

Supporting Information

Strain-dependent Anisotropic Nonlinear Optical Response in Two-Dimensional Functionalized MXene Sc_2CT_2 (T=O and OH)

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1. Electronic properties of Sc_2CT_2 (T=O and OH) MXenes monolayers

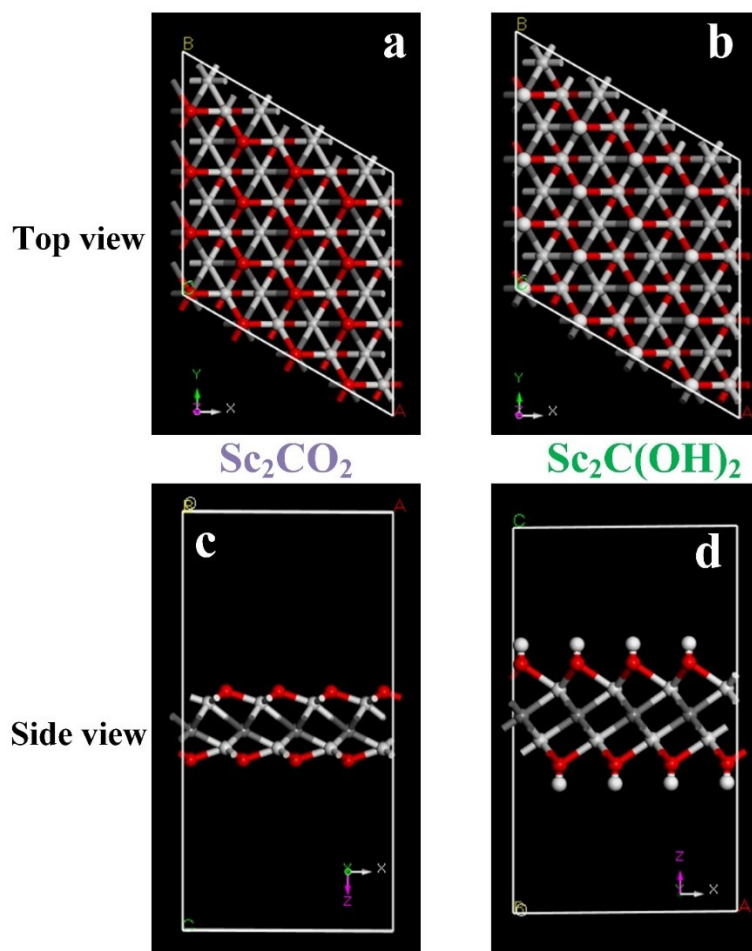


Figure S1 (a) Top view and (c) side view of the most stable configuration of monolayer Sc_2CO_2 ; (b) and (d) of monolayer $\text{Sc}_2\text{C(OH)}_2$.

The geometry optimization and optical properties of materials are performed using the plane-wave basis Vienna ab initio simulation package (VASP) based on universal density functional theory (DFT) calculations under the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional[1-3]. The optimized lattice parameters of 2D Sc_2CO_2 and $\text{Sc}_2\text{C(OH)}_2$ are 3.404 Å and 3.264 Å, respectively. The cutoff kinetic energies for plane waves are set as 400 eV. The relaxation of energy is taken as 1.0×10^{-5} eV. For the calculations of the strained monolayer Sc_2CT_2 (T=O and OH) structures, to avoid interactions between adjacent layers, a vacuum layer with a thickness of 15 Å is utilized.

To determine the optoelectronic properties of 2D monolayer Sc_2CT_2 (T=O and OH) as a function of strain, the biaxial tensile strain from 1% to 5% has been applied to 2D Sc_2CT_2 monolayers. The electronic properties of the strained Sc_2CT_2 monolayers are shown in Figure S2. The band structure of Sc_2CO_2 monolayer with 0%~2% strain shows indirect band-gap from valence band maximum (VBM) at the Γ point to conduction band minimum (CBM) at the K point as shown in Figure S2(a-c). For 3%~5% strained

Sc₂CO₂ monolayer, however, the band structure shows direct band gap from VBM at the K point to CBM at the K point as shown in Figure S2(d-f). The band structure of strained Sc₂CO₂ monolayer is consistent with previous results[4]. For Sc₂C(OH)₂ monolayer, the band structure displays direct band-gap from VBM at the Γ point to CBM at the Γ point at 0%~2% tensile strained state as shown in Figure S2(g-i), while the band structure exhibits indirect band-gap from VBM at the Γ point to CBM at the M point at 3%~5% tensile strained state as shown in Figure S2(j-l).

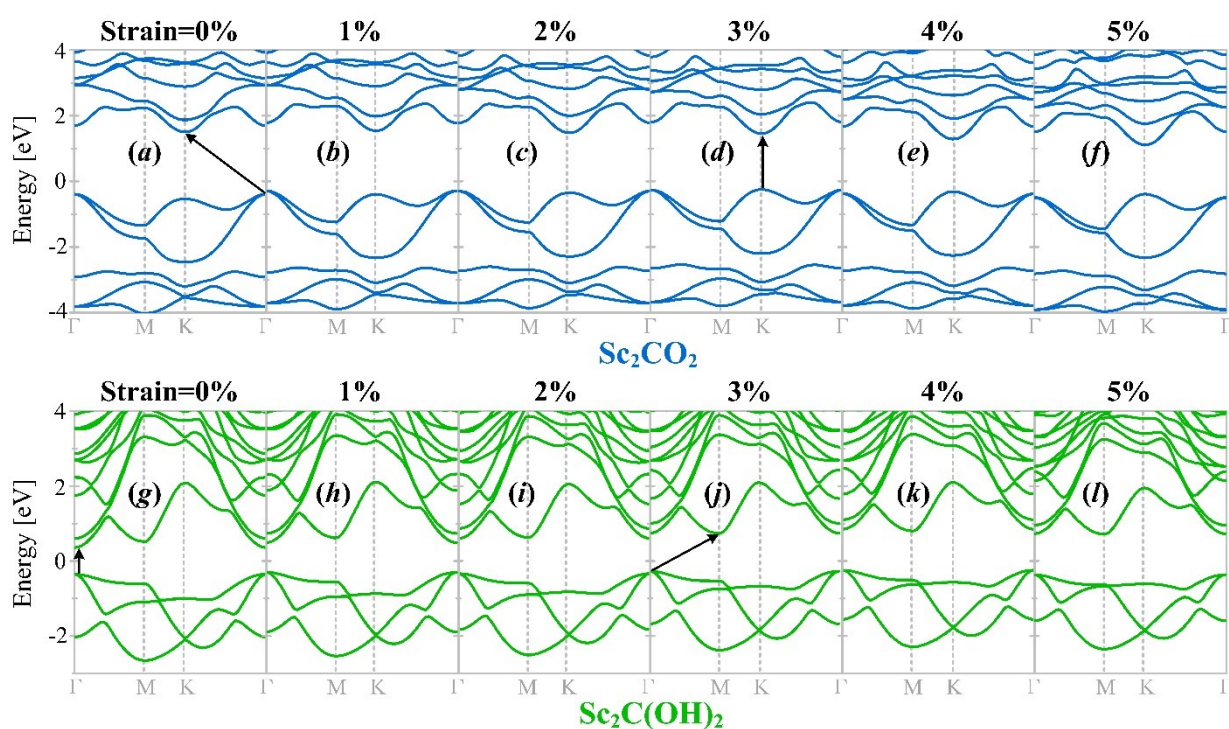


Figure S2 Band structures of O-terminated MXene [Sc₂CO₂ (a-f)] and OH-terminated MXene [Sc₂C(OH)₂ (g-l)] at different tensile strained states.

2. Linear optical properties of strained Sc₂CT₂ (T=O and OH) monolayers

The linear optical response is directly related to the complex dielectric function $\hat{\epsilon} = \epsilon_{re} + i\epsilon_{im}$, and the imaginary part of the dielectric function is given by the following equation (S1):

$$\epsilon_{im}^{ab}(\omega) = \frac{4\pi^2}{\Omega} \sum_{nm,k} f_{nm} \frac{r_{nm}^a r_{mn}^b}{\omega_{nm} - \omega} \quad (\text{S1})$$

Where superscripts a and b indicate Cartesian components; n and m represent the energy bands; $f_{nm} = f_n - f_m$ is the difference of the Fermi distribution functions; $\omega_{nm} = \omega_n - \omega_m$ is the frequency difference for bands n and m ; and Ω is the unit cell volume. r_{nm}^a is the matrix element of the position operator that is defined as $r_{nm}^a = -ip_{nm}^a / \omega_{nm}$. Where p_{mn} is the momentum matrix element. The real part of the dielectric function is obtained from $\epsilon_{im}(\omega)$ by Kramer–Kronig transformation. The linear optical properties such as the complex refractive index ($\hat{n} = n + i\kappa$) and the optical absorption (α) can be obtained by the calculated dielectric function as follows:

$$\hat{n}^2 = \hat{\epsilon}, \alpha = 4\pi\kappa/\lambda \quad (\text{S2})$$

where λ is the wavelength; n and κ are real and imaginary parts of the complex refractive index, respectively.

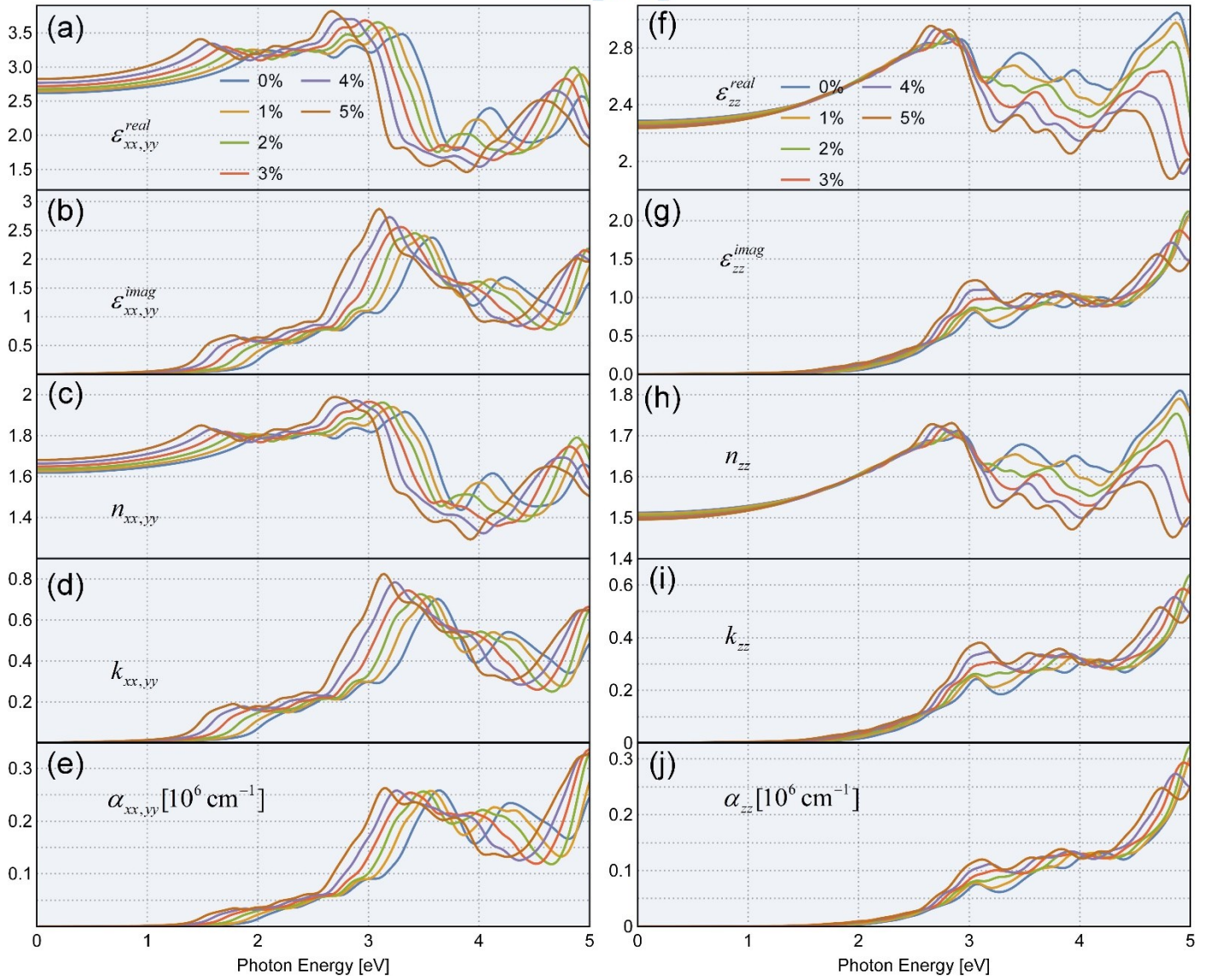


Figure S3. (a)~(f) In-plane and (g)~(l) out-of-plane of the linear optical coefficients including real (ϵ^{real}) and imaginary (ϵ^{imag}) parts of the dielectric function, real (n) and imaginary (κ) parts of the complex refractive index, and absorption coefficient α of strained Sc_2CO_2 monolayers as a function of photon energy.

Sc₂C(OH)₂

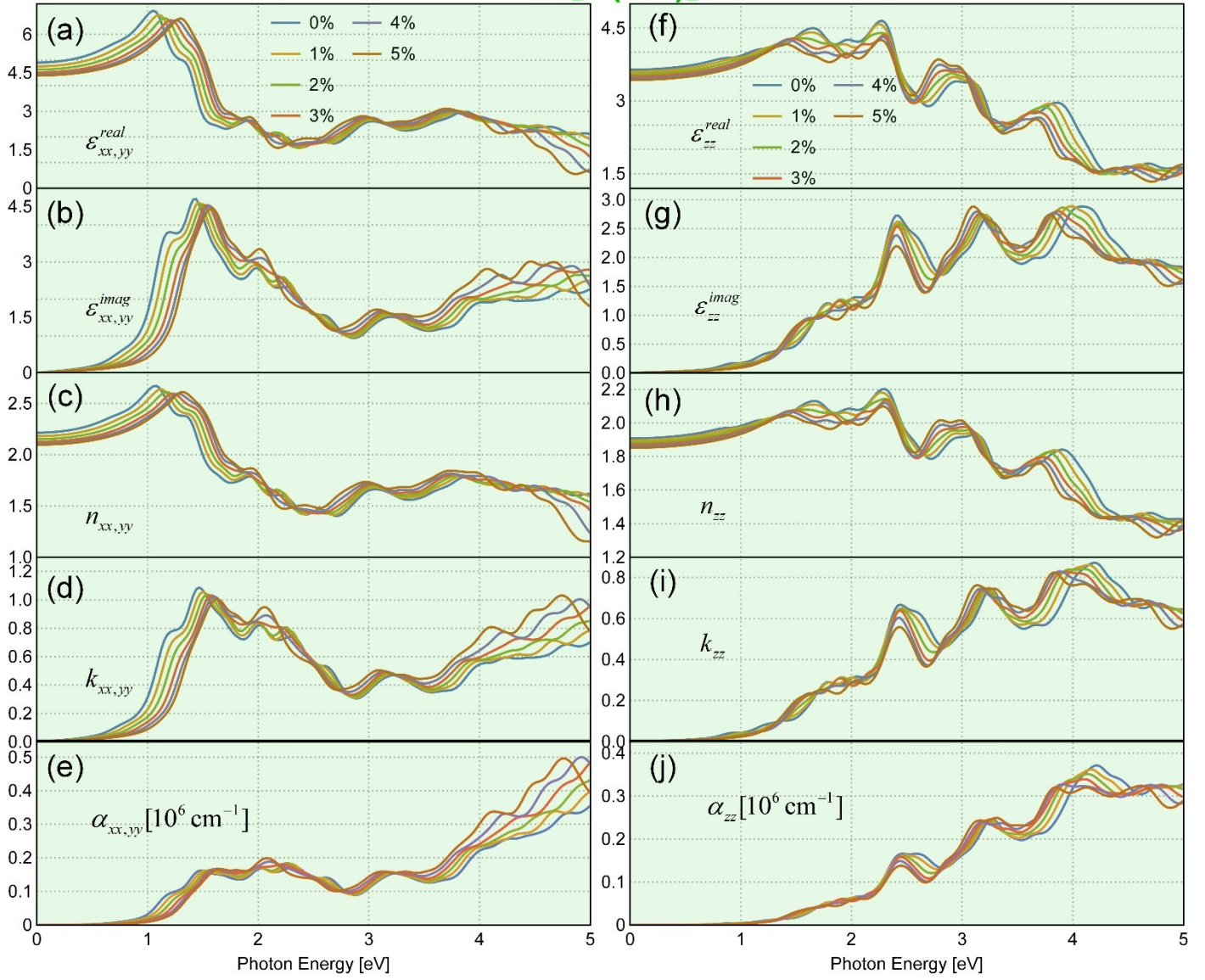


Figure S4. (a)~(f) In-plane and (g)~(l) out-of-plane of the linear optical coefficients including real (ϵ^{real}) and imaginary (ϵ^{imag}) parts of the dielectric function, real (n) and imaginary (κ) parts of the complex refractive index, and absorption coefficient α of strained Sc₂C(OH)₂ monolayers as a function of photon energy.

3. Photoelastic tensor of strained Sc₂CT₂ (T=O and OH) monolayers

The second-order nonlinear susceptibility $\chi^{abc}(-2\omega, \omega, \omega)$ corresponding formalism was derived in a simpler manner by Aversa and Sipe, and was rearranged by Rashkeev *et al* [5-7]. The second-order nonlinear susceptibility $\chi^{abc}(-2\omega, \omega, \omega)$, which consists of the contribution from the pure interband processes $\chi_e^{abc}(-2\omega, \omega, \omega)$, and the mixed interband and intraband processes $\chi_i^{abc}(-2\omega, \omega, \omega)$ can be described as:

$$\chi^{abc}(-2\omega, \omega, \omega) = \chi_e^{abc}(-2\omega, \omega, \omega) + \chi_i^{abc}(-2\omega, \omega, \omega) \quad (\text{S3})$$

The contribution from these two processes could be obtained by:

$$\chi_e^{abc}(-2\omega, \omega, \omega) = \frac{e^3}{\hbar^2 \Omega} \sum_{nml,k} \frac{1}{2} \frac{r_{nm}^a (r_{ml}^b r_{ln}^c + r_{ml}^c r_{ln}^b)}{(\omega_{ln} - \omega_{ml})} \left[\frac{2f_{nm}}{\omega_{mn} - 2\omega} + \frac{f_{ln}}{\omega_{ln} - \omega} + \frac{f_{ml}}{\omega_{ml} - \omega} \right] \quad (\text{S4})$$

$$\begin{aligned} \chi_i^{abc}(-2\omega, \omega, \omega) &= \frac{i}{2} \frac{e^3}{\hbar^2 \Omega} \sum_{nm,k} f_{nm} \left[\frac{2}{\omega_{mn}(\omega_{mn} - 2\omega)} r_{nm}^a (r_{nm;c}^b + r_{mn;b}^c) \right] \\ &+ \frac{1}{\omega_{mn}(\omega_{mn} - \omega)} (r_{nm;c}^a r_{mn}^b + r_{nm;b}^a r_{mn}^c) \\ &+ \frac{1}{\omega_{mn}^2} \left(\frac{1}{\omega_{mn} - \omega} - \frac{4}{\omega_{mn} - 2\omega} \right) r_{nm}^a (r_{mn}^b \Delta_{mn}^c + r_{mn}^c \Delta_{mn}^b) \\ &- \frac{1}{2\omega_{mn}(\omega_{mn} - \omega)} (r_{nm;a}^b r_{mn}^c + r_{nm;a}^c r_{mn}^b) \end{aligned} \quad (\text{S5})$$

Where r is the position operator; Ω is the unit cell volume; superscripts a, b and c are Cartesian components; $\hbar\omega_{mn} = \hbar\omega_m - \hbar\omega_n$, is the energy difference for the bands m and n; $r_{mn;a}^b$ is the generalized derivative of the coordinate operator.

$$r_{mn;a}^b = \frac{r_{nm}^a \Delta_{mn}^b + r_{nm}^b \Delta_{mn}^a}{\omega_{nm}} + \frac{i}{\omega_{nm}} \sum_l (\omega_{lm} r_{nl}^a r_{lm}^b - \omega_{nl} r_{nl}^b r_{lm}^a) \quad (\text{S6})$$

Where $\Delta_{mn}^a = (p_{nm}^a - p_{mn}^a) / m$ is the difference between the electronic velocities at the bands n and m; p is the momentum matrix element. At the zero-frequency limit, the **Equation (S5)** can be simplified as[5, 7]:

$$\chi_e^{abc} = \frac{e^3}{\hbar^2 \Omega} \sum_{nml,k} \frac{r_{nm}^a (r_{ml}^b r_{ln}^c + r_{ml}^c r_{ln}^b)}{(\omega_{ln} - \omega_{ml})} [\omega_n f_{ml} + \omega_m f_{ln} + \omega_l f_{mn}] \quad (\text{S7})$$

$$\chi_i^{abc} = \frac{i}{4} \frac{e^3}{\hbar^2 \Omega} \sum_{nm,k} \frac{f_{nm}}{\omega_{mn}^2} \left[r_{nm}^a (r_{mn;c}^b + r_{mn;b}^c) + r_{nm}^b (r_{mn;c}^a + r_{mn;a}^c) + r_{nm}^c (r_{mn;b}^a + r_{mn;a}^b) \right] \quad (\text{S8})$$

To simplify the rank of tensors, the second order nonlinear susceptibility $\chi_{ijk}^{(2)}$ is related to the second-order nonlinear coefficient d_{ul} as $\chi_{ijk}^{(2)}(\omega, \omega) = 2d_{ul}(\omega, \omega)$.

According to the relationship between the second-order nonlinear coefficient $d_{ul}^{(2,m\%)}$ and the strain $m\%$ [8, 9], the photoelastic tensor $p_{ul}^{m\%}$ can be obtained through the Equation (S9).

$$p_{ul}^{m\%} = \frac{d_{ul}^{(2,m\%)} - d_{ul}^{(2,0)}}{m\%} \quad (\text{S9})$$

Where $d_{ul}^{(2,0)}$ is the second-order nonlinear coefficient of the unstrained Sc_2CT_2 (T=O and OH) monolayers.

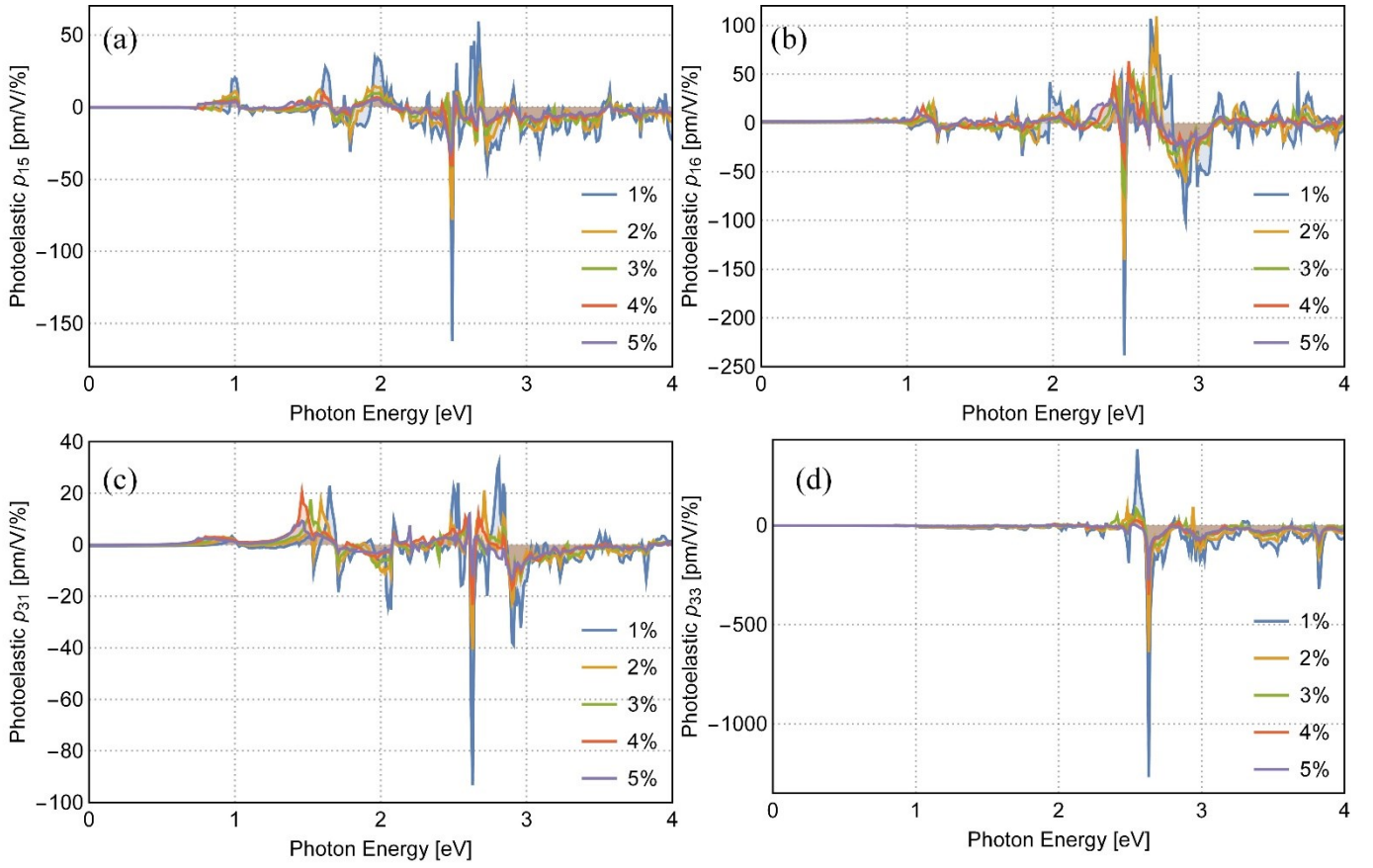


Figure S5 Photon energy-dependent photoelastic tensor elements p_{ul} of (a-d) monolayer Sc_2CO_2 at different tensile strained states.

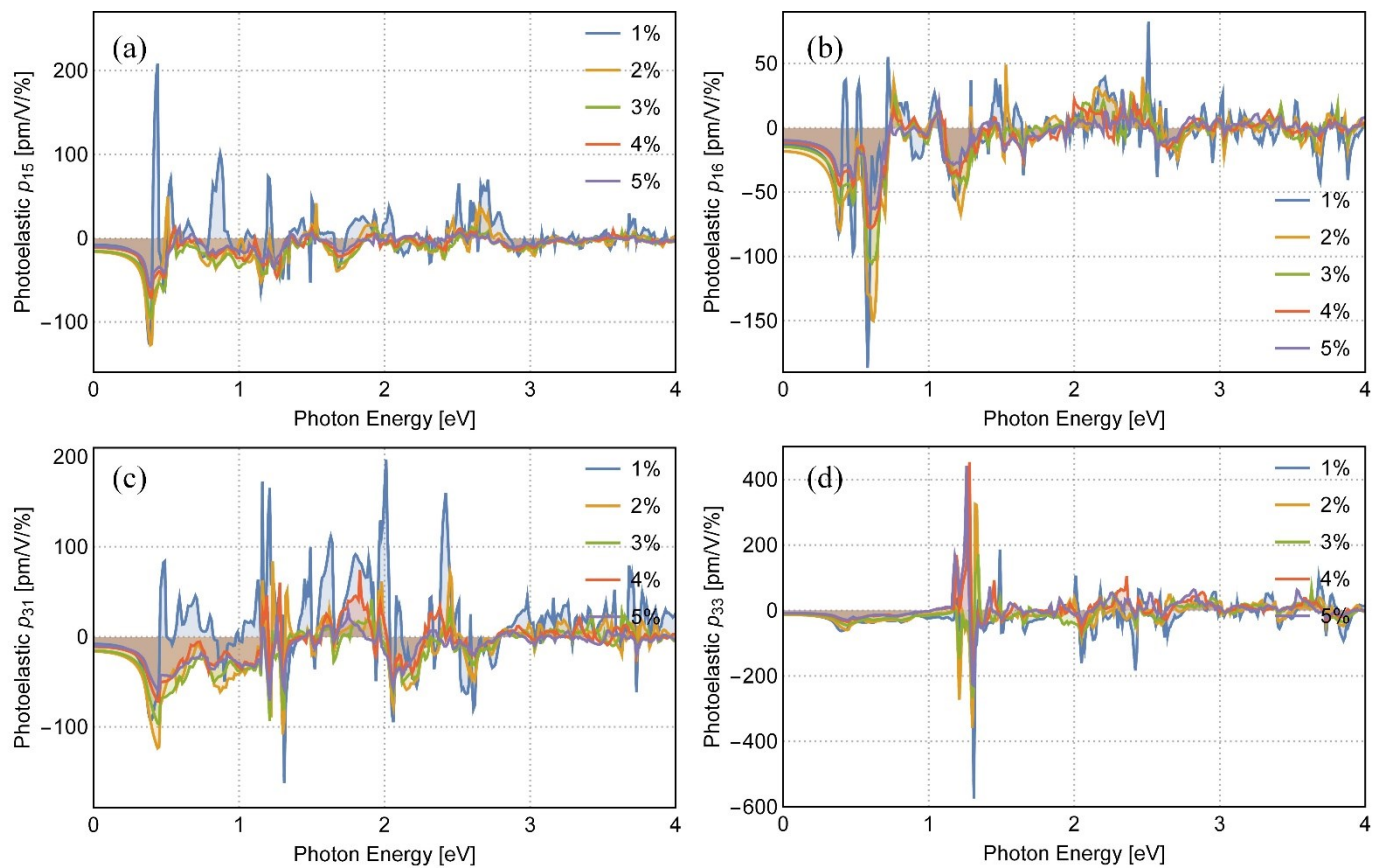


Figure S6 Photon energy-dependent photoelastic tensor elements $p_{\mu l}$ of (a-d) monolayer $\text{Sc}_2\text{C}(\text{OH})_2$ at different tensile strained states.

4. Second harmonic generation in strained Sc_2CT_2 (T=O and OH) monolayers

The schematic setup for the second harmonic generation (SHG) in a reflection configuration is shown in

Figure S7. The incident pump light is linearly polarized along the X direction with an incident angle θ to the sample surface. The electric field of the incident light can be given as:

$$\begin{bmatrix} E_X \\ E_Y \\ E_Z \end{bmatrix} = \begin{bmatrix} E_0 \cos[\theta] \\ 0 \\ E_0 \sin[\theta] \end{bmatrix} \quad (\text{S10})$$

The second order nonlinear susceptibility $\chi_{ijk}^{(2)}$ is related to the second-order nonlinear coefficient $d_{\mu l}$ as:

$$d_{\mu l} = \frac{1}{2} \chi_{ijk}^{(2)} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \quad (\text{S11})$$

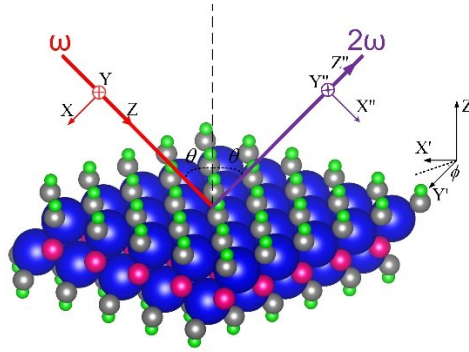


Figure S7 Schematic of SHG in a reflection configuration. XYZ and $X'Y'Z'$ represent the laboratory and crystal coordination, respectively.

The transformation tensor containing azimuthal angle could be obtained by a rotating operation $T(\phi)$.

$$d_{i,j,k}^{(2)'} = \sum_{f=1}^3 T_{i,f} \times \sum_{g=1}^3 T_{j,g} \times \sum_{h=1}^3 T_{k,h} \times d_{f,g,h}^{(2)} \quad (\text{S12})$$

$$T(\phi) = \begin{bmatrix} \text{Cos}[\phi] & \text{Sin}[\phi] & 0 \\ -\text{Sin}[\phi] & \text{Cos}[\phi] & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (\text{S13})$$

Here ϕ denotes the angle between the mirror plane in the crystal structure and the polarization of the pump beam; $T_{i,f}$, $T_{j,g}$ and $T_{k,h}$ is an element in $T(\phi)$. Thus, the SHG components can be expressed as:

$$\begin{bmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{bmatrix} = 2\varepsilon_0 d_{\mu l}'(\phi) \begin{bmatrix} E_x^2(\omega, \theta) \\ E_y^2(\omega, \theta) \\ E_z^2(\omega, \theta) \\ 2E_y(\omega, \theta)E_z(\omega, \theta) \\ 2E_z(\omega, \theta)E_x(\omega, \theta) \\ 2E_x(\omega, \theta)E_y(\omega, \theta) \end{bmatrix} \quad (\text{S14})$$

where ε_0 is the permittivity of the space. Thus, the dependence of the two polarization components (parallel and perpendicular) of SHG on sample orientation could be described as:

$$\begin{aligned} I_{//} &\propto [-P_x(d_{\mu l}, \phi) \cos[\theta] + P_z(d_{\mu l}, \phi) \sin[\theta]]^2 \\ I_{\perp} &\propto P_y^2(d_{\mu l}, \phi) \end{aligned} \quad (\text{S15})$$

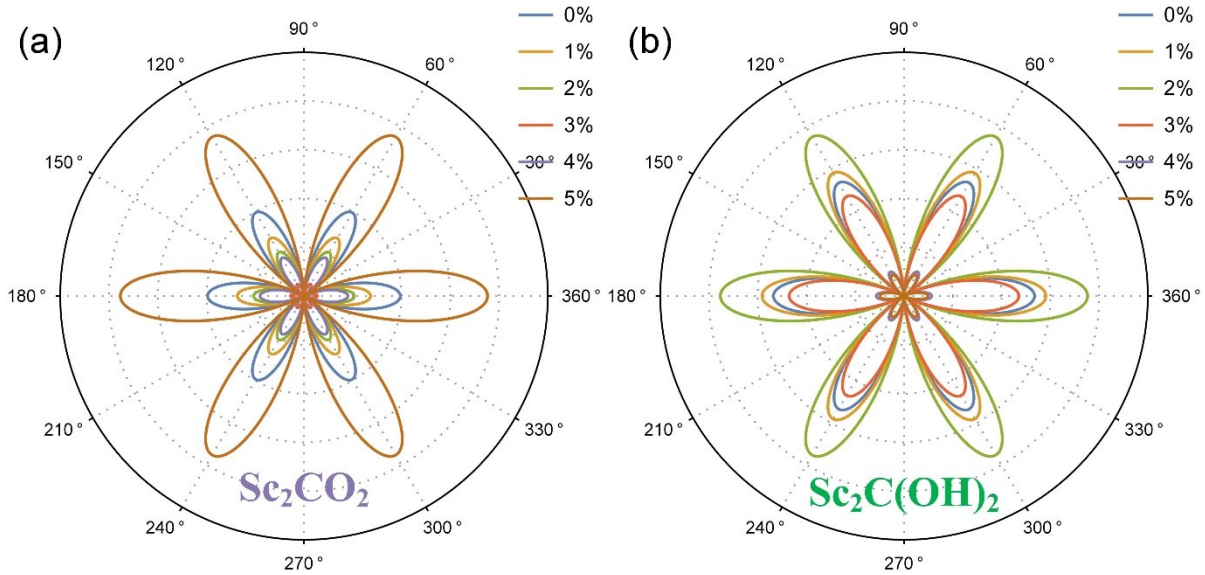


Figure S8. Perpendicular component of the SHG intensity under different tensile strained states for (a) Sc_2CO_2 monolayers and (b) $\text{Sc}_2\text{C}(\text{OH})_2$ monolayers.

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