Tunable Broadband Photoresponse Electron-Emission Nanostructure: Metasurface-Extended Spectrum-Selecting and Plasmon-Enhanced Emitting

Yan Shen, Yuchen Han, Huanjun Chen, Ningsheng Xu, and Shaozhi Deng*

Exploring novel nanotechnology schemes for tunable broadband vacuum photodetection devices is of great significance. Herein, a strategy to combine a field-emission cold cathode with plasmonic nanostructures to form a plasmon-enhanced field-emission metasurface array is proposed. Mo nanostructures with excellent emission properties act as field-emission cold cathode materials. Au nanospheres are applied to enhance the photocurrent of Mo nanopiramid emitters and to generate tunable resonance responses by plasmonic couplings. The response frequency and polarization can be selective in a broadband range from visible to near-infrared, which originates from the periodic couplings of the Mo–Mo microcavities and the Au–Mo interfaces in the designed metasurface emitter arrays. The amplitude of photodetection signals is experimentally demonstrated to be tunable not only by the geometrical dimensions of the Mo nanopiramid and the number of decorated Au plasmons, but also by the applied external electrostatic fields. This plasmon-enhanced photoresponse field-emission process is attributed to plasmon-mediated electron emission. Herein, a route to tunable broadband photoresponse electron-emission nanostructures at room temperature (≈300 K) and low energy consumption for photocathode and vacuum device applications is provided in the results.

1. Introduction

Photodetection over a broadband range is crucial in several fields of civil, military, and fundamental research. With the continued development of spectroscopy, imaging, communication, and other applications, studies on photodetectors with tunable frequencies, amplitudes, and polarizations have garnered increasing attention.¹⁻³ Nanotechnology has spawned various low-dimensional nanomaterials and their heterostructures, which can be assembled as photodetecting media to improve device applications, such as ultrasensitivity, miniaturization, and functionality.⁴⁻⁹ New mechanisms and novel nanostructures of photoelectric response must be explored to realize the next generation of high-performance tunable broadband photodetectors. This is particularly important for vacuum photoemission detectors based on photocathodes, which are used for specific purposes, such as outer-space photodetection and imaging and high-brightness emission. To date, most metal and semiconductor photocathodes operate under monochromatic excitation, and their quantum efficiency is generally low (ranging from 10⁻³ to 10⁻⁶).¹⁰ Herein, we propose a multi-field excited plasmon-mediated electron-emission (PMEE) strategy that combines a field-emission cold cathode with surface plasmons (SPs) and introduces the design of a metasurface array. The developed nanostructures exhibit flexible tunabilities within a wide spectral response range, such as selective frequency, polarization, and amplitude properties, which can be applied in active vacuum photodetecting devices.

The field-emission cold cathode is based on the quantum tunneling electron-emission process, which has the advantages of high current density, low energy consumption, transient response, and room-temperature operation, and is believed to be able to rapidly respond to and effectively convert light signals in a vacuum environment. High-melting metallic Mo has been demonstrated to be an attractive cold cathode material owing to its high conductivity, good thermal conductivity, and excellent high-temperature stability, and it has been successfully used in vacuum electron devices like traveling wave tubes, X-Ray tubes, and field-emission displays.¹¹⁻¹³ Recently, a series of Mo nanostructures based on self-assembly growth (e.g., nanowires,¹⁴ nanowalls,¹⁵ nanoscrews,¹⁶ and nanopyramids¹⁷) have been reported to exhibit excellent field-emission characteristics. In addition, self-assembled Mo–Mo microcavities have been experimentally demonstrated to exhibit strong localized light absorption and enhanced near-electromagnetic field under external light excitation, making Mo nanostructures a novel non-coinage-metal material for nanophotonics applications such as surface-enhanced Raman scattering (SERS).¹⁸,¹⁹

Y. Shen, Y. Han, H. Chen, N. Xu, S. Deng
State Key Laboratory of Optoelectronic Materials and Technologies
Guangdong Province Key Laboratory of Display Material and Technology
School of Electronics and Information Technology
Sun Yat-sen University
Guangzhou 510275, P. R. China
E-mail: stsdsz@mail.sysu.edu.cn

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Optical metamaterials, which are artificial assemblies of metallic, dielectric, or semiconductive resonators with pre-designed subwavelength dimensions,[20,21] have been widely studied by researchers because they can effectively select and tune the inherent characteristics of the detected light.[22–25] Well-designed metasurface arrays have been applied in solid-state photodetectors to achieve exact selectivities for the frequency, amplitude, and polarization of broadband light.[26–29] In addition, nanoscale coinage-metal materials (e.g., gold, silver, or copper) based on SPs exhibit outstanding properties in light trapping and electromagnetic field confining around nanostructures.[30–33] When combined into a metasurface array, these noble metal subwavelength structures at the plasmonic resonance frequency exhibit great advantages in producing an enhanced photoresponse performance in comparison with their dielectric and semiconductive counterparts.[20,34–36] They were also adopted as cathode materials for a specific light-driven electron-emission process, that is, the plasmonic photoemission (PPE).[37–40] However, coinage-metal nanostructures with strong SPs are generally not the best candidates for cold cathode materials. One of the reasons is that these plasmon-enhanced nanostructures (e.g., disks, gratings, grooves, or holes) do not possess the high-aspect-ratio geometrical features for strong localized electric field enhancement, and hence are not conducive to field-emission properties, such as low turn-on field- and large-emission current.[41]

Herein, we propose a photoresponse field-emission nanostructure by decorating plasmonic gold (Au) nanospheres onto a Mo nanopyramid to form a Au-on-Mo cold cathode material, which exhibits a tunable broadband response from the visible to the near-infrared region under photoelectric field excitation. When designed into a metasurface emitter array, the strong couplings from the Mo–Mo pyramidal microcavities promote high selectivity and tunability of the frequency and amplitude responses. Au SPs improve the intensities of light absorption and the near-electromagnetic field of the Mo nanopyramid array at their responsive characteristic peaks. Moreover, the newly generated selective dependencies of frequency and polarization for the Au-on-Mo nano-emitters are further demonstrated in the near-infrared band, which is based on the created Au–Mo interface plasmonic couplings. We attribute such tunable and enhanced photoresponse field-emission behavior to a novel PMEE process. In the experiments, we successfully prepared single-crystalline Mo nanopyramid films through self-assembly growth of nanomaterials. Au plasmonic nanospheres with specific resonance wavelengths were thereafter transferred and decorated onto Mo emitters to form Au-on-Mo nanopyramids. The decorated nanostructures exhibited a fivefold increase in photocurrent density, electron yield, quantum efficiency, light responsivity, and sensitivity compared with the pristine nanostructures under a moderate laser intensity of approximately 1 W cm⁻². The enhancement of the photoresponsive signal can be actively regulated by an external electrostatic field. It is not only demonstrated at some plasmonic resonance frequencies but also over the entire broadband of absorption excited by super-continuum white light (from 400 to 2400 nm).

The results of this study open a potential pathway for a vacuum photodetecting active device that can be tuned over a wide spectral range at room temperature. A reasonable cold cathode metasurface array scheme can also be used to realize optoelectronic devices with specific functional requirements. For instance, this field-emission-based photodetection scheme should be valuable for some space applications,[32,43] which require vacuum electronic devices to generate high-brightness electron beams and protect against harsh operating conditions, such as cosmic radiation, solar flares, and large temperature differences.

2. Results and Discussion

2.1. Nanostructure and Metasurface Array Design

The design concept of the tunable broadband photoresponse field-emission nanostructure and metasurface array can be described as follows: tapered metal nanostructures with high melting points are excellent field-emission cold cathode materials. High-melting Mo nanopyramids exhibit an appropriate geometry with a sharp top end and thick bottom, which is beneficial for excellent field-emission properties, such as low turn-on field- and large-current emission.[17–19] Therefore, Mo nanopyramids were first designed into a metasurface emitter array (Figure 1a). By selecting different geometric parameters of the pyramids, effective tunability of the frequency and amplitude of the broadband photoresponse can be realized. In addition, plasmonic Au nanospheres were designed to decorate Mo nanopyramids and form composite nano-emitters and their arrays. These Au SPs efficiently enhanced the photoresponse field-emission properties of the Mo nanopyramids by creating the Au–Mo interface couplings. This enhancement in photoresponse field emission can be interpreted as a PMEE process, which is shown in Figure 1b and has been described in detail in our previous work.[44,45] The corresponding energy-level diagram for the PMEE mechanism in this study is shown in Figure 1c. The decorated Au SPs are not directly responsible for emitting electrons, but act as a medium between light absorption and electron emission.[45] When the excited light matches the resonance frequencies of the Au SPs or the generated Au–Mo interfaces, the nearby photon absorption efficiency and localized electromagnetic field are significantly enhanced, and energetic hot electrons are generated by the non-radiative resonance decay of plasmons (see the left half of Figure 1c). These hot electrons can first be injected into their attached Mo nanopyramids to increase the supply of emitted electrons (see the yellow arrow) and subsequently emit into vacuum from the top ends of the Mo electron emitters with the help of an electrostatic field (see the purple line). In contrast, the laser-induced near-electric-field component acting on the material surface was enhanced by Au SPs. This helps to reduce the barrier width experienced by the electrons within the Mo emitters next to the Au nanospheres (see the green energy lines and double arrow). In PMEE, the light-driven electrons need much less photon energy to pump into vacuum, simultaneously realizing low-intensity excitation and high efficiency, which is beneficial for the sensitivity and miniaturization of vacuum photodetectors.

A finite-difference time-domain (FDTD) method was applied to study the light absorption and near-electromagnetic field response of the proposed nanostructures and their metasurface arrays. Figure 2a shows the calculated absorption cross-section
observed that the strongest near-field enhancements occurred periodically at the edges (Figure 2b) and corners (Figure S1, Supporting Information) of the nanopyramids, but not at their top ends.

The geometric dimensions of the designed Mo nanopyramids were thereafter tuned to detect the sensitivity of the emitters to incident light within a broadband spectral range from the visible to near-infrared region. Figure 2c shows the $\sigma - \lambda$ curves of the Mo nanopyramid metasurface arrays with different individual widths ($w$, corresponding to the grating period), but with a fixed height ($h$) of 500 nm. It is observed that as $w$ of the pyramid increases, the generated absorption peak appears as a red shift. In particular, when the value of $w$ increased from 600 to 1400 nm, the main absorption peak originally located in the visible region ($\approx$609 nm) shifted to the near-infrared region ($\approx$1445 nm), accompanied by an enlargement of the light absorption cross section (see inset in Figure 2c). Figure 2d shows the $\sigma - \lambda$ curves for the metasurface arrays with different individual heights ($h$, corresponding to the grating thickness), but with a fixed width ($w$) of 1000 nm. This shows that by adjusting the height of the Mo nanopyramid, the light absorption intensity can be regulated without changing the response frequency. In particular, when the value of $h$ increases from 300 to 800 nm, the $\sigma$ value of the main absorption peak of $\approx$1019 nm decreases from $8.72 \times 10^{-13}$ to $1.35 \times 10^{-13}$ m$^2$ (see inset in Figure 2d). The height dependence of the Mo pyramid is important in our study because it not only affects the light absorption rate, but also directly affects the aspect ratio and field enhancement factor of the electron emitter. The results indicate that a shorter pyramidal structure seems to be much better for strong light absorption and near-field enhancement. Conversely, for the field-emission process, an elongated structure and high aspect ratio are often required to obtain a stronger geometric electrostatic field enhancement ($\beta$). Therefore, it is necessary to comprehensively consider the construction of optical metasurface-based field-emission arrays, and coupling forms based on plasmonic enhancement is one way that is worth considering.

Plasmonic Au nanospheres were thereafter decorated onto the Mo nanopyramids to form Au-on-Mo nanostructures and their metasurface arrays. Figure 3a shows the light absorption cross-section ($\sigma$) curve when assuming that a Mo nanopyramid is adhered to by one Au nanosphere near the Mo top end (see the inset). Here, we used $\sigma_a$ of the area of interest instead of the absorption of the entire system to characterize the light absorption capacity of the models. This is because only the region near the top end of the Mo pyramid and the Au nanospheres within this region contribute to the electron emission in the PMEE process. In particular, the locations of the interface between the Au and Mo surfaces are of great concern, as $\sigma_a$ directly affects the internal quantum efficiency of photoelectric conversion. The Au nanosphere was set to $\approx$56 nm in diameter, presenting a plasmonic resonant absorption peak at $\approx$507 nm with a corresponding $\sigma_a$ of $4.98 \times 10^{-15}$ m$^2$ when inspected alone (Figure S2, Supporting Information). The absorbing peak of Au is very close to one of the absorption peaks ($\approx$502 nm) of the Mo nanopyramid metasurface array. After coupling with the Mo surface, the light-absorbing peak of the interface exhibited a significant red shift to $\approx$590 nm, with the corresponding $\sigma_a$ value being improved by nearly an order of magnitude ($\approx$1.21 $\times 10^{-14}$ m$^2$).
At this Au–Mo coupling interface, the electromagnetic near-field intensities also exhibited strong wavelength-dependent behavior. Figure 3b shows that at the strongest plasmon resonance wavelength of 590 nm, a significantly enhanced electromagnetic field can be observed at the Mo surface region adjacent to the Au SP (see the inset). The near-field plasmonic enhancement was more than 50 times ($\approx$52) that of the initial incident optical field. This led us to believe that Mo nanopyramids attached to Au nanospheres can create stronger light absorption and localized near-field enhancement in the Au–Mo coupling regions. This is conducive to the acquisition of photons and improvement of the conversion efficiency during light absorption and light-driven field-emission processes.

Figure 3c shows the $\sigma_a - \lambda$ curves for the individuals of Au-on-Mo nanopyramids when enlarging the analysis areas of $\sigma_a$ to cover the entire Mo top end (see the green boxes marked in the insets). In this case, the resonance absorption peak exhibited a slight blue shift to 538 nm, and a series of new absorption peaks were generated in the range of 1520 to 1720 nm. This was closely related to the existence of the entire Mo pyramid tip and the resulting new Au–Mo couplings. In addition, an overall enhancement of $\sigma_a$ for the system can be observed in the broadband wavelength range of 400–2000 nm with the participation of Au SPs, and such an enhancement becomes clearer with an increase in the number of decorated Au nanospheres. This result was also verified in a study of Au-on-Mo metasurface arrays. As shown in Figure 3d, the originally existing Mo–Mo coupling peaks can be further enhanced, and new characteristic peaks appear. With fixed geometric dimensions, metasurface field-emission arrays decorated with more Au nanospheres generally exhibit stronger absorption intensities at the three original characteristic peaks of 502, 750, and 1019 nm, and also produce new absorption peaks in the ranges of 1240–1360 and 1640–1760 nm. We propose that these newly generated peaks in the near-infrared range originate from periodic strong couplings between the Mo and Au SPs inside the metasurface array. Their intensities increase with an increase in the number of decorated Au nanospheres, exhibiting a nonlinear tendency (see the inset in Figure 3d). This is because the positions of the Au nanospheres distributed on the sides of the 3D Mo pyramid were different. The various
positions on the surface of the Mo pyramid have different electromagnetic coupling conditions, implying that not all Au spheres contribute equally to $\sigma_a$.

The light polarization sensitivities of the proposed nanostructures and metasurface arrays were further studied. The absorption cross-section ($\sigma_a$) curves as a function of the polarization angle ($\theta$) were simulated and illuminated by incident light of different wavelengths. Figure 4a shows that at the resonance frequency of the Au–Mo plasmonic coupling interface ($\approx 590$ nm), there are no changes in $\sigma_a$ intensities under different $\theta$ values for the Mo and Au-on-Mo nanostructure individuals with symmetric arrangements. Only a negligible change with a deviation of 2.74% (from 2.13 to 2.19 $\times 10^{-13}$ m$^2$) was detected for the Au-on-Mo nanopyramid with asymmetric Au SPs distribution. In the built-up metasurface array, the examined absorption intensities were also approximately the same for different polarization angles at the resonance excitation frequencies based on the Mo–Mo couplings (Figure S3, Supporting Information). However, metasurface arrays with periodic Au–Mo plasmonic couplings exhibit a sensitive selectivity to the polarization of the incident light, particularly for cases in which the Au SPs are arranged asymmetrically. For instance, the Au-on-Mo nanopyramid array with eight Au nanospheres asymmetrically arranged around Mo top end exhibits newly generated light absorption peaks at 1340, 1520, and 1680 nm. Their intensities varied significantly with the light polarization direction (Figure S4, Supporting Information). When illuminated at 1520 nm (Figure 4b), this nanopyramid array presents a distinct anisotropy of light absorption. The calculated $\sigma_a$ value is 1.58 $\times 10^{-13}$ m$^2$ for $\theta = 0^\circ$ while it is approximately 0.53 $\times 10^{-13}$ m$^2$ for $\theta = 90^\circ$, with a deviation of more than 66.46% (see the green curve in Figure 4b). We believe that the Au–Mo coupling strength is ultimately determined by the arrangement of the Au nanospheres. This indicates that the addition of plasmonic nanostructures to the Mo metasurface field-emission array can enhance the amplitude of photoresponse signals in a broadband from the visible to near-infrared range, and further realize the tunabilities of light frequency and polarization responses simultaneously.

2.2. Mo and Au-on-Mo Nanopyramids Preparation

To demonstrate the broadband photoresponse and tunability of the designed nanostructures, self-assembled Mo and Au-on-Mo nanopyramids were experimentally prepared. Single-crystalline Mo nanopyramids, as field electron emitters, were grown on a stainless steel substrate through a series of chemical reactions during the thermal evaporation process (Figure S5, Supporting Information).
Supporting Information). Next, Au nanospheres with a diameter of ≈56 nm were decorated onto the Mo surface through centrifugation, supernatant removal, dilution, and drying treatments (Figure 5a, see Experimental Section for details). The number of transferred Au nanospheres can be effectively controlled using different concentrations of the Au particle solution. In this study, we focused more on the top ends of Mo nanopyramids and nearby Au nanospheres. After statistical analysis (Figure S6, Supporting Information), two samples of Au-on-Mo nanopyramids, with different average numbers of Au nanospheres around the Mo tip, were selected for comparison with pristine Mo emitters. Figure 5b–d shows SEM images of typical individuals for these three samples. The prepared Mo nanopyramids typically exhibit a horizontal width of 1000 nm, a vertical height of approximately 500 nm, and a good single-crystalline nature (Figure 5b). In addition, it clearly shows that there are averaged 8 and 14 Au nanospheres adhered randomly around the Mo tip for Au-on-Mo Sample #1 (Figure 5c) and Sample #2 (Figure 5d), respectively. The energy-dispersive spectroscopy (EDS) spectrum (Figure 5e) and the EDS mapping analysis of the micro-region (insets in Figure 5e) further provide evidence that the composite nanostructure is completely composed of pure Mo (with an atom percentage of 99.3%) and Au (≈0.7%) without any other impurity elements.

SERS was further employed as an experimental tool to verify the enhancement of the light absorption properties of Mo nanopyramids with the participation of Au SPs. Methylene blue (MB) molecules were utilized as probe analytes to assess the SERS performance of the Mo and Au-on-Mo nanostructures. When the excitation frequency is in resonance with the electron transition of the probed molecule (with an absorption band centered at approximately 650 nm[15]), the Raman scattering intensity of the sample should be strongly enhanced.[46] Figure 5f shows the Raman spectra of MB molecules (10^{-4} M) adsorbed onto the pristine Mo nanopyramids, Au-on-Mo Samples #1 and #2, under 633 nm laser excitation. We observe that the recorded Raman bands are assigned to v(CC) ring + v(CN) ring mode (≈1620, 1391 cm⁻¹) and v(CC) ring mode (≈1428 cm⁻¹),[47] and no significant Raman shifts were observed among these three samples. However, the intensities of the Raman bands of the MB molecules for the Au-on-Mo samples were much stronger than those of the pristine Mo nanopyramids. In particular, the relative intensity ratio of the primary characteristic peak (≈1620 cm⁻¹) for the pristine Mo nanopyramids, Au-on-Mo Sample #1 (with eight Au SPs), and Au-on-Mo Sample #2 (with 14 Au SPs) was 1:3.2:7, and that for the secondary characteristic peak (≈1391 cm⁻¹) was calculated as 1:2.8. The recorded Raman intensity improved as the number of plasmonic Au nanospheres increased, indicating the enhancement of light absorption and a localized near-electromagnetic field based on the Au SPs. Raman mapping images were captured to characterize the reproducibility of the SERS performance and plasmonic enhancements. The mappings collected from the different samples were comparable, with clear differences in intensities. Under the same area (≈400 × 400 μm²), the samples with more Au SPs clearly exhibit more and brighter “hot spots” (Figure S7, Supporting Information). Figure 5g shows a typical Raman mapping image of the MB molecules adsorbed onto the Au-on-Mo nanopyramids (Sample #2), which exhibits good reproducibility of SERS and optical enhancement.

2.3. Plasmon-Enhanced Photosresponse Field-Emission Properties

The light-driven field-emission properties of the prepared nanostructures were comprehensively characterized under a laser plus electrostatic field co-operated mode (Figure S8, Supporting Information). In an ultrahigh vacuum environment, the field-emission current density versus the bias electrostatic field (J–E) and laser intensity (J–I laser) relationships were recorded (see Experimental Section for details). First, the initial field-emission properties of the three samples were compared when the laser was turned off. Here, the turn-on field (E_{th}) and threshold field (E_{th}) are defined as the applied electrostatic field to induce a field-emission current density (J) of 10 and 10 mA cm⁻², respectively. For the Mo nanopyramids and Au-on-Mo samples, there is no significant difference observed on the E_{th} (fluctuating from 7.75 to 8.75 V μm⁻¹) and E_{th} (ranging from 14.25 to 14.60 V μm⁻¹) values even with the participation of Au SPs (Figure S9, Supporting Information). All the transformed Fowler–Nordheim (F–N) plots (see insets in Figure S9, Supporting Information) exhibit approximately linear dependence. This indicates that the electron-emission behaviors of
both Mo and Au-on-Mo nanostructures under dark conditions (laser off) are consistent with the classical F–N theory in which the total current density of field emission can be expressed as follows:\textsuperscript{[41]}

\[
J = \frac{AF^2}{\phi^2(y)} \exp\left(-\frac{B\phi^{1/2}}{F} v(y)\right)
\]  

(1)

where \(A = 1.54 \times 10^{-6}\) represents the first F–N constant with units of \(A\cdot eV\cdot V^{-2}\), \(B = 6.83 \times 10^9\) is the second F–N constant with units of \(eV^{1/2}\cdot V\cdot m^{-1}\), \(\phi\) is the surface work function of the emitting material, and \(F\) is the localized field intensity of the emitters. In addition, \(t(y)\) and \(v(y)\) are elliptic functions, and one can take the following approximations of \(t(y) \approx 1\) and \(v(y) \approx 0.956 - 1.062y^2\) (\(y = 3.79 \times 10^{-1} F^{1/2}/\phi\)) when the external

Figure 5. Preparation and characterization of the Mo and Au-on-Mo nanopyramids. a) Cartoons that illustrate the preparation of the Mo and Au-on-Mo nanopyramids for photoresponse field emission. b–d) High-magnification scanning electron microscope (SEM) images of typical individuals of the pristine Mo nanopyramid, the Au-on-Mo sample (#1, with a statistical average of 8 Au nanospheres around the Mo tip), and another Au-on-Mo sample (#2, with a statistical average of 14 Au nanospheres around the Mo tip), respectively. e) energy-dispersive spectroscopy (EDS) spectrum of a typical Au-on-Mo nanopyramids sample. Insets: EDS mapping analysis of the selected area, and the corresponding element distribution maps of Mo and Au, respectively. f) Surface-enhanced Raman scattering (SERS) spectra of the three samples adsorbed with \(10^{-4}\) m methylene blue (MB) molecules at an excitation of 633 nm. g) Raman mapping image of the \(10^{-4}\) m MB molecules adsorbed onto the typical Au-on-Mo nanopyramids with a mapping area of \(400 \times 400 \mu m^2\). The mapping corresponds to the intensity of the Raman peak at \(1620\) cm\(^{-1}\).
electric field \((E)\) provided is not excessively large; thus, Equation (1) can be simplified as follows\(^{[44]}\)

\[
J = \frac{AF^2}{\phi} \exp\left(-\frac{B\phi^{3/2}}{F}\right)
\]

In Equation (2), parameter \(F\) is generally enhanced with respect to the external electric field \((E)\) under dark conditions \((F = F_0 = \beta E)\) because of the tip geometrical structure of the cold cathodes. Thus, the geometric field enhancement factor \((\beta)\) and surface work function \((\phi)\) were determined to be the only two factors that affect the field-emission current density. It was originally believed that the decoration of Au SPs may add a certain amount of protrusions on the surface of Mo pyramids, which gives the emitters an enhancement in \(\beta\) and acts as additional field-emission sites. However, by comparing the \(J-E\) and \(F-N\) behaviors of the different samples, this degree of change has almost negligible effects on the field-emission properties. One of the reasons is that the surface work function \((\phi)\) of those Au protrusions is higher than the Mo pyramids \((\approx 5.4\text{ eV for } \text{Au}^{[48,49]} \text{ and } \approx 4.3\text{ eV for Mo}^{[13]})\). The pumped electrons still mainly originated from the tips of the Mo nanopyramids instead of their adjacent Au nanospheres.

A continuous monochromatic laser with an incidence wavelength of 532 nm was selected to stimulate the samples. This wavelength was very close to the plasmonic resonance peak of the decorated Au nanospheres (≈507 nm) and the calculated light absorption peak of the Au–Mo nanocomposites (≈538 nm). The dependence of the total current density \((J)\) on the bias electric field \((E)\) under different laser intensities was recorded (Figure S10, Supporting Information). There was no change in the values of \(E_0\) and \(E_{\text{thrust}}\), but there was an increase in the total current density for the samples with the increase in laser intensity. We can observe that the Au–Mo nanoplanes exhibit a more significant increase in the \(J\) value than the pristine nanoplanes under the same excitation intensities. This conclusion is clarified by the values of the photocurrent density \((\Delta J)\), which should be \(\Delta J = J_{\text{laser on}} - J_{\text{laser off}}\) (see Figure 6). In the same excitations, the Mo emitters adhered with more Au SPs exhibit a stronger improvement in \(\Delta J\). For instance, \(\Delta J\) over 3.0 and 4.0 mA cm\(^{-2}\) can be obtained for the Au-on-Mo Samples #1 and #2, respectively, upon a stimulation condition of \(I_{\text{laser}} \approx 1.03\text{ W cm}^{-2}\) and \(E \approx 17.75\text{ V cm}^{-1}\). In contrast, the maximum value of \(\Delta J\) is only \(\approx 0.85\text{ mA cm}^{-2}\) for the pristine Mo nanoplanes. However, a nonlinear tendency in the higher \(E\) region was observed. This implies that the applied electrostatic field plays an important role in the photoresponse field-emission process. This makes it possible to actively tune the amplitude of the light response using electrostatic bias.

The photocurrent density \((\Delta J)\) versus laser intensities \((I_{\text{laser}})\) curves of different samples were directly compared under a fixed value of \(E\) of 17.25 V cm\(^{-1}\), as shown in Figure 7a. These \(\Delta J\) values were thereafter converted to photoresponse-emitting electron yields. The maximum numbers of emitted electrons for the pristine Mo nanoplanes, Au-on-Mo Sample #1, and Au-on-Mo Sample #2 were calculated as \(1.061 \times 10^{14}\), \(3.744 \times 10^{14}\), and \(4.992 \times 10^{14}\), respectively. This advantage of electron supply became even more apparent as the laser intensity increased with the help of Au SPs and the Au–Mo plasmonic couplings.

The photoelectric conversion external quantum efficiencies \((\eta)\) were also calculated as a function of the laser intensity \((I_{\text{laser}})\) for a fixed value of \(E\) of 17.25 V cm\(^{-1}\). The \(\eta\) value is an important index for inspecting whether electron emission is efficient for practical photodetection device applications. Thus far, most metal photocathodes have had very low quantum efficiency (≈10\(^{-5}\)–10\(^{-3}\) excited at UV wavelengths less than 266 nm), far from their semiconductor counterparts.\(^{[10]}\) Figure 7b shows that the obtained \(\eta\) values in this study exhibited an increased dependence on the excitation intensities without any saturation. The Au-on-Mo nanoplanes have the strongest \(\eta\) value of 4.55 × 10\(^{-3}\) (for Au-on-Mo Sample #2) when the laser intensity was provided as 1.03 W cm\(^{-2}\), which is ≈4.7 times higher than that of the pristine nanoplanes (≈0.97 × 10\(^{-3}\)). This has reached the highest level among commercial metal photocathodes. Moreover, sensitivity and light responsivity are also of concern. These parameters have a similar increasing trend.

![Figure 6](image-url). Laser-induced photocurrent density \((\Delta J)\) versus bias electric field \((E)\) curves of the Mo and Au-on-Mo nanoplanes under illumination of 532 nm laser. a) Pristine Mo nanoplanes, b) Au-on-Mo Sample #1 (with 8 Au nanospheres around the Mo tip), c) Au-on-Mo Sample #2 (with 14 Au nanospheres around the Mo tip). The laser intensity was fixed to 0 (laser off), 0.27, 0.52, 0.77, and 1.03 W cm\(^{-2}\), respectively. The discrete plots denote the experimental data and the dotted lines represent the fitting results based on Equation (2).
with increasing laser intensity. Figure 7c,d shows that the sensitivity (light responsivity) of the pristine Mo nanopyramids, Au-on-Mo Sample #1, and Au-on-Mo Sample #2 was calculated as 2.43% (0.83 $/C^2_{10}$ $/C_0^{3 \text{AW}}$), 7.32% (2.91 $/C^2_{10}$ $/C_0^{3 \text{AW}}$), and 9.41% (3.88 $/C^2_{10}$ $/C_0^{3 \text{AW}}$), respectively. With an increase in the number of decorated Au SPs, all of the aforementioned performance indicators exhibit approximately a fivefold improvement with a fixed high $E$ condition of 17.25 V $\mu$m$^{-1}$.

In the high $E$ regions, the Mo nanopyramids decorated with Au SPs exhibited more significant improvements in performance during the moderate-intensity light-excited field-emission process. Now, we further discuss this mechanism. Returning to the origin of field-driven electron tunneling emission, the derivation of the current density ($J$) is based on the energy distribution theory, and is determined by two elements: the electron supply function and the electron transmission coefficient as follows\[50\]

$$J = e \int_{-\infty}^{+\infty} P(W) dW = e \int_{-\infty}^{+\infty} N(W_x, W) D(W_x) dW_x dW$$

(3)

where $P(W) dW$ denotes the total number of electrons tunneling through the surface barrier. The term $N(W_x, W) dW_x dW$ is defined as the electron supply function, which represents the number of electrons per unit area and per unit time on an ideal metal surface ($x = 0$), with energy ranging from $W$ to $W + dW$ and its $x$ component ranging from $W_x$ to $W_x + dW_x$. After further derivations, it can be described as follows\[50\]

$$N(W_x, W) = \frac{4\pi m}{\hbar^3} \times \frac{dW_x dW}{1 + \exp[(W - \xi)/kT]}$$

(4)

where $m$ denotes the electron mass, $\hbar$ is Planck’s constant, $k$ is Boltzmann’s constant, and $\xi$ is the Fermi energy, which is related to the work function $\phi = -\xi$. In addition, the temperature $T$ here corresponds to the actual temperature gained by the electrons, not the lattice temperature.

$D(W_x)$ is another factor that affects the number of tunneling electrons in Equation (3), which is defined as the electron transmission coefficient and is obtained from quantum mechanics. Under the Wenzel–Kramers–Brillouin (WKB) approximation, the result of the transmission coefficient can be expressed as follows\[41\]

$$D(W_x) = \exp \left[ -\frac{8\pi^2 m |W_x|^{3/2}}{3\hbar eF} v(y) \right]$$

(5)

Figure 7. Comparison of the plasmon-enhanced field-emission properties of the pristine Mo nanopyramids and Au-on-Mo samples under excitation of a 532 nm laser and a fixed electric field of 17.25 V $\mu$m$^{-1}$. a) Photocurrent density increments versus laser intensities ($\Delta J$–$I_{\text{laser}}$) curves, which were also converted to the photoresponse electron yields ($N$). b–d) Calculated external quantum efficiencies ($\psi$), sensitivities, and responsivities as function of the laser intensities.
From Equation (4) and (5), it is observed that the parameters $T$ and $F$ directly affect the electron supply function and electron transmission coefficient, respectively, and further determine the total number of tunneling electrons. Under laser illumination, the parameter $F$ should be considered as the sum ($F = F_0 + F_{\text{plasmon}}$) of the localized electrostatic field ($F_0 = \beta E$) and the electric field component of the laser-induced near-electromagnetic field, which should be enhanced by the decorated Au SPs ($F_{\text{plasmon}} = \beta_{\text{plasmon}}E_{\text{optical}}$). However, under laser intensities as low as $\approx 25$ W cm$^{-2}$, such an electric field component is small compared to the applied electrostatic field bias, which can be ignored even in the presence of Au SPs (with the strongest $\beta_{\text{plasmon}}$ of 52 at the Au–Mo coupling interface). Consequently, the contribution of the plasmon-enhanced near-field to the field emission was small in our case. Herein, the increase in the temperature of the electrons ($T$) is considered the key factor that significantly improves the electron supply function, that is, the number of electrons available for emission. In Au-on-Mo nanopyramids, the decorated Au SPs act as light-trapping nanoantennas to adsorb incident light and confine the near-electromagnetic field. On the one hand, the aforementioned enhanced near-field induced by the plasmon resonances can accelerate the light absorption of the adjacent molybdenum, which consequently increases the electron energy inside the Mo nanopyramids. On the other hand, the non-radiative SP resonance decay generates high-energy hot electrons in the Au SPs, which are thereafter injected into the pyramids by passing through the barrier at the interface between Mo and Au, and subsequently tunnel into the vacuum from the Mo emitter tips (see Figure 1b). Both of these behaviors significantly increase the number of hot electrons supplied. It is apparent that by relying only on a sufficiently large electrostatic field to narrow the surface potential barrier of the cold cathode, these hot electrons have a greater chance to tunnel, and thus, the role of the Au SPs can be highlighted (see Figure 1c). This reflects the PMEE process, and the plasmon-enhanced metasurface field-emission array can be designed to support it.

To further demonstrate the moderate-intensity excitation and active tunability of the photoresponse amplitude within a broader spectral band, a focused supercontinuum white-light laser (400–2400 nm) was employed as the source to illuminate these three samples. The $J$–$E$ characteristics and transformed $F$–$N$ plots under different laser intensities of 0 (laser off), 0.97, 3.54, 5.91, and 7.82 W cm$^{-2}$ exhibit physical behavior exactly similar to those of monochromatic light excitation at 532 nm (Figure S11, Supporting Information). Figure 8a–c displays

![Figure 8](image-url)
the $\Delta J$–$E$ curves under various laser intensities, and one may observe that the maximum photocurrent densities for the pristine Mo nanopyrhids, Au-on-Mo Sample #1, and Au-on-Mo Sample #2 were recorded as 0.90, 5.75, and 6.30 mA cm$^{-2}$, respectively, with fixed conditions of $I_{\text{laser}} \approx 7.82$ W cm$^{-2}$ and $E \approx 17.75$ V $\mu$m$^{-1}$. Compared with the pristine samples, the maximum increment measured under white-light excitation can be enhanced by approximately 700% under the same biased electric field for Au-on-Mo Sample #2. These results demonstrate once again the mediating role and electron-supplying impact of Au SPs on the plasmon-enhanced photoresponse field emission, which is similar to the situation of monochromatic light excitation.

The dependence of electron emission on the specific excitation bands was thereafter studied. The $J$–$I_{\text{laser}}$ curves of different excitation bands with a fixed $E$ of 17.25 V $\mu$m$^{-1}$ were recorded (Figure S12, Supporting Information), and it is observed that these experimental values exhibit approximate linear distributions at low $I_{\text{laser}}$ regions (<0.5 W cm$^{-2}$), but tending to nonlinear distributions at higher $I_{\text{laser}}$ regions (>0.5 W cm$^{-2}$). After fitting the experimental data, the extracted $J$–$\lambda$ relationships of the three samples were compared under different $I_{\text{laser}}$ values (Figure 8d–f). In particular, the enhancement of the photocurrent density was more prominent in the wavelength range of 664–785 nm (with a central wavelength of 724.5 nm). In this band, the maximum $\Delta J$ of the pristine Mo nanopyrhids was 1.74 mA cm$^{-2}$, whereas it was over 5.20 mA cm$^{-2}$ for those decorated by the Au nanopiers. This wavelength band with the maximum amplitude enhancement did not cover the strongest plasmonic resonance wavelengths of the Mo–Mo coupling ($\approx$1019 nm) or the Au–Mo couplings from 1200 to 1800 nm. This is owing to the randomness of the self-assembly growth of the Mo nanopyrhids films in our experiment. The experimental $J$–$\theta$ behavior (Figure S13, Supporting Information) further confirmed this. For different light polarization angles ($\theta$), the obtained field-emission current densities exhibited isotropic properties. All of the detected deviations of the obtained current densities are small, being measured as 0.79% (35.17–35.45 mA cm$^{-2}$), 1.31% (41.42–41.97 mA cm$^{-2}$), and 0.47% (42.45–42.65 mA cm$^{-2}$) for the pristine Mo nanopyrhids, Au-on-Mo Sample #1, and Au-on-Mo Sample #2, respectively. We believe that after combining the metasurface design and advanced micromachined ordered array fabrication, more functionality can be acquired, such as tunable photoresponse frequency and polarization performance.

3. Conclusion

In conclusion, to develop a tunable broadband response vacuum photodetection application, we proposed a plasmon-enhanced field-emission nanostructure and the corresponding metasurface array. Molybdenum nanopyrhids were applied as the field-emission cold cathode, and plasmonic gold nanoparticles were used to enhance the photoresponse electron-emission properties and generate a resonance response by the Au–Mo couplings. In our design of metasurface field-emission arrays, the tunability of frequency and amplitude in the visible to near-infrared range can be achieved by periodic Mo–Mo micro-cavity couplings, and the frequency and polarization in the near-infrared range can also be tuned with periodic Au–Mo plasmonic couplings. The amplitude of the photodetecting signals can be passively tuned by the Au SPs decorated onto the Mo field emitters and actively tuned by external electrostatic fields, which has been demonstrated by light-driven field-emission measurements based on the prepared Au-on-Mo nanopyrhids. We attribute such tunable and enhanced photoresponse field emission to the PMEE process; consequently, the Au-on-Mo nanopyrhids exhibited an approximately fivefold increase in the photocurrent density, electron yield, quantum efficiency, sensitivity, and responsivity compared with the pristine nanopyrhids. Our study provides a route to develop photocathodes and vacuum photodetectors with tunable features and broadband response, particularly for devices operated at low energy consumption.

4. Experimental Section

Design of Nanostructure and Metasurface Array: The nanostructure and array designs of Mo and Au-on-Mo nanopyrhids and their electromagnetic responses were studied using an FDTD method (Lumerical FDTD solutions). The nanopyrhids was initially modeled with a horizontal width of 1000 nm and vertical height of 500 nm, and the diameter of the decorated Au nanopiers was set as 56 nm. For different Au-on-Mo nanostructures, the Au nanopiers were located on the surface of Mo pyramid, a part of them (the first 8 ones) were approximately 141 nm away from the tip of the pyramid, and another part (the last 6 nanopiers) were approximately 282 nm away from the tip. To calculate the absorption cross-section ($\sigma_n$) spectra and electromagnetic near-field enhancements, linearly polarized plane waves with wavelengths ranging from 400 to 2000 nm were launched onto the modeled nanostructures from their top ends. For the Mo nanopyrhids inidividual, a perfectly matched layer (PML) condition was employed in all directions. For the Au-on-Mo nanopyrhids array, a periodic boundary condition was employed in both $x$ and $y$ directions, and the PML condition was used in the $z$ direction. A plane wave incident along the $z$ direction and polarized in the $x$ direction was employed as the light source. The refractive indices of Au and Mo were obtained from literature work by Edward and Palik and Werner et al.[31,32] During the calculation, a mesh size of 1 nm was utilized in the Mo nanopyrhids and for the interface regions around the Au nanopiers. For further metasurface array design, the influences of the width and height of the pyramids, number of decorated Au nanopiers, and direction of incident polarization were simulated to obtain the best light absorption characteristics and near-field enhancements of these nanostructure arrays.

Preparation and Characterization: A modified thermal evaporation technique was utilized to prepare single-crystalline Mo nanopyrhids through the following reaction steps, which have been described in our previous work:[15–19] oxidation of the Mo source with residual oxygen in the cavity, disproportionation and decomposition of Mo oxides in the gas phase, condensation, and layered nucleation of Mo vapor atoms at specific temperatures. A piece of poly crystalline Mo bulk with high purity (\textapprox99.97%, ACHEMETAL Tungsten & Molybdenum Technology Co., Ltd., Luoyang) was placed as the evaporating Mo source, and the disc-shaped stainless steel substrates (#304, with diameter of \textapprox1.6 mm and area of \textapprox3.14 mm$^2$) were selected as the cathode platform considering the availability of electronic components. Inside a bell jar vacuum environment, the Mo source and substrates were placed opposite to each other (Figure S5, Supporting Information). The source was heated to more than 1873 K and held for more than 30 min in an atmosphere of high-purity Ar (\textapprox200 sccm) and hydrogen (\textapprox100 sccm). Mo nanopyrhids were thereafter synthesized after cooling down to room temperature.

Plasmonic Au nanopiers with uniform size were first prepared by a wet-chemical method. NaBH$_4$ was used to rapidly reduce the chloroauric acid (HAuCl$_4$·3H$_2$O) to generate Au nanocrystalline seeds solution with...
size of 1–2 nm. Then, a certain volume of this seed solution was injected into a growth solution containing cetyltrimethylammonium bromide (CTAB), AgNO₃, and ascorbic acid (AA). In such a growth solution, the Au atoms reduced by AA would continue to deposit on the Au nanocrystals, which started to grow slowly into Au nanospheres with a certain size. The diameter of these Au nanospheres was adjusted to about \( \approx 56 \text{ nm} \) by changing the volume of the injected seeds solution, the concentration of reactants, and the pH value of the growth solution.

The number of Au nanospheres transferred onto the Mo nanopyramids could be further effectively controlled by injecting different volumes of ultrapure water to dilute Au nanospheres solutions. The specific preparation process is as follows (shown in Figure 5a): first, ultrasonic pretreatment was applied to disperse the Au nanospheres in solution as much as possible. Second, the treated solution (\( \approx 20 \mu \text{L} \)) was injected into two centrifuge tubes, labeled as Solution #1 and Solution #2, respectively, and then centrifuged for 10 min. After this step, the Au nanospheres were mainly distributed in the lower layer of the solution and agglomerated into a cluster. Third, the supernatants in these centrifuge tubes were removed, and then the ultrapure waters with different volume of 40 and 20 \( \mu \text{L} \) were injected into Solution #1 and Solution #2, respectively, for diluting the solutions to different concentrations (with the corresponding volume ratio of 1:2 and 1:1). After another ultrasonic treatment, these two solutions were poured into two surface dishes to form droplets. The pristine Mo nanopyramids samples were then immersed into them for about 15 min. Finally, these two samples were taken out and dried naturally. The sample immersed in Solution #1 was labeled as Au-on-Mo Sample #1 while the other was labeled as Au-on-Mo Sample #2.

The microscopic morphology and elemental composition of the prepared nanostructures were characterized using a field-emission scanning electron microscope (FE-SEM, Supra 55 and Supra 60, Zeiss), while the other was labeled as Au-on-Mo Sample #2. The sample immersed in Solution #2 was labeled as Au-on-Mo Sample #2, respectively, and then centrifuged for 10 min. After this step, the Au nanospheres were mainly distributed in the lower layer of the solution and agglomerated into a cluster. Third, the supernatants in these centrifuge tubes were removed, and then the ultrapure waters with different volume of 40 and 20 \( \mu \text{L} \) were injected into Solution #1 and Solution #2, respectively, for diluting the solutions to different concentrations (with the corresponding volume ratio of 1:2 and 1:1). After another ultrasonic treatment, these two solutions were poured into two surface dishes to form droplets. The pristine Mo nanopyramids samples were then immersed into them for about 15 min. Finally, these two samples were taken out and dried naturally. The sample immersed in Solution #1 was labeled as Au-on-Mo Sample #1 while the other was labeled as Au-on-Mo Sample #2.

The microscopic morphology and elemental composition of the prepared nanostructures were characterized using a field-emission scanning electron microscope (FE-SEM, Supra 55 and Supra 60, Zeiss, \( \approx 10 \text{kV} \)) combined with an energy-dispersive spectroscopy (EDS, X-Max, Oxford Instruments, \( \approx 20 \text{kV} \)). The Raman spectra were measured using a confocal micro-Raman system (Renishaw inVia Reflex), equipped with a dark-field microscope (Leica, 50\(^\times\) objective, numerical aperture: 0.8), with an exciting laser wavelength at 633 nm. The signal acquisition time for extracting a typical Raman spectrum was set to 10 s. Based on this, the SERS performance was analyzed for the three different samples. The nanostructures were first immersed in a MB solution with molecule concentration of \( 10^{-4} \text{ M} \) for approximately 4 h, to allow for the adsorption of the MB molecules. These samples as the SERS substrates were then dried at room temperature, and were excited by the 633 nm laser with a focused diameter of 1 \( \mu \text{m} \). Raman mapping analysis was also conducted by scanning the sample to recording the corresponding spectrum from point to point in a testing area of \( 400 \times 400 \mu \text{m}^2 \). The mapping images correspond to the intensity of the Raman peak at 1620 cm\(^{-1}\), which indicates the primary characteristic peak of the MB molecules.

**Plasmon-Enhanced Field-Emission Measurement:** The light-driven field-emission properties of the prepared nanostructures were measured inside an ultrahigh vacuum chamber (\( \approx 7.5 \times 10^{-7} \text{Torr} \)), driven by a laser field plus electrostatic field operation mode (Figure 5b, Supporting Information). The plate metal anode was placed 200 \( \mu \text{m} \) away from the cold cathode samples, with a hole opened at the center to allow the laser beam to pass through and focus on the cathode. Laser excitation, in combination with a small electrostatic field, was applied to the samples to initiate electron emission. First, the samples were illuminated by a continuous monochromatic laser (LE-LS-532-100 TA, LEO) with an incident wavelength of \( 532 \text{ nm} \), which was near the plasmonic resonance wavelength of the Au nanosphere (at \( \approx 507 \text{ nm} \)), and the enhanced light-absorbing wavelength of the Au–Mo interface (at \( \approx 538 \text{ nm} \)). The electron-emission current density versus the bias electrostatic field (\( J–E \)) and versus the laser intensity (\( J–I_{\text{laser}} \)) behaviors was recorded to study the low-intensity driving field-emission properties. The \( I_{\text{laser}} \) values were calculated by dividing the incident laser power by the focused spot area, which was obtained using an optical power meter (UNO, GENTEC-EQO) and a spot analyzer (BM-USB-SP907-OS1, Spiricon). Next, these samples were continuously excited using a focused supercontinuum white-light laser (SC-Pro, OYSL Photonics, 400–2400 nm) under different \( I_{\text{laser}} \) values to evaluate the electron-emission characteristics over a broadband spectral range. For further optical frequency-dependence measurements, the incident laser beam was divided into various excitation bands through a pair of long- and short-wave pass filters (BLP01/FF01/BS01, Semrock). The relationship between the electron emission and light polarization was also studied by setting a polaroid in the incident light path. The polaroid was adjusted to different rotation angles to obtain the corresponding polarization angles.

**Supporting Information**

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

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**Conflict of Interest**

The authors declare no conflict of interest.

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. S.D. and N.S.X. conceived the idea, initiated the present study, and propose experimental scheme. Y.S. and Y.H. carried out the experiments. S.D. and Y.S. discussed and interpreted the results. H.C. assisted in the data analysis. Y.S., Y.H. and S.D. co-wrote the manuscript.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

Au-on-Mo nanopyramids, broadband photoresponse, cold cathode, field emission, metasurface array, plasmon-mediated electron emission, surface plasmon

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