resolved in $\overline{\Gamma}-\overline{X}$, whereas the band splitting of RSSs was tiny in $\overline{\Gamma}-\overline{M}$, suggesting anisotropic behavior of the RSSs. In their DFT calculations, spin-split surface bands (a typical characteristic of RSSs) were observed and showed excellent agreement with the experimental results. An additional Rashba spin orbital coupling (SOC) was included in the DFT calculations; without this Rashba SOC, the RSSs still existed but the band splitting in momentum was somewhat small. This anisotropic behavior of RSSs could be correlated to a warping effect caused by the crystal symmetry in α-Sn. Moreover, an estimated Rashba coefficient $\alpha_R \approx 1.5$ eV·Å is ~4.5 times larger than that of Au(111). Having RSSs coexisting with TSS1 could provide an efficient and gate-tunable spin-charge conversion, which offers great potential in the application of spintronics devices.

In summary, their work reports a comprehensive study on the electronic structure of compressively strained α-Sn/InSb(001). A transition from a topologically trivial to non-trivial phase was observed at the critical thickness of 6 BLs. A pair of RSSs was newly discovered in α-Sn films thicker than 30 BLs; they were regarded as a preformed TSS and this provided insights into the evolution of a TSS in a topological phase transition and the surface electronic structure of a Dirac material. As revealed by their results, α-Sn provides a rich playground for realizing various topological phases of matter, such as topological Dirac semimetal (TDS), TI, *etc*. The coexistence of RSSs and TSS1, as typified by an efficient and gate-tunable spin-charge conversion, may offer great opportunities for applications in the modern technology of spintronics. (Reported by Cheng-Maw Cheng)

This report features the work of Raynien Kwo, Cheng-Maw Cheng and their collaborators published in Phys. Rev. B **105** *, 075109 (2022).*

TLS 21B1 Angle-resolved UPS
- High-resolution ARPES
- Materials Science, Condensed-matter Physics

Reference
1. K. H. M. Chen, K. Y. Lin, S. W. Lien, S. W. Huang, C. K. Cheng, H. Y. Lin, C.-H. Hsu, T.-R. Chang, C.-M. Cheng, M. Hong, J. Kwo, Phys. Rev. B **105**, 075109 (2022).

A Simple and Efficient Method for Hydrogen Spillover and Storage

Atomic hydrogen spillover and storage was achieved and characterized for single-site catalysts through precise control of the coverage of Ti on graphene. This realization has potential to extend all graphitic materials to store hydrogen.

Since the beginning of the industrial revolution in the 18th century, coal has been increasingly used as an energy source for the operation of machines, which have made human life convenient. In the 19th century, the advent of the petrochemical industry accelerated technological development. Although industrial, economical, and technological advances have made human life considerably convenient, they have come at the price of an energy crisis and environmental issues such as global warming. Furthermore, petroleum is expected to be completely exhausted in the future. Therefore, identifying alternative clean energy sources is inevitable. Hydrogen energy is one of the most notable candidates for alternative clean energy because its conversion emits no carbon and produces only water as a by-product, thereby minimizing the progress of global warming. Accordingly, technologies for effective production and storage of hydrogen are warranted.

Chung-Lin Wu (National Cheng Kung University) and Chia-Hao Chen (NSRRC), in collaboration with the National Enterprise for nanoScience and nanoTechnology (NEST, Italy), discovered a high-efficiency hydrogen storage method. In early studies, graphene was revealed to be inert when exposed to hydrogen molecules but highly active when exposed to H atoms.[1,2] In their previous works, they demonstrated that single Ti atoms can adsorb on graphene at its energetically favorable hollow sites[3] and studied the structural variation of graphene upon Ti deposition and its hydrogen uptake by conducting scanning tunneling microscopy.[4] Drawing on these previous results, they further

used Ti atomic deposition to mimic a single-atom catalyst (SAC) on graphene.[5] Unlike the previous study,[6] in which dissociated hydrogen sources were used, the present study demonstrated that atomically dispersed Ti atoms on crystalline graphene can produce an efficient spillover for hydrogen, which is then chemisorbed around the anchored Ti SACs. The H storage capacity discovered in this study exceeded that of Ti nanocluster catalysts at similar Ti loading.

The hydrogen spillover is illustrated in **Fig. 1**; angle-resolved photoemission spectroscopy (ARPES) spectra at **TLS 08A1** reveal Ti-adatom-induced renormalization of the graphene band structure for low Ti coverage (~0.03 monolayer; ML). Compared with pristine graphene that the Ti coverage was too low to break the lattice symmetry of graphene and retain a linear and gapless feature. Moreover, the band structure renormalization could be attributed to strong Ti 3d and C $2p_z$ orbital hybridization of the isolated Ti atoms in the graphene hollow sites. When the sample was exposed to 4.5 L of H_2 near 300 K (1 L, exposure to 1×10^{-6} Torr for 1 s), linear dispersion of the band structure of graphene and a gap of approximately 280 meV was observed. These findings indicated that hydrogen atoms were chemisorbed on graphene, which is evidence for the dissociation of gaseous H_2 molecules and atomic hydrogen spillover by isolated Ti SACs. Without Ti, neither band structure modification nor renormalization was observed in the ARPES spectrum of graphene obtained after H_2 exposure. Thus, Ti catalyst facilitated the dissociation of molecular H_2 and hydrogenation of graphene at approximately 300 K under vacuum. The hydrogen spillover in the Ti SACs on the graphene system was characterized using ARPES and other qualitative and quantitative measurements, including X-ray photoemission (XPS) at **TLS 24A1** and X-ray
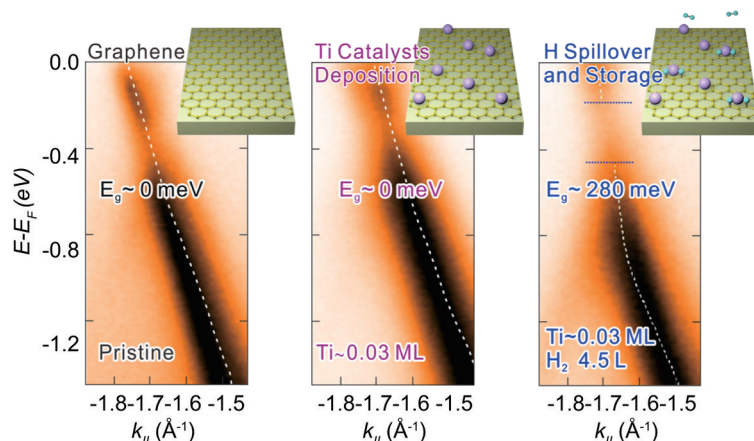
Fig. 1: ARPES measurements performed on pristine epitaxial graphene, after Ti deposition, and after a subsequent dose of H_2 molecules (4.5 L of H_2) at approximately 300 K. Band structure of pristine and Ti-doped graphene at a low coverage of 0.03 ML. The sample was then exposed to a 4.5-L dose of H_2. Data were measured along the direction K → Γ in the vicinity of the K point. White dashed lines indicate the energy dispersion fitted by the momentum dispersion curve. [Reproduced from Ref. 5]
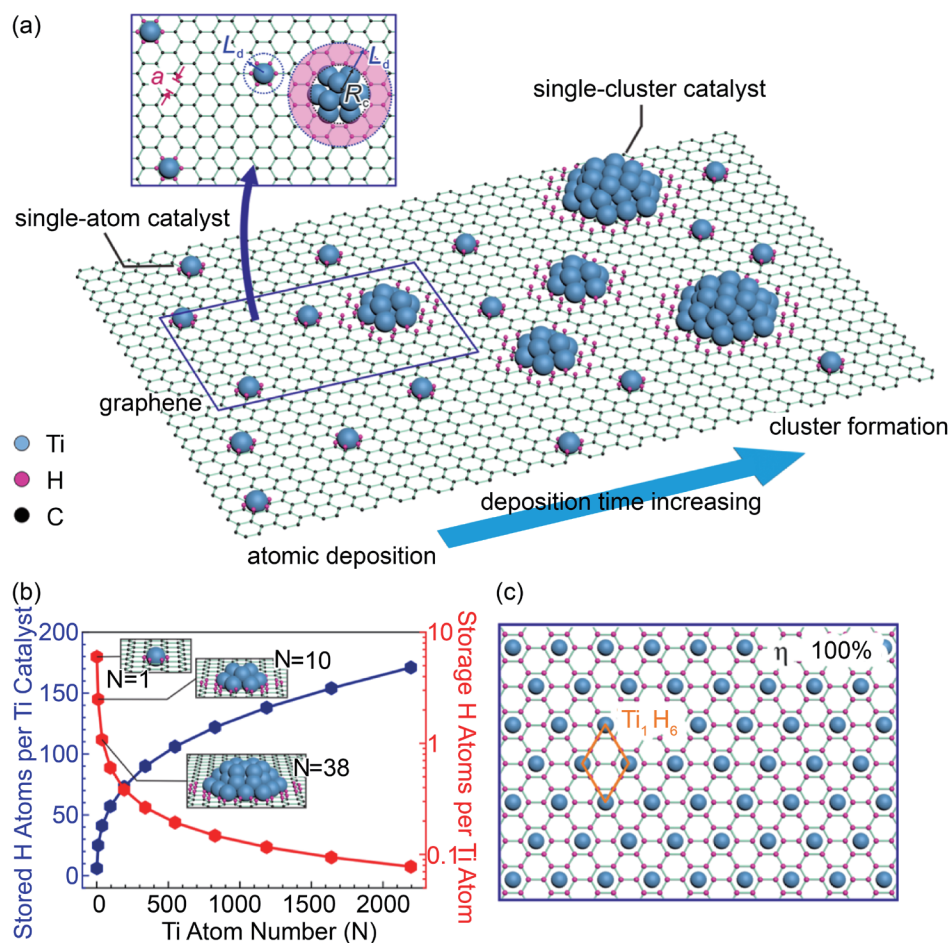
Fig. 2: (a) Schematic of hydrogen spillover from single-atom to single-cluster catalysts. Low-to-high Ti deposition yielded well-isolated atoms or nanocluster catalysts on graphene. From the spillover of H atoms on an isolated Ti atom and Ti nanocluster catalyst, the 2D-diffusion length L_d and nanocluster size (diameter R_c) could be used to estimate the H-storage capacity at low and high Ti coverage. (b) Calculation of H storage in the Ti SACs and Ti nanoclusters with a truncated-bipyramidal shape versus the number of Ti atoms N. (c) Schematic of full H storage ($\eta = 100\%$) on graphene obtained with Ti SACs through the formation of a TiH_6 structure. [Reproduced from Ref. 5]

absorption (XAS) at **TLS 09A2**. These findings indicate that a model based on the diffusion length of H on graphene and the size effect of Ti SACs should be developed. **Figure 2(a)** presents the hydrogen spillover and diffusion ability of the H atoms near each SAC and single-cluster catalyst. **Figure 2(b)** shows the simulated relationship between the number of atoms in the Ti SAC and the hydrogen storage efficiency. The result suggests that SACs have the highest hydrogen storage capacity. **Figure 2(c)** depicts the perfect condition for 100% hydrogen storage: a TiH_6 SAC structure on graphene.

In summary, Wu and Chen designed and simulated hydrogen spillover from single-atom to single-cluster catalysts by precisely controlling the coverage of Ti on graphene. The atomic nature of C–H bonds on graphene and the optimal H storage capacity were spectrally characterized using ARPES, XPS, and XAS. Given the short migration distance of H atoms diffusing on graphene at room temperature, the simulation results provide a general rule that will enable rational design of carbon-supported physisorbed metal catalysts for chemisorbed H storage through spillover. (Reported by Sheng-Shong Wong, National Cheng Kung University)

*This report features the work of Chung-Lin Wu, Chia-Hao Chen and their collaborators published in ACS Energy Lett. **7**, 2297 (2022).*

TLS 08A1 XPS, UPS
TLS 09A2 Spectroscopy
TLS 24A1 XPS, UPS, XAS, APXPS
- XPS, NEXAFS, UPS
- Materials Science, Chemistry, Surface, Interface and Thin-film Chemistry, Condensed-matter Physics, Chemical Materials

References

1. J.-X. Liang, J. Lin, X.-F. Yang, A.-Q. Wang, B.-T. Qiao, J. Liu, T. Zhang, J. Li, J. Phys. Chem. C **118**, 21945 (2014).
2. G. Srinivas, Y. Zhu, R. Piner, N. Skipper, M. Ellerby, R. Ruoff, Carbon **48**, 630 (2010).
3. J. W. Chen, H. C. Huang, D. Convertino, C. Coletti, L. Y. Chang, H. W. Shiu, C. M. Cheng, M. F. Lin, S. Heun, F. S. S. Chien, Y. C. Chen, C. H. Chen, C. L. Wu, Carbon **109**, 300 (2016).
4. T. Mashoff, M. Takamura, S. Tanabe, H. Hibino, F. Beltram, S. Heun, Appl. Phys. Lett., **103**, 013903 (2013).
5. J.-W. Chen, S.-H. Hsieh, S.-S. Wong, Y.-C. Chiu, H.-W. Shiu, C.-H. Wang, Y.-W. Yang, Y.-J. Hsu, D. Convertino, C. Coletti, S. Heun, C.-H. Chen, C.-L. Wu, ACS Energy Lett. **7**, 2297 (2022).
6. D. Lizzit, M. I. Trioni, L. Bignardi, P. Lacovig, S. Lizzit, R. Martinazzo, R. Larciprete, ACS Nano **13**, 1828 (2019).

Spatially Resolved Patterned Doping in Monolayer Transition-Metal Dichalcogenides

Area-selective doping of transition metals on the micron scale was achieved in tungsten-based dichalcogenides using a novel "open-replace-close" technique.

In recent years, monolayer transition-metal dichalcogenides (TMD) have attracted tremendous attention, owing to their potential for electronic, magnetic, optical, and catalytic applications. It has been recently recognized that substitutional doping of transition-metal atoms in monolayer TMDs is extremely useful for controlling their exotic physical and chemical properties, which can be improved for applications.[1–3] Substitutional doping of transition-metal atoms is an established method to tune material properties, which is typically carried out during the epitaxial growth of material films,[2] but it does not allow the spatial control of the doping material.[3] In a recent collaborative study reported in *Nanoscale*, researchers in Japan and Taiwan have developed a novel method to achieve area-selective doping on tungsten-based TMD monolayers.[4] In order to carry out spatial characterization of their micron-scale doping method, the authors used a combination of techniques, including optical spectroscopy, scanning-transmission electron microscopy (STEM), scanning photoelectron microscopy (SPEM), and micro-X-ray photoelectron spectroscopy (μ-XPS), and confirmed the efficacy of their "open-replace-close" (ORC) technique for the area-selective doping of monolayers.

Figure 1 (left panel, see next page) shows a schematic diagram of the three phases of the ORC substitution process for WSe_2 doped with Cr. In Phase I, the desorption of Se under the assistance of hydrogen proceeds according to the chemical reaction $WSe_2 \text{ (s)} + H_2\text{(g)} \rightarrow WSe_2\text{-}x\text{(s)} + H_2Se\text{(g)}$,