# Surface plasmon propelled high-performance CdSe nanoribbons photodetector

# Lin-Bao Luo,<sup>1,\*</sup> Wei-Jie Xie,<sup>1</sup> Yi-Feng Zou,<sup>1</sup> Yong-Qiang Yu,<sup>1</sup> Feng-Xia Liang,<sup>2</sup> Zi-Jun Huang,<sup>2</sup> and Ke-Ya Zhou<sup>3,4</sup>

 <sup>1</sup>School of Electronic Science and Applied Physics and Anhui Provincial Key Laboratory of Advanced Functional Materials and Devices, Hefei University of Technology, Hefei, Anhui 230009, China
 <sup>2</sup> School of Materials, Science and Engineering, Hefei University of Technology, Hefei, Anhui 230009, China
 <sup>3</sup> Department of Physics, Harbin Institute of Technology, Harbin, Heilongjiang 150001, China
 <sup>4</sup>zhoukeya@hit.edu.cn

\*luolb@hfut.edu.cn

**Abstract:** In this work, we present a plasmonic photodetector (PPD) with high sensitivity to red light illumination. The ultrasensitive PPD was composed of high-crystalline CdSe nanoribbons (NRs) decorated with plasmonic hollow gold nanoparticles (HGNs) on the surface, which were capable of coupling the incident light due to localized surface plasmon resonance (LSPR). Device analysis reveals that after modification of HGNs, both responsivity and detectivity were considerably improved. Further device performance analysis and theoretical simulation based on finite element method (FEM) find that the optimized performance is due to HGNs induced localized field enhancement and direct electron transfer.

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**OCIS codes**: (260.5150) Photoconductivity; (230.5160) Photodetectors; (160.4236) Nanomaterials; (240.6680) Surface plasmons.

#### **References and links**

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### 1. Introduction

As a promising class of materials, noble metal nanoparticles (NPs) have recently attracted increasing research interest for the localized surface plasmon resonance (LSPR), which is the coherent oscillation of electrons excited by light at an appropriate wavelength, resulting in very strong electromagnetic fields around their surface [1,2]. Au NPs have been considered as one of the most efficient light trapping platforms to boost the performance of light-harvesting systems in that the NPs can be employed to couple and trap freely propagating plane waves into a semiconductor [3,4]. On this account, plasmonic noble metal NPs have been widely applied in many fields such as solar cells [5,6], light emitting diodes (LEDs) [7,8], photocatalysts [9], photodetectors [10,11], and biomedical applications [12]. For example, Schaadt and associate reported that the decoration of Au nanoparticles on the surface of Si p-n photodiodes can substantially enhance the optical absorption as well as the photocurrent. What is more, Hashimoto et al. observed that coating of solid Au NPs could enhance the photocurrent of a photoelectronic hybrid device by more than eight times at a specific wavelength [13]. More recently, we reported on a surface plasmon resonance enhanced highly efficient planar silicon solar cell, the power conversion efficiency of the solar cells was considerably improved from 6.39 to 10.15% by the modification of Au NPs [14].

As one of the most important II-VI group semiconductors, cadmium selenium (CdSe) with a moderate direct band-gap of 1.7 eV at room temperature is of particular interest because of its potential as important building blocks for a variety of electronic and optoelectronic devices. Nanostructured CdSe in one dimensional form, including nanowires (NWs), nanoribbons (NRs), and nanobelts (NBs) have demonstrated marvelous versatility for novel and diverse applications including photodetectors (PDs) [15,16], solar cells [17,18] and LEDs [19] etc. Take photodetector for example, Jena and associate initiated the study of CdSe quantum-wire based PDs, the responsivity was estimated to be 0.1 A/W. To optimize the performance of CdSe PDs, Dai et al. resorted to n-type CdSe nanostructures obtained from high-temperature thermal evaporation method. They found that CdSe NB with very good crystallinity exhibited obvious photoresponse to 633 nm light illumination, with a responsivity as high  $1.5 \times 10^4$  A/W [20]. In addition, they also developed CdSe NB/graphene Schottky junction photodetector, the corresponding responsivity was estimated to be 10.2 A/W [21]. Despite of these efforts, however, the device performance of the CdSe PDs is still restricted by the relatively low responsivity. Extensive study has reveals that the poor device performance is mainly associated with the low cross-section of CdSe NWs, which are normally tens of nanometers in thickness [22]. Herein, we present a simple strategy to improve the device performance of CdSe NR based PD by modifying the surface with plasmonic HGNs. It is found that the HGNs@CdSe NR PD exhibits apparent sensitivity to 650 nm light with good reproducibility. What is more, compared with the device based on pure CdSe NR without surface functionalization, the photocurrent is observed to increase considerably, leading to increase in both responsivity and detectivity. We believe this study will open new opportunities for manipulating light and further improving the efficiency of semiconductor nanostructures based optoelectronic devices.

#### 2. Experimental setup

The CdSe NRs were synthesized by evaporating pure CdSe powder at 900 °C in a horizontal tube furnace via a conventional vapor-liquid-solid (VLS) progress. Briefly, a piece of Si wafer coated with 10 nm thick Au catalysts as substrates was placed at the downstream position, about 10 cm away from the CdSe source. Before heating, the system was evacuated to a base pressure of  $10^{-5}$  Torr, and then backfilled with an Ar and H<sub>2</sub> (5%) gas mixture with a constant flow rate of 100 Sccm (standard state cubic centimeter per minute) to a stable pressure of 150 Torr. Afterwards, the mixed powder was heated up to 900 °C and maintained at this temperature for 1.5 h. A layer of black wool-like product could be observed on the Si substrate. The HGNs were synthesized by a sacrificial galvanic replacement process [23,24], which begins with the synthesis of Co nanoparticles. At first, 100 mL ultra-pure water and 100  $\mu$ L sodium borohydride solution (1 M) were mixed with 400  $\mu$ L trisodium citrate dihydrate (0.1 M) in a three-neck flask which was deoxygenated by hydrogen gas flow throughout the reaction. Under rapid magnetic stirring, 100  $\mu$ L of 0.4 M cobalt hexahydrate solution was then added. During the reaction,  $H_2$  was formed as a by-product, and the generation of  $H_2$  will stop until the solution color changed from light pink to gray. A 0.1 M solution of chloroauric acid trihydrate was then added by 50  $\mu$ l aliquots at a step of 45 s. After reaction, the vessel was opened and cooled to ambient conditions under rapid stirring to allow the complete oxidation of any unreacted cobalt. The HGNs solutions were collected by centrifuging at 8000 rpm for 20 min. The phase, morphologies and crystal structures of the products were characterized by X-ray diffraction (XRD, Rigaku D/Max-y B with Cu Ka radiation), field-emission scanning electron microscopy (FESEM, SIRION 200 FEG), UV-Vis absorption spectrophotometry (CARY 5000), and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010, at 200 kV) equipped with selected area electron diffraction (SAED).

In order to compare the electrical property of CdSe NR before and after modifying HGNs, The device composed of an individual NR was assembled. In brief, the as-synthesized CdSe NRs were dispersed on a SiO<sub>2</sub> (300 nm thick)/Si wafer with a desired density, and then two parallel In electrodes as source and drain were defined by photolithography and a thermal evaporation method, followed by a lift-off process. The as-assembled device was then immersed into an ethylene glycol bis(3-mercaptopropionate) solutions for 6 hours to modify the NR surface with a layer of bis(3-mercaptopropionate). After washing with deionized water and ethanol, the device was finally immersed into an aqueous solution containing HGNs for 12 hours. The electrical property of the device was measured at room temperature by using a semiconductor characterization system (Keithley 4200-SCS). In this study, 650 nm-light was selected because CdSe has efficient absorption of 650 nm-light and the photocurrent of CdSe NR can reach a maximum at the wavelength of 650 nm. What is more, the photons with wavelength of 650 nm have the energy of 1.9 eV, which is large than the band gap of CdSe (1.7 eV). To explore the optoelectronic characteristics, incident light from a monochromatic light source system (Omni-l300) was perpendicularly focused and guided on the device.

We performed 3D simulation based on FEM with the aid of COMSOL Multiphysics. To simulate the optical properties of individual HGNs exposed in air, we employed a unit linear polarized light incident normally to a HGN with a fixed diameter 32 nm. The absorption efficiency is defined as  $Q_{abs} = W_{abs}/I_{in} A_{HGN}$ , in which  $W_{abs}$  is the energy absorbed by the HGNs,  $I_{in}$  is the incident irradiance,  $A_{HGN}$  is the particle cross-sectional area projected onto a plane perpendicular to incident beams.

# 3. Results and discussion

Figure 1(a) schematically illustrates the concept-of-proof PPD which is composed of an individual CdSe NR decorated with plasmonic HGNs. This surface functionalization was realized with the aid of bis(3-mercaptopropionate), whose thiol groups (–SH) can bridge both

Cd and Au atoms *via* strong chemical bonding [Fig. 1(b)]. According to the image shown in Fig. 1(c), the width and length of the CdSe NR are in the range of 1-8  $\mu$ m and tens of micrometers, respectively. The inset of Fig. 1(c) depicts the energy dispersive spectrometer (EDS) profile of CdSe NRs, which reveals an approximate atomic ratio of Cd:Se ~1:1. Further microstructure analysis in Fig. 1(d) demonstrates that the wurtzite phase CdSe NR grows along [0002] orientation with lattice spacing of 0.71 nm. Figures 1(e) and 1(f) show the TEM and HRTEM images of the as-prepared HGNs, respectively, from which a metallic shell and a hollow interior (cavity) can be easily visualized. The TEM images shown in both Figs. 1(g) and 1(h) suggest that HGNs have been successfully attached to the NR surface. According to our statistical study, the diameters of these HGNs are in the range of 27-37 nm, with an average diameter of 32 nm. In addition, the inner-to-outer radius aspect ratios range from 26% to 78%.



Fig. 1. (a) Schematic illustration of the PPD. (b) Schematic illustration of the CdSe NR decorated with HGNs *via* bis(3-mercaptopropionate) molecule. (c) TEM image of a single CdSe NR, the inset shows the corresponding EDS spectrum. (d) HRTEM image of a CdSe NR, the inset shows the corresponding SAED. (e) TEM image of the HGNs. (f) HRTEM image of a typical HGN. (g) TEM image of a CdSe NR decorated with HGNs. (f) TEM image of a CdSe NR decorated with HGNs at large magnification.

In order to study the plasmonic effect of HGNs on device performance of CdSe NR based PD, the photo-response of the PD before and after HGNs modification was compared. The green curve in Fig. 2(a) shows the typical *I-V* curves of single pure CdSe NR, in the dark and under light illumination with wavelength of 650 nm (5 mWcm<sup>-2</sup>). It is obvious that the dark current is only 1.4  $\mu$ A, but it will increase by approximately 60 times to 84  $\mu$ A when irradiated by light illumination at a bias voltage of 5 V. Interestingly, the on/off current ratio is much higher for the PPD modified with HGNs. The dark current is 0. 78  $\mu$ A, but the photo-response is highly reproducible. Figure 2(b) shows the photoresponse of pure CdSe and HGNs decorated CdSe NR, respectively, from which we can see that both devices can be alternatively switched between high- and low-conduction state when the light was turned on and off repeatedly. Further study reveals that photocurrent increasing gradually with increasing light intensity [Fig. 2(c)]. This light intensity dependent photocurrent can be expressed by a simple power law:  $I = AP^{\theta}$ , where *A* is the constant for a certain wavelength,

and exponent  $\theta$  determines the response of photocurrent to light intensity. By fitting this equation,  $\theta$  is estimated to be 0.93 and 0.97 for CdSe NR and CdSe NR@HGNs, respectively. Such nearly integer exponent means that after surface modification the trapping states have been considerably reduced, which is highly beneficial to photodetection capability. Figure 2(d) displays the spectral photoresponse of CdSe NR PDs before and after decoration with HGNs. It is interesting to note that the device assembled from HGNs@CdSe NR was also sensitive to the incident light with wavelength of ~550 nm, in addition to the peak sensitivity at 650 nm, corresponding to the band gap of CdSe nanostructures.



Fig. 2. (a) The *I-V* curves of CdSe NR before (green) and after (red) HGNs decoration, the inset is an FESEM image of the device. (b) Photoresponse of a pure CdSe NR and HGNs@CdSe NR PD under 650 nm light illumination at  $V_{\rm bias} = 1$  V. (c) The fitting of the relationship between the photocurrent and light intensity. (d) Spectral response of CdSe NR and HGNs@CdSe NR PD.

Next, we calculated several key parameters including responsivity (R), photoconductive gain (G) and detectivity (D\*), in order to quantitatively assess the effect of HGNs modification on the photoconductive property of the CdSe NRs. These three metrics can be calculated according to the following equations [25,26]:

$$R = \frac{I_p}{P_{opt}} \tag{1}$$

$$G = R(\frac{hc}{q\lambda})\frac{l}{\eta}$$
(2)

$$D^* = \frac{l}{\text{NEP}} \approx \sqrt{\frac{A}{2qI_d}}R.$$
 (3)

where,  $I_p$  is the photocurrent,  $P_{opt}$  the incident light power, q the elementary charge,  $\lambda$  the incident light wavelength, h the Planck's constant, c the light speed,  $\eta$  the quantum efficiency, A the PD area and  $I_d$  the dark current. Based on the above equations, R was estimated to be  $2.75 \times 10^4 \text{ AW}^{-1}$  for intrinsic CdSe NR and  $4.87 \times 10^4 \text{ AW}^{-1}$  for HGNs@CdSe NR, respectively. By using the method reported by Konstantatos [27], the internal quantum efficiency (IQE) was estimated to be 57% for pure CdSe NR and 66% for HGNs@CdSe NR

by IQE = EQE / (1 - R - T). The G was then calculated to be  $9.22 \times 10^4$  for pure CdSe NR and  $1.41 \times 10^5$  for HGNs@CdSe NR, respectively. What is more, the D\* was also found to increase from  $3.18 \times 10^{13}$  to  $7.5 \times 10^{13}$  cmHz<sup>1/2</sup>W<sup>-1</sup>. Table 1 briefly summarizes the key metrics of the present device and other CdSe nanostructure based PDs. It clearly shows that the R, G and D\* for the HGNs@CdSe NR device are much higher than other CdSe nanostructure based PDs, including CdSe NW [28,29], CdSe NW arrays [30], CdSe NPs [31], CdSe/ZnS QD [32], and CdSe NB [20], which corroborate that the plasmonic HGNs play an important role in determining the high performance of the nano-photodetector. It should be noted that in this table, the variation in device performance of other CdSe nanostructures is largely due to the following three factors: (1) The quality of the nanostructure. For example, the crystallinity of the semiconductor nanostructures, the surface states including the surface dangling bonds, the surface contaminant as well as surface absorbents; (2) The device geometry of the photodetectors, e.g., photo-conductive type, Schottky-junction photodiode type, and p-n nano-heterojunction type etc.; (3) The contact between the semiconductor nanostructures and metal electrode (Schottky contact or Ohmic contact). As matter of fact, similar phenomenon has been observed on other one-dimensional semiconductor nanostructures as well (e.g., ZnS [33, 34], and ZnSe [35, 36]).

 Table 1. Summary of the device performance of similar semiconductors nanostructures based PDs.

Materials	$R/AW^{-1}$	G	$D*/cmHz^{1/2}W^{-1}$	Ref.
HGNs@CdSe NR	$4.87 \times 10^4$	$1.41 \times 10^{5}$	$7.5 \times 10^{13}$	our work
CdSe NW	0.1	_	_	28
CdSe NW	1.7	_	$4.46 \times 10^{10}$	29
CdSe NW arrays	_	0.050	_	30
CdSe NPs	31	45	$6.9 \times 10^{10}$	31
CdSe/ZnS QD	$5.88 \times 10^3$	_	$7.06 \times 10^{7}$	32
CdSe NB	$1.5  imes 10^4$	$3.0 \times 10^{3}$	—	20

For the present plasmonic PD, when illuminated by visible light, the photo-generated current is mainly composed of three parts: (1) The contribution from photoconductivity. The photocurrent is owing to the generation of electron-hole pairs in the CdSe NR by photons with sufficient energy than the band gap of CdSe [37]. (2) Local field enhancement. The HGNs can act as an effective "antenna" that can enhance photocurrents as a result of plasmonic near-field coupling. (3) Direct electron transfer (DET). The HGNs can enhance the light absorption by localizing the incident field [38]. The plasmon resonance excites electrons and then transfers to the semiconductor nanostructures [22]. Such a charge injection mechanism is analogous to a dye sensitization process, in which the HGNs can absorb resonant photons and transfer the energetic electron formed in the process of the SPR excitation to CdSe NR.

We adopted finite element method (FEM) to study the optical property of plasmonic HGNs. Figure 3(b) plots the absorption of solid AuNPs and HGNs with varied inner-to-out radius aspect ratios ( $d_{in}/d_{out}$ , see Fig. 3(a)). Obviously, the solid NPs (namely AuNPs with aspect ratio of 0) exhibit typical light absorption at 500 nm. According to previous study, such a peak can be ascribed to the LSPR of HGNs [39]. Interestingly, when the aspect ratio is gradually increased from 26 to 78%, the absorption peak will red-shift from 500 to 550 nm, and the absorption efficiency is as high as 2.5 for HGNs with aspect ratio of 78%. It is worth noting that both electric effect field distribution and intensity are mainly determined by the aspect ratio of the HGNs. As shown in Figs. 3(c)-3(f), the solid AuNPs only exhibits hot spots at limited area. However, when the shell was reduced (equivalent to the increase of the  $d_{in}/d_{out}$ ), large-area hot spots with high field intensity was observed. Remarkably, hot spots throughout the inner and exterior part of the HGNs will appear when the radius aspect ratio is further increased to 78%. In addition, according to the color bar, the peak field intensity varies

with the aspect ratios of the HGNs. The peak field intensity for HGNs with aspect ratio of 78% is more than 3 times larger than that of HGNs with 26%. Such uniqueness in optical properties can be attributed to the special geometry of HGNs: unlike the solid AuNPs, the HGNs have two types of surfaces, one facing the exterior and the other within the cavity. The coupling of the two faces can provide surface field both inside the hollow part and on the outside surfaces [40]. Without question, the HGNs induced hot spots with large area distribution and high peak field intensity is highly beneficial to the device performance of CdSe NR based PDs.



Fig. 3. (a) Geometry of the HGNs. (b) Theoretical absorption curves of individual HGNs exposed in air, with different inner-to-outer radius aspect ratios range from 0 to 0.78, the diameter of HGNs are fixed at 32 nm. The illuminant is set as a unit linear polarized light range from 450 to 750 nm. (c)-(f) show the electric field distribution  $|\mathbf{E}|^2$  at the cross section of HGNs parallel to the polarization direction at LSP peaks, the color bar ranges from 0 to 14 or 60.

To explore the effect of modification of HGNs on the absorption of the CdSe NRs, the experimental absorption curves of both pure CdSe NR and HGNs@CdSe NRs were compared. As shown in Fig. 4, after decoration of HGNs, the absorption of CdSe NRs was considerably improved. Figure 5(a) compares the simulated absorption of the pure CdSe NR, solid AuNPs@CdSe NRs, and HGNs@CdSe NRs. Obviously, in comparison with pure CdSe NR, the absorption is increased in the range from 550 to 700 nm once solid AuNPs were decorated on the surface. As the solid AuNPs were replaced by hollow AuNPs (HGNs), much stronger absorption will be observed. Further separate simulation of HGNs and CdSe NR was carried out to unveil the origin of such increase in absorption. It is revealed that although the overall absorption of HGNs@CdSe nanostructure is increased, the absorption of sole CdSe NR decreases considerably [Fig. 5(c)], which is understandably related to the strong LSPR absorption of HGNs, as shown in Fig. 5(b). It should be noted that for CdSe NR decorated by HGNs with aspect ratio of 78%, the absorption of sole CdSe is reduced by more than 15% in the range from 500 to 650 nm [Fig. 5(c)]. Such a decrease in absorption is mainly due to the relative strong LSPR at 550, 650 nm light illumination, as shown in Figs. 5(d).



Fig. 4. Experimental absorption of both pure CdSe NR and HGNs@CdSe NR.



Fig. 5. (a) Theoretical simulation of absorption of HGNs decorated CdSe NRs, the HGNs have inner-to-inner-to-outer radius aspect ratios ranging from 0 to 78%. (b) Theoretical simulation of absorption of the HGNs, the HGNs are decorated on CdSe NRs surface. (c) Theoretical absorption of CdSe NR, the CdSe NR is decorated with HGNs on the surface. (d) Electric field distribution  $|\mathbf{E}|^2$  of CdSe NR decorated with HGNs under light illumination with wavelength of 650, 550 and 450 nm. For comparison, controlled simulation without HGNs was provided as well.

Figure 6 shows schematic illustration of the working mechanism. It is believed that the decoration of HGNs can induce DET from HGNs to CdSe NR and localized field enhancement. When HGNs were functionalized on CdSe NRs, due to their difference in the work function, the electrons in CdSe NR will transfer into HGNs, leading to a reduced dark current, band bending of semiconductor and formation of Schottky junction barrier. When the as-formed Schottky barrier was irradiated by light illumination, the energetic hot electrons from LSPR excitation of metallic plasmonic nanoparticles can couple the resonant photo energy, and then transfer to the nearby CdSe NR [41]. Such a DET mechanism is similar to a dye-sensitized solar cell without any dye layers, the HGNs essentially act as a sensitizer, absorbing resonant photons, and the energetic hot electrons with energy as high as 1-4 eV [41], would travel over the Schottky barrier and inject into the conduction band of CdSe NR [42,43]. Another equally important contributor is localized field enhancement. As mentioned

above, the HGNs can act as an effective "antenna" that can enhance photocurrents owning to plasmonic near-field coupling.



Fig. 6. Schematic illustration of LSPR assisted direct energy transfer mechanism.

The current device offers three obvious beneficial advantages over traditional plasmonic photodetector. (1) Reduced consumption of gold material. Thanks to the unique geometry, the shell can be as thin as several nm, as long as the shell is sufficiently concrete. Notably, such as reduce in gold consumption will not sacrifice the optical property of the gold nanostructures. (2) Improved device performance. As mentioned above, the HGNs exhibit much strong LSPR effect, compared to their solid counterparts with the same radius. Such a strong LSPR can contribute to device with high performance. (3) Tunable optical property. The SPR peaks of HGN can be readily tuned in a wide region by adjusting the inner-to-outer radius aspect ratio [23,24,44]. This convenience allows us to develop high performance optoelectronic device with very good spectral selectivity.

# 4. Conclusion

In summary, we reported on the fabrication of PPD based on the HGNs decorated CdSe NR. Optoelectronic property analysis finds that after surface modification with HGNs, the key parameters of the photodetector including R, G and  $D^*$ , all increase substantially. Further device performance analysis and theoretical simulation revealed that the optimized performance is due to HGNs induced localized field enhancement and direct electron transfer. The totality of this study will open up a new opportunity to optimize the device performance of semiconductor nanostructures based optoelectronic system.

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