Supporting Information

Thermally-Assisted Photocatalytic Conversion of CO$_2$-H$_2$O to Ethylene over Carbon Doped In$_2$S$_3$ Nanosheets

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1. Experimental section.

1.1 Chemicals. Indium chloride (InCl$_3$·4H$_2$O), L-cysteine, triethylenetetramine (TETA) and thiourea were purchased from Aladdin Ltd. The carbon dioxide (CO$_2$) gas was bought from Air Liquide (Tianjin) Co. Ltd. Deionized water (DIW) was used in all the experimental processes. All chemicals were of analytical grade and used without further purification.

1.2 Synthesis of carbon doping In$_2$S$_3$ (C-In$_2$S$_3$). The organic-inorganic hybrid precursor InS-TETA was synthesized by our previous method.$^1$ 0.2212 g InCl$_3$·4H$_2$O and 0.7269 g L-cysteine were dissolved in 12 mL H$_2$O and 6 mL TETA (triethylenetetramine) in an aqueous solution, stirred vigorously for 30 minutes, and then transferred to a 25 mL Teflon-lined stainless steel autoclave. The mixture was heated to 160 °C for 24 hours, then naturally cooled to room temperature. At the end of the reaction, the white product formed was washed three times with deionized water and absolute ethanol and placed in a vacuum drying oven for drying. The obtained organic-inorganic hybrid is called InS-TETA. 10 mg as-prepared hybrid InS-TETA was put into a solvent of 12 mL DIW in a 20 mL Teflon-lined stainless-steel autoclave under vigorous stirring for 30 minutes to form a homogeneous solution. The autoclave was sealed and kept at 180 °C for 10 h. The yellow precipitate was washed by DIW and absolute ethanol, respectively, and dried in a vacuum oven to obtain C-In$_2$S$_3$.

1.3. Synthesis of In$_2$S$_3$. As reported in the literature,$^2$ 0.5863 g InCl$_3$·4H$_2$O and 0.6089 g thiourea were put in an agate and mixed uniformly. Then the mixture was placed in a 6 mm diameter quartz tube and put into a tube furnace. Then the temperature was raised to 220 °C at a heating rate of 10 °C/min under the air atmosphere for 5 minutes. Finally, it was cooled down naturally to room temperature. The as-obtained powder was washed three times with hot DIW and ethanol to remove impurities and dried in a vacuum oven to obtain an orange-
red solid called $\text{In}_2\text{S}_3$.


Powder X-ray diffraction (XRD) was performed on a Bruker D8 Focus Diffraction System using a Cu Kα source ($\lambda=0.154178$ nm). SEM was conducted with a Hitachi S-4800 scanning electron microscope equipped with the Thermo Scientific energy-dispersion X-ray fluorescence analyzer. TEM, HRTEM were obtained with a JEOL-2100F system equipped with an EDAX Genesis XM2. XPS measurements were conducted with a PHI-1600 X-ray photoelectron spectrometer equipped with Al Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed on a photoelectron spectrometer using Al Kα radiation as the excitation source (PHI 5000 VersaProbe) with or without illumination. All the peaks were calibrated with the C 1s spectrum at a binding energy of 284.8 eV. UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded on a Lambda 750 UV-Vis spectrometer (PerkinElmer) equipped with an integrating sphere. The UV-Vis DRS spectra of solid samples were collected in 200-800 nm against BaSO$_4$ reflectance standard. Raman spectroscopy was recorded on Renishaw inVia reflex Raman microscope under an excitation of 532 nm laser light with a power of 20 mW. Ultraviolet photoemission spectroscopy (UPS) measurements were performed with an unfiltered He I (21.22 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV. Spectroscopy Photoluminescence (PL) was carried out on a Supermini 200 with a 50 kV X-ray tube. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis is carried out in a continuous-flow mode under Visible light irradiated and dark conditions, respectively, with external heating of 150 °C. And the results were calculated by the Kubelka-Munk function. The gas-phase product was measured on Agilent 7890A with thermal conductivity detector (TCD) and Shimadzu GC-2010 Plus with Barrier Discharge Ionization Detector (BID). Helium (He) was used as a carrier gas. The $\text{C}_2\text{H}_4$ generated by $^{13}\text{CO}_2$ and $\text{D}_2\text{O}$ isotope experiments were analyzed by the QP2010Ultra gas
chromatography-mass spectrometer.

3. Thermal assisted Photocatalytic CO₂ Conversion.

The thermal assisted photocatalytic conversion of CO₂ and H₂O was carried out in a stainless steel reaction chamber equipped with a quartz window at a chamber volume of 75 mL. Before the photoreaction, the sample (30 mg) was well dispersed in the reaction chamber, and the gas in the chamber was discharged by a mechanical pump. CO₂ was bubbled into the chamber with 0.1 mL water and reached atmospheric pressure. The products formed in the irradiated chamber were measured at regular intervals under the 300 W xenon lamp (Beijing Perfect light PLS-SXE-300UV) with the light intensity of 1 W/cm² and external heating at 150 °C.

When the products were subjected to barrier discharge ionization detection for gas chromatography analysis, the GC-2010 gas chromatograph equipped with an activated carbon packed column (carrier gas He) was used. The overall formula during the photocatalytic conversion of CO₂-H₂O to C₂H₄ over C-In₂S₃ is supposed to be

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \begin{cases} \text{CO} \\ \text{CH}_4 \\ \text{C}_2\text{H}_6 \\ \text{C}_2\text{H}_4 \\ \text{O}_2 \end{cases} \]

The evolution rate of different products was calculated using equations (1). The selectivity of C₂H₄ among all products and hydrocarbons were calculated using equation (2) and (3).

\[
\text{Evolution Rate (µmol/ g/ h)} = \frac{\text{peak area of } X \times C}{\text{peak area of standard gas} \times t \times m} \times V \quad (1)
\]

\[
\text{Selectivity(C}_2\text{H}_4) = \frac{\text{Evolution Rate of C}_2\text{H}_4}{\text{Evolution Rate of all products}} \quad (2)
\]
Selectivity($C_2H_4$) = \frac{\text{Evolution Rate of } C_2H_4}{\text{Evolution Rate of hydrocarbons}} \tag{3}

$X$: The different products including $H_2$, CO, CH$_4$, C$_2$H$_4$ and C$_2$H$_6$.

$C$: The concentration of $X$ in standard gas.

$t$: The illumination time.

$m$: The mass of used catalyst.

$V$: The volume of used reactor.

4 The measurement of Quantum Efficiency. The Quantum Efficiency (QE) of our system is measured under external heating at 150 °C. In a typical procedure of the measurement of QE, 100 mg photocatalyst was well-dispersed in a stainless steel reaction chamber equipped with a quartz window at a chamber volume of 75 mL. CO$_2$ was bubbled into the chamber with 0.1 mL water and reached atmospheric pressure. 180 W Light Emitting Diode (LED) Electro Luminescent (EL) with the light intensity of 10 mW·cm$^{-2}$ in the wavelength of 420 nm was used as the light source and the irradiation area was fixed to 1.0 cm$^{-2}$ under external heating at 150 °C. The details of QE calculation were blown.

(1) The number of absorbed photons ($N_{\text{absorbed}}$):

$$N_{\text{absorbed}} = \frac{t (s) \times P (W \cdot cm^{-2}) \times \lambda (m)}{h (J \cdot s) \times c (m \cdot s^{-1})}$$

$$N_{\text{absorbed}} = \frac{1(s) \times 0.01(W \cdot cm^{-2}) \times 1(cm^{2}) \times 420 \times 10^{-9}(m)}{6.626 \times 10^{-34}(J \cdot s) \times 3 \times 10^{8}(m \cdot s^{-1})} = 2.1 \times 10^{16}$$

(2) The QE of CO$_2$ reduction was obtained by:

$$\text{QE} = \frac{(2n_{CO} + 8n_{CH}_4 + 12n_{C_2H}_4 + 14n_{C_2H}_6) (mol) \times N_a (mol^{-1})}{N_{\text{absorbed}}} \times 100 \%$$

$$\text{QE} = \frac{(2 \times 10.04 \times 10^{-11} + 8 \times 7.91 \times 10^{-11} + 12 \times 3.0 \times 10^{-10} + 14 \times 2.01 \times 10^{-11}) \times 6.02 \times 10^{23}}{2.1 \times 10^{16}} \times 100 \% = 13.33 \%$$

$P$: The optical power.
\( \lambda \): The wavenumber of the incident light.

\( c \): The speed of light.

\( h \): Planck constant.

5. **In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).**

*In situ* DRIFTS analysis was carried out in two sequential steps in a continuous-flow mode. Firstly, the catalysts were desorbed for 1 h in the \( \text{N}_2 \) atmosphere under 200 °C. Next, Data was collected in a continuous steam-saturated high purity carbon dioxide flow for 30 min at 4 cm\(^{-1}\) resolution and 128-time points were recorded under 150 °C for each experiment, with and without the LED light (420 nm) illumination. It should be noted that the background was collected in the \( \text{N}_2 \) atmosphere under 150 °C to exclude the effect of residues on the catalyst surfaces.
6. Supplementary data and figures.

Figure S1. TEM (a) and HRTEM (b) images of C-In$_2$S$_3$.

Figure S1a reveals the morphology of C-In$_2$S$_3$. Figure S1b shows that the lattice fringes of (311) plane of C-In$_2$S$_3$ become disordered after doping with carbon.
Figure S2. SEM (a), TEM (b) and HRTEM (c) images of In$_2$S$_3$.

Figure S2 reveals that the morphology of In$_2$S$_3$ is the same as C-In$_2$S$_3$ and the orderly lattice of In$_2$S$_3$ without carbon doping.
**Figure S3.** Carbonaceous matters analysis of the C-In$_2$S$_3$ and In$_2$S$_3$ by Raman spectra.

Figure S3 shows the Raman spectra of C-In$_2$S$_3$ reveals additional peaks ~1340, and 1525 cm$^{-1}$, which matches the characteristic vibrational modes of 6 $A_{1g}$, and 6 $E_{2g}$, respectively, in doped amorphous carbon with pentatomic and heptatomic rings. And the In$_2$S$_3$ sample did not show any characteristic peak at 1200-1600 cm$^{-1}$ (Figure S3), which indicates that the non-carbon-doped In$_2$S$_3$ did not form any carbonaceous materials.
Figure S4. The XPS spectra for survey scan of C-In$_2$S$_3$ (a) and In$_2$S$_3$ (b).

To prove the impact of C doping instead of N doping, we performed the XPS spectra for a survey scan of C-In$_2$S$_3$ and In$_2$S$_3$. The N element can be detected from the XPS spectra of both samples in Figure S4. It can be seen from the XPS spectra that the intensity of the N 1s peak is almost the same in both samples, but C-In$_2$S$_3$ has a stronger C 1s peak than In$_2$S$_3$. The signals for N may come from the XPS chamber during the measurements. So, we ignore the effect of N doping, and the dominant effect of C doping leads to the differences of product distributions between our two samples. Additionally, the N doping effect was often ignored in the other reports.\(^4\)
**Figure S5.** The (a) SEM (inset) and HRTEM after CO$_2$ reduction test for five cycles at 150°C, (b-d) XPS spectra for C 1s (b) In 3d (c) S 2p survey scan (d) after CO$_2$ reduction test for five cycles at 150°C

Figure S5 shows the SEM, HRTEM image and XPS spectra for C 1s, In 3d and S 2p survey scan of C-In$_2$S$_3$ after long-term CO$_2$ reduction test at 150°C. These results demonstrate that the C-In$_2$S$_3$ catalyst preserves its morphology and components after a long-term CO$_2$ reduction test.
Figure S6. (a) The CO$_2$-H$_2$O reduction performances of C-In$_2$S$_3$ at different temperatures for five hours. (b) The product distribution of C-In$_2$S$_3$ reacted for five hours of photocatalytic and thermal assisted photocatalytic, respectively.

Figure S7. SEM image after CO$_2$ reduction test for (a) one cycle and (b) five cycles at 180 °C.
Figure S8. The production of O$_2$ as a function of the reaction time of C-In$_2$S$_3$ under room temperature and slightly negative pressure in an online quartz reactor.

To demonstrate the overall photocatalytic mechanism, the evolution rate of oxygen as the oxidation product under room temperature and slightly negative pressure in an online quartz reactor was measured. Figure S8 showed the O$_2$ evolution rate of C-In$_2$S$_3$. The O$_2$ evolution rates over C-In$_2$S$_3$ were 4.9 μmol g$^{-1}$ h$^{-1}$, equivalent to 39.2 μmol g$^{-1}$ h$^{-1}$ of electrons, respectively. In the reduction reaction, the C-In$_2$S$_3$ consumed about 13.87, 5.22 and 24.16 μmol g$^{-1}$ h$^{-1}$ of electrons, respectively, to produce H$_2$, CH$_4$, and C$_2$H$_4$ under room temperature. The electrons from the water oxidation were almost comparable to the consumed electrons for the reduction reaction on the C-In$_2$S$_3$. This result demonstrated that H$_2$O as an electron donor in the whole photocatalytic process.
Figure S9. The XPS spectra for a survey scan of C-In$_2$S$_3$ (a) before and (b) after five cycles of photocatalytic conversion.

We did not detect any oxidation products other than O$_2$ in the product. This also confirms that the water acts as the electron donor and photocatalytic water splitting provides hydrogen source for C$_2$H$_4$. 
Figure S10. *In situ* DRIFTS spectra for CO$_2$ / H$_2$O vapor adsorption on C-In$_2$S$_3$ under Visible light irradiation at different times.
Computational calculations

The Materials Studio software was supported by the National Supercomputing Center in Shenzhen. Performing spin-polarization first-principles calculation based on Density Functional Theory (DFT) using CASTEP. The description of exchange-correlation energy was utilized the Perdew-Burke-Ernzerhof (PBE) exchange-correlation-function of the generalized gradient approximation (GGA). For the pseudopotentials, the projector-augmented-wave (PAW) method was adopted. Setting 450 eV as the energy cutoff for the plane-wave basis expansion. Setting the force on each atom to 0.05 eV / Å for the convergence criterion. In order to avoid layer-to-layer interaction, the slab model was constructed with a 15 Å vacuum layer in the z-direction. According to the Monkhorst-Pack method, the sampling in the Brillouin zone was set with 1×2×1. The van der Waals interaction was considered using the DFT-D3 scheme. In$_2$S$_3$ was simulated by a slab p(1×1)-(311) surface with a thickness of ~ 9 Å, with five bottom layers fixed to represent the bulk features during geometry optimization and reaction calculations. The surface is dominated by three-coordinated In and S, which termination can minimize the dangling bonds. Carbon dopants are introduced to replace sulphur at the sublayers, without directly bonding with CO$_2$ and other intermediates, but dopants can affect the local geometries and electronic structures of surface atoms. The Computational models are displayed following:

Figure S11. The Computational models of In$_2$S$_3$ (a, b) and C-In$_2$S$_3$ (c).
Figure S12. Calculated reaction energy diagram of H$_2$O to H$^*$ + OH$^*$ over C-In$_2$S$_3$ and In$_2$S$_3$. 

Figure S12. Calculated reaction energy diagram of H$_2$O to H$^*$ + OH$^*$ over C-In$_2$S$_3$ and In$_2$S$_3$. 

Figure S13. Calculated reaction energy diagram of CH* to CH* \(_2^*\) (a) and 2CH* \(_2^*\) to C\(_2\)H\(_4\) (b) over C-In\(_2\)S\(_3\) and In\(_2\)S\(_3\).
**Figure S14.** Uv-Vis diffuse reflectance (a) and Tauc plots with both direct and indirect fittings (b) of C-In$_2$S$_3$ and In$_2$S$_3$.

Figure S14 shows that the ($E_g$) of In$_2$S$_3$ and C-In$_2$S$_3$ are obtained to be 1.96 and 2.18 eV by fitting the Uv-Vis diffuse reflectance spectrum with a modified Kubelka-Munk function.
Figure S15. Ultraviolet photoemission spectroscopy (UPS) study in the cutoff (a) and the onset energy (b) regions of C-In$_2$S$_3$ and In$_2$S$_3$ (c, d). (UV light source is He I, 21.2 eV (80 mA, 530 V, 5.0 x 10$^{-2}$ mbar): valence band, with 0 eV binding energy corresponding to the Fermi level.)

We carried out the study of ultraviolet photoemission spectroscopy (UPS) (Figure S15). The valence band of C-In$_2$S$_3$ is 1.28 eV, which is more positive than the valence band of 1.24 eV of In$_2$S$_3$, which indicate that C-In$_2$S$_3$ has a stronger ability to oxidize H$_2$O.$^9$
Figure S16. Schematic illustration of the band structure of In$_2$S$_3$ and C-In$_2$S$_3$.

Changing the band structure of a material has an important effect on adjusting the redox properties of the material. The band structure of In$_2$S$_3$ and C-In$_2$S$_3$ was confirmed by the results of the Uv-Vis diffuse reflectance spectra (Figure S14) and ultraviolet photoemission spectra (Figure S15), as shown in Figure S16. We adjust the bandgap of the semiconductor by introducing carbon in indium sulfide. After doping with carbon, it was found that the bandgap of In$_2$S$_3$ became wider and the conduction band position became more negative, so it had a stronger ability to reduce CO$_2$, while the valence band position was higher with the ability to oxidize water enhanced. Both the reductive and oxidative ability of catalysts can be enhanced after carbon doping, benefiting the multi-electron reduction process.
Figure S17. Spectroscopy Photoluminescence (PL) of C-In$_2$S$_3$ and In$_2$S$_3$.

To evaluate the composite ability of photogenerated charge carriers of prepared C-In$_2$S$_3$ and In$_2$S$_3$, the determination of photoluminescence (PL) was performed. The corresponding peaks at around 450 nm and 580 nm of C-In$_2$S$_3$ are relatively weaker than that of In$_2$S$_3$ (Figure S17), indicating that the photoinduced carrier recombination is greatly reduced, which may be due to carbonaceous matter and the interface charge transfer between C-In$_2$S$_3$ is enhanced.
Table S1. The total consumed electron number (TCEN) for CO₂ conversion of the C-In₂S₃ and other semiconductors.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Condition</th>
<th>Light source</th>
<th>H₂ (µmol g⁻¹ h⁻¹)</th>
<th>CO (µmol g⁻¹ h⁻¹)</th>
<th>CH₄ (µmol g⁻¹ h⁻¹)</th>
<th>C₂H₄ (µmol g⁻¹ h⁻¹)</th>
<th>C₂H₆ (µmol g⁻¹ h⁻¹)</th>
<th>CH₃OH (µmol g⁻¹ h⁻¹)</th>
<th>TCEN (µmol g⁻¹ h⁻¹)</th>
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<tbody>
<tr>
<td>C-In₂S₃</td>
<td>CO₂ +H₂O</td>
<td>UV-Vis</td>
<td>14.6</td>
<td>10.0</td>
<td>7.9</td>
<td>30.0</td>
<td>2.1</td>
<td>472.7</td>
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<tr>
<td>CdS/Ni₃S₉/Al₂O₃¹⁰</td>
<td>CO₂ +H₂O</td>
<td>Visible light</td>
<td>841.0</td>
<td>121.0</td>
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<td>242.0</td>
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<tr>
<td>ZnIn₂S₄¹¹</td>
<td>CO₂ +H₂O</td>
<td>Simulated sunlight</td>
<td>33.2</td>
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<td></td>
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<td>66.4</td>
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<tr>
<td>TiO₂-graphene¹²</td>
<td>CO₂ +H₂O</td>
<td>Full light</td>
<td>5.2</td>
<td>26.7</td>
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<td>224.0</td>
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<td>TiO₂/g-C₃N₄¹³</td>
<td>CO₂ +H₂O</td>
<td>Visible light</td>
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<td>43.2</td>
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<td>Visible light</td>
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<td>Pt/GaN¹⁵</td>
<td>80 kPa CO₂ +H₂O</td>
<td>Full light</td>
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<td>~14.8</td>
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<td>218.4</td>
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<td>WN-WO₃¹⁶</td>
<td>CO₂ +H₂O</td>
<td>Simulated sunlight</td>
<td>368.5</td>
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<td></td>
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Table S2. Chemical compositions of C-In$_2$S$_3$ and In$_2$S$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>In</th>
<th>S</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-In$_2$S$_3$</td>
<td>34.93</td>
<td>53.88</td>
<td>11.18</td>
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<tr>
<td>In$_2$S$_3$</td>
<td>38.74</td>
<td>58.12</td>
<td>3.14</td>
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</table>

Error±2-3 % (atomic %)
Table S3. The chemical composition of C-In$_2$S$_3$ after five consecutive cycles.

<table>
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<th>Element</th>
<th>In</th>
<th>S</th>
<th>C</th>
</tr>
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<td>36.03</td>
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</table>

Error±2-3 % (atomic %)
Table S4. The catalytic activity of CO₂ conversion on C-In₂S₃ under different conditions

<table>
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<tr>
<th>Feed gas</th>
<th>illumination</th>
<th>Temperature (°C)</th>
<th>Production (μmol g⁻¹ h⁻¹)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>CO₂+H₂O</td>
<td>sun light</td>
<td>Room temperature</td>
<td>34.68</td>
</tr>
<tr>
<td>CO₂+H₂O</td>
<td>sun light</td>
<td>150</td>
<td>61.89</td>
</tr>
<tr>
<td>CO₂+H₂O</td>
<td>dark</td>
<td>150</td>
<td>trace</td>
</tr>
<tr>
<td>CO₂+H₂</td>
<td>dark</td>
<td>150</td>
<td>/ [b]</td>
</tr>
</tbody>
</table>

[a]: n.d. = not detectable. [b]: hydrogen is not quantified due to the presence in the feed gas.
References


(14) S. Feng, M. Wang, Y. Zhou, P. Li, W. Tu and Z. Zou, APL Mater. 2015, 3, 104416.
