PHOTONICS Research

Self-powered lead-free quantum dot plasmonic phototransistor with multi-wavelength response

Yu Yu,¹ Yating Zhang,^{1,*} Lufan Jin,¹ Zhiliang Chen,¹ Yifan Li,¹ Qingyan Li,¹ Mingxuan Cao,¹ Yongli Che,¹ Haitao Dai,² Junbo Yang,³ and Jianguan Yao¹

¹Key Laboratory of Opto-Electronic Information Technology (Tianjin University), Ministry of Education, School of Precision Instruments and Opto-Electronics Engineering, Tianjin University, Tianjin 300072, China

²Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparing Technology, School of Science, Tianjin University, Tianjin 300072, China

³Center of Material Science, National University of Defense Technology, Changsha 410073, China *Corresponding author: yating@tju.edu.cn

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Because they possess excellent visible light absorption properties, lead-free colloidal copper-based chalcogenide quantum dots (QDs) have emerged in photoelectronic fields. By means of localized surface plasmonic resonance (LSPR), the absorption properties of QDs can be enhanced. In this paper, we fabricate a lead-free CuInSe₂ QD field effect phototransistor (FEpT) by utilizing the LSPR enhancement of Au nanoparticles (NPs). The plasmonic FEpT demonstrates responsivity up to $2.7 \ \mu A \cdot W^{-1}$ and a specific detectivity of 7×10^3 Jones at zero bias under illumination by a 532 nm laser, values that are enhanced by approximately 200% more than devices without Au NPs. Particularly, the FEpT exhibits a multi-wavelength response, which is photoresponsive to 405, 532, and 808 nm irradiations, and presents stability and reproducibility in the progress of ON–OFF cycles. Furthermore, the enhancement induced by Au NP LSPR can be interpreted by finite-difference time domain simulations. The low-cost solution-based process and excellent device performance strongly underscore lead-free CuInSe₂ QDs as a promising material for self-powered photoelectronic applications, which can be further enhanced by Au NP LSPR. © 2019 Chinese Laser Press

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1. INTRODUCTION

Self-powered photodetectors have advantages that include low power consumption, energy savings, and passive detection without any external power sources [1–4]. Unfortunately, traditional self-powered photodetectors made by Si, SiC, and InP still suffer from low responsivity [5]. By contrast, new types of functional nanomaterials can solve this problem owing to strong light absorption [6], particularly for colloidal quantum dots (CQDs).

CQDs have applications in a wide range of solutionprocessed photoelectronic devices, including solar cells [7–9], light-emitting diodes [10,11], infrared imaging [12], and photodetectors [13–16]. Particularly, quantum dot photodetectors (QDPDs) have focused largely on the utilization of IV-VI (PbS, PbSe) quantum dots (QDs) due to their near-infrared conduction band edge values and established synthetic procedures. However, the presence of Pb cations generally limits their application.

As one of the lead-free QDs, colloidal copper-based chalcogenide (CuIn X_2 , X = S and Se) QDs are attractive in a broad range of applications, specifically photovoltaics [17–21], photobiological labels [22–26], light-emitting devices [27–29], electrocatalysts [30,31], and photodetectors [32], due to their lower toxicity, better biocompatibility, and unique photoelectric properties [33]. Particularly, by exhibiting a tunable bandgap ranging from 0.96 to 1.65 eV [21], CuInSe₂ QDs have a higher optical absorption coefficient in the visible spectral range [17,21]. Therefore, they are considered more promising candidates for use in photodetection devices.

As we all know, metal plasma can be implemented to increase light absorbance and reduce recombination during charge transport to current collectors [33–36]; thus, it can improve the photoelectronic properties. As for CQDs, the localized surface plasmonic resonance (LSPR) effect has been utilized to increase photoelectric properties by coupling with incident light in many photodetectors [37–40]. For instance, Dong *et al.* [40] demonstrated a CsPbBr₃ QD photodetector overlapping with LSPR, which exhibited higher light ON–OFF and photocurrent than nonplasmonic CsPbBr₃ QDs. Chang *et al.* [37] reported InAs CQD photodetectors

enhanced by LSPR, demonstrating a 130% enhancement of photoresponse and detectivity. To our knowledge, field effect phototransistors (FEpTs) based on CuInSe₂ QDs enhanced by LSPR have never been studied.

In this paper, plasmonic lead-free CuInSe₂ FEpTs are fabricated by deposition of Au nanoparticles (NPs) for multiwavelength detection. Particularly, light signals can be efficiently converted into electrical signals at zero volt bias. Meanwhile, the device demonstrates responsivity up to 2.7 μ A/W, and detectivity of 7.2 × 10³ Jones. The plasmonic FEpT exhibits fast response (a rise time of 0.1 ms and a decay time of 0.06 ms), and excellent stability and reproducibility. Moreover, with the effect of Au NP LSPR for the device, the photocurrent is enhanced by approximately 200%. The enhancement mechanism is attributed to the coupling effect between CuInSe₂ QDs and Au NPs, which is confirmed by theoretical simulation through the finite-difference time domain (FDTD) method. Therefore, superior detection performance by the enhancement of the Au NP plasmonic effect promises great potential for future optoelectronic devices.

2. DEVICE STRUCTURE AND FABRICATION

The plasmonic CuInSe₂ QDs FEpT was fabricated by the following process. First, the substrate was prepared by a highly doped n-type silica wafer (n⁺ Si), and a silica dioxide (SiO₂) layer with thickness of 300 nm was thermally grown on the substrate. Sequentially, the substrate was cleaned by ultrasonic treatment in acetone, alcohol, and deionized water for 15 min. Second, Au NPs (purchased from Nanjing Muke Company) were deposited on the SiO₂ with a self-assembly method. In detail, Au NP solution added by pipette was deposited on the substrate by spin-coating at 6000 r/min for 60 s. Third, the lead-free CuInSe₂ QDs film was deposited at 3000 r/min for 60 s. Finally, utilizing a sophisticated shadow mask, drain and source electrodes were thermally evaporated at a rate of 8 Å \cdot s⁻¹ (1 Å = 0.1 nm) at pressure of 3.8×10^{-4} Pa. Each device was dried for 24 h in vacuum conditions before further measurements. All the measurements were performed in air at room temperature.

3. RESULTS AND DISCUSSION

Figure 1(a) depicts the schematic diagram of the plasmonic CuInSe₂ QDs FEpT. For the bottom-gate configuration, a highly doped n-type silicon wafer $(n^+ Si)$ covered with a 300 nm thick SiO₂ layer (capacitance C_{ox} of 11.5 nF \cdot cm⁻²) was used as the gate electrode. Then, the substrate was cleaned by ultrasonic treatment in propanol, acetone, and deionized water for 10 min each. After that, the charge trapping layer of 13 nm thick Au NPs [shown in the sectional scanning electron microscope (SEM) image in Fig. 1(b)] was transferred onto the substrate by the self-assembly method. Meanwhile, the transmission electron microscopy (TEM) image in the inset of Fig. 1(b) depicts the nearly monodisperse spherical shape of CuInSe₂ QDs [41]. The coverage of the Au NP layer configuration on the substrate was measured by atomic force microscopy (AFM). Figure 1(c) depicts a 1 μ m × 1 μ m topography image working at trapping mode, which exhibits good homogeneous surface morphologies. Next, colloidal CuInSe₂ QDs made by the hydrothermal synthesis method were spincoated on the device with rotating speed of 3000 r/min. Finally,



Fig. 1. (a) Schematic diagram of plasmonic $CuInSe_2$ QD FEpT architecture. (b) Cross-sectional SEM image of composite film between $CuInSe_2$ and Au NPs (inset: TEM image of pristine $CuInSe_2$ QDs). (c) AFM image of Au NPs on silicon substrate. (d) Optical absorption spectra of $CuInSe_2$ QDs with (red line) and without (black line) deposited Au NPs on glass substrate.

the source and drain electrodes of Cr/Au were deposited through a thermal evaporation method assisted by a shadow mask [42], where the channel length (L) and channel width (W) were defined as 0.1 mm and 2.5 mm, respectively. Notably, the thickness of the photosensitive layer is a key parameter for FEpTs, given the abilities of either light absorption or gate electrode modulation. Specifically, if the active layer is too thin, it cannot absorb sufficient light to convert photoexcitons. In addition, pinholes in the thin QD film will cause inhomogeneous conduction in the channel, while if the film is too thick, the bottom gate will modulate the channel ineffectively. After optimization, the thickness of the CuInSe₂ QD film prepared in the phototransistors is fixed at ~670 nm [shown in Fig. 1(b)]. The absorption properties of CuInSe₂ QD film with deposited Au NPs (red line) or not (black line), are depicted in Fig. 1(d). This indicates that the absorption properties can be enhanced by considering the Au NP LSPR. For measurement details, the source (with ground connection) and drain electrodes were connected with a Keithley 2400, the channel current flowing into the drain electrode $(I_{\rm DS})$ was also measured by a source meter of Keithley 2400, and the gate voltage (V_{GS}) was applied by a DC voltage source of HP6030A. Photoelectrical measurements were also performed based on this system under illumination by 405, 532, and 808 nm lasers.

To characterize the electronic properties of plasmonic CuInSe₂ QDs FEpTs, output characteristics of pristine CuInSe₂ QD FEpTs (in darkness, dashed lines; under illumination of 700 mW \cdot cm⁻² with a 405 nm laser, solid lines) with different gate voltages V_{GS} (0, ±1 V, ±2 V, ±3 V, ±4 V) are depicted in Fig. 2(a). The device exhibits typically ambipolar characteristics. To look further into the modulation of gate voltage, Fig. 2(b) depicts the transfer characteristics of typical CuInSe₂ FEpTs, with Au NP deposition (black line, in darkness; red line, under illumination of 845 mW \cdot cm⁻² by an 808 nm laser) and without Au NP deposition (blue line,



Fig. 2. Photoelectronic properties of the device. (a) Output characteristics ($I_{\rm DS} - V_{\rm DS}$ curves) under different $V_{\rm GS}$ (1 V increment) of plasmonic FEpT (dashed lines, in darkness; solid lines, under illumination of 700 mW \cdot cm⁻² of a 405 nm laser). (b) Transfer characteristics of typical CuInSe₂ FEpTs, after Au NP deposition (black line, in darkness; red line, under illumination of an 845 mW \cdot cm⁻² of 808 nm laser) and before Au NPs deposition (blue line, in darkness; green line, under illumination of 845 mW \cdot cm⁻² of an 808 nm laser) with applied bias voltage $V_{\rm DS} = 1.2$ V.

in darkness; green line, under illumination of 845 mW \cdot cm⁻² by an 808 nm laser) under bias voltage $V_{\rm DS} = 1.2$ V. Each device exhibits typically ambipolar characteristics, and the "V" shape of the transfer curves is particularly presented, manifesting either electron or hole transport in the n-type or p-type channels of the device, respectively. Particularly, for the plasmonic CuInSe₂ FEpT, the mechanism can be interpreted as that after the two materials contact each other, owing to the existence of accepter states in Au NPs, electrons are injected into these states [40]. The effective electric field determines the flowing direction and an amount of the electrons separated from photoexcitons tends to reside in the Au NP layer [43]. Therefore, the shift of minimum V-shaped transfer curve toward negative V_{GS} [the red line shown in Fig. 2(b)] can be ascribed to the efficient photoexciton separation and hole transfer at the interface [44]. Comparing with the condition without irradiation, the values of $|I_{\rm DS}|$ become larger. It can be understood that the photoinduced carriers can be generated under the condition of light irradiation. Therefore, the enhancements of $I_{\rm DS}$ are ascribed to the increase of the electron and hole concentrations [42]. Meanwhile, after considering the LSPR effect, the drain-source dark current in the plasmonic FEpT can be suppressed, and the V_{GS} shift is more significantly observed as the gate bias varies [40]. This is because more electrons are trapped in the surface of Au NPs, leading to a large width of the conducting channel [40]. Therefore, the bottom gate will effectively modulate the channel.

Corresponding to Fig. 1(d), CuInSe₂ QDs exhibit broad absorption ranging from 400 to 850 nm. Illuminated by light with different wavelengths (405, 532, and 808 nm), photoswitching curves of the device are presented in Figs. 3(a)-3(c)under periodic illumination intensity of 157 mW/cm². The device exhibits stable and excellent reproducibility in each illumination. Meanwhile, the photocurrents excited by 405, 532, and 808 nm are about 120, 100, and 60 nA, respectively. Physically, this indicates that the incident photo energy must be larger than the energy gap; in other words, photocurrent generation needs to match the basic condition. Only these incident photons with enough photon energy can excite electrons from the valence band maximum to the conduction band minimum (CBM), generating the photocurrent. Therefore, more



Fig. 3. Time-dependent response of the device at zero bias with different wavelengths and irradiation intensities. (a), (d) 405 nm; (b), (e) 532 nm; (c), (f) 808 nm.

electrons and photoexcitons can be excited with stronger incident photo energy light at the short wavelength and contribute more to photocurrent. Under the irradiation of stronger energy light at the shorter wavelength, it leads to a huge enhancement in the density of free carriers, which in turn results in easier carrier transport and tunneling, and thus to greatly enhanced photocurrents. Figures 3(d)-3(e) depict the drain-source currents (I_{DS}) versus illumination irradiance (E_e) under different wavelengths, in which photocurrent increases linearly with E_e at low irradiance, then tends to saturate at high irradiance. It is concluded that with larger irradiance, more photoexcitons can be excited, leading to lower built-in potential of the Schottky barrier and a higher probability to pass over the Schottky barrier. If the electrons pass over the Schottky barrier, then photocurrent will increase linearly in the progress of the carrier flowing to the external circuit. Note that, with irradiance continuing to increase, the quantity of photoexcitons is no longer increased in CuInSe₂ QDs, and thus they cannot be converted to photocurrent, leading to saturation of the photocurrent. To further investigate the photo properties of the device, as a vital parameter, photoresponsivity (R) is calculated by [45-47]

$$R = \frac{\Delta I_{\rm DS}}{P} = \frac{I_{\rm illu} - I_{\rm dark}}{E_e \times S},$$
 (1)

where I_{illu} and I_{dark} represent the drain current under illumination and in darkness. P, E_e , and S are power density, irradiance, and the effective channel area, respectively. The photoresponsivities of the plasmonic CuInSe₂ QDs FEpT as a function of irradiance under different wavelengths are shown in Fig. 4. Particularly, the maximum photoresponsivity (R) is calculated to be 2.7 μ A/W at irradiance of 0.5 mW/cm² under the illumination of a 532 nm laser. Other key parameters characterizing photodetector performance, such as detectivity (D^*) , noise equivalent power (NEP), and gain (G) can be given as [48] $D^* = RA^{1/2}/(2eI_{\rm DS})^{1/2}$, NEP = $A^{1/2}/D^*$, and $G = \frac{\hbar v}{e}R$, respectively, where R is the responsivity, A is the area of the detector, *e* is the charge of an electron, and I_{DS} is the dark current. The D^* , NEP, and G of the device are 7.2×10^3 Jones, 6.9×10^{-8} W/Hz, and 6.29×10^{-6} , respectively. Responsivities in plasmonic CuInSe₂ QDs FEpT under illumination of 405 nm exhibit a first increasing then decreasing trend. However, it decreases with the increasing irradiance in particular at wavelengths of 532 and 808 nm. This is attributed



Fig. 4. Photoresponsivity (R) of the device with or without deposited Au NPs as a function of irradiance under different wavelengths with chopper frequency of 3944 Hz at a bias of 0 V: (a) 405 nm, (b) 532 nm, and (c) 808 nm.

to the existence of acceptor states in Au NPs. To demonstrate in detail, we construct a measurement system referring to Ref. [49]. Meanwhile, as another key parameter for photodetectors, photoresponse speed determines the capability of a photodetector to follow a fast-switching optical signal. It also reflects a series of times during the whole transition progress in which it concludes the vital acceptor progress. To highlight this progress of the device, initially we adopt a pump laser with different light irradiance at each wavelength, varying the chopper frequency. Figure 5 shows the time-dependent drain current response of the device with the maximum light irradiance under [Fig. 5(a)] 405 nm, [Fig. 5(b)] 532 nm, and [Fig. 5(c)] 808 nm, with maximum chopper frequency of 3944 Hz. The drain current quickly increases as soon as the light switch is turned on and then decreases when the light switch is turned off. This indicates that the increased charge intensity lowers the effective barrier height upon illumination, which allows easier charge tunneling and transportation than that of the device in darkness. Particularly, the red dashed circles denote the progress of photo-induced electrons excited to the acceptor states in an Au nanoparticle. Furthermore, the amplitude of this progress decreases with the enhancement of wavelength. This indicates that more electrons and photoexcitons can be excited with larger incident photo energy light at the short wavelength and contribute more to photocurrent. This also indicates that electrons have to overcome the Schottky barrier during transport [50]. Under the illumination of larger energy light at the shorter wavelength, the built-in potential of the Schottky barrier decreases, resulting in a large increase in the free carrier density, leading to easier carrier transport and tunneling and thus to greatly enhanced photocurrents. Furthermore, the device exhibits photoresponse for a fluorescent lamp, indicating that our device has a strong light detection property for weak illumination.

To validate the experimental results, the software FDTD Solutions is utilized to better demonstrate the enhancement by effects of Au LSPR on CuInSe₂ QD photogenerated carriers.



Fig. 5. Time-dependent response of the device with or without deposited Au NPs as a function of irradiance under different wavelengths with chopper frequency of 3944 Hz at a bias of 0 V: (a) 405 nm, (b) 532 nm, and (c) 808 nm.

Figure 6(a) presents the simulation schematics of the plasmonic device. The electric field distribution in the vicinity of Au NPs is calculated by FDTD simulation. In concordance with experimental results, particularly in the SEM and TEM images, we assume that the 13 nm diameter Au NPs are packed in the x-yplane under the compact CuInSe₂ QD film in thickness of 670 nm [shown in Fig. 1(b)]. The incident light illuminates toward the top surface with propagating direction of -z. Figures 6(b)-6(d) show the field distributions in the *x*-*y* plane of a single Au NP deposited in the CuInSe₂ QDs film under light illumination with the wavelengths of 405 nm [Fig. 6(b)], 532 nm [Fig. 6(c)], and 808 nm [Fig. 6(d)]. Obviously, the enhancement of the electric field in the vicinity of the Au NPs can be observed after packing under the CuInSe₂ QD film. The degree of electric field distribution is indicated by the shading in red or blue. Particularly, as described in each map of Figs. 6(b)-6(d), the distributions of the strongest and weakest enhancement are represented by the dark red and dark blue, respectively. Compared with different distributions with LSPR enhancement for CuInSe₂ QDs, the enhancement degree under the wavelength of 405 nm [shown in Fig. 6(b)] is the strongest (approaching >2 times). This indicates that under the illumination of shorter wavelength light with larger energy, the photogenerated carrier density will have a large increase, so as to enhance photocurrents for the device. Therefore, the theoretical simulation is consistent with the experimental results.

In addition, as another parameter characterizing the properties of the photodetector, temporal photocurrent responses of the device with (solid lines) or without (dashed lines) Au LSPR under different wavelengths are shown in Fig. 5. The rise and decay times in the devices with Au NPs LSPR effect and without Au NPs are approximately 0.1 ms/0.06 ms and 0.05 ms/0.03 ms, respectively. This is attributed to the additional progress during photogenerated carriers trapped in the acceptor states. Recently, using pristine CuInSe₂, Guo *et al.* [41] reported switching times of FEpTs of \sim 80 ms



Fig. 6. (a) Structure diagram of FDTD simulation. The field distributions in the x-y plane under (b) 405 nm, (c) 532 nm, and (d) 808 nm light illumination.

Table 1. Comparison in Device Performance of CulnSe₂ FEpTs with or without Au NPs at the Strongest Enhancement with Wavelength of 405 nm

Device	I _{dark} [nA]	I _{illu} [nA]	$I_{ m dark}/I_{ m illu}$	Responsivity $[\mu A \cdot W^{-1}]$	D * [10 ³ Jones]	Rise/Decay Time [ms]
Without Au NPs	8.2	13.8	1.6	2.0	$7.0\\14.4$	0.05/0.03
With Au NPs	5.7	28.9	5.0	4.4		0.1/0.06



Fig. 7. Electronic band structure and working principle of the CuInSe₂ QD FEpTs with Au NPs.

and 150 ms. To compare characteristics without the Au NP LSPR effect, several key parameters are listed in Table 1.

The sensing mechanism of plasmonic CuInSe₂ FEpTs is schematically described in Fig. 7. According to band theory, electron-hole pairs (photoexcitons) are generated when the incident photon energy is greater than the bandgap of CuInSe₂ QDs. Then, electrons and holes are separated from photoexcitons by applying external bias, generating the photocurrent. Under continuous illumination, electrons can transport to the interface acceptor states in Au NPs. The conduction electrons are trapped at the acceptor states of Au NPs. Owing to the acceptor states during illumination, the conductivity also continuously decreases until the acceptor states are completely filled. Given short wavelength light with larger photon energy, more photogenerated electrons can be excited. Therefore, the amplitude at short wavelength varies significantly. Particularly, electrons can be excited into higher energy level of CuInSe₂ QDs illuminated by pump light with larger photon energy [shorter wavelength, 405 nm, shown in Fig. 5(a)], leading to the increase of photocurrent. The acceptor states in Au NPs are located between the high energy level and CBM in CuInSe₂ QDs. Therefore, the electrons in the higher energy level will energetically be transited into the acceptor states. After completion of filling to saturation, electrons in the saturated acceptor states will jump to the CBM in the CuInSe₂ QDs, leading to continued increase in the photocurrent. However, in darkness, vacancies will occur in saturated acceptor states and can be filled with electrons from the high energy level in CuInSe₂ QDs, leading to the decrease of photocurrent.

4. CONCLUSION

In summary, plasmonic lead-free CuInSe₂ quantum dot (QD) field effect phototransistors (FEpTs) were fabricated through a

low-cost, solution-processed strategy. The FEpTs exhibit selfpowered multi-wavelength response, particularly, for 405, 532, and 808 nm irradiations. It is worth mentioning that the relevant properties can be enhanced after considering the Au NP localized surface plasmonic resonance (LSPR) effect. Meanwhile, this enhancement has been revealed by the finite-difference time domain (FDTD) method. Furthermore, for photoelectronic properties in the plasmonic device, the responsivity and the detectivity are up to 2.7 $\mu A \cdot W^{-1}$ and 7×10^3 Jones, respectively. The plasmonic device presents stability and reproducibility in the progress of ON-OFF cycles, and fast rise and decay times of the photocurrent are ~ 0.1 and ~0.06 ms. Therefore, the low-cost solution-based process and excellent device performance strongly underscore lead-free CuInSe₂ QDs as a promising material for self-powered photoelectronic applications, which can be further enhanced by the Au NP plasmonic effect.

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