Supporting Information

Plasmonic Transition Metal Carbide Electrodes for High-Performance InSe Photodetectors

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Figure S1a shows the optical microscopy (OM) image of a liquid-exfoliated Ti$_2$CT$_x$ flake with lateral size >20 μm. Figure S1b is the AFM image of several Ti$_2$CT$_x$ flakes with similar thickness (~2 nm). Figure S1c presents the HRTEM image and SAED pattern of a Ti$_2$CT$_x$ flake, indicating clean surface and perfect crystallinity. Figure S1d is the Raman spectrum of an InSe nanoflake; the spectrum is similar to that previously reported. $^8$

Figure S1. a) OM image of liquid-exfoliated Ti$_2$CT$_x$ flake with lateral size >20 μm. b) AFM image of several liquid-exfoliated Ti$_2$CT$_x$ flakes with clean surfaces. c) High-resolution transmission electron microscopy (HRTEM) image of Ti$_2$CT$_x$ flake. Inset is the corresponding selected area energy diffraction pattern. d) Raman spectra of InSe nanosheet. Inset was the OM image of mechanical exfoliated InSe flake.
In order to confirm the stability of our Ti$_2$CT$_x$ electrode, we investigated the conductance change after exposing the Ti$_2$CT$_x$ electrode to air (Figure S2). We found that the Ti$_2$CT$_x$ electrode retained metallic properties without significant change in conductance after two months of exposure.

Figure S2. a) OM image of as-exfoliated Ti$_2$CT$_x$ device. Scale bar is 1 µm. b) OM image of Ti$_2$CT$_x$ device, as exposed in air for two months. Scale bar is 5 µm. c) Drain current as a function of gate voltage for the as-exfoliated Ti$_2$CT$_x$ device (black line) and after two months of the electrode exposure to air (red line).
AFM images in Figure S3a–d show the variation in morphology of Ti$_2$CT$_x$ flake with the plasma etching time. The surface profiles (along the white lines in Figures S3a-d) of the Ti$_2$CT$_x$ flake at different plasma etching times are presented in Figure S3e. With increasing ICP process time (0, 60, 120, and 180 s), a constant decrease in thickness (~1 nm) can be detected, which means that Ti$_2$CT$_x$ flake is etched layer by layer under the plasma condition. HRTEM and selective-area energy diffraction (SAED, inset) image of the plasma-treated Ti$_2$CT$_x$ flake is shown in Figure S3f. A well-maintained crystalline structure with a hexagonal electron diffraction pattern was observed.

![AFM images showing variation in morphology](image)

Figure S3. (a–d) AFM images of Ti$_2$CT$_x$ flake under different plasma etching times and (e) corresponding surface profile scans. Measured positions are marked by horizontal white lines. The inductively coupled plasma condition is Ar and SF$_6$ (flux ratio = 40:1) at 25 W and 30 mTorr. (f) HRTEM and selective-area energy diffraction (SAED, inset) image of the plasma-treated Ti$_2$CT$_x$ flake.
Figure S4a is the AFM image of ICP etched Ti$_2$CT$_x$ nanoribbon device. As shown in Figure S4b, after ICP plasma etching, Ti$_2$CT$_x$ nanoribbon shows similar high conductivity as the original Ti$_2$CT$_x$ flake. From the Kelvin probe force microscope (KPFM) measurement (Figure S4d), it was found that the work function difference between the ICP-treated MXene and original MXene is 0.02 eV, which does not affect device performance, considering the Schottky barrier height of 0.5 eV between the InSe and Ti$_2$CT$_x$ electrode in our top-contacted devices.

Figure S4. a) AFM image of Ti$_2$CT$_x$ nanoribbon device. Ti$_2$CT$_x$ nanoribbon was achieved by ICP plasma etching of Ti$_2$CT$_x$ flake. Scale bar is 1 µm. b) Drain current as a function of drain voltage of Ti$_2$CT$_x$ flake and Ti$_2$CT$_x$ nanoribbon. c) AFM image and d) KPFM image of Ti$_2$CT$_x$ electrode. Scale bar is 1 µm.
Figure S5a shows the AFM image of vertically stacked InSe and Ti$_2$CT$_x$ flakes after plasma etching. The whole InSe is covered by the Ti$_2$CT$_x$ flake. The periodic rectangular area is the etched part of the Ti$_2$CT$_x$ flake. The surface profile along the vertical line is shown in the inset. The thickness of the Ti$_2$CT$_x$ flake is 7.5 nm, measured with respect to the substrate, and the thickness measured with respect to the bottom InSe flake is 7.5 nm, as well. If the bottom InSe flake was etched by plasma (the plasma etching time was sufficiently long), the thickness of the Ti$_2$CT$_x$ flake measured with respect to the InSe flake should be higher than that measured with respect to the substrate. This indicates that only the Ti$_2$CT$_x$ flake was etched off during the plasma process. Figure S5b demonstrates the transfer curve of the InSe/Ti$_2$CT$_x$ FET before and after plasma etching. Before plasma etching, the channel material of InSe/Ti$_2$CT$_x$ FET device was Ti$_2$CT$_x$, which showed high metallic conductivity. After plasma etching, the exposed part of Ti$_2$CT$_x$ was etched off; consequently, the channel material was transformed to InSe, which showed a high on/off ratio of $\sim 10^5$.

![AFM image showing vertically stacked InSe and Ti$_2$CT$_x$ flakes after plasma etching. The InSe flake is covered by a Ti$_2$CT$_x$ flake. The periodic nanoribbon array region of the Ti$_2$CT$_x$ flake is etched by plasma. b) Drain current as a function of gate voltage of the InSe/Ti$_2$CT$_x$ heterostructure before and after plasma etching ($V_d = 1$ V).](image)
A high drain voltage was applied to the InSe/Ti$_2$CT$_x$ devices to study the electrical endurance and carrier transport under extreme operating conditions. A linearly increasing current level as a function of the applied drain voltage, instead of saturation, was observed (Figure S6a). We attribute the origin of the super-linear behavior to the avalanche phenomenon resulting from impact ionization by hot carriers in the InSe channel. Figure S6b is the distribution of the electric field at which carrier multiplication occurs with InSe/Ti$_2$CT$_x$ devices, which matches well with previously reported work$^{12}$. Hall measurements were performed to measure the carrier concentration (Figure S6c). The carrier concentration ($n_e$) is expressed as $n_e=(dB/dR_H)/e$, where $B$ is the magnetic field, $e$ is the electron charge, and $R_H$ is the Hall resistance of the device. $R_H$ is calculated by $R_H=V_H/I$. $V_H$ is the Hall voltage and $I$ is the current. An exponential increase in carrier concentration was observed under a high electric field, which supports the conclusion of carrier multiplication by the avalanche effect.

Figure S6. a) $I$-$V$ curve of InSe/Ti$_2$CT$_x$ devices showing avalanche and breakdown behavior. b) Statistics of the electric field at which carrier multiplication occurs with InSe/Ti$_2$CT$_x$ devices. c) Carrier concentration ($n_e$) as a function of applied electric field ($E$). Inset: Hall voltage ($V_H$) vs. applied magnetic field ($B$) for various electric fields.
A dark-field optical image in Figure S7b indicates the intensity of optical fields and the light absorption. The InSe with patterned Ti$_2$CT$_x$ nanoribbon shows a stronger optical field in comparison to the part without the Ti$_2$CT$_x$ nanoribbon. Photoluminescence (PL) intensity mapping images were collected in the 530–540 nm spectral range (Figure S7c). A significant enhancement in PL intensity of InSe with Ti$_2$CT$_x$ was observed.

Figure S7. a) Bright-field and b) dark-field optical image of InSe with patterned Ti$_2$CT$_x$ nanoribbon. c) Photoluminescence intensity mapping image. d) OM image of Ti$_2$CT$_x$ and InSe flake shown in figure c.
A significant absorption enhancement throughout the entire operation bandwidth of the device was demonstrated by the patterned Ti$_2$CT$_x$ thin film with resonance peak shifts as compared to the unpatterned device, shown in Figure S8a. The simulated light absorption of patterned and unpatterned Ti$_2$CT$_x$ thin film was compared (Figure S8b) by using a commercially available multiphysics tool, COMSOL, demonstrating good agreement with experimental results. In the simulation, the dielectric permittivity values of Ti$_2$CT$_x$ were adopted from the reported calculation works$^{3,4}$. A 15-nm-thick Ti$_2$CT$_x$ with a periodic width of 250 nm and a slit width of 250 nm (air) were built in the calculation. A periodic boundary condition and port excitation mode were applied, and a stationary solver was chosen to determine the light coupling effect at different wavelengths with plasmonic nanostructures.

Figure S8. a) Comparison of absorption spectra of patterned and unpatterned Ti$_2$CT$_x$ films. b) Comparison of simulated absorption spectra of patterned and unpatterned Ti$_2$CT$_x$ films.
Power-dependent temporal measurements of the patterned and unpatterned InSe/Ti$_2$CT$_x$ avalanche photodetectors under different illumination densities were performed and the results are demonstrated in Figure S9. With increase in the power density, the photocurrent always increases. Compared to the unpatterned InSe/Ti$_2$CT$_x$ photodetector, the patterned device always exhibits higher photocurrents.

Figure S9. Photoresponse curves of patterned and unpatterned InSe/Ti$_2$CT$_x$ photodetector under different power densities (0.17-625 W/m$^2$).
To extract the detectivity ($D^*$) of the photodetectors, the shot noise $S_{\text{shot}} = \sqrt{2qI}$, thermal noise $S_{\text{thermal}} = \sqrt{4kT/R_{\text{shunt}}}$, and 1/f noise ($S_{1/f}$) were calculated at $V_d=3$ V, $V_g=0$ V. For the patterned InSe/Ti$_2$CT$_x$ device, $S_{\text{shot}}$ is estimated to be 0.4 pA/Hz$^{0.5}$, $S_{\text{thermal}}$ is found to be 0.2 pA/Hz$^{0.5}$, and $S_{1/f}$ is measured to be 28 pA/Hz$^{0.5}$ (Figure S10a, at 10 Hz). For the unpatterned InSe/Ti$_2$CT$_x$ device, $S_{\text{shot}}$ is estimated to be 0.52 pA/Hz$^{0.5}$, $S_{\text{thermal}}$ is found to be 0.15 pA/Hz$^{0.5}$, and $S_{1/f}$ is calculated to be 31 pA/Hz$^{0.5}$ (Figure S10b, at 10 Hz).

![Figure S10a](image1.png)  
![Figure S10b](image2.png)

Figure S10. 1/f noise ($S_{1/f}$) for the a) patterned and b) unpatterned InSe/Ti$_2$CT$_x$ photodetectors.
Table S1 shows a comparison between the InSe/Ti$_2$CT$_x$ and InSe/graphene photodetectors, illustrating that the InSe photodetector with the Ti$_2$CT$_x$ electrode simultaneously demonstrates high responsivity and high NPDR.

Table S1. Performance comparison of InSe photodetectors fabricated with the Ti$_2$CT$_x$ electrode in this study, and the graphene electrode based InSe photodetectors reported in the literature.

<table>
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<tr>
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<th>Responsivity [A/W]</th>
<th>$T_r/T_f$ [ms]</th>
<th>NPDR [W$^{-1}$]</th>
<th>Spectral range [nm]</th>
<th>ref</th>
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<tbody>
<tr>
<td>Gr/GaSe/InSe/Gr</td>
<td>0.1</td>
<td>0.0019/0.002</td>
<td>5.8×10$^9$</td>
<td>250-900</td>
<td>$^s_5$</td>
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<tr>
<td></td>
<td>60</td>
<td>0.1/0.1</td>
<td>1.2×10$^{11}$</td>
<td>400-1000</td>
<td>$^s_6$</td>
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<tr>
<td></td>
<td>4000</td>
<td>1/10</td>
<td>7×10$^9$</td>
<td>633</td>
<td>$^s_7$</td>
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<tr>
<td>P- Ti$_2$CT$_x$/InSe/P- Ti$_2$CT$_x$</td>
<td>$1×10^5$</td>
<td>0.5/26</td>
<td>3.5×10$^{13}$</td>
<td>405-785</td>
<td>This work</td>
</tr>
<tr>
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<td>0.8/28</td>
<td>2.5×10$^{12}$</td>
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REFERENCES


