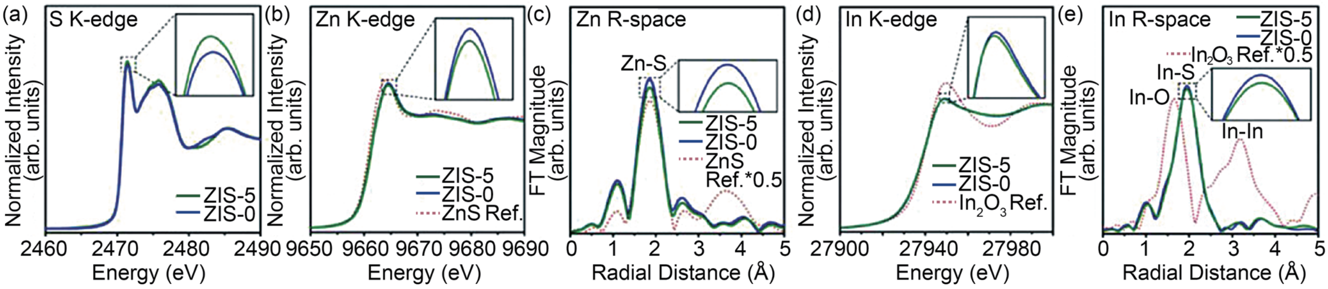

**Fig. 1**: (a) Normalized S K-edge XANES spectra for ZIS-0 and ZIS-5. (b) Normalized Zn K-edge XANES spectra and (c) Fourier transformed (FT) EXAFS spectra in R-space of ZIS-0, ZIS-5, and ZnS reference. (d) Normalized In K-edge XANES spectra and (e) FT EXAFS spectra in R-space of ZIS-0, ZIS-5, and $In_2S_3$ reference. [Reproduced from Ref. 1]

the ZIS structure plays a pivotal role in facilitating rapid charge transfer and effective charge separation, ultimately enhancing hydrogen production. This investigation meticulously explores how sulfur and indium vacancies improve charge dynamics and hydrogen evolution rates. By integrating the experimental data with multi-scale simulations, the study demonstrates how these vacancies optimize hydrogen production, offering valuable insights into the mechanisms by which structural vacancies in ZIS influence its electrochemical performance, particularly in hydrogen generation applications.

In summary, defect engineering of ZIS nanosheets with varying levels of indium and sulfur vacancies was successfully realized through hydrazine post-treatment of hydrothermally synthesized ZIS nanosheets. The photocatalytic HER rates show a positive correlation with the combined concentrations of indium and sulfur vacancies in the ZIS nanosheets. This study provides a detailed exploration of vacancy engineering in ZIS nanosheets, leveraging piezoelectric polarization in conjunction with the dipole field to enhance photocatalytic efficiency. (Reported by Yan-Gu Lin)

*This report features the work of Jih-Jen Wu and his coworkers published in Adv. Mater.* ***36****, 2403228 (2024).*

**TPS 32A Tender X-ray Absorption Spectroscopy**
**TPS 44A Quick-scanning X-ray Absorption Spectroscopy**

- XAS
- Materials Science, Chemistry, Condensed-matter Physics, Environmental and Earth Science

## Reference

1. W. J. Zhong, M. Y. Hung, Y. T. Kuo, H. K. Tian, C. N. Tsai, C. J. Wu, Y. D. Lin, H. C. Yu, Y. G. Lin, J. J. Wu, Adv. Mater. **36**, 2403228 (2024).

# Defect-Engineering for Selective Methanol Decomposition

*Undercoordinated Pt sites in $PtTe_2$ are crucial in facilitating methanol decomposition and promoting formaldehyde production.*

Two-dimensional transition metal dichalcogenides (TMDs) have garnered significant attentions in catalysis due to their unique electronic properties, high surface area, and tunable surface chemistry. Unlike conventional noble metal catalysts, which exhibit disadvantages such as high costs and susceptibility to poisoning, TMDs are promising alternatives owing to their structural versatility and defect engineering capabilities.[1,2] However, the basal planes of pristine TMDs are often inert, limiting their catalytic utility. Surface defects, particularly chalcogen vacancies, introduce the undercoordinated metal sites that can serve as highly active catalytic centers, significantly altering their chemical reactivity. Among TMDs, platinum telluride ($PtTe_2$) is of particular interest due to its intrinsic metallic nature, which provides superior conductivity compared to semiconducting TMDs such as $MoS_2$ or $WS_2$. A research team led by Meng-Fan Luo (National Central University), Jyh-Pin Chou (National Changhua University of Education), and Chun-Liang Lin (National Yang Ming Chiao Tung University) is investigating the catalytic properties of $PtTe_2$ with engineered Te vacancies. Their study focuses on $PtTe_2$, a metallic group-10 TMD, emphasizing the role of undercoordinated Pt ($Pt_{uc}$) sites at Te vacancies in methanol decomposition, which is a crucial reaction for hydrogen production and direct methanol fuel cells. To explore the catalytic behavior of $PtTe_2$, controlled $Ar^+$

bombardment was employed to selectively remove surface Te atoms, generating $Pt_{uc}$ sites while maintaining the structural integrity of the underlying Pt lattice. **Figure 1(a)** presents the scanning tunneling microscopy (STM) images before and after ion bombardment, confirming the introduction of single and multi-Te vacancies. **Figure 1(b)** further characterizes the defect structure through synchrotron-based photoelectron spectroscopy (PES), which reveals a shift in the Pt 4f binding energy. This shift indicates a lower oxidation state at $Pt_{uc}$ sites, which enhances their reactivity. To assess the influence of $Pt_{uc}$ concentration on catalytic performance, **Figs. 1(c) and 1(d)** quantify the methanol conversion probability as a function of vacancy density. At low $Pt_{uc}$ concentrations (≤10%), methanol conversion exceeds 90%, with high selectivity toward $CH_2O$ and $CH_4$. As $Pt_{uc}$ concentration increases (10%–20%), selectivity shifts, favoring C–O bond scission over dehydrogenation, which is further validated by near-ambient-pressure photoelectron spectroscopy (NAP-PES) and near-ambient-pressure mass spectroscopy results.

Methanol adsorption and decomposition were systematically investigated using synchrotron-based *in situ* NAP-PES and near-ambient pressure mass spectrometry (NAP-MS). As shown in **Fig. 2(a)**, the NAP-PES spectra for pristine $PtTe_2$ reveal that methanol does not undergo significant decomposition, confirming its catalytic inertness. In contrast, on defect-rich $PtTe_2$, the spectral intensity of methanol-related species ($CH_3OH$) decreases with increasing temperature, indicating the progressive methanol conversion. Concomitantly, peaks corresponding to $CH_2O$ (formaldehyde) and $CH_x$ species are observed, which demonstrate that $Pt_{uc}$ sites actively promote methanol dehydrogenation. NAP-MS results further confirm these findings by monitoring the gaseous products formed during the reaction (**Fig. 2(b)**). On $Pt_{uc}$-enriched $PtTe_2$, $CH_2O$ (formaldehyde) and $CH_4$ (methane) are the dominant products, whereas only trace amounts of CO and $CO_2$ are detected.

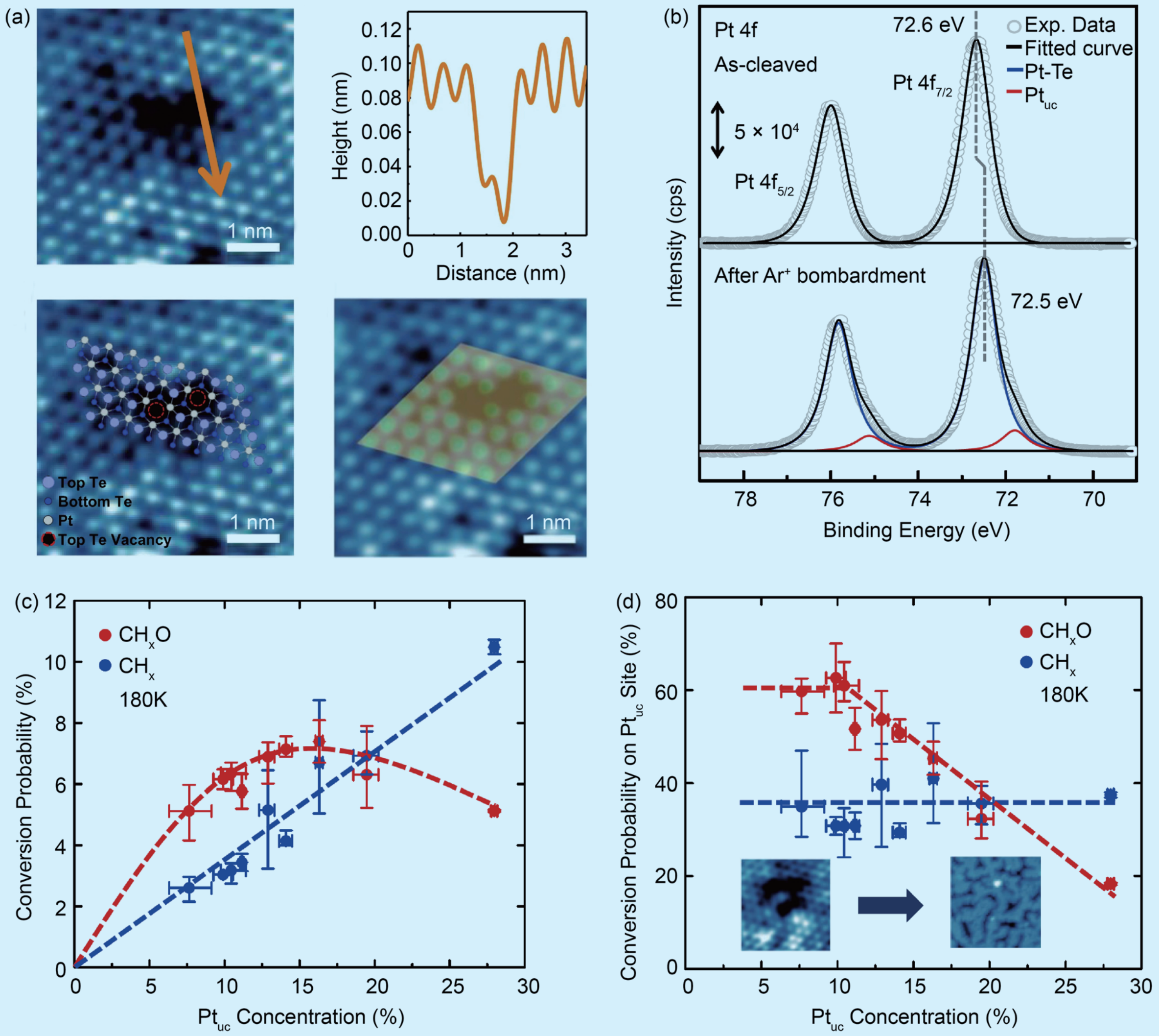

**Fig. 1**: (a) High-resolution image of two single-Te vacancies, the line profile across a single-Te vacancy, the overlap of the two single-Te vacancies model with the imaged ones and the overlap of the STM image with the DFT-simulated one produced based on the vacancy model. (b) PES spectra of Pt 4 f core level from layered $PtTe_2$ as cleaved and bombarded by $Ar^+$ (0.5 keV, 3 mins). (c,d) Varied reaction probabilities of methanol adsorbed on a $PtTe_2$ surface with $Pt_{uc}$ sites. Probabilities of conversion to $CH_xO^*$ (red circles) and $CH_x^*$ (blue) of monolayer methanol adsorbed on a $PtTe_2$ surface, and those on $Pt_{uc}$ sites as a function of the concentration of the surface $Pt_{uc}$. [Reproduced from Ref. 3]

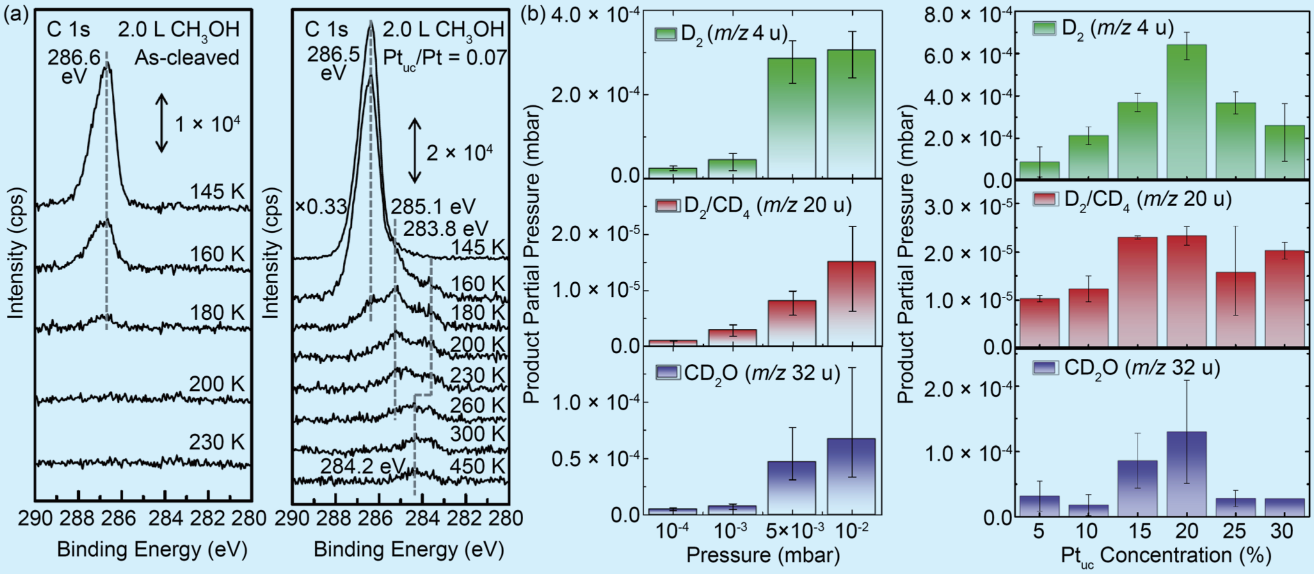

**Fig. 2**: (a) PES spectra of C 1s core level for methanol adsorbed on as-cleaved and Ar$^+$-bombarded PtTe$_2$ at 145 K and annealed stepwise to selected temperatures. (b) Production of $D_{2(g)}$ (*m/z* 4 u), $D_2O_{(g)}$ /$CD_{4(g)}$ (*m/z* 20 u), and $CD_2O_{(g)}$ (*m/z* 32 u) from PtTe$_2$ at 300 K, as a function of methanol-d$_4$ pressure (Pt$_{uc}$/Pt ratio 0.10) and Pt$_{uc}$ concentration ($10^{-2}$ mbar). [Reproduced from Ref. 3]

This highlights the selective nature of Pt$_{uc}$ sites, which favor formaldehyde formation over complete C–O bond scission, reducing unwanted CO poisoning, which is an issue commonly observed for conventional Pt catalysts. Additionally, the reaction selectivity shifts with increasing Pt$_{uc}$ concentration. At moderate defect densities (~10%), methanol decomposition predominantly follows the dehydrogenation pathway, producing $CH_2O$ and $CH_4$. However, at higher Pt$_{uc}$ densities (>10%), the C–O bond cleavage pathway becomes more competitive, leading to increased $CH_4$ and $H_2$ formation while slightly reducing $CH_2O$ selectivity. This trend is consistent with density functional theory (DFT)-calculated reaction barriers, which suggest that Pt$_{uc}$ sites lower the activation energy for selective dehydrogenation but can also facilitate C–O scission at higher defect concentrations.

In summary, this study establishes PtTe$_2$ with undercoordinated Pt sites as a highly efficient catalyst for methanol decomposition, offering superior activity and selectivity compared to conventional Pt catalysts. The unique triangular coordination and oxidation state variations of Pt$_{uc}$ sites play a crucial role in tuning the reaction pathways. By integrating advanced synchrotron-based PES, *in situ* NAP-PES/NAP-MS at **TLS 09A2** and **TLS 24A1**, and theoretical modeling, this work provides fundamental insights into defect engineering in TMDs. It lays the foundation for designing next-generation catalysts for methanol reforming, hydrogen production, and direct methanol fuel cells. (Reported by Hao Ming Chen, National Taiwan University)

*This report features the work of Meng-Fan Luo, Jyh-Pin Chou and Chun-Liang Lin published in Nat. Commun.* ***15****, 653 (2024).*

**TLS 09A2 Spectroscopy**
**TLS 24A1 XPS, UPS, XAS, APXPS**

- *In situ* NAP-XPS
- Materials Science, Thin-film Chemistry

## References

1. G. D'Olimpio, C. Guo, C.-N. Kuo, R. Edla, C. S. Lue, L. Ottaviano, P. Torelli, L. Wang, D. W. Boukhvalov, A. Politano, Adv. Funct. Mater. **30**, 1906556 (2020).
2. Y. Chen, S. Huang, X. Ji, K. Adepalli, K. Yin, X. Ling, X. Wang, J. Xue, M. Dresselhaus, J. Kong, B. Yildiz, ACS Nano, **12**, 2569 (2018).
3. J.-W. Hsueh, L.-H. Kuo, P.-H. Chen, W.-H. Chen, C.-Y. Chuang, C.-N. Kuo, C.-S. Lue, Y.-L. Lai, B.-H. Liu, C.-H. Wang, Y.-J. Hsu, C.-L. Lin, J.-P. Chou, M.-F. Luo, Nat. Commun. **15**, 653 (2024).