Hybrid van der Waals heterojunction based on two-dimensional materials

Cuicui Sun* and Meili Qi
School of Civil Engineering, Shandong Jiaotong University, Jinan 250300, China.
*Corresponding author’s e-mail: 204150@sdjtu.edu.cn

Abstract. Since the discovery of graphene, two-dimensional (2D) layered materials have always been the focus of material research. The layers of 2D materials are covalent bonds, and the layers are weakly bonded to adjacent layers through van der Waals (vdW) interactions. Since any dangling-bond-free surface could be combined with another material through vdW forces, the concept can be extended. This can refer to the integration of 2D materials with any other non-2D materials through non-covalent interactions. The emerging mixed-dimensional (2D+nD, where n is 0, 1 or 3) heterostructure devices has been studied and represents a wider range of vdW heterostructures. New electronic devices and optoelectronic devices based on such heterojunctions have unique functions. Therefore, this article depicts the research progress of (2D+nD, where n is 0, 1 or 3) vdW heterojunctions based on 2D materials.

1. Introduction
Since the peeling of graphene, the studies of thin 2D layers has received widespread attention. 2D materials cover various materials from insulators to semi-metals to semiconductors, which exhibit unique electronics, optics, and optoelectronic properties. The large specific surface area of 2D materials allows to adjust their inherent properties using various methods. Among them, the formation of van der Waals heterojunctions (vdWHs) has fascinated much vision, because 2D materials can not only be easily separated into different layers, but also be particularly easily to combine with other materials to build vdWHs. And any passivated surface without dangling bonds may attach with another material through vdW forces to form a mixed dimension: 2D+nD (n = 0, 1, and 3) vdWHs. Since there is no direct chemical bonding, vdWHs allows highly dispersed materials to be integrated together without being restricted by lattice matching. This provides a lot of freedom for the combination of 2D materials with other materials to create functional vdWHs.

2. 0D-2D van der Waals heterojunction
0D materials have strong light absorption, higher carrier transmission, adjustable optical band gap and good self-assembly function because of the quantum size effect and larger specific surface area. Therefore, 0D materials have been considered as one of the candidate materials for constructing hybrid vdWHs based on 2D materials.

2.1 0D-2D vdWHs based on metal nanoparticles
Generally, metal nanoparticles used as absorbers of electron to accelerate electron transport. Two-dimensional materials can inhibit the agglomeration of zero-dimensional particles, and can provide active sites for the reaction, and can also promote the separation of electron-hole pairs. In addition, the metal nanoparticle structure can focus and guide light with a specific frequency into the
2D material through design to increase the absorption rate, and lead to high spectral selectivity. Echtermeyer proved that the photodetector efficiency which were combined graphene with 0D nanoparticles can be increased by 20 times. Liu et al.[1] reported by transferring plasma gold nanoparticles to graphene, a high efficiency and high sensitive multicolor photodetector can be realized. The average peak light responsivity is approximately 2.2 mA W⁻¹, and the light responsivity is increased by 400%.

2.2 0D-2D vdWHs based on quantum dots
Depositing 0D quantum dots onto 2D materials could increase the device photodetection. PbS quantum dots (QDs) was integrated with graphene, which proved that the light guide gain is greater than 2×10⁸, the responsivity is about 10⁷ A W⁻¹. In order to optimize the properties, Kufer et al.[2] obtained a photodetector by coupling 0D PbS quantum dots and 2D MoS₂, which showed high light responsiveness as high as 10⁹ A W⁻¹ and can reduce dark current. In addition, the combination of graphene QDs and 2D MoS₂ can cause n-type doping[3], as shown in Figure 1(a), and the the barrier height was improved due to the doping effect at the MoS₂/InP device, making the power conversion efficiency of the prepared solar cells based MoS₂/InP device increased from 2.1% to 4.1%. Based on the MoS₂/quantum dot hybrid dimensional heterostructure, (Figure 1(b)) a reconfigurable optical memory with implanted photonic programming/electrical erasing operations is realized[4]. The special interaction between MoS₂ and QDs results in the removal of continuous n-doping on the MoS₂. So the long-lasting photocurrent and excellent optical storage characteristics were achieved.

3. 1D-2D van der Waals heterojunction
1D nanomaterials have a richer morphology, including nanowires, nanobelts, nanotubes, and so on. The research of 1D materials not only involves the electron, photon and phonon transmission, it also related to the research of nanometer and quantum size in the diameter direction. And the significant merit of one-dimensional materials have been expanded in the 1D-2D vdWHs.

3.1 1D-2D vdWHs electronic devices
The constructed 1D-2D hybrid structure can combine one-dimensional and two-dimensional materials to expand into three-dimensional space, depositing 1D nanomaterials on 2D ideal substrate. A controlled heteroepitaxial method was reported that to bond InAs nanowires to graphite films. And well-aligned vertical InAs arrays on a monolayer graphene substrate are prepared due to the same plane lattice between them[5]. This is of great significance for making full use of graphene InAs devices with excellent electrical properties. Semiconductor nanowire arrays vertically integrated on monolayers have been applied to many complex devices. The ZnSe nanowire/Si hybrid heterojunction has good diode characteristics, ideality factor (about 1.95), higher rectification ratio (about 10⁶), and lower rectification voltage (about 0.9 V). Moreover, the device also exhibits good photovoltaic behavior, and its photovoltaic cell efficiency is about 1.8%. The 1D-2D vdWHs combined of ZnO...
nanowires and single-layer BP is applied to build p-n diodes and BP-gated field effect transistors with n-ZnO channels. The diode shows static rectification, $10^4$ on/off ratio, and dynamic rectification in kilohertz, and the field-effect transistors excel in both electrostatic and kilohertz dynamics.

In addition, the use of 1D materials to modify 2D materials by assembling vdWHs can protect the original structure and inherent properties of 2D materials. The graphene-1D nanostructure vdWHs minimizes damage to the graphene lattice and retains its inherent electronic properties. Dry transfer of 1D Al$_2$O$_3$ nanoribbons to graphene retains the original characteristics of graphene and achieves a carrier mobility of up to $2.3 \times 10^4$ cm$^2$ V$^{-1}$ s$^{-1}$.

### 3.2 1D-2D vdWHs optoelectronic devices

The 1D materials not only has a longitudinal axis for absorbing incident sunlight, but also a radial minor axis for separating photo-generated charge carriers. Due to the large aspect ratio, 1D nanomaterials can be separated and recycled more easily after the photoreaction is completed. Moreover, the 1D materials have a large space surface area and enough reaction sites, which are suitable for building 1D-2D vdWHs.

Liu et al.[6] achieved a photoconductivity gain of about $10^5$ electrons/photons through CNT-graphene phototransistor by transferring CVD-grown graphene to CNT, as shown in Figure 2(a). The device has ultra-wide band light response, high light response and fast response time. Because both graphene and CNT have excellent mechanical strength, the fabricated flexible CNT-graphene photodetector not only has about 51 A W$^{-1}$ responsivity and about 40 ms response speed, but also has a high stability under severe bending conditions. In addition, nanorods arranged vertically on the 2D material can enhance its optoelectronic properties. For example, the 1D-2D hybrid structure constructed by depositing ZnO nanorods on a single layer of MoS$_2$[7] exhibits enhanced Raman and fluorescence emission than MoS$_2$, Figure 2(b). This is all result from the ZnO has the light antenna effect. UV photodetectors[8] was prepared by combining single-layer graphene and ZnO nanorods (Figure 2(c)). Under a bias voltage of -1 V, the responsivity was 113 A. W$^{-1}$, the photoconductive gain is about 385, which is much larger than a single graphene-based photodetector. The phototransistor and photoconductive sensor that use graphene mixed with other kinds of sensitizers can increase the responsiveness of the device. By combining graphene with different band gaps and 1D semiconductors (including CdSe nanoribbons and GaAs nanowires), a variety of photodiodes have been fabricated.

![Figure 2](a) A CNT-graphene phototransistor[6], (b) ZnO/MoS$_2$ photoluminescence structure[7], (c) ultraviolet photodetector that built by 1D ZnO array with a single-layer 2D graphene[8].

### 4. 2D-3D van der Waals heterojunction

In recent years, solar energy has become an alternative energy source to traditional fossil fuels. Compared with other renewable energy sources, solar energy has a bright future due to its abundant reserves. To use solar energy, semiconductor solar cells are developed to turn solar energy into electricity using photovoltaic effect. The conversion of solar energy into chemical fuels is essential to overcome the intermittency of solar radiation. While the photoelectrochemical system is considered to be a promising chemical fuel production method due to its low cost and energy consumption as well as the environmental protection.
4.1 Photovoltaic applications of 2D-3D vdWHs
The build of the metal/semiconductor heterojunction is a direct method for manufacturing photovoltaic devices. By selecting two materials with large differences in work function, a larger photovoltaic voltage can be obtained. However, the construction of the junctions tends to introduce interface effect, that could reduce the photovoltage. In addition, since the metal is opaque, the metal will reduce the light absorption in semiconductor. This will reduce the use of sunlight, thereby reducing energy conversion efficiency. Therefore, the addition of 2D layered materials on the basis of 3D semiconductors has opened up new areas for the design of devices with new functional interfaces and excellent optoelectronic properties.

Because the amorphous carbon film itself has high transparency, high photoelectric tunability, relatively high hardness and great chemical inertness, they could be introduced on silicon to form photovoltaic junctions. The power conversion efficiency of graphene/GaAs devices was increased to 15.5% by introducing trifluoromethanesulfonic acid doped graphene and alumina antireflection layer. It can lead to a higher Schottky barrier, and its power conversion efficiency can reach 23.8%. The MoS2/InP vdWHs[9] photovoltaic performance was improved by the gate effect. The conversion efficiency increased from 4.0% to 7.1% when the gate voltage was 6 V. In addition to the MoS2/semiconductor heterojunction, an ultra-thin WS2/Si vertical heterojunction is also constructed, which can be used as a photodetector with broadband optical response and good detection performance.

4.2 photoelectrochemical applications of 2D-3D vdWHs
As we all know, Most photoelectrodes used today are very susceptible to light corrosion. A popular way to solve the problems is to add a layer to construct a layered heterojunction protective film. Therefore, it is very necessary to use new two-dimensional protective layer materials to construct photoelectrode which is lower cost, higher efficiency and more stable. By integrating transparent graphene and semiconductor (silicon), a Schottky barrier can be formed to effectively separate carriers. In addition, graphene can act as a protector in the electrolyte solutions to prohibit the reactions in semiconductor. Therefore, integrating graphene with 3D semiconductors may simultaneously achieve higher stability, better transparency, and higher conductivity for photoelectrochemical devices. The graphene layer treated with N2 plasma deposited on the silicon nanowire photocathode as an efficient hydrogen evolution reaction catalyst. Due to the large number of defects introduced in the plasma treatment, the N-graphene layer can effectively promote the Faraday reaction by reducing the double-layer charge transfer resistance. The starting potential of the composite electrode is 0.09 V higher than that of Si nanowires. Hou et al.[10] reported the α-Fe2O3/graphene/BiV1-xMxO4 core/shell structure, as shown in Figure 3, in which the α-Fe2O3 nanorod used as core, the graphene used as interlayer and BiV1-xMxO4 used as shell. It is observed that the graphene oxide form a "bridge", covering and connecting the Fe2O3 array. This unique structural provides a connected interface between the nanorods and reduced graphene oxide, which helps to improve charge separation, thereby improving photoelectrochemical activity. The photocurrent density generated by the heterojunction is about 1.97 mA cm⁻².

Figure 3. Synthetic pathway of Fe2O3 nanoarray/graphene oxide/BiV1-xMxO4 heterojunction[10].
The great potential of 2D layered materials has promoted continuous progress in the research of two-dimensional materials. Several main elements Mo, W, S, C, and N in transition metal disulfides and graphene and their derivatives are abundantly stored in nature, providing prerequisites for large-scale industrial production. The various properties of two-dimensional materials (light, electricity, and magnetism) can also be modified in many different ways, which provides conditions for the functionalization of two-dimensional materials. Importantly, 2D layer materials can not only form 2D/2D vdWHs, but also be built to 0D/2D, 1D/2D and 2D/3D mixed-dimensional vdWHs, which provide new platform for structural engineering and functional design.

5. Conclusion
In general, the combination of 2D materials with other kinds dimensions of nanomaterials has greatly broaden the research field of 2D materials and become a material with potential in the next few years. This provides more ways for realizing any combination of 2D materials and other materials. In addition, through appropriate material selection, these heterojunctions can provide more innovative interaction methods stimulated by external factors. Clearly, the emergence of mixed-dimension vdWHs will make two-dimensional layered materials a permanent hot spot, which will eventually lead to major breakthroughs in new material devices. Moreover, although the mixed-dimensional heterostructure has been confirmed from the micro-scale mechanical peeling samples, the repeated synthesis of 2D materials is still in its infancy. In addition, unlike traditional semiconductor technology, most of the materials mentioned above have an interface thickness of less than 5 nanometers, which means that the quality and thickness uniformity of single crystal films are very important. In general, the huge integration possibilities brought about by the mixed-dimensional vdWHs indicate that this field has considerable future growth potential in terms of basic research and applied technology.

Acknowledgments
This work was supported by the Doctoral Scientific Research Foundation of Shandong Jiaotong University (BS50004943), Scientific Research Fund Project of Shandong Jiaotong University (Z201916), and the Natural Science Foundation of Shandong Province (ZR2020QE070).

References
[1] Liu, Y., Cheng, R., Liao, L., Zhou, H., Bai, J., Liu, G., Liu, L., Huang, Y., Duan, X. (2011) Plasmon resonance enhanced multicolour photodetection by graphene. Nat. Commun., 2: 579.
[2] Kufer, D., Nikitskiy, I., Lasanta, T., Navickaite, G., Koppens, F. H. L., Konstantatos, G. (2015) Hybrid 2D-0D MoS2-PbS Quantum Dot Photodetectors. Adv. Mater., 27: 176-180.
[3] Wang, P., Lin, S., Ding, G., Li, X., Wu, Z., Zhang, S. Xu, Z., Xu, S., Lu, Y., Xu, W., Zheng, Z. (2016) Enhanced monolayer MoS2/InP heterostructure solar cells by graphene quantum dots. Appl. Phys. Lett., 108: 163901.
[4] Sun, Y., Ding, Y., Xie, D., Sun, M., Xu, J., Yang, P., Zhang, Y., Ren, T. (2021) Reconfigurable optical memory based on MoS2/QDs mixed-dimensional van der Waals heterostructure. 2D Mater., 8: 025021.
[5] HONG Y J, LEE W H, WU Y, et al. van der Waals epitaxy of InAs nanowires vertically aligned on single-layer graphene [J]. Nano Letters, 2012, 12(3): 1431-1436.
[6] Liu, Y., Wang, F., Wang, X., Flahaut, E., Liu, X., Li, Y., Wang, X., Xu, Y., Shi, Y., Zhang, R. (2015) Planar carbon nanotube-graphene hybrid films for high-performance broadband photodetectors. Nat. Commun., 6: 8589.
[7] Zhang, K., Zhang, Y., Zhang, T., Dong, W., Wei, T., Sun, Y., Chen, X., Shen G., Dai, N. (2015) Vertically coupled ZnO nanorods on MoS2 monolayers with enhanced Raman and photoluminescence emission. Nano Res., 8: 743-750.
[8] Nie, B., Hu, J. G., Luo, L. B., Xie, C., Zeng, L. H., Lv, P., Li, F. Z., Jie, J. S., Feng, M., Wu, C. Y., Yu, Y. Q., Yu, S. H. (2013) Monolayer graphene film on ZnO nanorod array for high-performance Schottky junction ultraviolet photodetectors. Small, 9: 2872-2879.
[9] Lin, S., Wang, P., Li, X., Wu, Z., Xu, Z., Zhang, S., Xu, W. (2015) Gate tunable monolayer MoS$_2$/InP heterostructure solar cells. Appl. Phys. Lett., 107: 153904.

[10] Hou, Y., Zuo, F., Dagg, A., Feng, P. (2012) Visible Light-Driven α-Fe$_3$O$_4$ Nanorod/Graphene/BiV$_{1-x}$Mo$_x$O$_4$Core/Shell Heterojunction Array for Efficient Photoelectrochemical Water Splitting. Nano Lett., 12: 6464-6473.