

# Opposite Polarity Surface Photovoltage of MoS<sub>2</sub> Monolayers on Au Nanodot versus Nanohole Arrays

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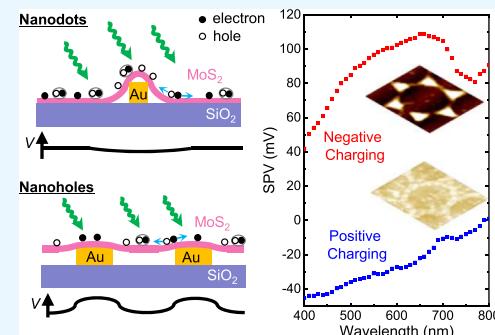
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**ABSTRACT:** We prepared MoS<sub>2</sub> monolayers on Au nanodot (ND) and nanohole (NH) arrays. Both these sample arrays exhibited enhanced photoluminescence intensity compared with that of a bare SiO<sub>2</sub>/Si substrate. The reflectance spectra of MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH had clear features originating from excitation of localized surface plasmon and propagating surface plasmon polaritons. Notably, the surface photovoltages (SPV) of these hybrid plasmonic nanostructures had opposite polarities, indicating negative and positive charging at MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH, respectively. Surface potential maps, obtained by Kelvin probe force microscopy, suggested that the potential gradient led to a distinct spatial distribution of photo-generated charges in these two samples under illumination. Furthermore, the local density of photo-generated excitons, as predicted from optical simulations, explained the SPV spectra of MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH. We show that the geometric configuration of the plasmonic nanostructures modified the polarity of photo-generated excess charges in MoS<sub>2</sub>. These findings point to a useful means of optimizing optoelectronic characteristics and improving the performance of MoS<sub>2</sub>-based plasmonic devices.

**KEYWORDS:** MoS<sub>2</sub>, localized surface plasmon, surface plasmon polariton, photoluminescence, surface photovoltage



## INTRODUCTION

The unique physical phenomena occurring in hybrid systems consisting of transition metal dichalcogenide (TMD) materials and metal nanostructures have received considerable research attention.<sup>1–13</sup> In TMD/metal hybrid systems, excitation of surface plasmons not only provides a means of overcoming the limitations of light–matter interactions but also enables tuning of the spectral response of TMD materials.<sup>1–11</sup> Thus, integration of plasmonic nanostructures can improve the performance of TMD-based devices for various applications, such as catalysis, sensing, light-emitting devices, and photovoltaics.<sup>1–3</sup>

Localized surface plasmons (LSPs) give rise to strong light confinement near metal nanostructures. LSP effects can markedly enhance optical absorption and emission in TMD layers on and under metal nanostructures.<sup>4–7</sup> Propagating surface plasmon polaritons (SPPs) along the metal/dielectric interface can also tune the optical characteristics of TMD layers.<sup>8–11</sup> Many researchers have revealed differences between the features of SPPs and those of LSPs in metal/TMD hybrid systems, including selective creation of specific excitons, strong exciton–plasmon coupling, and ultrafast transfer of hot electrons at the TMD/metal interface.<sup>8–11</sup>

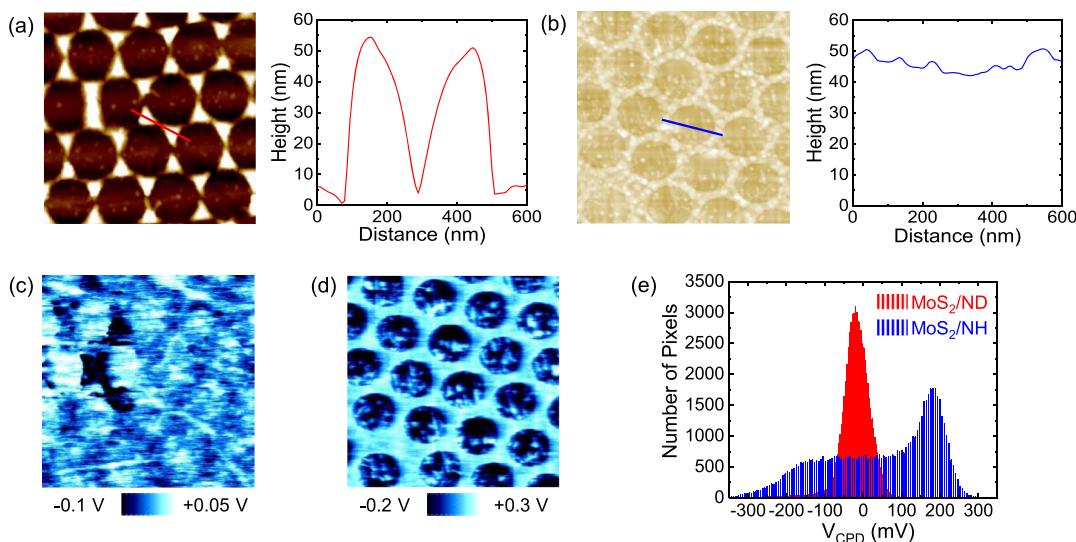
Nanosphere lithography (NSL) has notable advantages as a low-cost and high-throughput nanopatterning technique.<sup>14–17</sup>

There have been numerous NSL-based studies on the use of close-packed polystyrene (PS) beads as a shadow mask to fabricate hexagonal arrays of nanodots (NDs) through. In addition, etching of PS beads followed by metal deposition enables fabrication of nanohole (NH) arrays.<sup>16,17</sup> Metal ND arrays support LSP resonance, which have a spectral response that is mainly determined by dielectric functions of the metal and the geometry of the individual ND. Arrays of NHs in a metal film allow both the SPP and LSP modes to couple to incoming light. Plasmon–exciton coupling, mediated by both LSP and SPP contributions, provides us with the opportunity to better understand the rich physics of TMD/metal hybrid nanostructures.

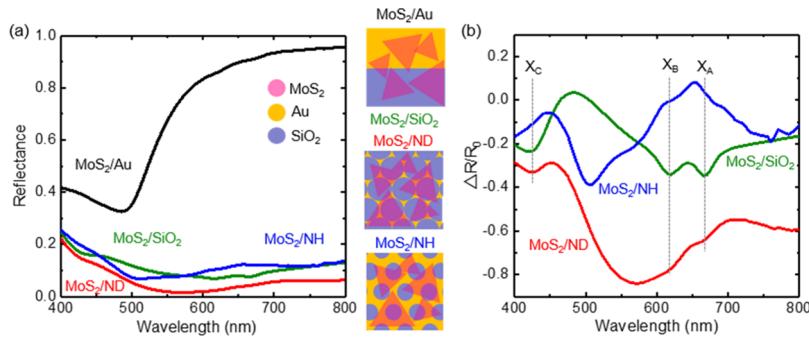
Contact potential difference (CPD) in the dark is determined by  $[(\text{work function of a sample}) - (\text{work function of a probe})]/|e|$  ( $e$ : the electron charge).<sup>13,18–21</sup> CPD measurements are a versatile technique for characterizing

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**Figure 1.** AFM images and height profiles of (a) MoS<sub>2</sub>/ND and (b) MoS<sub>2</sub>/NH. (c,d) Maps and (e) histograms of CPD<sub>D</sub> obtained from the same region in a and b. Total area of the AFM images and CPD<sub>D</sub> maps is 2 × 2  $\mu\text{m}^2$ .



**Figure 2.** (a) Reflectance and (b) differential reflectance spectra of MoS<sub>2</sub>/SiO<sub>2</sub> (green), MoS<sub>2</sub>/Au (black), MoS<sub>2</sub>/ND (red), and MoS<sub>2</sub>/NH (blue). (a) Schematic illustrations of the four sample types. X<sub>A</sub>, X<sub>B</sub>, and X<sub>C</sub> indicated by dashed lines represent A, B, and C excitons in MoS<sub>2</sub> monolayers, respectively.

semiconductor materials and their devices.<sup>6,13,18–21</sup> For example, dopant concentrations of semiconductors, band bending at semiconductor junctions, and electric dipole layers at interfaces can be measured through CPD.<sup>13,18</sup> A potential gradient and/or band offset can modify the spatial distribution of photo-generated charges. The resulting CPD change is called surface photovoltage (SPV).<sup>6,19–21</sup> The SPV is defined as  $[\text{CPD}_D - \text{CPD}_L]$ , where CPD<sub>D</sub> and CPD<sub>L</sub> are CPD measured in the dark and under light illumination, respectively. The polarity and density of excess charges determine the sign and magnitude of a SPV signal.<sup>19–21</sup> SPV characterization can reveal the influence of light illumination on charge dynamics in a variety of semiconductor materials. Moreover, optical and SPV spectra can be compared to probe defect states in semiconductor materials and their optoelectronic devices.<sup>21</sup>

In this work, MoS<sub>2</sub> monolayer flakes were transferred onto the Au ND and NH arrays fabricated by NSL techniques. Contributions of plasmonic effects were apparent in the optical characterization of the MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH samples. In addition, measured CPD maps and SPV spectra, which directly depend on the net charges at the surface, provide us opportunities to unveil photon–plasmon–exciton coupling phenomena in our MoS<sub>2</sub>/Au hybrid nanostructures.

## RESULTS AND DISCUSSION

Figure 1a,b shows atomic force microscopy (AFM) images and height profiles of the MoS<sub>2</sub> flakes transferred onto the ND and NH patterns, respectively. The ND pattern consists of triangular-shaped Au NDs with hexagonal symmetry. The NH pattern is a continuous Au thin film with an array of NHs (diameter: 400 nm). The peak-to-valley heights for both MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH were almost the same as the thickness of the Au(50 nm)/Ti(3 nm) film (Figure S1, Supporting Information). The thickness of the metal layer is similar to those used in other TMD/metal nanostructures.<sup>4,5</sup> As shown in Figure 1a, a large portion of the MoS<sub>2</sub> flakes in MoS<sub>2</sub>/ND contacted the SiO<sub>2</sub> surface except for a limited region close to the Au NDs. In MoS<sub>2</sub>/NH, the MoS<sub>2</sub> flakes were suspended over the NHs (Figure 1b). The morphology of the MoS<sub>2</sub> layers could be determined by the distinct geometric configuration of the ND and NH patterns since the fabrication procedures for the two samples were identical.

The CPD<sub>D</sub> maps of the MoS<sub>2</sub> flakes on the ND and NH patterns, obtained by Kelvin probe force microscopy (KPFM), are shown in Figure 1c,d, respectively. In MoS<sub>2</sub>/ND, the measured CPD<sub>D</sub> near the NDs was negative but that at the SiO<sub>2</sub> surface was positive. MoS<sub>2</sub>/NH had much clearer CPD<sub>D</sub> contrast, compared with that of MoS<sub>2</sub>/ND. This suggests that the electronic interaction at the MoS<sub>2</sub>/Au contact rather than

the ND-induced local strain dominantly affected the CPD<sub>D</sub> maps of MoS<sub>2</sub>/ND.<sup>12,13</sup> The CPD<sub>D</sub> of the suspended MoS<sub>2</sub> region was negative, whereas that of the MoS<sub>2</sub> on the Au layer was positive. At the MoS<sub>2</sub>/Au contact, charge redistribution can modify the carrier concentration in MoS<sub>2</sub> and increases CPD<sub>D</sub> of MoS<sub>2</sub>.<sup>13</sup> The CPD<sub>D</sub> difference in MoS<sub>2</sub>/NH clearly visualizes such strong electronic interactions.

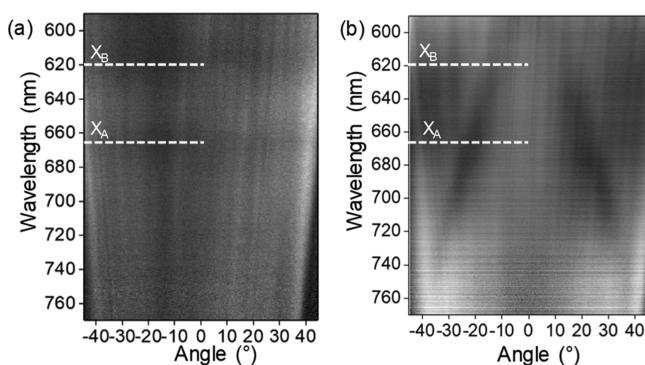
The histogram in Figure 1e shows the CPD<sub>D</sub> distributions in MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH. MoS<sub>2</sub>/NH had a more pronounced CPD<sub>D</sub> contrast than that of the MoS<sub>2</sub>/ND, as expected from their CPD<sub>D</sub> maps (Figure 1c,d). The maximum magnitude of the measured CPD<sub>D</sub> in MoS<sub>2</sub>/ND was less than 100 mV, whereas that of the MoS<sub>2</sub>/NH was greater than 200 mV. The MoS<sub>2</sub> region on the Au layer in MoS<sub>2</sub>/NH had the largest positive CPD<sub>D</sub>, and the suspended MoS<sub>2</sub> region in MoS<sub>2</sub>/NH had the smallest negative CPD<sub>D</sub>. The local CPD and its variation respectively reflect the electric potential and electric field (i.e., the potential gradient) at a specific location.<sup>6</sup> In MoS<sub>2</sub>/ND, electrons tend to move toward the MoS<sub>2</sub> region on the SiO<sub>2</sub> surface for positive CPD and holes move toward the Au NDs for negative CPD. In MoS<sub>2</sub>/NH, electrons and holes move toward the MoS<sub>2</sub> region on the Au layer for positive CPD and the suspended MoS<sub>2</sub> region for negative CPD. These differences should be considered to understand the behaviors of excess charges in the hybrid nanostructures under light illumination.

Figure 2a shows reflectance (R) spectra of MoS<sub>2</sub>/ND, MoS<sub>2</sub>/NH, and MoS<sub>2</sub> monolayer flakes on a flat 50 nm thick Au thin film (MoS<sub>2</sub>/Au) and MoS<sub>2</sub> monolayer flakes on a SiO<sub>2</sub>/Si substrate (MoS<sub>2</sub>/SiO<sub>2</sub>). MoS<sub>2</sub>/Au had a much larger R value than the other samples, and the spectrum was similar to that of a bare Au thin film (Figure S2a, Supporting Information). As shown in Figure 2a, both the Au nanopatterns gave a lower R value than that with a 100 nm SiO<sub>2</sub>/Si substrate, and MoS<sub>2</sub>/ND had the smallest R among all measured samples (see Figure S2a,b, Supporting Information). Figure 2b had a differential reflectance,  $\Delta R/R_0$ , defined as  $(R - R_0)/R_0$ , where R and R<sub>0</sub> are the reflectance of the sample and a bare SiO<sub>2</sub>/Si substrate, respectively. The SiO<sub>2</sub>/Si substrate does not exhibit destructive interference in the wavelength ( $\lambda$ ) range from 400 to 800 nm (Figure S2a, Supporting Information) because the optical path difference of the 100 nm-thick SiO<sub>2</sub> layer is small.<sup>23</sup> The  $\Delta R/R_0$  spectrum of the MoS<sub>2</sub>/SiO<sub>2</sub> (Figure 2b) had local minima at  $\lambda = 665, 620$ , and 440 nm, which originate from the A, B, and C excitonic resonances, respectively (also see Figure S2b, Supporting Information).<sup>24</sup> Features of such excitons also appeared in the spectra of MoS<sub>2</sub>/SiO<sub>2</sub>, MoS<sub>2</sub>/ND, and MoS<sub>2</sub>/NH, as indicated by the dashed lines in Figure 2b. The measured spectra of the bare samples were compared with those obtained by numerical calculations (Figure S2a, Supporting Information). Good agreement between them suggested that the defects in the NSL-fabricated nanopatterns did not significantly affect their optical spectra in the visible wavelength range, as reported by Jensen et al.'s work.<sup>14</sup>

The reflectance spectra strongly depended on the geometric configuration of the Au nanopatterns. The  $\Delta R/R_0$  value of MoS<sub>2</sub>/ND was less than  $-0.5$  at  $\lambda > 500$  nm and had a minimum at  $\lambda \approx 570$  nm (Figure 2b). This marked reduction of R is attributed to enhanced optical absorption in the MoS<sub>2</sub> layers through LSP excitation. Also, the absorption in the Au NDs and the underlying Si substrates is increased, as shown in the notable antireflection effects of the bare ND sample

(Figure S2a, Supporting Information). Conversely, MoS<sub>2</sub>/NH did not have any notable anti-reflection effects compared with MoS<sub>2</sub>/SiO<sub>2</sub>. The  $\Delta R/R_0$  value of MoS<sub>2</sub>/NH had local minima at  $\lambda \approx 520$  and 730 nm, which are attributed to excitation of SPPs and LSPs.<sup>14</sup>

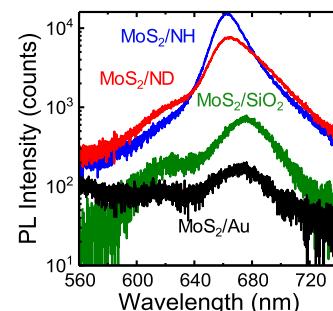
Angle-resolved differential reflectance spectra of MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH are shown in Figure 3a,b, respectively. The



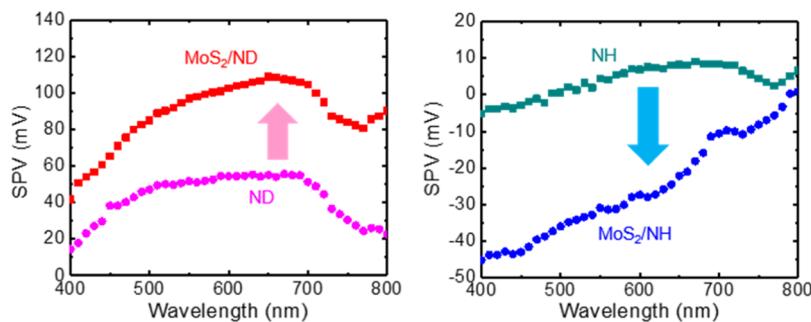
**Figure 3.** Angle-resolved differential reflectance spectra of (a) MoS<sub>2</sub>/ND and (b) MoS<sub>2</sub>/NH. X<sub>A</sub> and X<sub>B</sub> indicated by dashed lines represent A and B excitons of MoS<sub>2</sub> monolayers, respectively.

measurements were performed using a home-built angle-resolved microscopy setup.<sup>25</sup> The reflectance of the Au thin film was selected as a reference to calculate the differential reflectance of the sample to clarify the roles of the nanopatterns. MoS<sub>2</sub>/ND did not show any noticeable angle dependence, whereas MoS<sub>2</sub>/NH featured dips and a red-shift at wider angles. The clear angle dependence of the MoS<sub>2</sub>/NH is attributed to the dispersion relation of the SPP mode, which is supported by the periodic Au NH.<sup>15</sup> Furthermore, somewhat weak dips appeared at 665 and 620 nm, originating from A and B exciton states in MoS<sub>2</sub> (labeled as X<sub>A</sub> and X<sub>B</sub> in Figure 3), respectively.<sup>24</sup> The SPP-exciton coupling in MoS<sub>2</sub>/NH is in the weak coupling regime, and anti-crossing cannot be seen in the reflectance spectrum. The SPP mode wavelengths are close to the exciton resonance wavelengths; hence, SPP-exciton coupling is expected in MoS<sub>2</sub>/NH.

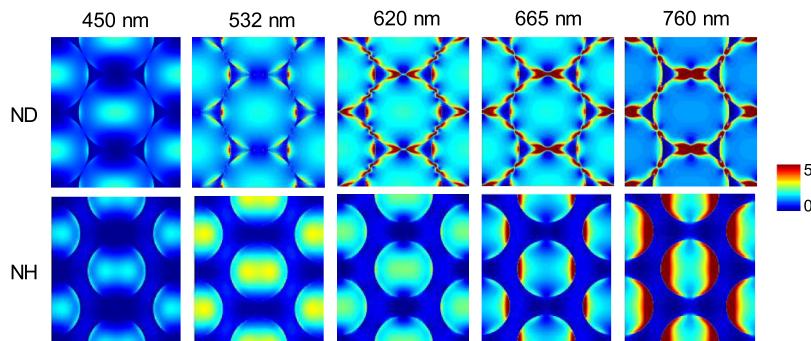
Figure 4 shows photoluminescence (PL) spectra of MoS<sub>2</sub>/Au, MoS<sub>2</sub>/SiO<sub>2</sub>, MoS<sub>2</sub>/ND, and MoS<sub>2</sub>/NH. MoS<sub>2</sub>/Au exhibited much weaker PL intensity than that of the other samples. Such PL quenching has been explained by charge transfer at the MoS<sub>2</sub>/Au interface and resulting suppression of the radiative recombination of photo-generated excitons.<sup>6,13</sup> The PL intensity of MoS<sub>2</sub>/NH and MoS<sub>2</sub>/ND was



**Figure 4.** PL spectra of MoS<sub>2</sub>/Au (black), MoS<sub>2</sub>/SiO<sub>2</sub> (green), MoS<sub>2</sub>/ND (red), and MoS<sub>2</sub>/NH (blue).



**Figure 5.** SPV spectra of a bare ND (magenta), MoS<sub>2</sub>/ND (red), a bare NH (cyan), and MoS<sub>2</sub>/NH (blue) in the visible wavelength range.



**Figure 6.** Calculated electric field intensity distributions of ND and NH under illumination of light with  $\lambda = 450, 532, 620, 665$ , and  $760$  nm.

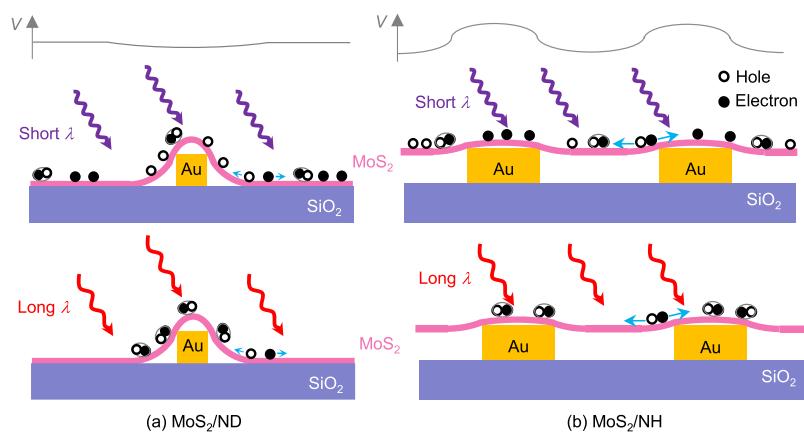
considerably enhanced, although the samples had an Au layer. The enhanced PL intensity of both MoS<sub>2</sub>/NH and MoS<sub>2</sub>/ND suggested that plasmonic enhancement of excitation and emission efficiency can exceed the nonradiative processes at the MoS<sub>2</sub>/Au interface. The strong and weak PL intensity peaks, as shown in Figure 4, originate from the A and B excitons, respectively.<sup>24</sup> The PL spectra were measured with the use of a micrometer-sized laser beam from several different locations of each sample. The measured PL intensity varied depending on the location, owing to the nonuniformity of the MoS<sub>2</sub> layers and nanopatterns.<sup>14–17</sup> The PL spectra in Figure 4 show the greatest peak intensities of each sample, which reflect that the signals measured from other regions also had a similar tendency. The PL spectra revealed that the peak position shifted depending on the underlying layer. Neutral excitons typically have larger binding energies than those of charged excitons.<sup>24</sup> Charge transfer from a metallic surface and/or trapped charges at the MoS<sub>2</sub>/dielectric interface can change the carrier concentration of MoS<sub>2</sub>.<sup>6,13</sup> Hence, the doping level in MoS<sub>2</sub> can affect the relative population of neutral and charged excitons, causing the PL peak to shift.<sup>24</sup>

Figure 5 shows SPV spectra of (left) ND and MoS<sub>2</sub>/ND, and (right) NH and MoS<sub>2</sub>/NH samples with respect to the reference Au probe in the dark steady-state. The SPV signals are the averages over the 2 mm diameter probe area. Both the NH and ND samples without MoS<sub>2</sub> had a relatively small positive SPV across the measured wavelength range. Positive (negative) SPV signals revealed the accumulation of electrons (holes) at the surface.<sup>19–21</sup> Downward band bending occurred at the interface of the SiO<sub>2</sub> and p-type Si; hence, photo-generated electrons (holes) moved toward (away from) the surface during light illumination. Consequently, band bending became less severe, leading to the SPV becoming more positive.<sup>26</sup> The magnitude of the SPV measured from a bare SiO<sub>2</sub>/Si substrate was as great as 300–400 mV in the visible

wavelength range (Figure S3, Supporting Information). Metal thin films cannot support either accumulation or depletion of electrons under light illumination, owing to the large number of free electrons. Thus, the SPV signals were considerably reduced for the MoS<sub>2</sub> on Au films (Figure S3, Supporting Information). The surface plasmon excitation markedly increased the absorption and scattering cross-section of the Au nanostructures.<sup>4–12</sup> Such plasmonic effects and shadowing effects of the Au nonpatterns reduced optical absorption in the exposed SiO<sub>2</sub>/Si region. As a result, the ND and NH samples exhibited a small positive SPV compared with that of the bare SiO<sub>2</sub>/Si substrates (Figure S3, Supporting Information).

The SPV signals measured from MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH were of greater magnitude than those from the bare ND and NH samples (Figure 5). Clearly, photo-generated charge carriers in the MoS<sub>2</sub> monolayers contributed to this difference. Notably, the SPV signals of MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH had opposite polarity across the measured wavelength range: [SPV of MoS<sub>2</sub>/ND] > 0 and [SPV of MoS<sub>2</sub>/NH] < 0 (Figure 5). Thus, positive and negative charging occurred at the MoS<sub>2</sub> surface of MoS<sub>2</sub>/NH and MoS<sub>2</sub>/ND, respectively. In addition, the SPV spectra of MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH had distinct behaviors in their wavelength dependence: the magnitude of the SPV for the former had a maximum at  $\lambda \approx 650$  nm, whereas that of the latter decreased as the wavelength increased.

The top-view electric field intensity maps for ND and NH, under illumination of light with  $\lambda = 450, 532, 620, 665$ , and 760 nm, are shown in Figure 6. The simulation was performed using the finite difference time domain method (Lumerical Solutions) with a normally incident plane wave light source. The optical constants of Si, SiO<sub>2</sub>, Ti, and Au were taken from the literature.<sup>27,28</sup> The electric field intensity was estimated at 20 nm above the SiO<sub>2</sub> surface. At  $\lambda \geq 532$  nm, the electric field intensified at the edge of the Au NDs. LSP excitation



**Figure 7.** Schematic illustrations of electric potential ( $V$ ) distributions (top) and expected behaviors of photo-generated excitons and charge carriers in (a) MoS<sub>2</sub>/ND and (b) MoS<sub>2</sub>/NH at short and long wavelengths (bottom). Blue arrows indicate drift motion of charges.

concentrated incident light near the NDs leading to broadband antireflection effects, as shown in the  $R$  and  $\Delta R/R_0$  spectra of MoS<sub>2</sub>/ND (Figure 2a,b).<sup>14–17</sup> The map of NH at  $\lambda = 532$  nm clearly showed a large electric field near the center of the holes. Such a strong field should enhance absorption in the MoS<sub>2</sub> monolayer, resulting in a negative  $\Delta R/R_0$  of MoS<sub>2</sub>/NH, as shown in the  $\Delta R/R_0$  spectrum (Figure 2b). A large field in the middle of the NHs in Au and Ag thin films has been reported in earlier works and explained by radial propagation and interference of SPPs from adjacent NHs.<sup>29,30</sup> The electric field intensity near the edge of the Au layer was strong for the NH sample at  $\lambda = 665$  and 760 nm, where  $\Delta R/R_0$  of MoS<sub>2</sub>/NH is negative and has a relatively large magnitude (Figure 2b). These results suggest that a large portion of incoming long-wavelength light should be absorbed at the near-hole-edge region of MoS<sub>2</sub>/NH. The density of photo-generated excitons is proportional to the intensity of incident light at the MoS<sub>2</sub> monolayers.<sup>23</sup> Thus, the optical simulation results in Figure 6 should be considered to understand the SPV spectra in Figure 5.

Figure 7 illustrates how photo-generated charge carriers affect the distinct features of the measured SPV spectra in Figure 5. The CPD<sub>D</sub> maps (Figure 1c,d) show the electric potential ( $V$ ) distributions of MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH, as schematically illustrated in the top of Figure 7. The gradient of  $V$  drives separation of excitons and drift of charge carriers, as discussed above. The resulting spatial distribution of charges should affect the CPD<sub>L</sub>. In-plane movement of charges are considered in Figure 7 because out-of-plane motion of charges is impossible in atomically thin MoS<sub>2</sub> monolayers. In MoS<sub>2</sub>/ND, the optical simulation results in Figure 6 suggest that a relatively large number of excitons are created at the MoS<sub>2</sub> region on the SiO<sub>2</sub> surface under illumination by short-wavelength light. The potential gradient around the Au NDs causes separation of the photo-generated excitons and drift of electrons away from the Au NDs, as illustrated in Figure 7. The resulting negative charging of the MoS<sub>2</sub> region on the SiO<sub>2</sub> surface causes CPD<sub>L</sub> to decrease compared with CPD<sub>D</sub>, resulting in a positive SPV. At longer wavelengths, hot spots appear (Figure 6) that create more excitons near the Au NDs. Thus, the contribution of the MoS<sub>2</sub>/Au region is important for determining the overall long-wavelength SPV of MoS<sub>2</sub>/NDs despite the small area fraction of the whole sample surface. Because MoS<sub>2</sub> monolayers on Au thin films have small SPV

signals (Figure S3, Supporting Information), the magnitude of the measured SPV was reduced at long wavelengths (Figure 5).

In MoS<sub>2</sub>/NH, illumination of short-wavelength light produced many excitons in the suspended MoS<sub>2</sub> region, owing to the strong light intensity (Figure 6). From the  $V$  distribution in the MoS<sub>2</sub>/NH (Figure 7b), electrons are supposed to move toward the Au layer. The depletion of photo-generated electrons induced positive charging of the suspended MoS<sub>2</sub> region, leading to a negative SPV signal (i.e., CPD<sub>D</sub> < CPD<sub>L</sub>). At longer wavelengths, the local density of photo-generated excitons near the Au NH edges increased because of the strong light confinement (Figure 6). This effect decreased the number of net charges in the suspended MoS<sub>2</sub> region and the magnitude of the measured SPV.

The interfacial band alignment allows charge transfer at the MoS<sub>2</sub>/Au contacts, which was considered to explain the CPD maps (Figure 1) and the PL quenching results (Figure 4).<sup>6,13</sup> Au thin films have a large number of free electrons, hence the Au nanopatterns in both ND and NH can act as charge reservoirs. As a result, the MoS<sub>2</sub> region in contact with the Au layer cannot show a large SPV signal, as shown in Figure S3. KPFM-measured CPD mappings of the samples also show the relatively small CPD changes at the MoS<sub>2</sub>/Au contact region under illumination of a 635 nm wavelength laser diode (Figure S4, Supporting Information). Thus, the averaged SPV signals of both the MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH depend on the area fraction of the MoS<sub>2</sub>/SiO<sub>2</sub> region. Moreover, the spatial distributions of light intensity and resulting photo-generated excitons play an important role in understanding the SPV spectra in Figure 5. Complementary studies of the optical and SPV characteristics of MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH allow us to explain photon–plasmon–exciton coupling behaviors in the hybrid nanostructures.

## CONCLUSIONS

MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH hybrid nanostructures were fabricated using NSL and exfoliation-transfer techniques. Angle-resolved reflectance spectra of MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH clearly indicated excitation of LSPs and SPPs. The LSP- and SPP-exciton coupling in these hybrid nanostructures enhanced the PL intensity of the MoS<sub>2</sub> monolayers. Notably, the SPV data revealed the opposite polarity of the excess photo-generated charges in MoS<sub>2</sub>, that is, negative and positive charging in MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH, respectively. This distinct SPV polarity is attributed to the electric potential

distributions in MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH. Furthermore, the local density of the photo-generated excitons, extrapolated from the finite difference time domain simulations, allowed us to explain the SPV spectra. This work shows that properly designed plasmonic nanostructures enable control over the spatial distribution of photo-generated carriers in MoS<sub>2</sub>/metal hybrid nanostructures.

## METHODS

**Sample Fabrication.** The two kinds of Au nanopatterns, ND array and NH array, were fabricated on SiO<sub>2</sub>(100 nm)/Si wafers using the NSL technique. Monolayers of a hexagonal PS bead array (diameter: 520 nm) were prepared on the wafers. Then, 50 nm Au thin films with 3 nm Ti adhesion layers were deposited on the PS-coated wafers by electron-beam evaporation, and the ND pattern was obtained after removal of PS beads. To make the NH pattern, the diameter of the PS beads was reduced to 400 nm by reactive ion etching. The Au(50 nm)/Ti(3 nm) thin films were deposited on the etched loose-packed PS bead monolayer. MoS<sub>2</sub> monolayer flakes, whose typical size is 10–20  $\mu\text{m}$ , were grown by chemical vapor deposition on Si substrates with 300 nm-thick SiO<sub>2</sub> layers.<sup>22</sup> The MoS<sub>2</sub> monolayer flakes were then transferred onto the ND and NH patterns by a wet-transfer method.

**KPFM Measurements.** The surface topography and CPD maps were obtained by an AFM system (NX-10, Park Systems) with a glovebox. All measurements were carried out in a N<sub>2</sub> atmosphere to avoid artifacts caused by the ambient gas adsorption. Pt/Ir-coated Si cantilevers were used as the tip, and its work function was calibrated against a highly ordered pyrolytic graphite (SPI Suppliers) reference sample. A near-infrared laser diode (wavelength: 930 nm) was used to detect the deflection of the cantilever. The presence of MoS<sub>2</sub> flakes was confirmed from the CPD data (Figure S1, Supporting Information).

**Macroscopic Reflectance Measurements.** Specular reflectance spectra were measured with the use of a quantum efficiency measurement system (QuantX-300, Newport). A xenon arc lamp and a monochromator were used to generate monochromatic light in the range of 400–800 nm, where the beam size was approximately 1 mm<sup>2</sup>. A high–low reflectance standard (product number: 603414) was used for calibration before measurements. After calibration, the samples were sequentially mounted on the sample stage and the reflectance spectrum of each sample was measured with the use of QuantX software during measurements.

**Angle-Resolved Micro-Reflectance and PL Measurements.** Angle-resolved micro-reflectance spectra were collected using a home-built angle-resolved microscopy setup. White light was focused onto the sample by a 60 $\times$  microscope objective (numerical aperture NA = 0.7), and the focused beam size is  $\sim$ 10  $\mu\text{m}$ . In the angle-resolved reflectance measurements, the back focal plane of the objective lens was projected to the entrance slit of a spectrometer equipped with a charge-coupled device detector (Princeton Instruments, 512  $\times$  2048 pixels) by a set of lenses. PL spectra were collected using the same home-built microscopy setup, and the beam diameter was 1.0  $\mu\text{m}$ . As an excitation source, an argon-ion laser at 457.9 nm (continuous wave) was focused through the objective lens, and the signal through the same objective was collected by an optical fiber, which was coupled to the spectrometer.

**SPV Spectroscopy Measurements.** SPV signals were measured in air with a scanning Kelvin probe apparatus (SKP5050, KP Technology) using a 2 mm diameter vibrating probe (frequency = 67 Hz). The tungsten lamp illumination was from the top side of the sample. The SPV spectra were measured with continuous monochromatic light at wavelengths in the range from 800 to 400 nm, selected using a linear variable filter.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c14563>.

AFM images, contact potential in dark maps, and height profiles of MoS<sub>2</sub>/ND and MoS<sub>2</sub>/NH; optical reflectance spectra of a bare SiO<sub>2</sub>/Si substrate, 50 nm Au-coated SiO<sub>2</sub>/Si substrate, bare Au ND, and bare NH; SPV spectra of a bare SiO<sub>2</sub>/Si substrate, MoS<sub>2</sub> flakes on a bare SiO<sub>2</sub>/Si substrate, and MoS<sub>2</sub> flakes on a 50 nm Au-coated SiO<sub>2</sub>/Si substrate; and KPFM-measured CPD mappings of the bare Au ND, MoS<sub>2</sub>/ND, bare NH, and MoS<sub>2</sub>/NH samples in dark and under illumination (PDF)

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## Notes

The authors declare no competing financial interest.

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