Intermediate-state imaging of electrical switching and quantum coupling of molybdenum disulfide monolayer

Zixiao Wang,1,2 Ben Niu3,4, Bo Jiang, Hong-Yuan Chen,3 and Hui Wang1

To investigate the electrical switching of the MoS2 monolayer we measured the optical intensity variation of plasmonic images of single AuNPs on MoS2 monolayer-covered substrate tuning by potential. The distinct phase change of individual AuNPs interplaying between a single metal nanoparticle and molybdenum disulphide monolayer, and the transient intermediate states during the switching event can be directly imaged by a plasmonic technique.

Results and Discussion

To investigate the electrical switching of the MoS2 monolayer we measured the optical intensity variation of plasmonic images of single AuNPs on MoS2 monolayer-covered substrate tuning by potential. The distinct phase change of individual AuNPs interplaying between a single metal nanoparticle and molybdenum disulphide monolayer, and the transient intermediate states during the switching event can be directly imaged by a plasmonic technique.

Significance

Thin transparent semiconductors of two-dimensional materials are attractive for the practical applications in next-generation nanoelectronic and optoelectronic devices. Probing the electron states and electrical switching mechanisms of a molybdenum disulphide monolayer with atomic-scale thickness (6.5 Å) allows us to unlock the full technological potential of this nanomaterial. We introduced a plasmonic phase imaging method to uncover the underlying mechanism and detailed switching dynamics of an electrical-state switching event. This dramatic phase change can be attributed to the reversible switching of classical electromagnetic coupling and quantum coupling effects interplaying between a single metal nanoparticle and molybdenum disulphide monolayer, and the transient intermediate states during the switching event can be directly imaged by a plasmonic technique.
gold film in 0.1 M NaF electrolyte by tuning the electrochemical gate potential (Fig. 1).

Zheludev and coworkers have demonstrated much beautiful work about plasmonic properties tuning by phase-change materials which have guided the development of plasmonic study (19–22). The plasmonic imaging technique has been demonstrated to show ultrasensitivity to the subtle variation of the surface charge density of nanomaterials (23–26). Based on this imaging method, the electron transport on a typical MoS2 monolayer surface changes local carrier density, which is externally manifested as the variation of plasmonic intensity. The plasmonic imaging setup combined with a typical electrochemical construction of a three-electrode system is schematically illustrated in Fig. 1A, where the p-polarized incident light is directed onto the gold film to excite a plasmonic plane wave on the surface and the scattering light of the plasmonic wave can be captured by a complementary metal–oxide–semiconductor (CMOS) transistor imager with low noise level (for more details see Materials and Methods).

We transferred and placed an MoS2 monolayer onto a gold film and then deposited individual AuNPs on the top of it. The MoS2 monolayer acts as the working electrode immersing in 0.1 M NaF electrolyte with a Pt foil and an Ag/AgCl wire, which serve as counterelectrode and reference electrode, respectively. Representative experimental and simulated plasmonic imaging results of single AuNP (d = 100 nm) are shown in Fig. 1A attributed to the oscillations of free electrons near the surface of gold film, which is excited by the incident light with an appropriate resonance angle. At this angle, the light can be absorbed by surface plasmons and changes the reflected light intensity that is imaged with our plasmonic system. Each AuNP reveals a parabolic fringe with a bright spot originating from the scattering of plasmonic wave (23, 25, 27). The images from a scanning electron microscope (SEM) show the symmetrical round shape of AuNPs on the gold substrate, and the average diameter of individual nanoparticles is obtained from the corresponding statistical analysis (SI Appendix, Fig. S1).

Unlike graphene, one of the distinct electrical characterizations of two-dimensional MoS2 is a large intrinsic band gap between its valence and conduction bands of 2.6 eV (28–30). Tuning of the gate potential leads to the dynamic electrical switching of the MoS2 monolayer, which is manifested as the local refractive index variation of individual metal nanoparticles attributed to the change of local charge density. This dynamic switching event between the electron-doping regime and the near-complete suppression of the conductivity regime for MoS2 monolayer insertion affects local electrical interaction between the individual AuNP and MoS2 monolayer (Fig. 1B). From the transmitted image and atomic force microscope (AFM) characterization in the same location, the MoS2 monolayer shows a smooth surface morphology and the average thickness is about 0.65 nm (Fig. 1C and D), so the evanescent field from the surface plasmonic wave can reach the AuNPs on it. The Raman spectrum and high-resolution transmitted electron microscope

**Fig. 1.** Schematic illustration of the plasmonic imaging technique and working principle of tuning electrical interplay between a single AuNP and an MoS2 monolayer. (A) Experimental setup of a single nanoparticle on an MoS2 monolayer by plasmonic imaging combined with three-electrode system, where WE is working electrode, RE is reference electrode, and CE is counterelectrode. The reference electrode is Ag/AgCl wire and the counterelectrode is Pt foil. (Insets) The false-color experimental and simulated plasmonic images of a single AuNP with a typical parabolic pattern. (B) Schematic view of the two different electrical states between the AuNP and MoS2 monolayer. (C) The bright-field imaging of the MoS2 monolayer covered on a bare gold substrate. The black arrows point out the edge of the MoS2 monolayer. (D) The corresponding AFM image of the MoS2 monolayer covered on a bare gold substrate and the height profile of the edge. The white arrows point out the edge of the MoS2 monolayer. The thickness of the MoS2 monolayer is ~0.65 nm. (E) The plasmonic intensity of MoS2 monolayer and bare gold regions tuning by the potential in 0.1 M NaF aqueous solution. The red dashed arrows point out the trend of optical signals. The frame rate is 100 frames per second.
Appendix

The plasmonic intensity variations of the MoS$_2$ monolayer-covered region and bare gold region have been investigated by tuning potential as shown in Fig. 1E. The plasmonic intensity for the MoS$_2$ monolayer-covered region exponentially decays with sweeping potential to positive a direction and then reaches a plateau near 0 V. This trend can be attributed to the switching of two electrical states for the MoS$_2$ monolayer (31, 32). In the electron-doping regime, the MoS$_2$ monolayer can let electrons flow by applying negative potential and it is gradually weakened in the positive potential scan, which is manifested as a decrease of plasmonic intensity. When the conductivity of the MoS$_2$ monolayer is fully hindered from 0 V to a positive value of potential, the electron flow is hindered and local charge density will not change with tuning potential corresponding to the plateau of plasmonic intensity variation. This observation is further validated by the bright-field imaging technique (SI Appendix, Figs. S3–S5). The transmitted intensity variation of the MoS$_2$ monolayer also reveals a trend similar to the plasmonic result. However, the plasmonic intensity response of the bare gold region is proportional by inversion to the applied potential, which matches with our previous work of a double-layer charging effect in a bare gold surface recorded by plasmonic imaging technique according to $\Delta \theta = 1/\alpha \cdot c \Delta E$. In this equation, $\alpha$ is a constant (47 C-m$^{-2}$-deg$^{-1}$ for bare gold surface), $c$ is the interfacial capacitance per unit area, and $\Delta E$ is potential change (33, 34). The potential dependence of quantum capacitance of the MoS$_2$ monolayer is calculated from the plasmonic intensity, and the corresponding energy diagrams indicate the switching of different electrical states (SI Appendix, Figs. S3–S5). This electrochemical plasmonic imaging technique offers the possibility for directly visualizing the various electrical intermediate states and switching dynamics of semiconductors.

By applying a potential step to dynamically tune the electrical switching states, the plasmonic images of individual AuNPs on gold substrate gapped with the MoS$_2$ monolayer are captured as shown in Fig. 2 and Movie S1. The single-nanoparticle plasmonic image shows periodic switching back and forth between negative and positive potentials, one with a bright center and the other one with a dark center of parabolic pattern for one AuNP. Fig. 2 A–D show the snapshots of switching events and the corresponding line profiles across the plasmonic pattern in the horizontal direction, revealing that two distinct electrical states induce a phase difference of 180° for a single AuNP on the MoS$_2$ monolayer. Our previous work has demonstrated that the large phase shift of a single-nanoparticle plasmonic pattern can be attributed to the switching from classical electromagnetic coupling regime to a quantum coupling regime (27). For near-complete suppression of the conductivity regime at positive potential, the electrical flow of the MoS$_2$ monolayer can be hindered and is consistent with previous work (3). The quantum coupling effect between individual AuNPs and the MoS$_2$ monolayer is hindered and the classical coupling effect dominates, which is manifested as the dark center of the parabolic pattern from the single-nanoparticle plasmonic image. For the electron-doping regime at negative potential, the optical response of the MoS$_2$ monolayer remains a linear dependence, with the applied potential indicating good electrical contact and the lack of any Schottky barrier at the MoS$_2$–gold electrode interface (Fig. 1E). The electron flow and strong quantum coupling effect between single AuNPs and the

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### Fig. 2. The switching of two different electrical states of a single AuNP (diameter = 100 nm) on MoS$_2$ monolayer tuning by potential step in 0.1 M NaF aqueous solution. (A) The plasmonic image of a single AuNP on an MoS$_2$ monolayer at +0.3 V, revealing the dark center of the parabolic pattern. (B) The false-color plasmonic image of the same nanoparticle in A and the intensity profile across the pattern of the single AuNP in the transverse direction. The black dashed line shows the center point of the parabolic pattern of the single AuNP. (C) The plasmonic image of the same AuNP on an MoS$_2$ monolayer at −0.3 V, revealing the bright center of the parabolic pattern. (D) The false-color plasmonic image of the same nanoparticle in C and the corresponding intensity profile across the pattern of a single AuNP in the transverse direction. The black dashed line shows the center point of the parabolic pattern. (E) Time-lapsed plasmonic intensity curve of the center region of the nanoparticle pattern in A–D and the corresponding modulated potential. The frequency of applied potential is 0.5 Hz. (F) The dynamic 2D line profile across the parabolic pattern of a single-nanoparticle plasmonic image in the transverse direction versus time. The frame rate of plasmonic images is 100 frames per second.

### Fig. S10. This electrochemical plasmonic imaging technique offers the possibility for directly visualizing the various electrical intermediate states and switching dynamics of semiconductors.

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(HRTEM) image of the MoS$_2$ monolayer further validate its single-layer characteristic (SI Appendix, Fig. S2).

The plasmonic intensity variations of the MoS$_2$ monolayer-covered region and bare gold region have been investigated by tuning potential as shown in Fig. 1E. The plasmonic intensity for the MoS$_2$ monolayer-covered region exponentially decays with sweeping potential to positive a direction and then reaches a plateau near 0 V. This trend can be attributed to the switching of two electrical states for the MoS$_2$ monolayer (31, 32). In the electron-doping regime, the MoS$_2$ monolayer can let electrons flow by applying negative potential and it is gradually weakened in the positive potential scan, which is manifested as a decrease of plasmonic intensity. When the conductivity of the MoS$_2$ monolayer is fully hindered from 0 V to a positive value of potential, the electron flow is hindered and local charge density will not change with tuning potential corresponding to the plateau of plasmonic intensity variation. This observation is further validated by the bright-field imaging technique (SI Appendix, Figs. S3–S5). The transmitted intensity variation of the MoS$_2$ monolayer also reveals a trend similar to the plasmonic result. However, the plasmonic intensity response of the bare gold region is proportional by inversion to the applied potential, which matches with our previous work of a double-layer charging effect in a bare gold surface recorded by plasmonic imaging technique according to $\Delta \theta = 1/\alpha \cdot c \Delta E$. In this equation, $\alpha$ is a constant (47 C-m$^{-2}$-deg$^{-1}$ for bare gold surface), $c$ is the interfacial capacitance per unit area, and $\Delta E$ is potential change (33, 34). The potential dependence of quantum capacitance of the MoS$_2$ monolayer is calculated from the plasmonic intensity, and the corresponding energy diagrams indicate the switching of different electrical states (SI Appendix, Figs. S3–S5). This electrochemical plasmonic imaging technique offers the possibility for directly visualizing the various electrical intermediate states and switching dynamics of semiconductors.

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metal-state MoS$_2$ monolayer take place and lead to a bright center of parabolic pattern for plasmonic images of individual AuNPs.

The switching of different plasmonic coupling effects between single a AuNP and the MoS$_2$ monolayer is shown in Fig. 2 $E$ and $F$ by applying a periodic potential step to control the electrical switching of the MoS$_2$ monolayer. An on–off switching event of electron flow is uncovered and generates a large phase shift of single-nanoparticle plasmonic images corresponding to bright- or dark-centered pattern. This characteristic property can make the MoS$_2$ monolayer operate as a logical inverter by converting a logical signal 0–1 and as a universal logical NOR gate electronic directly visualized by the electrochemical plasmonic imaging technique.

To validate the above conclusion of plasmonic coupling switching, we systematically performed control experiments of insulated polystyrene nanoparticles (PSNP) on an MoS$_2$ monolayer, AuNPs on a bare gold substrate, and AuNPs on an MoS$_2$ monolayer with the same potential modulation period, respectively (SI Appendix, Figs. S6–S8). By applying a square-wave potential from +0.3 V to −0.3 V, the plasmonic images and dynamic two-dimensional (2D) line profile across the parabolic pattern in a transverse direction for a single PSNP on an MoS$_2$ monolayer always revealed a dark center during the whole modulation process, as shown in SI Appendix, Fig. S6, which can be attributed to the insulated property of nanoparticles without any electron flow and quantum coupling effect between the insulator nanoparticles and the MoS$_2$ monolayer. In this situation, only classical electromagnetic coupling exists between the insulated nanoparticle and MoS$_2$ monolayer substrate. We further performed the modulation measurement of single AuNPs on a bare gold substrate without MoS$_2$ molecular monolayer insertion in SI Appendix, Fig. S7. The center of the parabolic pattern is bright and the electron flow takes place during the whole periodic tuning process of potential, corresponding to the quantum coupling effect between the metal nanoparticle and metal substrate. Remarkably, the plasmonic images of a single AuNP on an MoS$_2$ monolayer switch from a dark-centered pattern to a bright-centered pattern by applying the potential from +0.3 V to −0.3 V, as shown in SI Appendix, Fig. S8. This characteristic switching of a single AuNP on an MoS$_2$ monolayer from a classical coupling regime to a quantum coupling regime is highly reversible and quickly reaches kinetic equilibrium with different frequencies of potential (SI Appendix, Fig. S9), which can be demonstrated as stable conductors and an electron-blocking layer in polymer light-emitting diodes (LEDs).

We further uncover transient intermediate states and detailed dynamics of a coupling switching event of single AuNPs interplaying with an MoS$_2$ monolayer in Fig. 3. The triangle-wave potential has been introduced to gradually tune the switching process of electrical states of the MoS$_2$ monolayer, and the corresponding plasmonic images of a single AuNP is captured to extract a time-lapsed 2D line profile across the parabolic pattern in a transverse direction. This gradual variation of plasmonic intensity for the single AuNP region reveals various transient intermediate states between a classical electromagnetic coupling effect and a quantum coupling effect for an MoS$_2$ monolayer. The electron flow between the individual metal nanoparticle and MoS$_2$ monolayer is slowly hindered in a positive potential scan. Interestingly, the first-order derivative of the plasmonic intensity of the single AuNP reproduces well the switching of different coupling regimes as shown in Fig. 3B. Approaching the negative potential, the variational tendency reveals a sudden increase attributed to the quantum coupling event.

The experiments described above bring out the electrochemical plasmonic imaging technique with high sensitivity to monitor tiny changes and intermediate states of electron flow and the coupling effect of a single metal nanoparticle on a sub-nanometer monomolecular MoS$_2$ layer. The inherent mechanism of this imaging technique for single nanoparticle is the interference between a planar wave and a circular wave, which can be treated as the superposition of the initial plasmonic field and scattered plasmonic field in the direction of reflection (for more details see SI Appendix, Fig. S10). The relation between the total reflected light intensity recorded by the camera ($I$) and the total surface plasmon field ($E_{SP}$) is given by (35)

$$I = |E_r + \beta E_{SP}|^2,$$

where $E_r$ is the partially reflected light at the interface and $\beta$ is a constant describing the fraction of the scattered plasmonic wave in the direction of reflection. The plasmonic image of a single AuNP is simplified and described by

$$I(r', \tau') = |E_r(r) + E^{0}_{SP}(r) + \alpha E^{0}_{SP}(r'), e^{-i \kappa |r - r'|} e^{-i \omega |r - r'|}|^2,$$

where $r'$ is the position of the AuNP, $E^{0}_{SP}(r)$ is the surface plasmon field without any nanoparticle at position $r$, $\alpha$ is a scattering coefficient representing the polarizability of the nanoparticle, and $\alpha E^{0}_{SP}(r') e^{-i \kappa |r - r'|} e^{-i \omega |r - r'|}$ is the scattered wave by single AuNP at position $r'$. $\kappa$ is the plasmonic wave number.
and \( |E_c(r) + E_{sp}(r)|^2 \) is the background image without any nanoparticle at position \( r \).

The plasmonic images for a single AuNP and the corresponding intensity line profile across the plasmonic pattern in the transverse direction with the phase difference of 180° are simulated and plotted in Fig. 4 A and B. The plasmonic intensity of a single nanoparticle is affected by the amplitude (\( |\alpha_0| \)) and phase (\( \delta \)) simultaneously, as shown in Fig. 4 C and D. These two parameters change with the switching event of quantum plasmonic coupling and classical electromagnetic plasmonic coupling effects, which are consistent with the above experimental data. From the simulated results, the variation of phase extracted from the single-nanoparticle plasmonic pattern is more sensitive to reveal the tiny change of switching event of different plasmonic coupling effects. The intrinsic mechanism of phase shift can be attributed to the electrical switching of the MoS\(_2\) monolayer, which is manifested as the switching from a bright-centered to a dark-centered plasmonic pattern of the single metal nanoparticle.

To further verify the switching event of plasmonic coupling effects, the scattering spectrum for a single AuNP on different substrates is measured by tuning the potential from +0.3 V to –0.3 V (Fig. 5). For a bare gold substrate, the scattering intensity of a single AuNP reveals a tiny change at three representative potentials (+0.3 V, 0 V, and –0.3 V), as shown in Fig. 5A. The electron flow between the metal nanoparticles and metal electrode substrate takes place during the whole modulated process. For the MoS\(_2\) monolayer substrate, the scattering intensity of a single AuNP dramatically decreases with the potential from a positive to negative direction as shown in Fig. 5B, which can be attributed to the increasing of adsorption for the MoS\(_2\) monolayer (2, 18). A blue shift for the main peak location of the scattering curve for a single AuNP on an MoS\(_2\) monolayer is observed, corresponding to the switching from a classical electromagnetic coupling regime to a quantum coupling regime. Time-lapsed 2D dynamics of the single-nanoparticle scattering spectrum uncovers more details for sweeping the potential from a positive to a negative direction in Fig. 5C. To further validate the coupling mechanism mentioned above, the extinction spectra of a single AuNP on an MoS\(_2\) monolayer has been performed, as shown in Fig. 5D. The main peak reveals a red shift in wavelength when the switching event happens, which is consistent with previous work (36, 37). For incident light of plasmonic imaging approach with a wavelength of 680 nm, the sign of real part of polarizability changes and the plasmonic pattern for individual AuNPs reverses phase component.

### Conclusions

In this work, we first demonstrated a plasmonic-based phase imaging technique to directly visualize the dynamic electrical switching and plasmonic coupling events of single AuNPs on molybdenum disulfide monolayer tuning by potential within...
the nonfaradic regime. The switching between different electrical intermediate states of an MoS$_2$ monolayer can be modulated between an electron-doping regime and near-complete suppression of a conductivity regime, which correspond to a quantum coupling effect and classical electromagnetic coupling effect of a single metal nanoparticle, respectively. The key feature for the switching event of two plasmonic coupling effects has been directly monitored by the plasmonic imaging technique and validated by the simulation of a theoretical model. The characteristic phase switching of single-nanoparticle plasmonic images on an MoS$_2$ monolayer is highly reversible and quickly reaches equilibrium state, which can be demonstrated as stable conductors and electron-blocking layer in polymer LEDs. These observations form the basis for establishing logic gates under electrical modulation and offer the intriguing possibility to directly image the working principle of the on–off transistor in nanoelectronics and optoelectronics areas. This electrochemical plasmonic phase imaging technique with high sensitivity also can be utilized to study visualized electro-optical modulators and semiconductors at nanoscale.

Materials and Methods

**Chemicals.** Au nanoparticle aqueous solution (diameter: 100 nm) was purchased from Nanopartz and diluted in deionized water (18 MΩ·cm; Milli-Q, Millipore Corp.). The 200-nm polystyrene nanoparticle aqueous solution was purchased from Janus New-Materials. The NaF powder was purchased from Adamas-Beta and diluted in deionized water as the electrolyte in all experiments.

**Preparation of the MoS$_2$ Monolayer-Covered Gold Film.** Gold films were prepared by thermally evaporating 2 nm Cr and 47 nm Au onto freshly cleaned MoS$_2$ monolayer of MoS$_2$ on sapphire substrate (XFNANO) was transferred to gold film using a surface-energy-assisted transfer method (38).

**Scattering Spectrum Measurements by Tuning Potential.** A 660-nm p-polarized superradiant LED light source was introduced to excite surface plasmons and equipped with an inverted microscope (Nikon Ti-E) using a 60× high-numerical-aperture (NA) oil-emersion objective lens (NA = 1.49) and a CMOS camera (Hamamatsu, C11440-22C). An electrochemical cell made of polydimethylsiloxane was placed on top of the MoS$_2$ monolayer-covered gold film. To reliably control the experimental potential, a standard three-electrode system was used, including a working electrode (MoS$_2$-covered gold film, bare gold film, or ITO), a reference electrode (Ag/AgCl wire), and a counterelectrode (Pt foil) in 0.1 M NaF aqueous solution as electrolyte. The potentials with different waveforms can be applied by a potentiostat (Pine Research Instrumentation) combined with a function generator (Agilent, 33220A).

The optical transmitted imaging was performed with the same inverted microscope (Nikon, Ti-E) equipped with the 60× objective lens and CMOS camera. The incident light from a quartz tungsten halogen source (Nikon, D-LH/IC) passed a band-pass filter at 655 ± 15 nm and then illuminated the sample from the top to improve the sensitivity.

Raman spectra was collected with using a 488-nm laser under ambient condition (InVia-Reflex) with a 100× objective lens. The HRTEM image was acquired with a JEOL 2100 instrument at 200 kV. The SEM characterization of AuNPs was carried out by JSM-7800F to get the morphology and size information. The AFM images were captured in air with silicon nitride tips (Agilent Technologies, AFM 5500) and the scanning rate was 0.5 line per s.

**Scattering Spectrum Measurements by Tuning Potential.** The optical imaging of a single AuNP on an MoS$_2$ monolayer-covered gold film was measured by an inverted dark-field microscope (Eclipse Ti-U, Nikon), which was equipped with an oil-immersed dark-field condenser (NA = 1.20 to 1.43), a water-immersed objective lens, and a CMOS camera (Hamamatsu, C11440-22C). An electrochemical cell made of polydimethylsiloxane was placed on top of the MoS$_2$ monolayer-covered gold film. To reliably control the experimental potential, a standard three-electrode system was used, including a working electrode (MoS$_2$-covered gold film, bare gold film, or ITO), a reference electrode (Ag/AgCl wire), and a counterelectrode (Pt foil) in 0.1 M NaF aqueous solution as electrolyte. The potentials with different waveforms can be applied by a potentiostat (Pine Research Instrumentation) combined with a function generator (Agilent, 33220A).

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objective lens (NA = 0.6, 40x, part number MR08430), and a quartz tungsten halogen lamp (LV-H50PC, Nikon) as the light source. The dark-field scattering spectrums of a single AuNP on MoS₂ monolayer-covered gold film were captured by a grating spectrometer (Acton Spectra Pro SP-2300, Princeton Instruments) equipped with a liquid-nitrogen-cooled charge-coupled device (CCD). The extinction spectra of individual AuNPs on MoS₂ monolayer surfaces were measured by a spectrometer (SP-2-300, Princeton Instruments) and an electron-multiplying charge-coupled device (EMCCD) camera (ProEM+, Princeton Instruments). The electrochemical measurements were carried out with three-electrode system by an Autolab (Autolab PGSTAT302N, Metrohm AG). The square step measurements). The electrochemical measurements were carried out with three-electrode system by an Autolab (Autolab PGSTAT302N, Metrohm AG). The square step measurements. The potential can be applied on the sample and the corresponding current of the entire electrode is recorded by the Autolab. The Ag/AgCl wire and Pt coil were used as the reference electrode and the counterelectrode, respectively. The MoS₂ monolayer-covered gold film was the working electrode. The electrolyte is 0.1 M NaF aqueous solution.

Data Availability. All study data are included in the article and/or supporting information.

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PNAS 2022 Vol. 119 No. 22 e2122975119 https://doi.org/10.1073/pnas.2122975119 7 of 7