

Towards Atomically Thick LEGO

With the progress of graphene research, two-dimensional materials related to graphene attract wide attention in recent years. The common feature of these materials is that the bulk 3D crystals are stacked structures, with a van der Waals (vdW) interaction between adjacent sheets and strong covalent binding within each sheet. Due to the nature of vdW interaction, these stacked 2D materials are also known as vdW materials. These materials span a wide range from graphene with the simplest structure, to transition-metal dichalcogenides (TMD), transition-metal oxides and topological insulators, etc., containing diverse electronic structures and physical properties. VdW materials thereby possess diverse potential applications. Even more interestingly, because of the nature of their weak interlayer force, vdW materials are proposed to be able to stack as atomically thin LEGO to construct artificial superlattices

with designated functionalities.¹ To achieve such an ultimate goal, a thorough understanding of the intrinsic properties of vdW materials is essential.

In this regard, several research teams applied photoelectron spectroscopy (PES) with synchrotron radiation to study the fundamental electronic and chemical properties of various vdW materials in 2015.

The research team led by Forest Shih-Sen Chien (Tunghai University) utilized soft X-rays delivered by BL09A1 as a reducing agent for graphene oxide (GO), and made use of the character of PES, such as the sensitivity to surface and chemical states, to study the reduction dynamics of GO induced by soft X-rays.² By tuning the incident photon energy and the sample current density (SCD), Chien analyzed the evolution of the C

1s PES line shape and valence band maximum position of GO in detail; the evolution of carbon moieties upon soft X-ray irradiation and the deduced rate coefficients for GO reduction are shown in Figs. 1(a) and 1(b), respectively. These results indicate that the exposure to soft X-rays resulted in the dissociation of hydroxyl and functional carbonyl groups and in the formation of trigonal C–C bonds of GO; the dependence of the rate of X-ray reduction on the SCD exhibiting the reduction was attributed to the X-rays excited secondary electrons emitted from substrate. In summary, Chien's work yields clear experimental evidence regarding the mechanism of the GO reduction with soft X-rays, which might lead to an efficient method for mass production of high-quality graphene.

On the other hand, Ku-Ding Tsuei and his co-workers from NSRRC and National University of Singapore tackled another aspect of graphene properties, the many-body effects near the neutrality point of bilayer graphene (BLG). The ideal tool to investigate such effects is with angle-resolved photoemission spectroscopy (ARPES) as it probes directly BLG's band structures with information about both energy and momentum.

Fundamentally, a highly doped BLG behaves similar to an ordinary metal and is described with Fermi liquid theory, in undoped BLG, such as mechanically exfoliated BLG (ExBLG), this description is expected to fail; the system can be considered as quantum-critical, when the Fermi level (E_F) resides at the Dirac energy (E_D) and the system has no gap. In Tsuei's recent work,³ as shown in Fig. 2, using the ARPES system at BL21B1, they demonstrated that ExBLG on a Si substrate with native oxide has no gap and does not behave as a Fermi liquid. Tsuei's team observed for the first time in such charge-neutral BLG an electron-phonon coupling strongly dependent on anisotropic momentum space near the K-point as well as a directly observed non-Fermi liquid behaviour; their observations strongly support the existence of 2D quantum-critical points at the charge-neutrality point. Furthermore, the experimental evidences indicate that the thickness of vdW materials strongly affects their electronic structure, even in the simplest form of graphene. This information is of great importance when vdW superlattices are to be assembled.

Another family member of vdW materials that attracts much attention comprises TMD. Bulk TMDs are indirect band-gap semiconductors, but, interestingly, when thinned to a monolayer,

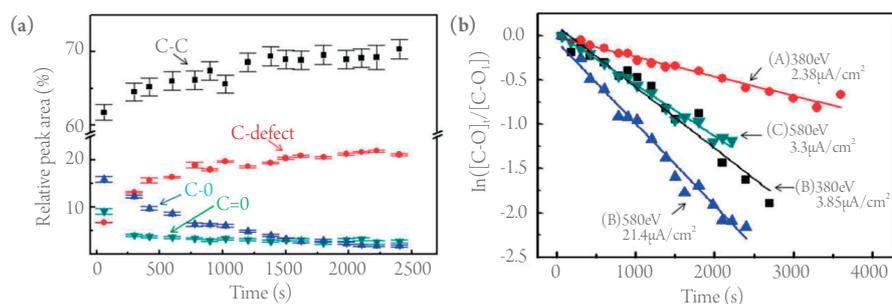


Fig. 1: (a) Evolution of C 1s core-level areas of C–C, C–O, C=O and C-defect signals with duration of exposure under X-radiation at 580 eV. (b) Logarithm of area ratio of the number of C–O moieties after exposure for period t and the number of C–O moieties of GO as deposited; $\ln([C-O]_t/[C-O]_i)$, versus period of soft X-ray exposure for four SCD. [Reproduced from Ref. 2]

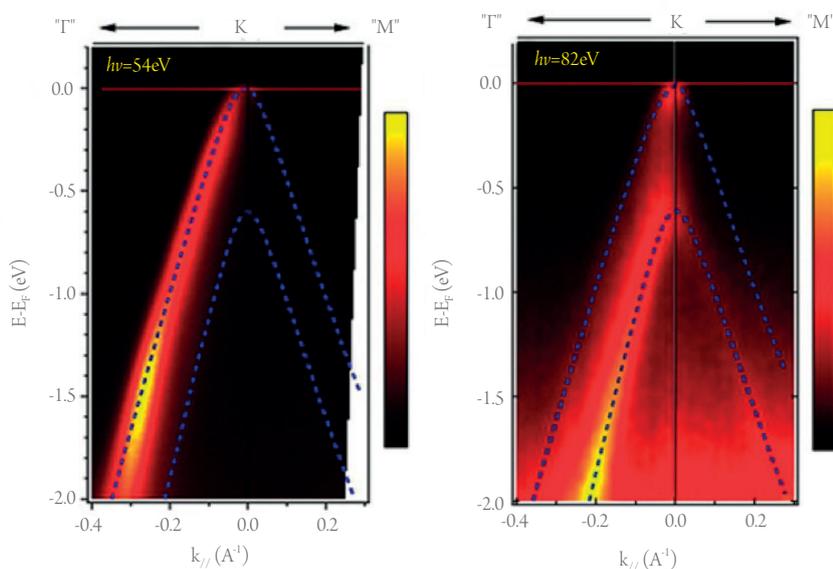


Fig. 2: Mapping of photoemission intensity of band dispersion around the K point taken at photon energies 54 and 82 eV. Whereas measurements at 54 eV enhance the outer band and suppress the inner band, measurements at 82 eV exhibit the opposite effect. [Reproduced from Ref. 3]

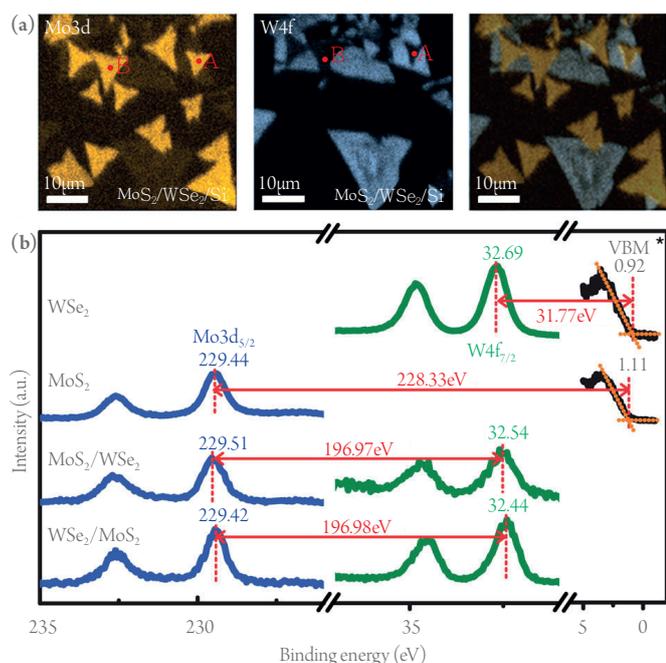


Fig. 3: SPEM measurements on stacked $\text{MoS}_2/\text{WSe}_2$ and $\text{WSe}_2/\text{MoS}_2$ heterostructures. (a) $\text{Mo}3d$ and $\text{W}4f$ mappings for the same physical area. The right figure is an overlapped mapping that allows the identification of $\text{MoS}_2/\text{WSe}_2$ stacked areas. Points A and B indicate a typical stacking area in which XPS is recorded. (b) Spectra of selected isolated WSe_2 and MoS_2 flakes, stacked $\text{MoS}_2/\text{WSe}_2$ and $\text{WSe}_2/\text{MoS}_2$ heterostructures. [Reproduced from Ref. 4]

they become direct band-gap semiconductors, which means that their heterojunctions (HJ) are ideal platforms for atomic layer optoelectronic applications. Since HJ band offset is the key parameter for the design of HJ-based electronic or photonic devices, an accurate determination of this parameter is critically important.

To understand the band alignment of TMD, Chih-Kang Shih (University of Texas at Austin, USA) Lain-Jong Li (Academia Sinica/King Abdullah University of Science and Technology, Saudi Arabia) and their co-workers, employed a scanning photoelectron microscopy (SPEM) located at **BL09A1**, to study the band alignment of single layer $\text{MoS}_2/\text{WSe}_2$ heterostructure.⁴

Using micro-focused soft X-rays delivered from SPEM (Fig. 3), in conjunction with scanning tunnelling spectroscopy, Shih and his collaborators determined the band alignment in TMD heterostructures. A type-II alignment in $\text{WSe}_2/\text{MoS}_2$ with a valence band offset 0.83 ± 0.07 eV and a conduction band offset 0.76 ± 0.12 eV was determined. The team discovered further that the TMD and its supporting graphite form also a semiconductor/semimetal heterostructure such that a transitivity holds for heterostructures formed between TMD and TMD/graphite.

All works describe above were aimed to elucidate the fundamental physical or chemical properties of vdW materials. Although we are still far from playing with vdW materials as LEGO, all this accumulated knowledge definitely bring us closer to this ultimate goal! (Reported by Chia-Hao Chen)

This report features the works of Ming-Hui Chiu, Chih-Kang Shih, Lain-Jong Li and their co-workers published in Nat. Commun. 6, 7666 (2015); of Cheng-Maw Cheng, Ku-Ding Tsuei, Barbaros Özyilmaz and their co-workers published in Sci. Rep. 5, 10025 (2015); and of Chi-Yuan Lin, Shih-Sen Chien and their co-workers published in J. Phys. Chem. C 119, 12910 (2015).

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How the Structure of Metallic or Bimetallic Nanocatalysts Affects the Reactivity of a Direct Methanol Fuel Cell

Green chemical energy is a promising source of energy in the pursuit of a natural environment free of pollution. By adopting the decomposition or oxidation of methanol on metallic nanocatalysts supported on oxides in electrochemical cells, the direct methanol fuel cell (DMFC) offers an efficient conversion to electricity and an abundant source of hydrogen, but the structure of a metallic or hetero-metallic nanocatalyst is found to play an important role in the electrochemical reactions in the design of a highly efficient cell or to improve the performance of DMFC operations. In 2015, scientists attempted to bridge the material gap between single metallic or core-shell nanocrystals (NC) and real catalysts by characterizing catalytic processes on supported metal or core-shell nanoclusters. A research team of Meng-Fan Luo (National Central University) investigated the

dependence on cluster size of supported rhodium (Rh) nanocatalysts in the decomposition of methanol. As Rh has been widely used and can be alloyed with primary platinum (Pt) catalysts in a DMFC, an investigation of the reaction mechanism and the cluster size in this model system might shed light on the design of a highly efficient catalytic system. From the hetero-structural point of view, another team of Tsan-Yao Chen (National Tsing Hua University) reported the effect of the bimetallic core-shell structure on electrochemical oxidation of MeOH in a full-stack module of a DMFC. Both reports illustrate the importance of catalytic structures on the efficiency of the methanol reaction in a DMFC cell.

From their investigation,^{1,4} the former team demonstrated the decomposition of methanol

and methanol- d_4 on Rh clusters supported on an ordered thin film of $\text{Al}_2\text{O}_3/\text{NiAl}(100)$ under UHV conditions with various surface techniques and calculations with density-functional theory. To investigate the correlation between structures of the Rh nanocatalyst and the methanol decomposition, the team performed advanced research in applying X-ray photoemission spectroscopy (PES) at **BL09A2**. In their work, the oxide-supported Rh nanocatalysts were carefully controlled *in situ* to imitate the conditions prepared in the NCU laboratory. To avoid contamination from the reactive gases in air, the research team performed PES measurements *in situ* immediately after the preparation of samples.

As Fig. 1 (a) shows, the C 1s PES spectra display the temperature dependence of the decomposition of