Engineering Light Outcoupling in 2D Materials

Der-Hsien Lien, Jeong Seuk Kang, Matin Amani, Kevin Chen, Mahmut Tosun, Hsin-Ping Wang, Tania Roy, Michael S. Eggleston, Ming C. Wu, Madan Dubey, Si-Chen Lee, Jr-Hau He, and Ali Javey

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 WSe2, resulting in a ∼11 times increase in Raman signal and a ∼30 times increase in the photoluminescence (PL) intensity of WSe2. On the basis of the interference model, we also propose a strategy to control the photonic and optoelectronic properties of thin-layer WSe2. 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
has proven to be viable for facilitating the light incoupling so as to achieve improved absorption.\textsuperscript{18–20} Another intuitive approach improved the interaction by modifying the dielectric surrounding of TMDCs.\textsuperscript{15,16} Substrate interference has been applied in the past as a simple way to precisely quantify the thickness of SiO\textsubscript{2} films grown on Si substrates by evaluating its reflection color.\textsuperscript{21} Such effects have also been used to tune the contrast/visibility/color of graphene and MoS\textsubscript{2} on Si/SiO\textsubscript{2} substrates, which allows monolayers to be seen and thicknesses to be identified under an optical microscope.\textsuperscript{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\textsubscript{2} is used for this demonstration because of its distinct PL and Raman responses and its well-studied optical properties. WSe\textsubscript{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.\textsuperscript{24} Figure 1a and b present the aforementioned schematic and optical images of a WSe\textsubscript{2} flake transferred on SiO\textsubscript{2}/Si substrates with different SiO\textsubscript{2} thicknesses. When sitting on different substrates, the color contrast of the monolayer WSe\textsubscript{2} shows apparent differences, indicating the interference between the substrate and flake is wavelength-dependent. These 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\textsubscript{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\textsubscript{2} monolayers.\textsuperscript{6,25} In addition, the Raman peak at ~250...
Letter

Figure 3. (a) Calculation of the thickness-dependent Raman intensities for WSe₂. (b) Enhancement ratio \((I_{\text{max}}/I_{\text{min}})\) extracted from the relative intensity map. (c) Calculation and experimental results for WSe₂ 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 SiO₂ thickness. The PL intensity of WSe₂ on 90 nm SiO₂ is enhanced the most, by 11 times, when compared to its PL on 185 nm SiO₂, whereas its Raman signal is enhanced the most, by 30 times, on 260 nm SiO₂ 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.⁵,²⁶ Considering multiple interfaces in this structure, incident light will encounter the boundaries of PMMA/WSe₂, WSe₂/SiO₂, and SiO₂/Si, undergoing multiple reflections. The four media, including PMMA, WSe₂, SiO₂, 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 WSe₂ layer can be deduced as

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

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 MoS₂.¹⁶,²⁶

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 SiO₂ thickness, as shown in Figure 2c. Here, the map presents the emission wavelength ranging from 300 to 900 nm and the SiO₂ 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 WSe₂) and 532 nm are specified, which correspond to the PL emission and Raman scattering wavelengths of WSe₂, respectively. For PL emission, the maximum intensity is seen at a SiO₂ thickness of \(\sim 90\) nm. For Raman scattering, the maxima are at \(\sim 90\) and 260 nm SiO₂ 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 SiO₂ 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 \(\sim 11\) times enhancement of PL and 30 times enhancement of Raman compared to those in destructive cases.

The thickness of WSe₂ also has an effect on light outcoupling. Figure 3a shows a calculated Raman intensity map as a function of WSe₂ NL and SiO₂ thickness. For thinner flakes (NL < 10), two enhancement regions are located at the thicknesses of \(\sim 90\) and 260 nm, corresponding to the constructive interference as mentioned above. To highlight the interference–NL dependence, the enhancement ratio \((I_{\text{max}}/I_{\text{min}})\) is plotted as shown in Figure 3b, where \(I_{\text{max}}\) and \(I_{\text{min}}\) are the maximum and minimum intensities, respectively, within the range defined in this map (SiO₂ 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 WSe₂ 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 SiO₂ thickness, whereas for NL = 71 and 121 the SiO₂ thickness dependence becomes weak. The results demonstrate that thinner layers are more sensitive to the substrate effect, agreeing well with the calculation shown in
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 provide constructive interference to facilitate the incoupling of light to flake. 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 ($d = \lambda/4n$; $d = \sim26$ 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).

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
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 \(\sim\)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 \(\sim\)11 times increase in Raman signal and \(\sim\)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\(_2\)O 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 \(\mu\)W power. A \(\sim\)0.5 \(\mu\)m 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 sample 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 RSof. The refractive index values of WSe\(_2\) at different wavelengths used in these simulations are provided in Supporting Information S7.
Information Figure S9. The intensity map in Figure 2C shows distinctive discontinuities between 750 and 800 nm because the refractive index values of WSe2 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.

**AUTHOR INFORMATION**

Corresponding Authors
*E-mail: ajavey@eecs.berkeley.edu.
*E-mail: jrhau.he@kaust.edu.sa.

Author Contributions
These authors contributed equally to this work.

Notes
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors acknowledge Joint Center for Artificial Photosynthesis (JCAP), Lawrence Berkeley National Laboratory, for providing access to the Raman and PL measurement tool.

**REFERENCES**