NMR spectra of corresponding cations with TBP coordination.

Figure 4. HRTEM images of (a) Au@Ag₂Te and (b) Au@Ag₃AuTe₂ NRs. The Fourier transform from the shell (inset in b) shows the expected crystal structure of Ag₃AuTe₂. c) Dark field STEM image, EDS STEM elemental mapping and compositional profile of Au@Ag₃AuTe₂ NRs.

Figure 5. a) HRTEM image of Au@CdTe NRs. Fourier transform in inset demonstrates the high crystallinity of the shell. b) STEM image, EDS elemental mapping and compositional profile of Au@CdTe NRs. c) HRTEM image of Au@Hg_xCd_{1-x}Te NRs. d) STEM image and EDS elemental mapping of Au@Hg_xCd_{1-x}Te NRs.

Figure 6. a) Normalized extinction spectra of Au, Au@Ag₂Te, Au@Ag₃AuTe₂, Au@CdTe, and Au@Hg_xCd_{1-x}Te NRs. b) Normalized extinction spectra of Au@CdTe NRs with different shell thickness.

Figure 7. a) Schematic illustration of the hybrid graphene/Au@Hg_xCd_{1-x}Te NRs photodetector device. b) Photogating mechanism between graphene and Au@Hg_xCd_{1-x}Te NRs. c) Transfer curves of graphene/Au@Hg_xCd_{1-x}Te NRs with and without light illumination. d) Light intensity-dependent photocurrent (dark current was subtracted) at 1200 nm, e) wavelength-dependent photocurrent at different power intensities and f) wavelength dependent photoresponsivity of the graphene/Au@Hg_xCd_{1-x}Te NRs, graphene/Hg_xCd_{1-x}Te NRs and graphene/Au@Ag₃AuTe₂ NRs photodetectors. ($V_{bias}=4$ V, $V_g=-40$ V).

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