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Engineering Light Outcoupling in 2D Materials

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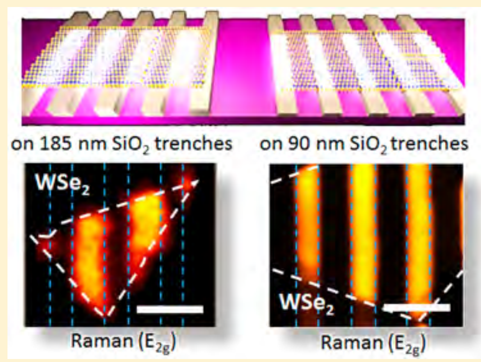
Supporting Information

ABSTRACT: When light is incident on 2D transition metal dichalcogenides (TMDCs), it engages in multiple reflections within underlying substrates, producing interferences that lead to enhancement or attenuation of the incoming and outgoing strength of light. Here, we report a simple method to engineer the light outcoupling in semiconducting TMDCs by modulating their dielectric surroundings. We show that by modulating the thicknesses of underlying substrates and capping layers, the interference caused by substrate can significantly enhance the light absorption and emission of WSe_2, resulting in a ∼11 times increase in Raman signal and a ∼30 times increase in the photoluminescence (PL) intensity of WSe_2. On the basis of the interference model, we also propose a strategy to control the photonic and optoelectronic properties of thin-layer WSe_2. This work demonstrates the utilization of outcoupling engineering in 2D materials and offers a new route toward the realization of novel optoelectronic devices, such as 2D LEDs and solar cells.



KEYWORDS: *2D materials, light outcoupling, substrate interference, photoluminescence, Raman*

Atomically thin two-dimensional (2D) transition metal dichalcogenides (TMDCs), such as MoS_2 and WSe_2, have recently positioned themselves as strong candidates for future optoelectronics.[1−5] When assessing the optical, electronic, and structural properties of these materials, micro-Raman and photoluminescence (PL) spectroscopies are often considered as quick and nondestructive methods. These techniques allow for the emission intensity and the peak energy position of emitted photons to be examined, which provide an informative matrix for evaluating the quality of materials.[6−8] Previously, it has been demonstrated that suspending the 2D materials can enhance the resolution of their optical signals. For example, suspended graphene and MoS_2 have shown enhanced PL/Raman signals, which are attributed to the diminishment of detrimental interactions between the materials and substrates, such as nonradiative recombination, charge transfer, and excitonic transitions.[9−13] On the other hand, the dielectric surroundings around the atomically thin 2D materials could optically regulate the incoupling and outcoupling of light, yielding a dramatic variation of the emission intensity.[14−17] However, the effect has not been explored in detail and is often overlooked. In this study, we show that the PL/Raman emission intensity of suspended 2D materials could be either enhanced or suppressed depending on the thickness of the underlying substrates or the depth of the trenches for suspended samples. Through modeling and experiments, we comprehensively investigate the roles of underlying substrates and surface coatings and their optical interference effects on TMDCs. By modulating the thickness of underlying substrates and capping layers, the absorption and emission of light can be engineered, giving tunable PL and Raman intensities by up to 11 and 30 times, respectively. Our results suggest an extremely simple way to significantly enhance the outcoupling of thin-layer TMDCs, which is crucial for optoelectronic devices built with semiconducting TMDCs, such as 2D LEDs, lasers and photonic components. Most notably, the concept enables the control of 2D materials' photonic properties, which provides design criteria for their photonic and optoelectronic components.

In an effort to improve the light−matter interaction, incorporating plasmonics and microcavities with 2D materials

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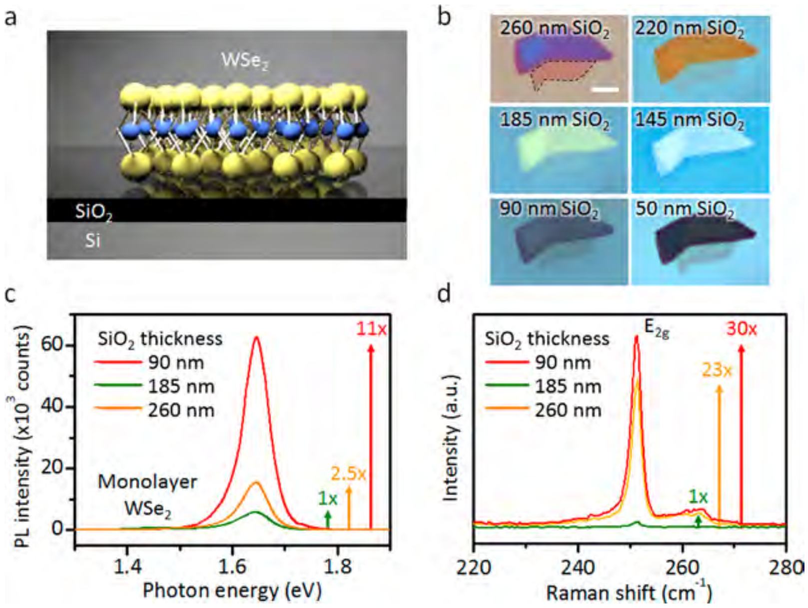

Figure 1. (a) Schematic of a single-layer WSe_2 on a SiO_2/Si substrate. (b) Optical images of a WSe_2 flake transferred onto SiO_2/Si substrates with different SiO_2 thicknesses. The white scale bar in the figure indicates 10 μm. (c) PL and (d) Raman spectra of WSe_2 flakes on substrates with 90, 185, and 260 nm SiO_2.

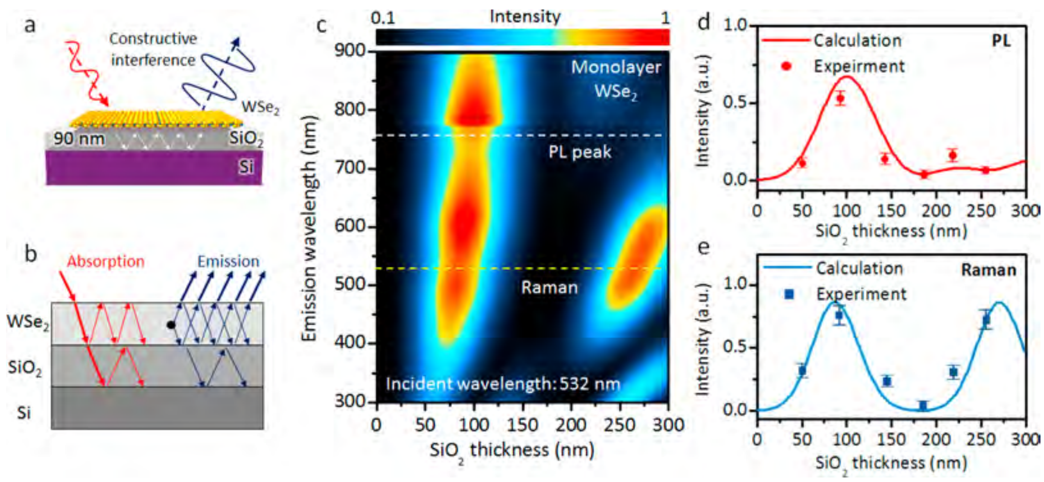

Figure 2. (a) Illustration of the outcoupling mechanism considering absorption and emission of light. (b) Illustration of the multiple reflections within the structure and the optical paths for absorption and emission processes. (c) Intensity map for light outcoupling as a function of both the emission wavelength and the SiO_2 thickness. Experimental and calculation results of (d) PL (at 752 nm) and (e) Raman (532 nm) scattering intensities.

has proven to be viable for facilitating the light incoupling so as to achieve improved absorption.[18−20] Another intuitive approach improved the interaction by modifying the dielectric surrounding of TMDCs.[15,16] Substrate interference has been applied in the past as a simple way to precisely quantify the thickness of SiO_2 films grown on Si substrates by evaluating its reflection color.[21] Such effects have also been used to tune the contrast/visibility/color of graphene and MoS_2 on Si/SiO_2 substrates, which allows monolayers to be seen and thicknesses to be identified under an optical microscope.[22,23] Here, we demonstrate that engineering substrate interferences can be also used to enhance the light outcoupling of 2D materials, which is applicable to all 2D materials systems. WSe_2 is used for this demonstration because of its distinct PL and Raman responses and its well-studied optical properties. WSe_2 flakes were prepared by micromechanical exfoliation and characterized by atomic force microscopy to identify the number of atomic layers (NL) of each flake. Then the flakes were transferred onto different substrates using poly(methyl methacrylate) (PMMA) as the transfer medium.[24] Figure 1a and b present the aforementioned schematic and optical images of a WSe_2 flake transferred on SiO_2/Si substrates with different SiO_2 thicknesses. When sitting on different substrates, the color contrast of the monolayer WSe_2 shows apparent differences, indicating the interference between the substrate and flake is wavelength-dependent. Theses color changes also imply that the light output intensity can vary with respect to the emission wavelengths. To verify these phenomena, we examine the PL and Raman spectra of the same monolayer WSe_2 on different substrates, as shown in Figure 1c and d. For PL measurements, peak values are at 1.65 eV, corresponding to the bandgap of WSe_2 monolayers.[6,25] In addition, the Raman peak at ~250

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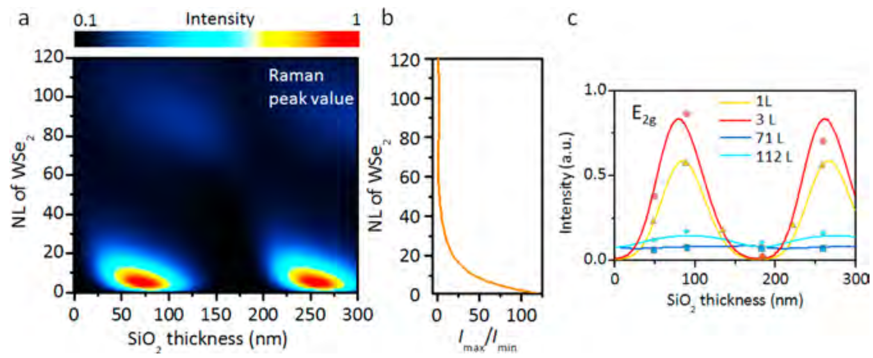

Figure 3. (a) Calculation of the thickness-dependent Raman intensities for WSe_2. (b) Enhancement ratio (I_{max}/I_{min}) extracted from the relative intensity map. (c) Calculation and experimental results for WSe_2 as a function of NL.

cm^{-1}, corresponding to the E_{2g} in-plane atomic vibration mode, is examined in this study. Note that all samples performed in this study were carried out under identical measurement conditions (see Methods). Due to the different emission wavelengths for PL and Raman measurements, their enhancements depend differently on SiO_2 thickness. The PL intensity of WSe_2 on 90 nm SiO_2 is enhanced the most, by 11 times, when compared to its PL on 185 nm SiO_2, whereas its Raman signal is enhanced the most, by 30 times, on 260 nm SiO_2 substrates. Note that the intensity change is reversible, as demonstrated by transferring the flake back onto the previous substrates (Supporting Information Figure S1). Here, sample-to-sample variation could be eliminated because the dry-transfer method used allowed for the same flake to be measured. We also show that the Raman intensity changes without a measurable peak shift, indicating that strain does not play a significant role in these results.[6]

The enhancement of light outcoupling assisted by substrate-induced light interferences can be explained simply by employing the multiple reflection model, as shown in Figure 2a and b.[25,26] Considering multiple interfaces in this structure, incident light will encounter the boundaries of PMMA/WSe_2, Wse_2/SiO_2, and SiO_2/Si, undergoing multiple reflections. The four media, including PMMA, WSe_2, SiO_2, and Si, are denoted as i = 0, 1, 2, and 3, respectively (Figure 2b). As both the absorption and emission are taken into account, the intensity of light outcoupled from the WSe_2 layer can be deduced as

$$I = \int_0^d |E_{ab}(x)E_{em}(x)|^2 dx$$

where d is the thickness of the flake, and $E_{ab}(x)$ and $E_{em}(x)$ are the electric field amplitudes within the flakes and light emitting out the flakes, respectively (Supporting Information S2). Note that according to previous reports,[16] the oblique incidence caused by the objective (numerical aperture = 0.9) will only lead to minute changes in the spectral response, so the assumption of a majority of normal incidence is still valid. We also note that this simplified model was used before to design substrates that increase the optical contrast between graphene and MoS_2.[16,26]

On the basis of the multiple reflection model, we are able to create a two-dimensional map quantifying the light outcoupling strength as a function of both the emission wavelength and SiO_2 thickness, as shown in Figure 2c. Here, the map presents the emission wavelength ranging from 300 to 900 nm and the SiO_2 thickness ranging from 0 to 300 nm. As shown in Figure 2d and e, the intensity at 752 nm (1.65 eV; direct bandgap emission of monolayer WSe_2) and 532 nm are specified, which correspond to the PL emission and Raman scattering wavelengths of WSe_2, respectively. For PL emission, the maximum intensity is seen at a SiO_2 thickness of ~90 nm. For Raman scattering, the maxima are at ~90 and 260 nm SiO_2 thicknesses. Those are in good agreement with the experimental results shown in Figure 1c and d. Note that changing the incident wavelength will produce a new set of light outcoupling maps based on the equations provided in the supplementary. The improved outcoupling is attributed to a combined effect of enhanced absorption and emission modulated by substrate-induced interference (Supporting Information Figure S3). Because the incident light is fixed (532 nm), the amount of light absorption is mainly governed by the Fabry–Perot interference, which shows a periodic variance with SiO_2 thickness. On the other hand, the strength of emission shows an irregular profile due to the combined effects of substrate interference and the wavelength-dependent refractive index. Enhanced outcoupling occurs when both absorption and emission meet constructive interference, which yields ~11 times enhancement of PL and 30 times enhancement of Raman compared to those in destructive cases.

The thickness of WSe_2 also has an effect on light outcoupling. Figure 3a shows a calculated Raman intensity map as a function of WSe_2 NL and SiO_2 thickness. For thinner flakes (NL < 10), two enhancement regions are located at the thicknesses of ~90 and 260 nm, corresponding to the constructive interference as mentioned above. To highlight the interference–NL dependence, the enhancement ratio (I_{max}/I_{min}) is plotted as shown in Figure 3b, where I_{max} and I_{min} are the maximum and minimum intensities, respectively, within the range defined in this map (SiO_2 thickness from 0 to 100 nm and NL from 1 to 120 L). The curve demonstrates that the enhancement becomes pronounced as the number of layers is reduced. For instance, the ratio for monolayer WSe_2 is over 100, whereas for the thicker flakes (NL > 30) the substrate effect is almost diminished (enhancement ratio <2). To compare the simulated maps with experiments, we measured the Raman (E_{2g}) intensity of 1, 3, 71, and 121 layers thick flakes on different substrates, as shown in Figure 3c. The NL of the flakes is obtained by AFM and then the flakes are transferred onto different substrates via the same technique described above. For NL = 1 and 3, the response shows apparent variance with changing SiO_2 thickness, whereas for NL = 71 and 121 the SiO_2 thickness dependence becomes weak. The results demonstrate that thinner layers are more sensitive to the substrate effect, agreeing well with the calculation shown in

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Nano Lett. 2015, 15, 1356–1361

Figure 3b. Note that the same effect is also valid for PL responses though a direct to indirect transition with increasing layers dominates the PL intensity rather than the substrate effect (see Supporting Information Figure S4).

From finite-difference time-domain (FDTD) simulations shown in Figure 4, a concentrated electric field is observed at the surfaces of 90 and 260 nm SiO_2 substrates, indicating that standing waves are formed. On the other hand, a valley of intensity is observed at the surface of a 185 nm SiO_2 substrate. The effect of the double layer structure is similar to a resonant cavity where a reflecting Si surface with a transparent SiO_2 layer can be regarded as a half cavity. When the substrate thickness equals a quarter the wavelength of incident light, the substrates provides constructive interference to facilitate the incoupling of light to flakes. It also shows that as the substrate thickness is varied, the electrical intensity within thinner WSe_2 (smaller window) will experience a more dramatic variation than the thicker WSe_2 (smaller window). Such a substrate effect will be minimized as the 2D materials become thicker than a quarter wavelength ($d = \lambda/4n$; $d = \sim 26$ nm corresponding to NL = 37),[14] in accordance with the observations shown in Figure 3. Recently, rise of advanced techniques in Raman spectroscopy, such as tip-enhanced Raman spectroscopy (TERS) and surface-enhanced Raman spectroscopy (SERS), have provided the ability to better resolve the absorbances, defects, and heterojunctions of 2D systems.[27] Compared to those techniques, this work provides an alternative strategy, namely, substrate-enhanced Raman spectroscopy, to achieve higher resolution for 2D materials characterization simply by adjusting the substrate (see Supporting Information Figure S5).

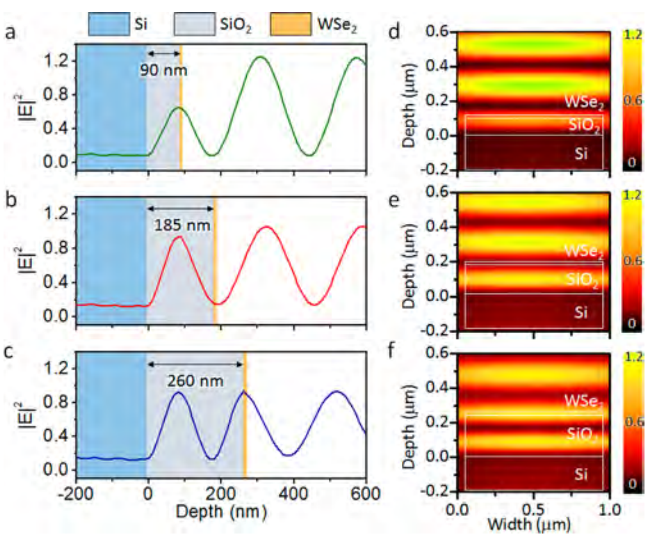

Figure 4. (a, b, c) Intensity of light as a function of penetration depth for different SiO_2 substrate thicknesses. (d, e, f) Intensity map for different SiO_2 substrate thicknesses. Note that the incident light comes from the top and the incident wavelength is 532 nm, corresponding to the experimental conditions. The depths at which Si, SiO_2, and WSe_2 are located are marked in the figures as white boxes.

In addition to being used for materials characterization, this technique can be also used for controlling the photonic properties of 2D materials, which paves a new way for the fabrication of 2D photonic components. As an example, Figure 5 shows that the light outcoupling of WSe_2 can be locally engineered by manipulating the refractive index of the substrates. To modify the substrates, electron-beam lithography is used to define periodic trenches on SiO_2/Si substrates. The SiO_2 layer in the trenches is fully etched so that the depth of the trenches are the same as the thicknesses of the SiO_2 layer. Here, substrates with 90 and 185 nm SiO_2 are used, which correspond to the most constructive and destructive substrates, respectively. Due to the difference of refractive indices between the SiO_2 (n = 1.46) and air (n = 1), the substrate forms a discrete refractive index variance along the surface. Figure 5a and b show the optical and Raman mapping images of the WSe_2 flakes after they were transferred onto the trenches. Apparent signal difference between the SiO_2 and gap regions can be observed. From the line scan shown in Figure 5c, a strong signal at the gap region is observed for 185 nm SiO_2 trenches, whereas it shows a suppression of signal at the gap region for the 90 nm trenches. The intensity difference is in accordance with the calculation results (see Supporting Information; Figure S6). From the data set, it is clear that the emission intensity for WSe_2 flakes on the SiO_2 substrate and suspended are both governed by the interference instead of doping effect. By using subwavelength gaps, the light emission of 2D materials can be locally engineered to achieve desired patterns with tunable emission strengths. This type of control of photonic properties on 2D materials has not been explored before and is compatible to current optoelectronic techniques.

Besides the substrate effect, the outcoupling can also be tailored by modifying the SiO_2 capping layer on 2D materials (an illustration is shown in inset of Figure 6a). Similar to the

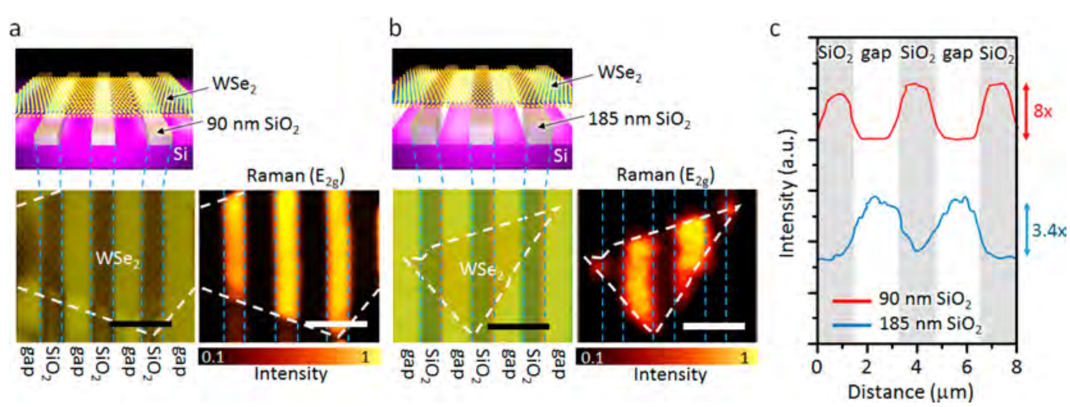

Figure 5. Optical microscope images and Raman mapping of the WSe_2 flakes after transfer onto (a) 90 nm and (b) 185 nm trenches. (c) Intensity line scans corresponding to the mapping in panels a and b. The scale bars in the images are 5 μm.

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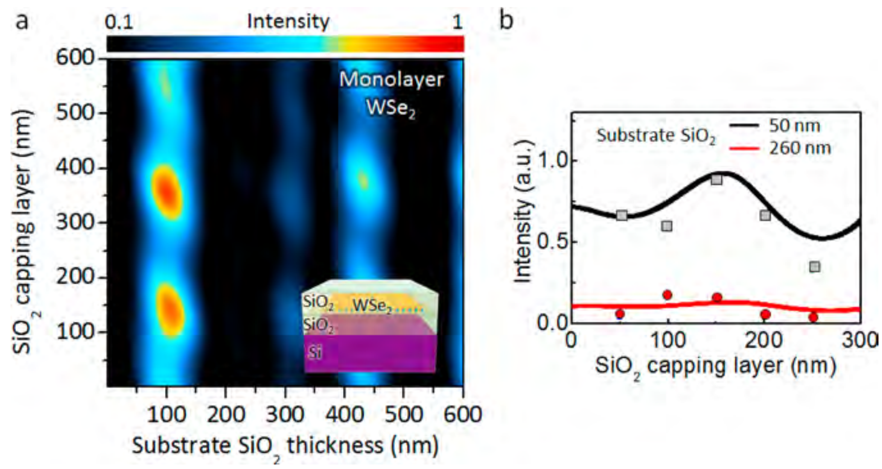

Figure 6. (a) Calculated PL intensity map for WSe_2 as a function of substrate and capping SiO_2 thicknesses. (b) Measured PL intensity for WSe_2 with different thicknesses of SiO_2 capping layers.

substrate effect where the outcoupling strength can be adjusted by changing the substrate thickness, enhanced coupling for a sandwich structure can be achieved by tuning the thickness of the capping SiO_2 layer. Considering the capping layer, a new model considering multiple reflections is built. The full derivation is given in the Supporting Information S7. Figure 6a shows the color map representing the light outcoupling as a function of substrate and capping SiO_2 thicknesses. The emission intensities are maximized at substrate thicknesses of ~100 nm and are diminished at the thicknesses between 150 to 300 nm (Supporting Information S8a), showing a similar trend as that in Figure 2d (substrate effect without capping layer). This indicates that the electrical profile within the dielectric layer is less relevant to the capping thickness, in agreement with the FDTD simulations in Figure 4. On the other hand, the capping layer will determine the boundary conditions of the air-dielectric junction and affect the electrical intensity at the 2D materials (Supporting Information S8b). Experimentally, monolayer WSe_2 flakes are prepared on substrates, and PL is measured as the thickness of the capping layer is increased, as shown in Figure 6b. As expected, the signal shows maximum enhancements as the interference reaches the constructive condition at a substrate thickness of 90 nm and a capping thickness of 150 nm, where the reflection phase is the same as the incident part. This notion allows one to modify the emission intensity from minimum to maximum by simply changing the thickness of the capping layer, which can be a passivation layer for 2D optoelectronics.

In conclusion, via both experimental results and simulations, we have demonstrated ~11 times increase in Raman signal and ~30 times increase in PL intensity of WSe_2 simply by engineering its dielectric surroundings. By modulating the thicknesses of underlying substrates and capping layers, we create a constructive interference between the absorption and emission of light and significantly enhance the outcoupling of WSe_2. Our work proposes an extremely simple way to control the photonic and optoelectronic properties of thin-layer WSe_2, which can be also applied to other direct gap semiconducting two-dimensional materials, such as single-layer MoS_2. Considering the robust and thin body nature of TMDCs, further utilization of outcoupling engineering in 2D materials will make a meaningful contribution to the realization of novel optoelectronic devices, such as 2D materials-based LEDs and solar cells.

Methods. Bulk WSe_2 (Nanosurf) was mechanically exfoliated using the adhesive tape method initially onto a 260 nm SiO_2/Si substrate. Due to the refractive index of WSe_2 and its optical interference with SiO_2/Si, the color contrast between WSe_2 thin layers is the greatest on 260 nm SiO_2/Si. This allows for the flakes of desired thickness to be mapped simply using an optical microscope. For multilayer flakes, atomic force microscopy (DI AFM Nanoscope Dimension 3100) was used to measure their exact thicknesses because it is difficult and inaccurate to figure out the thickness of a multilayer flake just by evaluating its color contrast. Using a poly(methyl methacrylate) (PMMA) membrane as the transfer media, the mapped flakes were then dry-transferred onto substrates with different SiO_2 thicknesses. After removing PMMA with dichloromethane, different thicknesses of SiO_2 were deposited as capping layers using plasma enhanced chemical vapor deposition (Oxford Plasmalab 80 Plus) at 200 °C with a power of 20 W, pressure of 900 mTorr, and precursor flow rates of 800 sccm N_2O and 100 sccm 10% SiH_4 in Ar.

Electron beam lithography is used to define periodic trenches on SiO_2/Si substrates using the PMMA as the resist. Dry etching was then done using CF_4 and O_2 to achieve anisotropic etching. Gas flows of CF_4 and O_2 were set to 90 and 30 sccm, respectively, and an RF power of 300 W was used for etching. After the etching step, PMMA resist was removed in acetone at room temperature.

Raman and PL measurements (Horiba Scientific LabRAM HR 800) were performed in backscattering geometry using a 532 nm laser with 8−80 μW power. A ~0.5 μm spot size was obtained by focusing through a 100× objective. The lowest laser power with a reasonable signal-to-noise ratio (SNR) was chosen to avoid heating effects in WSe_2 thin layers. High-resolution Raman mapping (WITec Alpha 300RA) was also performed with the same laser conditions while scanning the sampling on a piezo stage. Note that the measurement variation/error of the PL/Raman signals in our system is about 10%.

The multiple reflection simulations were performed using LabView and the FDTD simulations were done using RSoft. The refractive index values of WSe_2 at different wavelengths used in these simulations are provided in Supporting

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Nano Lett. 2015, 15, 1356−1361

Information Figure S9. The intensity map in Figure 2C shows distinctive discontinuities between 750 and 800 nm because the refractive index values of WSe_2 used for this calculation show steep variations in this range. The full-wave calculation, which is based on the finite difference method, was used to solve the Maxwell equations in time domain. During this analysis, the resolution of mesh grid was set at 10 nm in the simulation space and a 532 nm plane wave was used as the incident light source.

■ ASSOCIATED CONTENT

Supporting Information

Experimental and calculation details are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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