Boosting quantum yields in two-dimensional semiconductors via proximal metal plates

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Monolayer transition metal dichalcogenides (1L-TMDs) have tremendous potential as atomically thin, direct bandgap semiconductors that can be used as convenient building blocks for quantum photonic devices. However, the short exciton lifetime due to the defect traps and the strong exciton-exciton interaction in TMDs has significantly limited the efficiency of exciton emission from this class of materials. Here, we show that exciton-exciton interaction in 1L-WS₂ can be effectively screened using an ultra-flat Au film substrate separated by multilayers of hexagonal boron nitride. Under this geometry, induced dipolar exciton-exciton interaction becomes quadrupole-quadrupole interaction because of effective image dipoles formed within the metal. The suppressed exciton-exciton interaction leads to a significantly improved quantum yield by an order of magnitude, which is also accompanied by a reduction in the exciton-exciton annihilation (EEA) rate, as confirmed by time-resolved optical measurements. A theoretical model accounting for the screening of the dipole-dipole interaction is in a good agreement with the dependence of EEA on exciton densities. Our results suggest that fundamental EEA processes in the TMD can be engineered through proximal metallic screening, which represents a practical approach towards high-efficiency 2D light emitters.
Transition metal dichalcogenides (TMDs) are layered materials where the forces between its constituent layers are mediated by weak van der Waals interaction. In particular, the 1H phase of TMD monolayers with MX₂ (M = Mo, W and X = S, Se) stoichiometry has a direct bandgap at the high symmetry K (K′) points of the Brillouin zone\(^1\). Due to strong two-dimensional (2D) confinement, Coulomb bound electron-hole pairs, commonly known as excitons, can be formed upon optical excitation within the light cone at the K (K′) points, where they would subsequently undergo radiative recombination to yield photoluminescence (PL)\(^2\). However, the quantum yield (QY) of monolayer (1L)-MX₂ is fundamentally limited by various nonradiative decay pathways. This includes the conversion of bright excitonic states into spin- and valley-forbidden states (dark states)\(^3\). Numerous efforts have been recently made to improve the QY through investigating and/or even controlling the limiting mechanisms. It was found that as-exfoliated semiconducting TMDs, such as 1L-WS₂ and 1L-MoS₂, are inherently n-type, which have excess free carriers and thus promote the formation of trions and their nonradiative recombination\(^4\). In addition, the presence of boads of defects in 1L-TMDs (especially chalcogen vacancies, \(\sim 10^2 \text{cm}^{-2}\)) can serve as nonradiative recombination centers leading to low QYs\(^5\). Various methods such as defect passivation or charge transfer were proposed to improve the QY\(^7,10-14\). For example, a near-unity QY in sulfur-based 1L-MoS₂ has been reported through passivation of defect-mediated nonradiative recombination by super-acid treatment\(^12\) and atomic healing of sulfur vacancies were also observed by scanning transmission electron microscopy\(^10\). The current understanding is that the compensation of n-doping, such as via chemical treatment or by electrostatic doping, restores the predominance of neutral excitons, and therefore, enhance the PL efficiency of the 1L-TMDs\(^12-14\).

However, even in the ideal pristine 2D MX₂, the QY can still be quenched when the exciton-exciton interaction dominates to cause strong exciton Auger recombination, so-called exciton-exciton annihilation (EEA)\(^15-19\). This density-dependent fundamental process occurs at high exciton densities under strong light illumination. Most notably, experimentally reported EEA rate constants revealed a very large variation across different device configurations with values ranging from a few \(10^{-3}\) \(\text{cm}^2/\text{s}\) to \(10^{-3} \text{cm}^2/\text{s}\) for 1L-WS₂. These reported EEA rate constants are also orders of magnitude higher than those typically observed in semiconducting quantum-well systems\(^20\). Since electroluminescence (EL) in 2D TMDs arises as a consequence of radiative excitonic transition\(^21\), EEA practically determines the quantum efficiency of a light-emitting device at the exciton density under typical brightness\(^22,23\). Without question, the EEA process represents one of the key technological bottlenecks for achieving energy-efficient and bright EL devices even in otherwise pure, high-quality samples\(^8\). Despite experimental reports that the use of high-index substrates\(^24\) or hBN encapsulation\(^15,25\) resulted in largely reduced EEA rates in 1L-TMDs accompanied by the relative increase of PL, its physical origin was not well understood. Active suppressions of EEA were reported through the intentional formation of defects\(^8,27\) or by applying the strain\(^28\). Fundamental understanding of EEA, and strategies in alleviating EEA and the accompanying QY drooping at high exciton densities are of utmost importance to high-efficiency light-emitting devices.

Although an exciton in the 1s state is charge neutral and has no higher multipole moments, it can assume an induced dipole moment by the presence of other exciton. As schematically depicted in Fig. 1a, the dipolar interaction between the electron-hole pairs that form the excitons and its Coulombic fields can be strongly influenced by the presence of a proximal metallic plate because the image dipoles in the metal renders exciton-exciton interaction essentially quadrupolar. In this work, we provide the first systematic study of EEA and QY enhancement in this device geometry using ultra-flat Au substrates with atomically controlled hBN spacers. Our simple approach of controlling the exciton interaction via proximal metal plates provides an efficient and feasible route towards practical applications using highly efficient light-emitting devices derived from 1L-TMDs.

Results and discussion

Substrate-dependent PL intensity at low-density regime. Figure 1a illustrates a schematic of the sample configuration, with 1L-WS₂ prepared on an ultra-flat Au surface separated by a multilayered hBN spacer to serve as an insulating barrier, compared with 1L-WS₂ directly on SiO₂. Coulombic fields between two excitons would be substantially suppressed by metallic screening due to the presence of the Au substrate. Our goal is to investigate the anticipated reduction in Auger scattering between excitons, or EEA, due to such screening. In Fig. 1b, c, the atomic force microscopy (AFM) image and the PL intensity map of the actual sample are shown, respectively, where the thickness of the hBN layer on the Au surface was measured to vary in the range of 7–36 nm. We used the low laser power of 2 nW to assess the QY without the effect of EEA. The PL spectra of 1L-WS₂ obtained on the SiO₂/Si substrate and on Au at several hBN thicknesses are displayed in Fig. 1d. As shown in Fig. 1c, d, we observed that the PL intensity is highly dependent on the hBN thickness, where the corresponding PL intensities are summarized in Fig. 1e as a function of hBN thickness. Multiple samples were investigated, and the measured data obtained from the different 1L-WS₂ flakes are denoted by different symbols. We found that the PL intensities of 1L-WS₂ samples showed a consistent general trend, namely, a gradual increase of PL with the hBN thickness up to an optimum thickness of 33 nm, followed by a rapid decrease beyond this value.

Optical interference has to be accounted for in order to understand the origin of the measured changes in the PL intensity. The detected PL is proportional to both the optical absorption and the exciton emission yields of 1L-MX₂, hence it is critically affected by optical interference due to the multi-layered substrate\(^29,30\). To properly account for the optical interference effect, we modeled the optical enhancement factor (EF) as a function of hBN thickness on the Au substrate relative to the control configuration of air-suspended 1L-WS₂ using the Fresnel equation under normal incidence\(^29\) (Details for the estimation of the EF are described in the Supplementary Information). The estimated EF is overlaid (red line) with the measured PL-intensity data in Fig. 1e. The calculated EF corroborates very well with the measured PL intensity, indicating that the optical interference effect dominates the observed PL dependence on the hBN thickness. Differential reflection spectra of 1L-WS₂ also confirmed stronger absorption at thicker hBN on the Au substrate and we showed that the effect of the hBN thickness on the measured PL intensity can be nearly flattened by encapsulating 1L-WS₂ with thick (~50 nm) hBN (Supplementary Figs. 2 and 3 in the Supplementary Information).

For direct comparison, we measured the PL intensity of 1L-WS₂ on the SiO₂/Si substrate, which is denoted by the star on the left vertical axis in Fig. 1e. At first glance, it seems that the relative PL intensity from 1L-WS₂ on 7 nm hBN/Au is 2.5 times higher than that from 1L-WS₂ directly on the SiO₂/Si substrate (Fig. 1d, e). However, we confirmed that the actual QY of the former is about five times larger since the SiO₂/Si substrate gains the PL brightness via the EF by more constructive interference of multiple internal reflections, as denoted by the star on the right vertical
Substrate-dependent PL lifetime at the low-density regime. The proximal Au surface also showed a notable impact on the lifetime of photoexcited excitons in 1L-WS₂. We first considered the low photo-excitation regime where EEA can be neglected. Figure 2a shows the PL intensity map of 1L-WS₂ flakes prepared on the SiO₂/Si substrate, of which some parts are sitting on the hBN spacer of 27 nm in thickness (highlighted by the white dashed line in Fig. 2a). As shown in the PL intensity map (Fig. 2a) and the representative PL spectra obtained from 1L-WS₂ on SiO₂/Si and hBN/SiO₂/Si (Fig. 2b), the PL intensity from 1L-WS₂ on hBN/SiO₂/Si was lower than its counterpart on SiO₂/Si, whose difference can be accounted for by the optical interference effect (See the Supplementary Information). In 2D research community, hBN is frequently used as substrate and encapsulation layers for TMDs, since it preserves the pristine quality of TMDs and has the effect of refining the spectral properties such as narrowing of the spectral linewidth⁵,²⁵,²⁶,³⁵,³⁶. However, the role of hBN on the PL lifetime is rarely discussed. It was recently argued that hBN encapsulation alleviates EEA but also leads to an overall reduction in the PL lifetime⁵. A separate study also reported the reduction of the PL lifetime in hBN-encapsulated 1L-WS₂ and attributed it to enhanced exciton diffusion towards non-radiative traps⁶.

We measured the PL lifetimes of 1L-WS₂ on hBN/SiO₂/Si and SiO₂/Si by time-resolved photoluminescence (TRPL), and their representative PL decay curves are shown in Fig. 2c. The extracted PL lifetimes were found to be 940 ± 65 ps and 143 ± 38 ps for the SiO₂/Si and hBN/SiO₂/Si substrates, respectively, as shown in Fig. 2e. Due to the very low pump fluence of 2.6 nj/cm² (corresponding to an initial exciton density of 3.6 × 10⁹ cm⁻²), EEA can be ignored and the PL decay curves indeed exhibit a simple trend of a single exponential decay. In this regime, the PL lifetime of 1L-TMDs should be mainly determined by the rate of nonradiative capture by lattice defects⁹. The reduced PL lifetime of 1L-WS₂ on hBN/SiO₂/Si is consistent with the previous studies²⁵,²⁶.
Fig. 2 Excitonic PL at the low-density regime. a PL intensity image and b PL spectrum of 1L-WS2 on SiO2 (dark blue) out of the white dashed region in a and that for 1L-WS2 on hBN/SiO2 (dark red) from the dashed area in a, respectively. The scale bar in a corresponds to 4 μm. Normalized TRPL data obtained at an exciton density below $5 \times 10^{12} \text{cm}^{-2}$, free from EEA, from c 1L-WS2 on SiO2 (dark blue) and hBN/SiO2 (red) and d 1L-WS2 on Au (orange) and hBN/Au (black), respectively. Corresponding PL lifetimes are shown with the values in e and f with the same colors of the substrate conditions in c and d. The schematic structures of the samples are displayed, in which the solid lines are the guides to the eye. The colored shades in a and d indicate the range of the data trace, and the error bars in e and f indicate the standard deviation, observed from other samples with the same geometries.

Then, we examined the PL lifetimes for Au substrates. Figure 2d, f show the PL decay curves and the average PL lifetimes obtained from 1L-WS2 on hBN/Au, and directly on Au. The PL lifetimes of 1L-WS2 prepared on hBN/Au and Au exhibit average lifetimes of 1008 ± 220 ps and 897 ± 89 ps, respectively, which are comparable to the values of 1L-WS2 prepared on the SiO2/Si substrate. We observed similar trends for all the thicknesses of hBN below 20 nm, including the case for no hBN layer on the Au substrate. To the best of our knowledge, this is the first observation of the PL lifetime increase in 1L-TMDs on hBN due to the proximal Au surface. Our observation here reconciles with the concurrent enhancement of the PL efficiency due to electron depletion discussed previously in Fig. 1f, g and similarly to the PL enhancement in n-type 1L-MoS2 and 1L-WS2.

**PL lifetime vs. exciton density and hBN thickness.** We now discuss the effect of the Au substrate on the exciton dynamics in 1L-WSe2 at high exciton densities, where exciton-exciton interaction cannot be neglected. We obtained the PL transients for different exciton densities by varying pump fluences (labeled with colors shown in the legend) for our samples with hBN thicknesses of 36, 16, and 7 nm between 1L-WSe2 and Au. The corresponding normalized time traces are displayed in Fig. 3b–d. The normalized PL transients of 1L-WSe2 on the SiO2 substrate are included for comparison in Fig. 3a. As the density of photoexcited excitons in 1L-WSe2 increases, the PL decay time gradually decreases, and such density-dependent exciton decay is characteristics of EEA in 1L-TMDs.

While Fig. 3b-d clearly show that the PL lifetimes decrease with increasing exciton densities on hBN/Au substrates, the overall effect is weaker for thinner hBN layers. For example, the short component of the PL lifetime of 1L-WSe2 on the 7-nm-thick hBN on the Au surface decreased from 919 ps at $1.24 \times 10^{8} \text{cm}^{-2}$ to only 376 ps at $1.44 \times 10^{11} \text{cm}^{-2}$, which is a much smaller reduction (by about factor of 3) as compared to that of the sample on the SiO2 substrate, where it decreases from 890 ps at $8 \times 10^{8} \text{cm}^{-2}$ to 122 ps at $1.95 \times 10^{11} \text{cm}^{-2}$. To quantify the density-dependent PL decay rate, we used the rate equation to fit the PL decay curves:

$$\frac{dn_{ex}}{dt} = -\frac{n_{ex}}{\tau_{0}} - \gamma n_{ex}^{2},$$

where $n_{ex}$ is the exciton density, $\tau_{0}$ is the measured PL lifetime at a low exciton density, and $\gamma$ is the EEA rate constant. The solution to Eq. (1) can be simplified to $n_{ex}(t) = \gamma \tau_{0} \exp(t/\tau_{0})$, where the coefficient $\gamma$ is extracted from the slope of $\ln(n_{ex}(t)/\tau_{0})$ vs $\exp(t/\tau_{0})$ as shown in Fig. 3e (Justification of this approach is provided in the Supplementary Information). Figure 3f shows the plot of the estimated $\gamma$ value vs. the hBN thickness. Note that $\gamma$ of 1L-WSe2 on SiO2 of $(1.26 \pm 0.40) \times 10^{-11} \text{cm}^{2} \text{s}^{-1}$ is consistent with previous reports on 1L-WSe2. Such strong exciton interaction will critically degrade the QY of 1L-TMDs at high exciton densities. The estimated $\gamma$ value for 7-nm-thick hBN on the Au surface, however, was only $(1.78 \pm 0.94) \times 10^{-12} \text{cm}^{2} \text{s}^{-1}$, an order of magnitude lower than $\gamma$ of that prepared on the SiO2 substrate. The dramatic improvement in the exciton lifetime at high exciton densities strongly suggests that the Au surface is very effective in screening the exciton-exciton interaction, rendering EEA much less effective. Particularly, directly on the Au surface where the metal screening should be maximized, $\gamma$ was measured to be $(5.43 \pm 0.61) \times 10^{-2} \text{cm}^{2} \text{s}^{-1}$, which is larger than those on the hBN layers on Au. We believe that the direct contact of 1L-WSe2 to the Au surface may have affected the measurement of $\gamma$ through the possible charge inhomogeneity of the Au surface and the expedited exciton decay due to energy or charge transfer. (We ignore hereafter the $\gamma$ value for direct contact with Au in discussing the trend of $\gamma$ with the thickness of hBN.) Regardless,
we emphasize the robust general trend of decreasing $\gamma$ with the increased proximity of 1L-WS$_2$ to the metal substrate. The PL measurement of hBN-encapsulated 1L-WS$_2$ on Au also confirmed that the effect of metal proximity suppressing EEA is higher at thinner hBN on Au (Supplementary Fig. 4).

Enhanced absolute QY by suppressed EEA. To quantitatively assess the effect of metal screening on exciton emission of 1L-WS$_2$ at high exciton densities, we measured the absolute QY (a-QY), the ratio of the emitted photon number to the absorbed photon number, of 1L-WS$_2$ prepared on the Au surface with the 7-nm-thick hBN spacer as a function of generation rate (Fig. 4a) (Details for the a-QY measurement of 1L-WS$_2$ and the estimation of the generation rate from the excitation intensity are described in the Supplementary Information). The a-QYs of 1L-WS$_2$ either on hBN/Au or SiO$_2$ substrates exhibit a stiff droop, regardless of the substrate configuration, as the excitation or exciton density increases, which is typical of EEA. However, the onset of the QY droop for the two cases is quite different; more specifically, the QY droop in the hBN/Au substrate occurred at much higher excitation levels, herein found to be more than an order of magnitude higher, strongly supporting the conclusion that EEA is effectively suppressed in this structure. For example, we provide the PL spectra of 1L-WS$_2$ (adjusted with the substrate effect on absorption and emission to show the relative QYs) on hBN/Au (black) and on SiO$_2$/Si (orange) at $G$ of $\sim 6.8 \times 10^{16}$ cm$^{-2}$s$^{-1}$ and $\sim 7.5 \times 10^{20}$ cm$^{-2}$s$^{-1}$ (indicated with the light blue arrows in Fig. 4a) in Fig. 4b, c, where 3 times and 18 times enhancements in the a-QY were observed, respectively, clearly demonstrating the role of the hBN/Au substrate in effectively screening the Coulomb interaction between excitons, thereby suppressing EEA.

Theoretical model and analysis. In what follows, we present a theoretical model to understand the effects of the proximal metal gate on EEA and the QY. From classical electrostatics, the introduction of a perfect conductor (i.e., a metal) in a system containing charges screens the electrostatic fields. The reason for
Fig. 4 Enhanced QY by suppressed EEA. a a-QY of 1L-WS2 on hBN (7 nm)/Au (black dots) and SiO2/Si (orange dots) under the generation rate (G) varying from 2 × 10^{16} cm^{-2} s^{-1} to 2 × 10^{21} cm^{-2} s^{-1} with the substrate interference effects properly taken into account. The solid curves with each color code are fits to the experimental QY calculated with Eq. (5). The dotted lines are guides for eyes and mark the points where the QY droop starts (grey arrows). b and c PL spectra of 1L-WS2 on hBN (7 nm)/Au (black) and SiO2/Si (orange) at the G value indicated by light blue arrows in a. The PL spectra are adjusted with the substrate interference effect to show the relative a-QY's.

this is that the metal effectively creates mirror charges opposite to the original ones, transforming the charges and dipoles in the original system effectively into dipoles and quadrupoles, respectively, which renders the electric fields to be more screened and short-ranged\(^{38}\). In the case investigated here, where charges are in a monolayer semiconductor separated from the metal by an hBN spacer, a treatment involving image charges becomes less clear and the screened interaction potentials are more conveniently obtained by solving the Poisson equation, taking account of the various numbers of hBN layers on Au. We consider a system consisting of four regions, each with a distinct dielectric constant, representing the metal (Au), multilayer hBN, 1L-WS2 and vacuum. The solution of the electrostatic potential due to an electron at the 1L-WS2 region is:

\[
\Phi(\rho, z) = \frac{e}{4\pi\varepsilon_0} \int_0^\infty dk I_0(k\rho)\frac{\epsilon(k)}{\epsilon(k)}.
\]

(2)

where \(I_0(k\rho)\) is the zeroth-order Bessel function of the first kind and \(\epsilon(k) = \epsilon_{WS2}/[A(k)e^{kz} + B(k)e^{-kz} + 1]\) is the static dielectric function in reciprocal space. \(A(k)\) and \(B(k)\) are coefficients to be determined through the application of the electrostatic boundary conditions at the interfaces between vacuum, 1L-WS2, hBN and Au, and were calculated using a transfer matrix scheme proposed in ref. \(^{39}\). A similar approach has been proposed also in ref. \(^{40}\). The only parameters needed for such calculation are the thickness and dielectric constants of 1L-WS2 and hBN layers, which can be found in ref. \(^{39}\). The metal is accounted for by setting its dielectric constant to infinite as a boundary condition at the interface between hBN and Au. Note that the \(A(k)\) and \(B(k)\) coefficients depend on the size of the multilayer h-BN region, since its variation implies the changes in the h-BN/WS2 and WS2/vacuum interface positions. The electrostatic interaction between the source electron and a hole in the same region (\(z = 0\)) at a distance \(\rho\) from the origin is thus \(V_{\text{el}}(\rho) = e\Phi(\rho)\). It can be straightforwardly demonstrated that the electrostatic potential in Eq. (2), with the effective \(\epsilon(k)\) calculated as previously described\(^ {39,40}\) exhibits all the expected limits: it converges (i) to the Rytova-Keldysh form\(^ {31,42}\) (i.e. with \(\epsilon(k)\) linear in \(k\)) in the limit of infinitely thick hBN spacer (i.e. when the screening due to the metal is negligible), (ii) to the Coulomb interaction potential in the presence of image charges, previously used in calculations for e.g. plasmons in graphene\(^ {43}\), in the limit of an infinitely thin WS2 slab, and (iii) to the Coulomb interaction potential (i.e. with constant \(\epsilon(k) = \epsilon_{WS2}\)) in the limit of an infinitely thick WS2 slab.

To calculate the electrostatic potential between two excitons, we first sum the contributions of all pairs of charges

\[
V_{XX}(\rho_{\alpha\beta}; \rho_{\beta\gamma}; \rho_{\gamma\delta}; \rho_{\delta\alpha}) = \frac{e}{2}\left[\Phi(\rho_{\alpha\beta}) + \Phi(\rho_{\beta\gamma}) - \Phi(\rho_{\gamma\delta}) - \Phi(\rho_{\delta\alpha})\right],
\]

(3)

where the arguments represent the electron-electron, hole-hole, and electron-hole distances, respectively. Note that interactions between charges with the same (opposite) sign are positive (negative) due to the repulsive (attractive) force between them.

From here onward, we follow two approaches to investigate the effect of Au and hBN on EEA. In the first one, we model EEA as a nonradiative scattering problem between two excitons. Several pathways of Auger processes can lead to nonradiative exciton-exciton scattering: for example, one can consider an Auger process where the interaction between electrons in the conduction band of two different excitons lead to a final state where one of the excitons recomines, while its energy is used to ionize the other exciton, resulting in a hot unbound electron-hole pair in the final state. Other possibilities involve interactions between electrons in conduction and valence bands, and/or phonons\(^ {44,45}\). We simplify our discussion by assuming, as an approximation, only the former case of scattering, as illustrated in Fig. 5a, which we refer to as the direct Auger process. Other processes are expected either to behave similarly as we increase the hBN thickness, or to exhibit negligible contributions. We point out that, despite the fact that we have an initial state composed by two excitons and a final state with a single electron-hole pair in our model, recombinaction of the first exciton still preserves charge and spin in the overall process. In what follows, as well as in the Supplementary Information, we will use similar notation as in refs. \(^ {19,44,45}\), where more details on the theoretical model for such direct Auger process can be found.

According to Fermi’s golden rule, the scattering time is inversely proportional to the scattering probability which, for the direct Auger process considered here, is given by

\[
\frac{1}{\tau_{\text{EEA}}} = \frac{2\pi}{\hbar} \sum_k |M_{\text{dir}}(K_1 + K_2, K_2, K_1)|^2 \left[ E_k - 2E_B + E_K(K_1) \right] \\
+ E_K(K_2) - E_K(K_1) - 2\hbar^2k_f^2/M \int f(K)f(K_2),
\]

(4)

where \(\tau_{\text{EEA}}\) is the Auger lifetime of excitons, \(f(K)\) is the Boltzmann distribution function for classical exciton gas\(^ {19}\), \(E_K(K) = (k_f^2 - k_0^2)/2M\) is
the kinetic energy of the exciton, \( M \) is the effective exciton mass, \( E_x \) is the quasi-particle gap, \( E_b \) is the exciton binding energy, and the sum is made over different values of initial momenta \( K_1 \) and \( K_2 \) of the initial pair of excitons. While the Dirac delta function in Eq. (4) accounts for the conservation of energy, momentum conservation is imposed in the scattering matrix term \( M_{\text{dir}} \), whose calculation is demonstrated in detail in the Supplementary Information. The scattering matrix term encodes the electron-electron interaction potential and exciton envelope wave functions, which are both affected by the metal screening, thus rendering \( \tau_{\text{EEA}} \) effectively dependent on the hBN thickness, i.e. on the proximity to the Au substrate.

As an alternative approach to understand the observed reduction in the EEA rates as the 1L-WS\(_2\) is made closer to the Au substrate, we investigate how screening due to the metal affects exciton-exciton pair interactions. In order to do so, we numerically solve the Schrödinger equation, within the Wannier-Mott model, for the two-exciton system, whose screened interaction potential is given by Eq. (3). Details of this calculation are provided in the Supplementary Information. As an approximation, we consider pairs of excitons separated by a distance \( R \) given, on average, by the inverse of the square root of the exciton density. Results are shown as the blue squares in Fig. 5b, where the dependence of the exciton-exciton interaction energy on the hBN thickness is shown together with the experimental EEA rate constants (black squares) and the theoretically estimated EEA rate constants (red stars) considering the direct Auger rate calculated by Eq. (4), for the sake of trend comparison.

Indeed, the nonradiative Auger scattering rate is indicated to be significantly reduced by the proximity to the metal, which corroborates with our experimental observation as shown in Fig. 5b. These results also indicate that 1L-hBN layer on Au could provide a much stronger screening than \( N = 21 \) (smallest hBN thickness in our measurement), suggesting the efficacy to suppress EEA and boost the QY with our scheme by further reducing the thickness of hBN. As shown in Fig. 5b, the measured EEA rate constants at various hBN thicknesses on Au and on SiO\(_2\) substrates via the TRPL experiment follow the same trend as the theoretical ones via direct Auger scattering calculated with Eq. (4), with a single scaling factor, as well as the exciton-exciton interaction energy (see the right blue vertical axis) calculated at the exciton density of \( 1 \times 10^{11} \text{ cm}^{-2} \).

Furthermore, we related the a-QYs measured by CW laser excitation to the EEA rate by deriving an expression for the a-QYs from the rate equation\(^{46}\):

\[
QY = QY_0 \left( 2 \sqrt{1 + \frac{G_0}{G_\text{th}}} - 1 \right) \tag{5}
\]

where \( QY_0 \) is the QY at the low excitation intensity (non-EEA regime) and \( G_0 = 1/4\gamma\tau_0^2 \). In Fig. 4a, we showed the results of fitting the QY versus \( G \) to data to Eq. (5) with the EEA rate constants as fitting constants for hBN thickness of 7 nm on Au and for SiO\(_2\)/Si substrate. The EEA rate constants determined from fitting the a-QY measurement obtained by CW laser excitation are somewhat higher than those determined via time-resolved measurements that used pulsed excitation. This discrepancy was also observed previously\(^{26}\) and could originate from transient reduction of the exciton density due to diffusion of exciton at the central part of laser excitation in the TRPL measurement. However, the qualitative trend of increasing EEA rates with hBN thickness are observed in both CW and pulsed excitations, as shown in Fig. 5c.

In summary, we have demonstrated that exciton-exciton interaction and annihilation in 1L-WS\(_2\) can be effectively screened by using hBN/Au substrates, improving the QY by more than an order of magnitude in the high exciton density regime. Spectroscopic signatures of PL intensity and lifetime, and EEA rate constants, all showed the systematic dependence on the atomic thickness between 1L-WS\(_2\) and Au plate, whose qualitative features can be accounted by exciton-exciton scattering calculations, involving a nonradiative Auger-like process, for interacting charges in 1L-WS\(_2\) in proximity to a metal. Our result provides a simple scheme to regulate the fundamental process of EEA and paves the way for highly luminescent 2D light-emitting devices based on 2D-TMDs.

**Methods**

**Sample preparation.** hBNs and 1L-WS\(_2\) were mechanically exfoliated onto PDMS from bulk crystals\(^{45}\); WS\(_2\) bulk crystals were purchased from HQ graphene and hBN bulk crystals were provided by the National Institute for Materials Science, Japan. Exfoliated hBN flakes on PDMS generally come in various thicknesses and were identified by an optical microscope and subsequently pressed and peeled off.
onto ultra-flat Au substrates (Platypus Technologies) or a 300-nm-thick SiO2 layer on a Si wafer at the substrate temperature of 100 °C. Here, ultra-flat Au substrates were used to reduce the substrate roughness which may induce strain or incidental doping to 1L-WSe2. Our samples were then annealed at 150 °C in a vacuum oven for 12 h. The PL from the exfoliated 1L-WSe2 on PDMS was measured before the transfer. 1L-WSe2 samples were subsequently transferred onto the hBN/Au or hBN/ SiO2/Si substrates kept at 70 °C and then were annealed at 70 °C in the vacuum oven for 1 h. The thicknesses of hBN flakes were confirmed by atomic force microscopy (XE-120, Park Systems).

Optical measurements. PL images and spectra were obtained with a commercial confocal microscope (Alpha-300s, WITec Instrument GmbH) equipped with a 100x objective lens (N.A. = 0.9) and a frequency-doubled neodymium-doped yttrium aluminum garnet laser for 532 nm CW excitation. For TRPL measurements, the same microscope was used under pulsed excitation at 488 nm (BDL-800, Becker & Hickl GmbH), with the pulse width of 70 ps and the repetition rate of 80 MHz and an high-speed hybrid detector (HPM-100-40, Becker & Hickl GmbH) and a time-correlated single-photon counting module (TCSPC, Becker & Hickl GmbH). All measurements were conducted at room temperature.

Data availability. All data are available within the Article and Supplementary Files, or available from the corresponding authors on reasonable request.

Code availability. Codes used in the theoretical calculation are available from the corresponding authors on reasonable request.

Received: 15 October 2020; Accepted: 18 November 2021; Published online: 07 December 2021

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PRONEX/FUNCAP and PQ programs. A. Chaves also acknowledges financial support by the Research Foundation - Flanders (FWO). A. Chernikov gratefully acknowledges financial support by Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through SFB 1277 (Project-ID 314695032) project B05, Emmy-Noether Grant CH 1672/1 (Project-ID: 28702282), and the Würzburg-Dresden Cluster of Excellence on Complexity and Topology in Quantum Matter ct.qmat (EXC 2147, Project-ID: 390858490). K.W. and T.T. acknowledge support from the Elemental Strategy Initiative conducted by the MEXT, Japan (Grant Number JPMXP0112101001), JSPS KAKENHI (Grant Numbers 19H05790, 20H00354 and 21H05233) and A3 Foresight by JSPS.

Author contributions
T.L. and J.K. conceived and supervised the project, analyzed the data, and wrote the manuscript. T.T.T. and Y.K prepared the samples, performed the optical measurements. Y.L. analyzed the data and wrote the manuscript; J.D.S.F., A. Chaves, A.K., and T.L. performed theoretical calculation and wrote the manuscript. S.R. and Y.L. measured QY. T.T. and K.W. synthesized and discussed the role of high-quality hBNs. A. Chernikov and J.I.J. analyzed the data and wrote the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-021-27418-x.

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Peer review information Nature Communications thanks the anonymous reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

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