Understanding the remarkable excitonic effects and controlling the exciton binding energies in two-dimensional (2D) semiconductors are crucial in unlocking their full potential for use in future photonic and optoelectronic devices. Here, we demonstrate large excitonic effects and gate-tunable exciton binding energies in single-layer rhenium diselenide (ReSe2) on a back-gated graphene device. We used scanning tunneling spectroscopy and differential reflectance spectroscopy to measure the quasiparticle electronic and optical bandgap of single-layer ReSe2, respectively, yielding a large exciton binding energy of 520 meV. Further, we achieved continuous tuning of the electronic bandgap and exciton binding energy of monolayer ReSe2 by hundreds of milli–electron volts through electrostatic gating, attributed to tunable Coulomb interactions arising from the gate-controlled free carriers in graphene. Our findings open a new avenue for controlling the bandgap renormalization and exciton binding energies in 2D semiconductors for a wide range of technological applications.

INTRODUCTION
Atomically thin two-dimensional (2D) semiconductors usually exhibit large bandgap renormalization and extraordinary excitonic effects due to quantum confinement and reduced dielectric screening (1–4). As a result, light-matter interactions in these systems are primarily governed by the enhanced excitonic effects, which have been exploited to develop exciton-based devices operated at room temperature (RT) (5). Future progress in this area hinges on the ability to control the excitonic effects of 2D semiconductors by precisely tuning their exciton binding energies (Eg). This is crucial for realizing the full potential of 2D semiconductors in photonic and optoelectronic applications.

One unique aspect of 2D semiconductors is their unprecedented tunability in both their electronic and optical properties, due to high susceptibility to the doping and environmental screening (1, 6–12). It has been theoretically predicted and experimentally demonstrated that Coulomb interactions in 2D semiconductors can be engineered to tune their quasiparticle (QP) bandgap (Eg) and Eg using different methods such as chemical doping (6), electrostatically gating (7), and engineering environmental screening (1, 8, 9, 11, 12). Among all the methods reported, electrostatic gating offers additional advantages including continuous tunability and excellent compatibility for integration in modern device technologies. Recent studies involving the use of optical measurements demonstrated that gate-controlled excitonic effects can be achieved in monolayer transition metal dichalcogenides (TMDs) (7). However, an overlap of the band-edge absorption step with strong excitonic resonances generally makes it challenging to accurately determine Eg of 2D semiconductors from their optical absorption spectrum (13).

To probe Eg of 2D semiconductors directly, one can use scanning tunneling spectroscopy (STS) and optical spectroscopy (e.g., differential reflectance or photoluminescence spectroscopy) to measure Eg and optical bandgap (Eopt), respectively (1, 14). Here, we used this approach to demonstrate the gate-tunable Eg and excitonic effects in monolayer ReSe2 on a back-gated graphene field-effect transistor (FET) device, as sketched in Fig. 1A. We observed a large Eg of 520 meV for monolayer ReSe2 at zero gate voltage (Vg = 0 V). Moreover, we show that Eg of monolayer ReSe2 can be continuously tuned from 460 to 680 meV by electrostatic gating, which can be mainly attributed to screening from gate-controlled free carriers in graphene. This is distinct from the previous study of gate-tunable Eg in 2D semiconductors wherein the semiconductors’ own free carriers play a major role (7). These 2D semiconductor/graphene heterostructures have been widely used in the fabrication of transistors (15–17), photo detectors (18), and energy–harvesting devices (19). The ability to precisely tune the bandgap and excitonic effects of 2D semiconductors on graphene provides a new route for the optimization of the interfacial charge transport or light-harvesting efficiency. Therefore, we expect that our findings would have a profound impact in the field of novel electronic and optoelectronic devices based on artificially engineered van der Waals heterostructures.
monolayer ReSe2 flake onto a clean back-gated graphene FET device. The two lattice vectors (a and b) are outlined by red lines. The lattice constants are a = 6.6 Å and b = 6.7 Å. The angle between a and b is 118.9°. (C) A representative STM image of a monolayer ReSe2 flake on graphene/h-BN. The STM image reveals the unique 1D chains consisting of diamond-shaped Re4 units along a direction (highlighted by orange line). The cross (X) marks the position where the differential conductance (dI/dV) spectra were taken.

We then probed the local electronic properties of ReSe2 using STS. We note that differential conductance (dI/dV) spectra acquired in several moiré regions exhibit similar features (refer to section S3 for more details). Figure 3A shows a representative dI/dV spectrum acquired over monolayer ReSe2 (marked by a cross in Fig. 1D) at Vg = 0 V together with the local density of states (LDOS) calculated by density functional theory (refer to section S5 for more details). A wide bandgap and several prominent resonant peaks located close to both the conduction band (CB) and valence band (VB) edges have been captured in the dI/dV spectrum taken on the clean surface region (solid blue line in Fig. 3A). These features can be well reproduced in the calculated LDOS of a free-standing monolayer ReSe2 (dashed red line in Fig. 3A and refer to section S5 for more details). A close examination of the calculated band structure of monolayer ReSe2 allows us to identify that the origin of the prominent resonant peaks at the CB side (C1) is attributed to the dispersionless electronic bands as indicated in fig. S5.

We identify the band edges of each dI/dV spectrum using the method previously reported (I). The VB maximum (VBM) and the CB minimum (CBM) are found to be located at −1.27 ± 0.01 eV and 0.72 ± 0.01 eV, respectively, which yields Eg of 1.99 ± 0.02 eV for monolayer ReSe2. In addition, we observe the Fermi level (EF) to be closer to the CBM than the VBM, indicating a low n-doping of ReSe2, which is presumably due to the presence of donor-like defects with shallow mid-gap states (fig. S4A).

Electronic structure of monolayer ReSe2

We then probed the local electronic properties of ReSe2 using STS. We note that differential conductance (dI/dV) spectra acquired in several moiré regions exhibit similar features (refer to section S3 for more details). Figure 3A shows a representative dI/dV spectrum acquired over monolayer ReSe2 (marked by a cross in Fig. 1D) at Vg = 0 V together with the local density of states (LDOS) calculated by density functional theory (refer to section S5 for more details). A wide bandgap and several prominent resonant peaks located close to both the conduction band (CB) and valence band (VB) edges have been captured in the dI/dV spectrum taken on the clean surface region (solid blue line in Fig. 3A). These features can be well reproduced in the calculated LDOS of a free-standing monolayer ReSe2 (dashed red line in Fig. 3A and refer to section S5 for more details). A close examination of the calculated band structure of monolayer ReSe2 allows us to identify that the origin of the prominent resonant peaks at the CB side (C1) is attributed to the dispersionless electronic bands as indicated in fig. S5.

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Gate-tunable QP bandgap renormalization

One unique aspect of this study is that we can probe the QP band structures as a function of gate voltage. Figure 3C shows the gate-dependent dI/dV spectra taken at the same position over monolayer ReSe2. We observed that a gate-dependent rigid shift of the CBM and C1 toward EF when Vg is changed from −63 to +45 V (Fig. 3, B and C). Unexpectedly, the VBM remains nearly constant at different gate voltages as shown in Fig. 3 (B and C). The distinct shift of the CBM and VBM with the increase in the applied gate voltage therefore indicates a monotonic reduction of Eg. The QP bandgap of monolayer ReSe2 is determined to be 2.15 ± 0.01 eV at Vg = −63 V and 1.93 ± 0.02 eV at Vg = 45 V, respectively.

Probing the optical bandgap of monolayer ReSe2

We performed the differential reflectance spectroscopic measurement of monolayer ReSe2/graphene/h-BN at 5 K to probe its optical bandgap. Differential reflectance spectra of the sample after the background subtraction are shown in Fig. 3D (refer to fig. S6A for more details). At Vg = 0 V, Eopt of monolayer ReSe2 is determined to be 1.47 ± 0.01 eV at 5 K based on the peak position of differential reflectance spectrum (Fig. 3D), consistent with previous results (22). To probe the electrostatic gating effect on Eopt, we monitored the evolution of the peak position of the hybrid ReSe2/graphene device as a function of gate voltage.
We found that $E_{\text{opt}}$ remains nearly constant at all the gate voltages as opposed to the monotonic reduction of $E_g$ (Fig. 3, C and D). It reflects that the renormalization of $E_g$ is nearly fully offset by the change of $E_b$, in agreement with Koopmans’ theorem adapted for semiconductors and previous experimental studies (9, 29, 30). To further verify this, we performed photoluminescence measurement of monolayer ReSe$_2$/graphene/h-BN at different gate voltages at RT. The gate-dependent photoluminescence spectra acquired at RT also reveal a nearly constant $E_{\text{opt}}$ of monolayer ReSe$_2$ (fig. S6B).

Gate-tunable exciton binding energy

The exciton binding energy is directly determined from the equation ($E_b = E_g - E_{\text{opt}}$). As shown in Fig. 4A, a large gate-tunable bandgap renormalization of ReSe$_2$ can be achieved in our hybrid device, whereby $E_b$ can be precisely tuned over a wide energy range from $680 \pm 20$ meV to $460 \pm 20$ meV when $V_g$ increases from $-63$ to $+45$ V. The pertinent question to be addressed in this work is the physical origins of the gate-tunable QP bandgap renormalization and exciton binding energy in monolayer ReSe$_2$. We are able to exclude the contribution from the out-of-plane field-induced polarization of CBM and VBM wave functions (namely, Stark effects). The vertical field induced polarization of electrons and holes in monolayer TMDs is negligible due to their extreme confinement in the in-plane direction (7). In addition, the screening by graphene substrate substantially reduces the vertical electric field effect for monolayer TMDs is negligible due to their extreme confinement in the in-plane direction (7). In addition, the screening by graphene substrate substantially reduces the vertical electric field effect for monolayer ReSe$_2$.

On the other hand, free carriers in both ReSe$_2$ and adjacent graphene can, in principle, contribute to the renormalization of $E_g$ and tunable $E_b$ in single-layer ReSe$_2$. It has been predicted that $E_g$ of a free-standing 2D semiconductor can be substantially reduced because of the presence of free carriers (31, 32). Further, the dominant contribution to the QP bandgap renormalization in these systems is predicted to arise from the Coulomb-hole self-energy and screened-exchange self-energy (31). However, a detailed analysis of the experimental data reveals that the renormalization of $E_g$ and tunable $E_b$ is not likely to arise from the presence of free carriers in ReSe$_2$. First, the set of gate-dependent $d/dV$ spectra shows that $E_g$ never crosses the band edge of ReSe$_2$ (Fig. 3C), suggesting the absence of free carriers residing in the band edge states. We also considered the potential free carriers contributed from point...
To directly compare with experimental results, we need to convert the carrier density in graphene to the corresponding gate voltage \( V_g \). The carrier density in the ReSe\(_2\)/graphene hybrid system depends linearly on the gate voltage: \( n = \alpha(V_g - V_0) \). Here, \( \alpha \) is estimated to be around 7.1 \( \times 10^{10} \) cm\(^{-2}\) V\(^{-1}\) using a standard capacitor model (consisting of \( \sim 285\)-nm SiO\(_2\) and \( \sim 15\)-nm h-BN as dielectric materials) (33, 34). Note that \( n \) is the initial doping of the system at \( V_g = 0 \) V. Since the density of defects with mid-gap states is extremely low (3.9 (± 1.5) \( \times 10^{11} \) cm\(^{-2}\)) compared with the total gate-induced free-carrier density (\( \Delta n = 7.7 \times 10^{12} \) cm\(^{-2}\)) and \( E_b \) is away from band edges of ReSe\(_2\), this rationalizes that most of the gate-induced free carriers are injected into the underlying graphene. When \( V_0 \) is set as \(-64 \) V, we find the calculated \( E_b \) as a function of gate voltage agrees with the observed gate-dependent \( E_b \) (Fig. 4A). This suggests that the graphene underneath monolayer ReSe\(_2\) is strongly n-doped at \( V_g = 0 \) V, in line with the charge transfer analysis discussed in section S9.

**DISCUSSION**

In summary, we have successfully tailored the QP bandgap and the exciton binding energy in a 2D semiconductor by controlling the doping in the underlying graphene using electrostatic gating. Our results show that screening from a graphene substrate has a profound impact on Coulomb interactions in adjacent 2D semiconductors and leads to broad tunability of the electronic bandgap and exciton binding energy. Our findings not only result in the unprecedented understanding of many-electron physics in hybrid 2D semiconductor/graphene systems but also pave the way toward controlling the excitonic effects and precisely tuning the exciton binding energies in 2D semiconductors for a wide range of technological applications.

**MATERIALS AND METHODS**

**Sample preparation**

We fabricated the graphene/h-BN sample based on the recipe reported previously (35). We then used the well-established dry transfer technique to place a monolayer ReSe\(_2\) on top of graphene/h-BN sitting on SiO\(_2\)/Si substrate (36). The key steps for the sample treatment include the following: (i) The h-BN/SiO\(_2\)/Si substrate was annealed in the furnace at 500°C for 2 hours before the transfer of graphene. (ii) After the transfer of graphene, graphene/h-BN/SiO\(_2\)/Si sample was annealed in furnace with a flow of 100 sccm (standard cubic centimeters per minute) H\(_2\) and 200 sccm Ar at 350°C for 5 hours. (iii) ReSe\(_2\)/graphene/h-BN was annealed at 300°C in the ultrahigh vacuum chamber for 12 hours.

**STM and STS measurements**

Our STM and STS measurements were conducted at 4.5 K in the Omicron LT-STM system with a base pressure lower than 10\(^{-10}\) mbar. The STM tip was calibrated spectroscopically against the surface state of Au(111) substrate. All the dI/dV spectra were measured through a standard lock-in technique with a modulated voltage of 5 to 10 mV and the frequency of 700 to 800 Hz.

**Differential reflectance and photoluminescence measurements**

The differential reflectance measurements and photoluminescence measurements were conducted at 5 K and at RT, respectively, using a
custom-built confocal spectrometer. For differential reflectance measurements, samples were illuminated by the white light from broadband source (hydrogen-halogen lamp) focused into the spot of ~2 μm. Reflectance spectra from monolayer ReSe₂ (R_{\text{ReSe₂}}) and substrate (R_{\text{sub}}) were collected in confocal geometry. Differential reflectance spectra (DR) are obtained by DR = (R_{\text{sub}} – R_{\text{ReSe₂}})/R_{\text{sub}}. For photoluminescence measurements, samples were excited with a 532-nm laser through the 100× objective lens (numerical aperture of 0.9) with a power below 0.5 mW.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/7/eaaw2347/DC1

Section S1. Atomic force microscopy measurement of monolayer ReSe₂

Section S2. Moiré pattern of single-layer ReSe₂ on graphene

Section S2.1. Moiré patterns for various twist angles

Section S2.2. A comparison between experimental and theoretical moiré patterns

Section S3. Gate-dependent d-spectra of a different device.

Section S4. Band structure of monolayer ReSe₂

Section S5. Band structure of monolayer ReSe₂

Section S6. Differential reflectance spectrum and gate-dependent photoluminescence spectra of monolayer ReSe₂

Section S7. Gate-dependent d-spectra of graphene/monolayer ReSe₂

Section S8. Calculation of E_g in monolayer ReSe₂ as a function of the carrier density in graphene substrate

Section S9. Charge transfer at the interface of ReSe₂/graphene

Fig. S1. Identify the thickness of monolayer ReSe₂.

Fig. S2. Moiré lengths of ReSe₂/graphene as a function of twist angle.

Fig. S3. Gate-dependent d-spectra of a different device.

Fig. S4. STM images and STS measurements of defects in ReSe₂.

Fig. S5. Band structure of monolayer ReSe₂ calculated using the first-principle density functional theory calculations with the Perdew-Burke-Ernzerhof exchange-correlation functional using the QUANTUM ESPRESSO code.

Fig. S6. Differential reflectance spectrum and gate-dependent photoluminescence spectra of monolayer ReSe₂ on graphene/h-BN.

Fig. S7. Gate-dependent d-spectra of graphene/monolayer ReSe₂.

Fig. S8. Exciton binding energy (E_r) and Thomas-Fermi screening radius (r_s) as a function of electron concentration (n) in graphene.

Fig. S9. Charge transfer at ReSe₂/graphene interface.

Table S1. Geometrical properties of the moiré patterns of ReSe₂/graphene.

References (37–46)

**REFERENCES AND NOTES**


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Author contributions: J. Lu supervised projects. Z.Q. performed STM measurements and data analysis with the help of H.F. H.F. performed atomic force microscopy measurements. M.Tr. devised the model with contributions from A.H.C.N. and S.A. I.V. performed photoluminescence measurements and data analysis with the help of G.E. S.G. performed the calculation for estimating charge transfer at ReSe2/G interface. K.W. and T.T. grew the h-BN on device. P.L., J. Li, and Z.Q. fabricated the device. J.S. and M.Te. helped with the STM measurements. J. Lu and Z.Q. prepared the manuscript with the contribution from M.Tr., L.V., G.E., S.G., L.Y., E.L., and J.W. All authors contributed to the scientific discussion and helped in writing the manuscript.

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Giant gate-tunable bandgap renormalization and excitonic effects in a 2D semiconductor

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