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Article

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Achieving high carrier density and high mobility in graphene using monolayer tungsten oxyselenide

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Abstract

Highly doped graphene holds promise for next-generation electronic and photonic devices. However, chemical doping cannot be precisely controlled, and introduces external disorder that significantly diminishes the carrier mobility and therefore the graphene conductivity. Here, we show that monolayer tungsten oxyselenide (TOS) created by oxidation of WSe$_2$ acts as an efficient and low-disorder hole-dopant for graphene. When the TOS is directly in contact with graphene, the induced hole density is $3 \times 10^{13}$ cm$^{-2}$, and the room-temperature mobility is 2,000 cm$^2$/V·s, far exceeding that of chemically-doped graphene. Inserting WSe$_2$ layers between the TOS and graphene tunes the induced hole density as well as reduces charge disorder such that the mobility exceeds 20,000 cm$^2$/V·s and reaches the limit set by acoustic phonon scattering, resulting in sheet resistance below 50 Ω/□. An electrostatic model based on work-function mismatch accurately describes the tuning of the carrier density with WSe$_2$ interlayer thickness. These films show unparalleled performance as transparent conductors at telecommunication wavelengths, as shown by measurements of transmittance in thin films and insertion loss in photonic ring resonators. This work opens up new avenues in optoelectronics incorporating two-dimensional heterostructures including infrared transparent conductors, electro-phase modulators, and various junction devices.
The development of versatile doping techniques capable of controlling carrier density over a wide range is a key to fabricating advanced electronic and photonic devices.\textsuperscript{1-3} For graphene, doping is key to achieving high conductivity and tunable work function to realize its promise as a material for transparent electrodes and near- and mid-infrared (IR) photonics.\textsuperscript{4,5} In this and other two-dimensional (2D) materials, conventional techniques such as ion implantation have not proven effective,\textsuperscript{6} and surface-charge-transfer doping has instead been the most commonly employed technique. For example, hole-doping with NO\textsubscript{2} gas achieves hole density \(< 2 \times 10^{12} \text{ cm}^{-2}\) and sheet resistance of \(\sim 300 \Omega/\square\).\textsuperscript{7} Wet chemical doping has been demonstrated using a variety of inorganic and organic dopants, and achieves higher densities (> \(5 \times 10^{12} \text{ cm}^{-2}\)) with sheet resistance as low as 150–200 \(\Omega/\square\).\textsuperscript{8-10} However, chemical doping can suffer from poor long-term stability and large device-to-device variability,\textsuperscript{10-11} and introduces significant charge disorder which limits the carrier mobility to < 1,000 \(\text{ cm}^2/\text{V} \cdot \text{s}\). In contrast, solid-state dopants are preferable for doping graphene due to their high repeatability, CMOS compatibility, and long-term stability. For instance, non-stoichiometric insulators such as SiN\textsubscript{x} and AlO\textsubscript{x}\textsuperscript{12-13} have been utilized to optimize charge injection in 2D semiconductors, but have not been widely studied for use with graphene.

Here, we demonstrate low-disorder and tunable high-density doping of graphene on the basis of work-function mismatch-induced charge transfer with a nearby two-dimensional layer using solid-state oxide. We utilize a high work-function monolayer tungsten oxyselenide (TOS) formed by room-temperature UV-ozone oxidation of WSe\textsubscript{2} which we have previously shown that this process is self-limiting in nature\textsuperscript{14} and thus allows precise layer-by-layer control as well as low disorder, a significant improvement over other oxidation technique with the advantage of starting from a crystalline layered source giving rise to reduced charge disorder.\textsuperscript{15} We found that TOS layer induces high hole density of > 3 \(\times 10^{13} \text{ cm}^{-2}\) in a neighboring graphene layer preserving high mobility (2,000 \(\text{ cm}^2/\text{V} \cdot \text{s}\)) and low sheet resistance of 118 \(\Omega/\square\). When the TOS layer is separated from the graphene by WSe\textsubscript{2}, the mobility rises dramatically, in a similar fashion to modulation doping in III-V semiconductor heterostructures where the separation reduces impurity scattering.\textsuperscript{16} As a result, the graphene shows phonon-limited mobility at densities of 5 \(\sim 10 \times 10^{12} \text{ cm}^{-2}\) and further reduction of sheet resistance down to 48 \(\Omega/\square\). This highly conductive graphene is also highly transparent in the infrared: we demonstrate near-ideal transmittance (99.2%) and low insertion loss (0.012 dB/\(\mu\text{m}\)) at IR frequencies using the TOS-doped graphene.
Figure 1a shows the process flow of fabricating TOS-doped monolayer graphene. The device is fabricated by first stacking 1L-WSe$_2$, graphene, and bottom $h$-BN using a polycaprolactone (PCL) polymer-based dry transfer process.$^{17}$ The heterostructure is then etched into Hall-bar structures for accurate extraction of carrier densities and conductivities of graphene, with edge-contacted metal electrodes (Cr/Au) formed using standard lithography processes (Fig. 1b).$^{18}$ Finally, the monolayer WSe$_2$ is oxidized into monolayer TOS at room temperature (RT) by exposing the sample to ozone under UV illumination for 30 min (see Methods for further device fabrication and UV-ozone oxidation details). In particular, the combination of UV and ozone is important as UV exposure creates local surface defects which facilitate the oxidation of the topmost WSe$_2$ layer upon subsequent ozone exposure at room temperature. We note that this is in contrast to prior studies utilizing only ozone without any UV exposure$^{19}$ which required elevated temperature together with longer exposure time to completely oxidize the topmost WSe$_2$ layer. We also note that another added benefit of our TOS-doping method is the self-cleaning nature of UV-ozone oxidation, as evidenced by the reduction in surface roughness due to the removal of polymer residue on the surface (Figs. S1b). This is further corroborated by the suppression of hysteresis arising from carrier (de-)trapping at the surface states formed by polymer residue$^{20}$ for all of our devices after oxidation (Figs. S2 and S3).

We first determine the type of the carriers induced in our TOS-doped monolayer graphene using Raman spectroscopy, as shown in Fig. 1c. We find a clear blueshift of both G and 2D peaks (18.1 and 4.3 cm$^{-1}$, respectively) to their original positions in pristine graphene,$^{21}$ which indicates that graphene gets hole-doped. This is corroborated by $I_{2D}/I_G$ ratio getting reduced by threefold and full-width half maxima (FWHM) of the G peak reduced from 7.3 to 5.9 cm$^{-1}$ after oxidation (Fig. 1c, inset). Four-probe resistance ($R_{4p}$) of graphene as a function of the back-gate bias ($V_{GS}$) at RT also shows a drastic shift of the Dirac peak from $V_{GS} = 30$ V to beyond the measurement range, after the formation of the TOS layer (Fig. 1d). This, together with the $R_{4p}$ decreasing with negative bias voltage, clearly indicates that an ultra-high density of holes is induced in graphene. As a result, the RT sheet resistance ($R_{sh}$) of our TOS-doped graphene shows a remarkably low value of $\sim 118 \, \Omega/\square$ at zero gate bias voltage. Note that a weak secondary peak shown in $R_{sh}$ can be attributed to small spatial inhomogeneity in the sample or formation of the moiré potential from an unintentional atomic alignment of graphene with the bottom $h$-BN.$^{22}$ We further note that any
contribution of the TOS layer to the measured conductivity can be ruled out by independent electrical measurements which confirm that it is insulating (Fig. S4).

**Fig. 1. Electrical and Raman characterization of TOS-doped graphene.** a, Device structure at different steps in the measurement process. UV-ozone only oxidizes the topmost monolayer WSe\textsubscript{2} into monolayer TOS, while the underlying graphene layer remains intact and gets heavily p-doped. b, Optical image of the TOS-doped graphene devices with a Hall-bar geometry. c, Raman characterization of the graphene device showing blueshifts in G and 2D peaks after oxidation, indicative of the hole-doping. Note that the h-BN peak was used as a reference for calculating peak shifts. The insets show a clear reduction in $I_{2D}/I_G$ and FWHM of G peak after oxidation. d, Four-point resistance $R_{4p}$ as a function of $V_{GS}$ for TOS-doped graphene before and after doping. Dirac peak shifts from $V_{GS}$ of 30 V to beyond our measurement range after doping, indicative of ultra-high p-type doping of graphene. e, Sheet resistance $R_{sh}$ of TOS-doped graphene showing 118 $\Omega/\square$ at zero gate voltage.

To gain further insight into the nature of the TOS layer, we investigate its structural properties using selected-area electron diffraction (SAED). Figure 2a and b shows the SAED patterns of 1L-WSe\textsubscript{2} flake after oxidation, indicating complete disappearance of the hexagonal symmetry along the [0001] zone axis. This suggests that the resultant TOS layer is amorphous. However, few-layer
WSe$_2$ shows hexagonal single-crystal diffraction patterns even after oxidation as shown in Figs. 2c and d, confirming that the UV-ozone process presented in our work is self-limiting in nature (only oxidizes the topmost layer) and thus the underlying WSe$_2$ layers remain in pristine form (see Fig. S5 for transmission electron microscope (TEM) images of monolayer and few-layer WSe$_2$). The self-limited nature of our oxidation process is further corroborated by the energy-dispersive X-ray spectroscopy (EDS) measurements of 1L-WSe$_2$ that show the presence of selenium atoms even after oxidation (Table S1). We note that this self-limited nature allows for repeated oxidization and etching of multilayer WSe$_2$ flake in a monolayer-by-monolayer fashion$^{14}$ (Fig. S1a) as well as the removal of the TOS-doping method by simply etching the TOS layer, as indicated by the shift of the Dirac point back to $V_{GS} = 0$ V (Fig. S1c). On the atomistic level, this indicates that the TOS layer acts as a high diffusion barrier preventing further penetration of ozone molecules to the underlying layers.$^{23}$

Figure 2e and f show the X-ray photoelectron spectroscopy (XPS) spectra of W 4f and Se 3d core levels before and after the oxidation of CVD monolayer WSe$_2$. We find a dominant formation of multivalent oxidation states of W (W$^{5+}$ and W$^{6+}$) after the oxidation, which verifies that 1L-TOS is sub-stoichiometric. Note that weak W-O and Se-O signals present before oxidation are presumably attributed to intrinsic defects present in CVD grown samples. We further note that defects in amorphous nature of the TOS layer can cause surface adsorption of water and oxygen molecules leading to time-dependent degradation.$^{24}$ Figure S6 depicts the PMMA encapsulation layer as a potential solution to prevent this degradation. A slight initial decrease in the zero-gate bias hole density $p$ of our TOS-doped graphene to $7 \times 10^{12}$ cm$^{-2}$ immediately after the PMMA encapsulation can be attributed to chemical reaction with solvent at a high baking temperature of 180 °C. However, $p$ remains nominally unchanged thereafter (~14% decrease in $p$ over one month after the PMMA encapsulation), showing the use of PMMA encapsulation to enhance the stability of our TOS-doping method.
**Fig. 2. Structural characterization of monolayer TOS.** a,b, SAED patterns of 1L-WSe$_2$ and c,d, few-layer WSe$_2$, before and after the UV-ozone process. Single-crystal diffraction patterns with zone axis [0001] are visible before UV-ozone and are completely removed after the UV-ozone process, indicating the amorphous nature of the TOS layer. In contrast, few-layer WSe$_2$ still shows crystalline patterns even after oxidation, indicating a self-limiting process. e,f, XPS characterization of 1L-WSe$_2$ and 1L-TOS indicating the W 4f and Se 3d peaks, respectively. A comparison of W 4f peaks show the creation of multivalent oxidation states of W ($W^{5+}$ and $W^{6+}$) in the TOS layer confirming the sub-stoichiometric nature of the TOS layer.

**Figure 3a** shows the measured hole density ($p$) of TOS-doped graphene extracted from Hall effect measurements. We first focus on the case where the TOS is directly in contact with the graphene. We find that the hole density is $3.2 \times 10^{13}$ cm$^{-2}$ at $V_{GS} = 0$ V, consistent with the estimate from the Raman measurements. Applying $V_{GS}$ can further tune $p$ up to $3.7 \times 10^{13}$ cm$^{-2}$, demonstrating that the back-gate capacitance is electrostatically decoupled from the top TOS layer. This doping level is equivalent to ~1% of the graphene atomic density ($3.82 \times 10^{15}$ cm$^{-2}$), and similar to the maximum achievable in silicon using substitutional doping. The doping level is also beyond what can be achieved by electrostatic gating through solid dielectrics. For example, a graphite back-gated structure with $h$-BN dielectric can only achieve carrier densities on the order
of $\sim 6 \times 10^{12}$ cm$^{-2}$ in graphene, and a perfect dielectric with a high electrical-breakdown dielectric strength of 1 V/nm can only accumulate $\sim 2 \times 10^{13}$ cm$^{-2}$.

Fig. 3. Tuning carrier density and mobilities in TOS-doped graphene with WSe$_2$ interlayers. 

**a**, Hole density, **b**, corresponding Fermi-level of graphene with respect to its $E_{\text{CNP}}$, and **c**, sheet resistance as a function of back-gate bias, extracted from Hall-effect measurements. Increasing the number of WSe$_2$ interlayers between the TOS doping and graphene reduces the hole density in the graphene. High hole doping densities push the Fermi-level deep into the valence band as shown in the inset. **d**, Hole mobility as a function of hole density for TOS-doped graphene with WSe$_2$ interlayers at room temperature. TOS-doped graphene with 3L- and 4L-WSe$_2$ interlayers extend the LA phonon-limited hole mobility, previously achieved in h-BN-encapsulated graphene (black points), to higher hole densities. These mobilities are significantly higher than other chemical doping techniques providing similar doping densities, highlighted in the bottom gray zone. At extremely high hole densities for TOS-doped graphene without and with 1L-WSe$_2$ interlayer, our work shows a significant (> 10×) mobility improvement compared to electrolyte gating.

The self-limiting nature of the oxidation process provides a straightforward method to tune the induced hole density: when multilayer WSe$_2$ is utilized, the top layer is converted to TOS and the
remaining layers remain pristine, increasing the separation between the dopant layer and the channel. As we vary the interlayer WSe$_2$ thickness from 1 to 4 layers (1L to 4L), the induced $\rho$ decreases monotonically to $0.4 \times 10^{13}$ cm$^{-2}$ (Fig. 3a and Fig. S8 at 1.5 K), and remains additionally tunable by the back-gate. The corresponding Fermi energy ($E_F$) can be extracted using the relation

$$E_{\text{CNP}} - E_F = \hbar v_F \sqrt{\pi p},$$

(1)

where $E_{\text{CNP}}$ is the energy of charge neutrality point (Dirac point), $\hbar$ is the reduced Planck constant, and $v_F$ is the Fermi velocity in graphene ($\approx 10^6$ m/s). We find that $E_F$ can be tuned from -0.1 to -0.7 eV, by simply changing the WSe$_2$ layer number together with the back gate (Fig. 3b).

We show the measured sheet resistance of the graphene in Figure 3c. At zero back gate voltage, the TOS-graphene sample shows sheet resistance ($R_{sh}$) of 118 $\Omega/\square$. For comparison, the undoped graphene has $R_{sh}$ of a few k$\Omega/\square$ and state-of-the-art chemically-doped graphene has $R_{sh}$ of $\sim$140 $\Omega/\square$, demonstrating superiority of our doping method. Remarkably, for the 3L and 4L samples, $R_{sh}$ is even smaller, falling below 50 $\Omega/\square$ (see also Fig. S9). This indicates an increase in carrier mobility that more than offsets the reduced carrier density.

To explore the electrical performance of the TOS-doped graphene in more detail, we plot the carrier mobility (at RT) derived from the measured sheet resistance and carrier density in Figure 3d,e. With no interlayer WSe$_2$, the mobility is $\sim$2,000 cm$^2$/V·s, more than an order of magnitude higher than that achieved in graphene with similar high carrier density induced by either chemical doping$^{4,8,9}$ or electrolyte gating.$^{27-30}$ In spite of this dramatic improvement, the mobility still falls below the limit predicted from acoustic phonon scattering, indicating dominant scattering from charged impurities. The density of such impurities can be estimated from the measured low-temperature mobility $\mu \approx 20 \left( e/\hbar p_{imp} \right)$, where $p_{imp}$ is the impurity density, $\hbar$ is the Planck constant, and $e$ is the elementary charge (Fig. S8b,c).$^{31}$ From this relation, we estimate $p_{imp}$ of $\sim$4.6 $\times$ 10$^{11}$ cm$^{-2}$, well below that of electrolyte-gated graphene ($6 \times 10^{12} - 10^{13}$ cm$^{-2}$)$^{32}$. This indicates that the charge disorder in the TOS layer is much lower than for other dopants.

With insertion of interlayer WSe$_2$, the mobility improves dramatically, reaching values of $\sim$17,000 cm$^2$/V·s for the 3L sample and $\sim$24,000 cm$^2$/V·s for the 4L sample at zero gate voltage. Remarkably, these values are at the limit set by longitudinal-acoustic (LA) phonon scattering.$^{18}$
This indicates that three layers of WSe$_2$ (~2 nm) can screen the charged impurities in the TOS layer so that the impurity scattering is reduced by more than an order of magnitude. This is consistent with previous studies showing that the charged-impurity scattering rate decreases rapidly as a function of the distance between the impurities and the graphene layer.$^{33}$ The mobility improvement achieved in this way is analogous to the modulation doping technique in conventional semiconductor heterostructures, whereby the physical separation of dopant from the active channel drastically increases carrier mobility by minimizing impurity scattering by dopant atoms.$^{16}$

To understand the origin of the charge transfer between TOS and graphene, we focus on two important electrostatic boundary conditions imposed in our devices in equilibrium: (1) constant Fermi level $E_F$ across the entire system and (2) continuous vacuum level without any discontinuities. We first note that the charge neutrality point of graphene lies deep in the bandgap of WSe$_2$, so that we can effectively treat WSe$_2$ as a dielectric.$^{34}$ Therefore, the resultant electrostatic boundary condition in our TOS-doped graphene with interlayer WSe$_2$ can be expressed in terms of the work function $\Phi$ of the individual layers (TOS and graphene) as

$$\Phi_{\text{TOS}} = \Phi_{\text{Gr}} + pt/\varepsilon, \quad (2)$$

where $\Phi_{\text{TOS}}$ ($\Phi_{\text{Gr}}$) is the work function of TOS (graphene) with respect to the vacuum level, $t$ is the distance between graphene and TOS, and $\varepsilon$ is the dielectric constant of WSe$_2$. Here, we use $\varepsilon = 3.8.$.$^{35}$ The final term in eq. (2) is the potential drop developed across TOS and graphene as a result of charge transfer, which can be determined from Poisson’s equation.$^{36}$ From eq. (2), $p$ in graphene can be simply expressed in terms of $t$ and the work-function mismatch between the two layers as $p = \varepsilon(\Phi_{\text{TOS}} - \Phi_{\text{Gr}})/t$. We find that our model fits well our data for $E_F$ in our TOS-doped graphene as a function of $t$ (Fig. 4a), indicating that the charge transfer is dictated by the work function mismatch between the two layers. Note that the extracted $\Phi_{\text{TOS}}$ of ~5.6 eV is in good correspondence with previous studies on non-stoichiometric tungsten oxides.$^{37}$

To validate our model of work-function mediated charge transfer, we study the TOS-doped graphene devices with different stacking orders of graphene and TOS layer (Gr/TOS and TOS/Gr) as well as with different insulating interlayer (TOS/2L h-BN/Gr; Fig. S10). Raman spectra clearly show hole-doping of graphene irrespective of the stacking order or the type of insulating interlayer.
This not only verifies the work-function mediated charge transfer but also rules out the possibility doping due to fixed dipoles, as seen for self-assembled monolayers and ferroelectric insulators. The densities extracted from the Raman shifts of $>2.5 \times 10^{13}$ cm$^{-2}$ for the TOS/graphene sample and $\sim1 \times 10^{13}$ cm$^{-2}$ for the graphene/TOS sample, as well as $\sim2 \times 10^{13}$ cm$^{-2}$ for TOS/2L $\alpha$-BN/graphene sample are in good agreement with our Hall-effect measurements. A slight decrease in doping density of the graphene/TOS sample (compared to TOS/graphene) can be attributed to chemical processing at elevated temperatures during the stacking and cleaning processes.

The proposed doping mechanism indicates that TOS can be an effective hole-dopant for many other materials with suitable work function mismatch. We test this by interfacing TOS with semiconductors spanning various dimensions – 1D semiconductor (single-walled carbon nanotube, SWCNT), 2D semiconductor (4L-WSe$_2$), and 3D organic semiconductor (Dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene, DNTT) (fabrication details can be found in the Methods section). Figs. S11 – 13 clearly show that hole densities increase in these systems after the placement of TOS on their surface, indicating that that high work-function TOS can universally p-type dope a wide range of materials based on work-function mismatch.

We next perform self-consistent electrostatic simulations using the extracted $\Phi_{\text{TOS}}$ of $\sim5.6$ eV to gain further insight into the role of the WSe$_2$ interlayer in the charge transfer process (simulation details can be found in our previous work). The additional material parameters are provided in Table S2. Specifically, we study the effect of defects in WSe$_2$ on the resultant $p$ in graphene at RT as shown in Fig. 4c (here we assume that defects are equivalent to acceptors/donors $N_A$ and $N_D$). For defect densities lower than $5 \times 10^{11}$ cm$^{-2}$, our simulations show that $p$ can be well understood in terms of eq. (2) for any layer number of WSe$_2$ interlayers. However, $p$ departs from eq. (2) at higher defect densities due to additional charge transfer from acceptors (donors) in WSe$_2$ to graphene, which further decreases (increases) the resultant hole density in graphene. In our studies, we use high-purity flux-grown WSe$_2$ with low defect densities ($<10^{11}$ cm$^{-2}$). Therefore, the simulations support the model of charge transfer dictated by work-function mismatch and validate the assumption of treating interlayer WSe$_2$ as a simple dielectric. In this low defect density limit, our simulations further show that the induced charge densities in the WSe$_2$ interlayer are orders of magnitude lower than that in graphene (Fig. 4d and Fig. S14). This indicates that the electrical
characteristics of our devices are dominated by the bottom graphene layer with negligible WSe$_2$ contribution.

Fig. 4. Work function mediated charge transfer in TOS-doped graphene. a, Graphene hole density $p$ as a function of the distance $t$ between TOS layer and graphene. Our model based on work-function mediated charge transfer provides excellent fits to the experimental data. b, Raman map of 2D vs. G peak frequencies for pristine graphene (gray), graphene on 1L-TOS (red), 1L-TOS on graphene with 2L $h$-BN spacer (orange) and 1L-TOS on graphene (dark red). The gray and purple dotted lines indicate a peak shift of G and 2D peaks with different carrier density and strain, respectively. A clear blueshift obtained from the G and 2D peaks in graphene along the $\epsilon = -0.2\%$ line can be seen after the TOS doping, irrespective of the TOS location. The shifts are in good agreements with previous work on p-type carrier modulation in graphene devices by Das et al. (shown in sky blue). c, Self-consistent electrostatic simulation of induced hole density in TOS-doped graphene as a function of defect density for different thickness of WSe$_2$ interlayer. d, The same simulation for 4L-WSe$_2$ interlayer device shows negligible charges in the WSe$_2$ interlayers compared to the bottom graphene.
We now explore the potential of TOS-doped graphene in optoelectronic applications. One immediate advantage of our technique is the ability to strongly suppress interband absorption for photon energies up to $2E_F$ due to Pauli blocking.\textsuperscript{5} Figure 5a shows the measured transmittance spectra of chemical vapor deposition (CVD)-grown 1L-WSe\textsubscript{2}/graphene films on quartz before and after UV-ozone oxidation (see Fig. S15 and Methods for the detailed measurement setup). Before oxidation, the transmittance is near graphene’s intrinsic value (97.7\%) for photon energies less than 1.4 eV since the top WSe\textsubscript{2} is transparent in the near-IR region, and shows a dip at 1.67 eV that corresponds to the excitonic bandgap of WSe\textsubscript{2}. In contrast, the near-IR transmittance significantly improves after oxidation, increasing to 99.2\% at telecommunication wavelengths ($\lambda \sim 1550$ nm). From the transmittance data, we can infer that $E_F$ of $\sim$0.6 eV for our TOS-doped graphene, in reasonable agreement with that from electrically measurements for the exfoliated sample discussed above (0.65 eV). Furthermore, the TOS-doped graphene is highly transparent even in the visible regime (see insets) indicated by the reduction of the WSe\textsubscript{2} absorption peak. The weak presence of the excitonic peak is due to thickness inhomogeneity in the top CVD-grown WSe\textsubscript{2} layer within the area of illumination ($\sim$6\% of the area is covered by 2L-WSe\textsubscript{2} as shown in Fig. S15c). Figure 5b shows that our TOS-doped graphene displays superior performance at telecommunication wavelength (1550 nm) as compared to other conventional transparent conducting films, including indium tin oxide (ITO), zinc-doped indium oxide (IZO), zirconium-doped indium oxide (IO:Zr), hydrogen-doped indium oxide (IO:H), zinc oxide (ZnO), and aluminum-doped zinc oxide (AZO).\textsuperscript{43-47} In general, traditional transparent conductors suffer from a trade-off between transmittance and sheet resistance. In contrast, our CVD TOS/Gr and exfoliated TOS/3L-WSe\textsubscript{2}/Gr samples provide exceptionally higher transmittance while maintaining remarkably low sheet resistance, >99\% transmittance at 197 $\Omega$/\textsquare and 97.7\% at 48 $\Omega$/\textsquare, respectively. This highlights the both the intrinsic suppression of interband transitions in highly doped graphene, and the ability of the TOS-doping technique to achieve high carrier density while maintaining high mobility.

Finally, we demonstrate the ability to utilize TOS-doped graphene as a transparent gate electrode and high-speed phase-modulator in near-IR photonic circuits.\textsuperscript{48} We probe the optical response of TOS-doped graphene embedded on planarized low loss silicon nitride (SiN) waveguides, in a microring resonator cavity (Fig. 5c; see Methods for detailed fabrication
processes). Notably, our planar photonic structure comprises a TOS/Gr/\textit{h}-BN/SiN composite waveguide with a strong optical mode overlap when compared to out-of-plane measurements. The normalized ring transmission spectra show that the bare low-loss cavity is weakly coupled to the straight waveguide (under-coupled regime), thereby yielding a low extinction of ~3 dB on resonance, with narrow linewidth (Fig. 5d). After the transfer of WSe$_2$/Gr/\textit{h}-BN on the planarized SiN substrate, we extract an insertion loss of 0.077 ± 0.014 dB/µm in our composite waveguide from the optical response as shown in gray of Fig. 5d (see Methods and Supporting Information for insertion loss extraction).\textsuperscript{49} We attribute the high insertion loss to the undoped graphene in WSe$_2$/Gr/\textit{h}-BN stack, which causes the resonator linewidth to broaden considerably, increasing the cavity loss and over-coupling the waveguide to the cavity. The insertion loss is lowered by about 85% to 0.012 ± 0.0022 dB/µm after UV-ozone oxidation, consistent with Pauli blocking of absorption. The significant lowering of insertion loss leads to the condition where the coupling rate between waveguide and ring resonator equals the optical decay rate (loss) in the cavity, thereby exhibiting a critically coupled resonance transmission response (shown in red in Fig. 5d), where the extinction is ~60 dB, with the spectral sharpening of the resonance. The 2% change measured in the out-of-plane transmission (Fig. 5a) is magnified to an 85% change in the in-plane transmission due to the enhanced optical mode overlap in integrated photonic circuits. This low insertion loss of 0.012 dB/µm uniquely places TOS-doped graphene as an ideal alternative to traditional transparent conducting materials such as ITO, which has at least two orders of higher insertion loss (1.6 dB/µm) with similar device geometries.\textsuperscript{50}
**Fig. 5. Optical properties of TOS-doped graphene.**

**a.** Transmittance of CVD-grown 1L-WSe$_2$ on graphene before and after the UV-ozone oxidation. Shaded area indicates the standard deviation. The dashed line indicates the transmittance of intrinsic graphene (97.7%). Before UV-ozone, the transmittance for photon energies less than 1.4 eV remains around graphene’s intrinsic absorption. An excitonic band gap peak of WSe$_2$ is also seen at 1.67 eV. After UV-ozone treatment, the peak is reduced significantly along with an increment in the transmittance from 97.2 to 99.2% at telecommunication wavelength (1550 nm). The insets show different CVD stacks on quartz substrate to compare transparency in visible regime.

**b.** Comparison of optical transmission at 1550 nm for TOS-doped Gr with widely-used transparent conducting films as a function of sheet resistance. The thickness of the films is indicated in parentheses.

**c.** Top-view and cross-sectional schematics of a microring resonator with TOS(WSe$_2$)/Gr/h-BN composite stack on planarized SiN waveguide.

**d.** Normalized resonator transmission spectra of the planarized SiN ring configuration before transfer (blue), after transfer (grey) and after UV-ozone oxidation (red) of the stack. The black dashed lines indicate the numerical fit of the ring resonator equation with the measured transmission response of the ring resonator. Before transfer (blue), the ring resonator is in the under-coupled regime, where the ring resonator and bus waveguide exhibit weak coupling due to
the ultra-low loss waveguides (2.326 dB/cm). After transfer (grey), the insertion loss in the composite SiN waveguides increases to 0.077 ± 0.014 dB/µm, which over-couples the ring resonator to the waveguide, causing significant broadening of the resonator linewidth. The high loss in the ring can be attributed to the undoped graphene. After UV-ozone oxidation, the transmission spectra exhibit a critical coupling condition, where the insertion loss due to the stack is reduced by 85% to 0.012 ± 0.0022 dB/µm. The error range in the insertion loss measurement for before and after-oxidation arises due to the uncertainty in the length of the stack transferred on the ring resonator (see inset).

**Conclusion**

In this study, we utilize the work-function mediated charge transfer to achieve degenerate p-type doping of graphene using monolayer TOS prepared by a room-temperature UV-ozone oxidation of monolayer WSe\textsubscript{2}. Our TOS-doped graphene (1L-TOS/1L-Gr) shows excellent hole mobilities (~2,000 cm\textsuperscript{2}/V·s) even at high hole density (>3 × 10\textsuperscript{13} cm\textsuperscript{-2}) which results in low sheet resistance (118 Ω/□) at room temperature. We further demonstrate tunable carrier density together with enhanced mobility reaching the phonon-limited scattering rate at room temperature by inserting WSe\textsubscript{2} interlayers, further reducing graphene sheet resistance to ~50 Ω/□. Our self-consistent electrostatic model based on work-function mismatch can well describe the charge transfer mechanism as well as the tunable carrier density with WSe\textsubscript{2} interlayer. Finally, our TOS-doped graphene displays exceptionally high optical transmittance (>99%) and low insertion loss (0.012 dB/µm) at telecommunication wavelength. Our work opens up new avenues for incorporating vdW heterostructures into photonic circuits as a transparent gate electrode and high-speed phase-modulator for near-IR applications.
Methods

Fabrication and characterization of graphene device

WSe₂, graphene, and h-BN flakes were prepared on SiO₂/Si substrate by mechanical exfoliation. The thickness of each flake was determined by the contrast difference in optical microscopic images and Raman spectra. Only monolayer graphene was used while the WSe₂ thickness varied from 1L to 5L to see the layer dependence. The stacking of flakes was conducted by the dry transfer method using PCL polymer at 50~58 °C to pick up flakes that are then transferred onto a 285-nm SiO₂/Si at 80 °C to melt the polymer. To remove the polymer, the sample was annealed at 340 °C under vacuum condition. Edge contacts were formed to the graphene layer by etching through the layers and subsequently depositing e-beam evaporated metal. Cr/Au (2/80 nm) contacts were deposited by e-beam evaporation after reactive-ion etching (RIE) of the WSe₂, graphene and h-BN layers with CHF₃ to form the edge contact. UV-ozone oxidation (Samco UV-2 located in class 100 cleanroom controlling humidity < 40% and temperature < 20 °C) was conducted at room temperature for 30 minutes with an oxygen flow rate of 3 L/min. The system has a separate discharge type ozone generator and the generated ozone flows into sample chuck underneath the UV light source. The UV lamp is a mercury grid lamp with primary wavelength of 254 and 185 nm, and output power of ~10 mW/cm². Chuck temperature was maintained < 50 °C during the oxidation process. The etch to remove TOS was conducted using 1M KOH diluted in deionized water followed by a deionized water rinse and vacuum annealing at 300 °C. Electrical measurements were performed with both a semiconductor parameter analyzer (Keysight B1500A) and lock-in amplifiers (Stanford Research SR830) connected to a cryostat containing a tunable perpendicular magnetic field under vacuum conditions.

Fabrication of SWCNT, WSe₂, and DNTT devices

SWCNT device: CNTs were grown on a SiO₂/Si substrate at 890 °C. The locations of SWCNTs were identified using SEM and AFM scans. Cr/Pd (2/20 nm) contacts were then fabricated on selected SWCNTs using the lift-off method. 1L-WSe₂ was transferred and subsequently oxidized after the initial electrical measurements of the SWCNT (without TOS) were completed.
**WSe$_2$ device:** 4L-WSe$_2$ was stacked on h-BN using the same dry-transfer process used with graphene. E-beam evaporation and lift-off was used to create top surface contacts of Pd/Au (20/50 nm) to WSe$_2$. Electrical measurements of the same device before and after UV-ozone oxidation are presented in the manuscript.

**DNTT device:** Two devices were made on the same chip, one with and one without TOS. To create the device with TOS, we first exfoliated 1L-WSe$_2$ on a SiO$_2$/Si substrate followed by lift-off metallization with Ti/Pd/Au (2/20/20 nm). 1L-WSe$_2$ was converted into monolayer TOS through UV-ozone oxidation. Contacts were also concurrently patterned in areas without TOS to form the second device. Then, 40 nm of DNTT was deposited by sublimation. The channel areas were defined by coating the sample with PMMA, patterning with e-beam lithography, and etching away the semiconductor with SF$_6$ plasma, leaving the active channel area (see Fig. S13).

**Transmittance measurements**

The transmittance of CVD-grown 1L-WSe$_2$/Gr directly on a quartz substrate (purchased from 2D Semiconductors) was measured under ambient condition using a custom setup built around a Nikon TE-300 inverted microscope as shown in Fig. S15. The output of a tungsten halogen lamp was focused onto a 50 μm pinhole and an aspheric condenser lens to obtain collimated white light, which was focused at the sample plane through the quartz substrate using a long working distance 50x objective (0.55 NA). The transmitted light was collected with a 40x (0.6 NA) objective focused at the sample plane from below and was sent to an f/4 spectrograph (Princeton Instruments SpectraPro HRS300) equipped with a cooled InGaAs array detector (Princeton Instruments PylonIR). Order sorting filters were used to avoid higher-order diffraction signals. Transmittance was calculated by dividing the transmitted intensity measured on the sample by the transmitted intensity through a nearby blank area of quartz, with dark counts subtracted from both measurements. The system was optimized to ensure that the instrument error was <0.5% over the whole spectral range for each measurement as indicated shaded area of the spectrum.

**Fabrication of SiN photonic platform with TOS-doped graphene**

To fabricate low-loss silicon nitride waveguides, we use e-beam lithography to define 1300 nm wide waveguides on a stack of 360 nm PECVD SiO$_2$ hard mask and 330 nm high silicon nitride
(SiN), deposited using LPCVD at 800 °C and annealed at 1200 °C for 3 hours on 4170 nm thermally oxidized SiO₂. We use CHF₃/O₂ (52/2 sccm) chemistry in Oxford 100 Plasma ICP RIE to etch the hard mask of 360 nm SiO₂ and subsequently use an optimized etch recipe CHF₃/O₂/N₂ (47/23/7 sccm) that uses a higher oxygen content which reduces both polymerization and side-wall roughness. We use 360 nm SiO₂ as a sacrificial hard mask for etching SiN, since increasing the O₂ flow significantly lowers the selectivity of etching. Following the etch, we deposit about 600 nm of PECVD SiO₂ on the waveguides. We planarize the SiO₂ to about 70-100 nm above the SiN waveguides using standard chemical planarization (CMP) techniques to create a uniform surface for the transfer of the WSe₂/Gr/h-BN stack on the ring resonator. Subsequently, a stack of 1L-WSe₂/1L-Gr/20~25 nm h-BN was transferred onto the planarized SiN waveguides using a PCL dry transfer method. To remove the polymer, the sample was annealed at 340 °C under vacuum conditions. Finally, UV-ozone oxidation is performed to oxidize WSe₂ into TOS and dope graphene. Notably, microring resonators allows for high fidelity measurement of the optical propagation loss induced by TOS-doped graphene due to the enhanced sensitivity of a high-quality factor (Q) cavity (~ 300,000 in our case) to small changes in phase and absorption.

**Optical loss measurement and insertion loss estimation**

We couple transverse electric (TE) polarized light from a tunable near-infrared laser (1550 ~ 1650 nm) to the input of the SiN microring resonator (Input of schematic in Fig. 5c) using a tapered single-mode fiber, which is then collected from the SiN ring output, using a similar tapered fiber. Transmission measurements were taken from the same device before transfer to account for the insertion loss of planarized SiN substrates, once after the transfer to account for the insertion loss due to undoped graphene, and finally, after UV-ozone oxidation to measure the propagation loss so the composite waveguide with doped graphene. The original normalized transmission responses are shown in Fig. S16. We normalize each of the ring transmission spectra by the maximum transmission power at the output at a wavelength detuning (Δλ), where the cavity does not interact with the incoming light. We estimate the insertion loss by fitting the experimental normalized ring transmission to the theoretical ring transmission (T) obtained from the following resonator equation,
\[ T = \left| 1 - \frac{\frac{2}{\tau_e}}{f(\omega - \omega_0) + \frac{1}{\tau_0} + \frac{1}{\tau}} \right|^2, \]  

(3)

where \( \frac{1}{\tau_e} \) is the decay rate (coupling rate) from the waveguide (bus) to the ring resonator, \( \frac{1}{\tau_0} \) is the decay rate due to the loss in the ring, and \( \omega - \omega_0 \) is the frequency detuning with \( \omega_0 \) as the resonant frequency. The quality factor (Q) of the ring resonator is related to the \( \tau_0 \) and \( \alpha \) (insertion loss in linear scale) through the equation \( Q = \frac{\omega_0 \tau_0}{\alpha \lambda_0} \approx \frac{2\pi n_g}{\alpha \lambda_0} \), where \( n_g \) is the group index and \( \omega_0 = \frac{2\pi c}{\lambda_0} \) with \( \lambda_0 \) as the resonant wavelength.

**Data availability**

The data that support the findings within this paper are available from the corresponding authors upon reasonable request.

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**Author contributions**

M.S.C., A.N., and Y.J. designed and conducted initial experiments under J.H. and J.T.T.’s supervision. M.S.C. and A.N. stacked, fabricated, and conducted electrical, optical, and material characterizations of the samples with B.S.Y.K.’s contribution. B.S.Y.K. establish a model for a

**Additional information**

M.S.C., A.N., A.B., Y.J., J.H., and J.T.T. filed for a US non-provisional patent regarding the technology reported in this article. Correspondence and requests for materials should be addressed to J.H. and J.T.T.

**References**


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