Exploration of the origin of the excellent charge-carrier
dynamics in Ruddlesden-Popper oxysulfide perovskite

\( Y_2Ti_2O_5S_2 \)

Yisen Yao\(^ {1,2} \), Qiaoqiao Li\(^ 3 \), Weibin Chu\(^ 5 \), Yi-min Ding\(^ 2 \), Luo Yan\(^ 3 \), Yang Gao\(^ {2,3} \), Arup Neogi\(^ 2 \), Alexander Govorov\(^ {2,4,*} \), Liujiang Zhou\(^ {1,3,*} \), Zhiming Wang\(^ {1,2,*} \)

\(^ 1 \) Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, China.
\(^ 2 \) Yangtze Delta Region Institute (Huzhou), University of Electronic Science and Technology of China, Huzhou 313001, China.
\(^ 3 \) School of Physics, University of Electronic Science and Technology of China, Chengdu 610054, China.
\(^ 4 \) Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701, United States.
\(^ 5 \) Key Laboratory of Computational Physical Sciences (Ministry of Education), Institute of Computational Physical Sciences, Fudan University, Shanghai 200433, China.

* Corresponding authors

Part 1 The orbital overlap features in \( Y_2Ti_2O_5S_2 \)

The crystal orbital Hamilton populations (COHP) is calculated here to study the overlap between atoms (Figure 1S). The distance between two atoms can also reflect the bonding characteristics to a certain extent (Table 1). The distance between Y and S atoms is 2.82 Å, which is far from than Y–S single bond, indicating an ionic bond. The ELF Figure in text also confirmed this. However, there is still a little overlap between Y–\( d_{xy} \) and S–\( p_{x,y} \) orbital that contributes to CBM and VBM, respectively (Figure 1S (b)). The distance between Ti and O atom is 1.82 Å, which is smaller than Ti–O single covalent bond, indicating a weak covalent bond between Ti and O atom. From Figure 1S (b) we can find no overlap between Ti–\( d_{xy} \) and S–\( p_{x,y} \) orbital.
Figure S1. The COHP of selected atom (a) and selected orbital (b) in $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$. Ti$-d_{xy}$ orbital and S$-p_{x,y}$ orbital are the major contributors to CBM and VBM individually. We can discover that the optical transition between Ti and S atoms cannot happen because of the no overlap between Ti$-d_{xy}$ orbital and S$-p_{x,y}$ orbital.

Table S1. The table of bond length in our optimized structure and the covalent radii tested by Pekka Pyykkö.1-4

| The bond length of $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ (unit: Å) |  |
|---|---|---|
| O$_{\text{equator}}$ | O$_{\text{apex}}$ | S |
| Ti | 1.82 | 1.96 | 2.92 |
| Y | 2.44 | - | 2.82 |

<table>
<thead>
<tr>
<th>Covalent radii of the element involved in $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti single-bond</td>
<td>1.36</td>
</tr>
<tr>
<td>Y single-bond</td>
<td>1.63</td>
</tr>
<tr>
<td>O single-bond</td>
<td>0.63</td>
</tr>
<tr>
<td>S single-bond</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Part 2 The transition dipole moment (TDM) of $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$, CsPbI$_3$ and Ta$_3$N$_5$.

Figure S2. The TDM of $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ (a), CsPbI$_3$ (b) and Ta$_3$N$_5$ (c). Although the transition at $\Gamma$ point is allowed in $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$, it is still very weak compared to CsPbI$_3$ and Ta$_3$N$_5$. 
Part 3 The influence spectra, uACF and pure-dephasing function

Hefei-named packages are used based on hopping probabilities between the two states obtained as:\(^5\):
\[ P_{j\rightarrow k}(t,\Delta t) = \frac{2R[c_j c_k^* d_{jk}]\Delta t}{c_j^* c_j} \]  \hspace{1cm} E1
\[ d_{jk} = \langle \varphi_j | \frac{\partial}{\partial t} | \varphi_k \rangle = \sum_l \left( \langle \varphi_j | \nabla_{R_l} H | \varphi_k \rangle / (\epsilon_k - \epsilon_j) \right) R_l \]  \hspace{1cm} E2

\( c \) are the coefficients of wave functions. \( d_{jk} \) is the NAC between Kohn–Sham states \( j \) and \( k \). \( H \) is the Kohn-Sham Hamiltonian, \( \varphi_j, \varphi_k, \epsilon_k \) and \( \epsilon_j \) are the wave functions and eigenvalues for electron states \( j \) and \( k \). \( R_l \) is velocity vector of the nuclei. \( \langle \varphi_j | \nabla_{R_l} H | \varphi_k \rangle \) expresses the time-dependent orbital coupling including the overlap of two states. \( \epsilon_k - \epsilon_j \) express the bandgap here. The elastic scattering can be presented by the decay time in pure-dephasing function and the unnormalized autocorrelation functions (uACF). The uACF can be written as:\(^6,7\)
\[ C(t) = <\Delta E(t)\Delta E(0)>_T \]  \hspace{1cm} E3
where \( \Delta E(t) = E(t) - <E> \) is the fluctuation of the energy gap between the two states forming a coherent superposition from its average value. The pure-dephasing function is given by:
\[ D(t) = \exp[-\frac{1}{\hbar^2} \int_0^t dt' \int_0^{t'} dt'' C(t'')] \]  \hspace{1cm} E4

Fourier transforms (FTs) of the fluctuations for VBM-CBM energy gaps induced by phonon\(^6,8,9\), named influence spectra or spectral density, can reflect the phonon mode that participates in e-ph coupling and is given by:
\[ I(\omega) = \frac{1}{2\pi} \left| \int_{-\infty}^{\infty} dt e^{-i\omega t} C(t) \right|^2 \]  \hspace{1cm} E5

Part 4 The distribution of band edge and ELF in SrTiO\(_3\).
Figure S3 (a)(b) The partial charge density of VBM (a) and CBM (b) in SrTiO$_3$ with isosurface value 0.02 e/Å$^3$. (c) Electron localization function (ELF) in the (100) plane of SrTiO$_3$. The Ti–O bond is a mixture of ionic and covalent bonding, forming the network distribution of 0.2<ELF<0.7 in whole bulk.

**Part 5 The weak exciton effect in Y$_2$Ti$_2$O$_5$S$_2$.**

Figure S4 (a) The imaginary parts of the frequency-dependent dielectric function of Y$_2$Ti$_2$O$_5$S$_2$. The optical calculations with e-h interaction are presented, based on BSE level. (b) side view of exciton wave functions of Y$_2$Ti$_2$O$_5$S$_2$. A 5 × 5 × 1 supercell was adopted. The iso-value value is 8×10$^{-9}$ e/Å$^3$. The hole position is marked by a black spot in the rock-salt layer. The electron mainly distributes in the perovskite layer, which finely explains its extremely small density distribution of excitons.

**Part 6 The Robustness of electron-hole separated transport.**
Figure S5 The VBM and CBM’s partial charge density of snapshots at room temperature in Y$_2$Ti$_2$O$_5$S$_2$. We can find the robustness of electron-hole separated distribution, which is also the main character of electron-hole separated transport.