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Recent trends in covalent functionalization of 2D materials

Jae Hwan Jeong,^a Sojung Kang,^b Namwon Kim,^{bcd} Rakesh Joshi^e and Gwan-Hyoung Lee^{id}*^{bfg}

Covalent functionalization of the surface is more crucial in 2D materials than in conventional bulk materials because of their atomic thinness, large surface-to-volume ratio, and uniform surface chemical potential. Because 2D materials are composed of two surfaces with no dangling bond, covalent functionalization enables us to improve or precisely modify the electrical, mechanical, and chemical properties. In this review, we summarize the covalent functionalization methods and related changes in properties. First, we discuss possible sites for functionalization. Consequently, functionalization techniques are introduced, followed by the direct synthesis of functionalized 2D materials and characterization methods of functionalized 2D materials. Finally, we suggest how the issues may be solved to enlarge the research area and understanding of the chemistry of 2D materials. This review will help in understanding the functionalization of 2D materials.

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1. Introduction

Research on two-dimensional (2D) materials has exploded since the mechanical exfoliation of graphene using a scotch tape method was invented.¹ After graphene, other 2D materials, such as transition metal dichalcogenides (TMDCs),^{2,3} hexagonal boron nitride (hBN),^{4,5} black phosphorous (BP),^{6–8} MXene,^{9–11} and 2D oxides,^{12,13} have been found and studied. The unique properties of 2D materials, such as their atomic thinness, van der Waals (vdW) gap, dangling-bond-free surface, and high crystallinity, allow precise control of properties by electrical modulation and surface absorption, leading to extensive research into the properties and applications of 2D materials.^{14–22}

However, wide application of 2D materials has been hindered by their limitations. Atomic-level thinness and large

^a Department of Materials Science and Engineering, Yonsei University, Seoul, 03722, Republic of Korea. E-mail: pee8379@yonsei.ac.kr

^b Research Institute of Advanced Materials (RIAM), Seoul National University, Seoul 08826, Korea. E-mail: n.sojung.kang@gmail.com

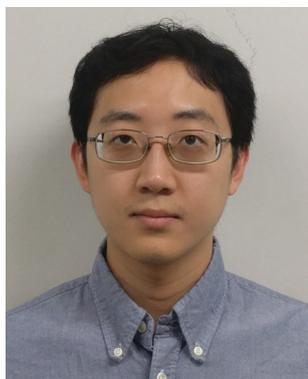
^c Ingram School of Engineering, Texas State University, San Marcos, TX 78666, USA. E-mail: namwonkim@txstate.edu

^d Materials Science, Engineering, and Commercialization (MSEC), Texas State University, San Marcos, TX 78666, USA

^e School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia. E-mail: r.joshi@unsw.edu.au

^f Institute of Engineering Research, Seoul National University, Seoul, 08826, Korea. E-mail: gwanlee@snu.ac.kr

^g Department of Materials Science and Engineering, Seoul National University, Seoul 08826, Korea



Jae Hwan Jeong

Jae Hwan Jeong is a graduate student at Yonsei University under the supervision of Prof. Gwan-Hyoung Lee.



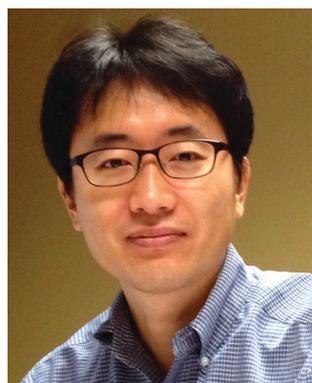
Sojung Kang

Dr Sojung Kang is a postdoctoral researcher at Seoul National University under the supervision of Prof. Gwan-Hyoung Lee. She received a PhD in Materials Science and Engineering from Yonsei University.

surface area result in high defect sensitivity in 2D materials. Exfoliation or dispersion of 2D materials, which are mandatory for most chemical modification processes, can introduce many defects.^{23–25} Several 2D materials, such as BP, are susceptible in the ambient environment and degrade over time.^{26,27} Therefore, making 2D materials more versatile has been an attractive issue to researchers for some time. With proper modification or treatment on 2D materials, more intriguing properties can be achieved for wide-ranging application. Compared with conventional bulk materials, 2D materials are more likely to be affected by traditional surface modification techniques, such as substitutional element doping,^{28,29} defects generation,^{30–32} composite formation with polymers,^{33–35} decoration with metal nanoparticles,^{36,37} and functionalization by physisorption.^{38–40} Conversely, 2D materials allow new modification methods that are inapplicable to traditional 3D materials, including assembly of stacked heterostructures,^{41–50} the intercalation of other ions

or molecules between layers,^{51–54} and the modification of structures by ripple^{55–57} or rolling.^{57–59} Among them, covalent functionalization, which introduces covalent bonds between functional groups and 2D materials, has been widely studied for its versatility. Covalent functionalization of many 2D materials, such as graphene,^{60–67} graphene oxide (GO),^{60,68,69} TMDCs,^{70–74} BP,^{75–77} hBN,^{78,79} MXene,⁸⁰ 2D oxides,^{72–74,81} and others,^{40,82} have been extensively studied for a variety of applications, including biology,^{73,75,81,83–95} polymer composites,^{33–35,96} environmental technology,^{35,97–99} energy,^{60,100–103} electrical,^{100,104–108} optics,⁶⁰ and catalytic engineering.^{106,109–112}

There are plenty of review papers that cover the covalent functionalization of 2D materials. However, most of them are focused on specific 2D materials, applications, functionalization techniques, or functional groups, and there was no review paper dedicated to covalent functionalization techniques for general 2D materials. In this paper, we review various covalent functionalization methods and their related applications. As shown in Fig. 1, the discussion begins with the functional group at different locations, followed by individual functionalization techniques and the direct synthesis of functionalized 2D materials. Finally, common characterization techniques for functionalized 2D materials will be briefly introduced. From here on, the term covalent functionalization indicates functionalization by forming a covalent bond between 2D materials and functional groups. Other surface modification techniques, such as non-covalent and substitutional doping, are not discussed in this paper.



Namwon Kim

Namwon Kim is an associate professor of Ingram School of Engineering at Texas State University. He received his PhD from the Department of Mechanical Engineering at Louisiana State University in 2009 and worked as a postdoctoral researcher at Columbia University and the Center for BioModular Multi-Scale Systems. His research interests focus upon advanced multi-scale manufacturing and surface engineering, experimental

microfluidics and optical measurements, and transport phenomena as related to micro/nano-systems for bio-medical/analytical applications.

2. Sites for covalent functionalization

Location is a critical factor for the functionalization of 2D materials because different reaction sites require different reaction mechanisms between functional groups and 2D materials. In this section, we focus on the reaction mechanisms at each site, with the functionalization examples order of edge, vacancy, grain boundary, basal plane, local strain, and existing functional group.



Rakesh Joshi

Rakesh Joshi FRSC is an Associate Professor at the School of Materials Science and Engineering, UNSW Sydney, leading the graphene research group. Before joining UNSW, he was a Marie Curie International Fellow at the University of Manchester. A/Prof. Joshi is among a select group of researchers who have been awarded each of the world's most prestigious relevant International Research Fellowships; the JSPS Invitation Fellowship, the Hum-

boldt Fellowship and the Marie Curie International Fellowship. Rakesh Joshi has over 95 journal articles (and 4 patents), with over 75 articles as the first/corresponding author.



Gwan-Hyoung Lee

Gwan-Hyoung Lee is an associate professor at Seoul National University. He received a PhD in Materials Science and Engineering from SNU. Then, he worked for Samsung Electronics. In 2010, he joined Columbia University as a postdoctoral researcher. After five years at Yonsei University, he is now with SNU since 2019. His research activities include the investigations of electrical, mechanical, and optical properties of

2D materials as well as 2D-material-based heterostructure devices for electrical and optoelectronic applications.

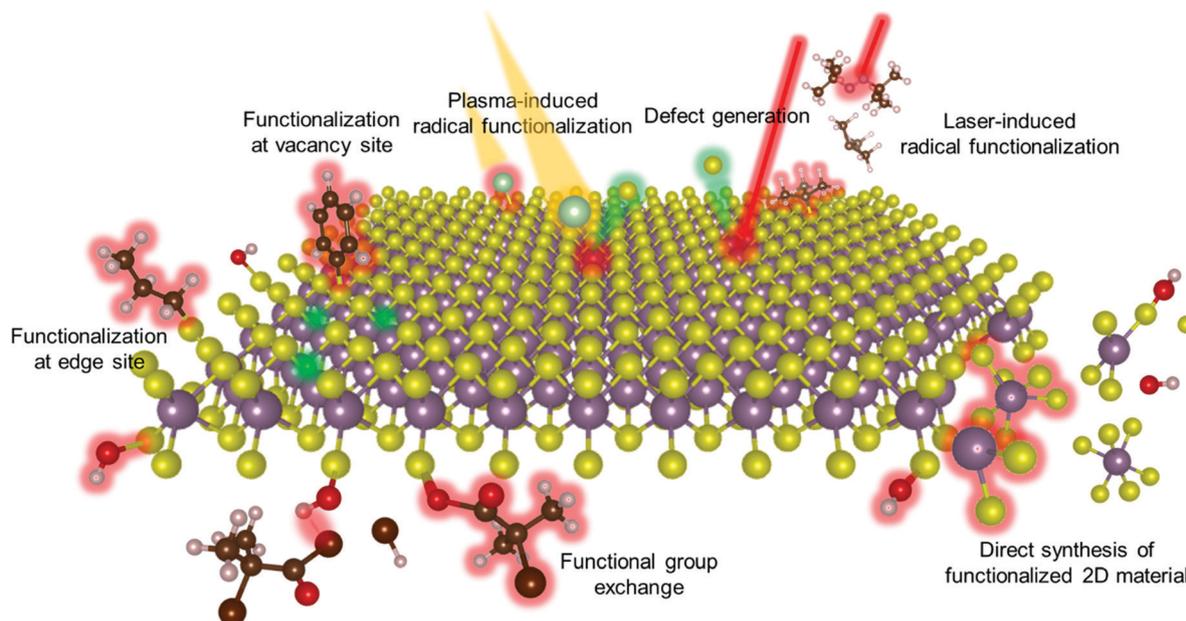


Fig. 1 Schematic illustration of functionalization sites and various techniques for covalent functionalization of 2D Mater.

2.1 Edge

Despite the fact that the surfaces of 2D materials are dangling-bond-free, their inevitable edges have dangling bonds. The high chemical potential of the edges can be utilized as catalysts for hydrogen evolution reactions (HER)^{113,114} and active sites to attach to the functional group.^{115,116}

The introduction of more edge sites to 2D materials has been widely studied^{117,118} for relatively stable 2D materials, such as graphene and hBN,^{115,116} where the edges spontaneously bond with other molecules or atoms. For example, sonication with water^{119,120} or ball milling with NaOH solution¹²¹ can functionalize hBN with a hydroxyl group (–OH). Other groups or elements, such as halogen (F, Cl, Br, I),^{122,123} hydrogen,¹²⁴ nitrogen,¹²⁵ and NH₂¹²⁶ are similarly functionalize the edge using the ball-mill method under selected environmental conditions. These naturally or intentionally generated functional groups become highly concentrated at the edge site rather than at other locations, allowing edge-specific functionalization with complex molecules through the functional group exchange mechanism, which will be discussed in more detail at Section 2.6.

The functionalization reaction at the edge or other specific sites can be limited depending on the molecule's shape and size.^{127–129} For example, 1,2-dithiolanes only bond to the edge of MoS₂ with two adjacent S vacant spaces,¹²⁷ and dibenzothiophene selectively bonding to the point corner site of the MoS₂ triangle.¹²⁸ Furthermore, edge functionalization facilitates the exfoliation of 2D materials as the edge functional groups repulse each other, inducing delamination and allowing the surrounding solvent to penetrate between layers.^{122,130–132} Fig. 2(a) shows edge-functionalization-induced delamination of graphene with maleimide as a functional group.¹³¹

2.2 Vacancy defect

Even in 2D materials with high crystallinity, vacancy defects are inevitable. In addition to intrinsic vacancies, extrinsic vacancies can be introduced by annealing, plasma treatment, ion bombardment, chemical/mechanical exfoliation, or electron beam (e-beam) irradiation.^{30–32,111}

The vacancy on the 2D material surface has high chemical potential, attracting other molecules, and forming a covalent bond spontaneously.^{133–135} Molecules with thiol groups (–SH) are a notable example of vacancy functionalization, which are favorable for bonding with S vacancies of MoS₂ unless the chemical bonding is disturbed by the molecule's geometry.^{136–142} (Fig. 2(b)) Zhang *et al.*¹³⁶ fabricated fluorophore-attached thiol molecules to illuminate S vacancies using selective bonding between thiol groups and vacancies to make vacancies clearly visualized using an optical fluorescent microscope (Fig. 2(c)). Healing or passivation of defects also can be achieved *via* vacancy functionalization. For example, the S vacancy of the MoS₂ surface can be repaired by thiol functionalization followed by breakage between the S and C bond.^{137,138}

2.3 Grain boundary

Chemical vapor deposition (CVD) is one of the most widely used methods to synthesize 2D materials,^{143,144} for large-area single-layer 2D material films with sizable grain sizes and high crystallinity. However, the formation of grain boundaries (GBs) is inevitable for CVD-synthesized 2D material films unless a particular technique is used to align the crystal orientation, such as a single crystal substrate or super slow precursor supply.^{145–147} GBs are reported to affect the electronic and mechanical properties of 2D materials,^{148–150} and the additional properties are expected to be observed from GB functionalization.¹⁵¹

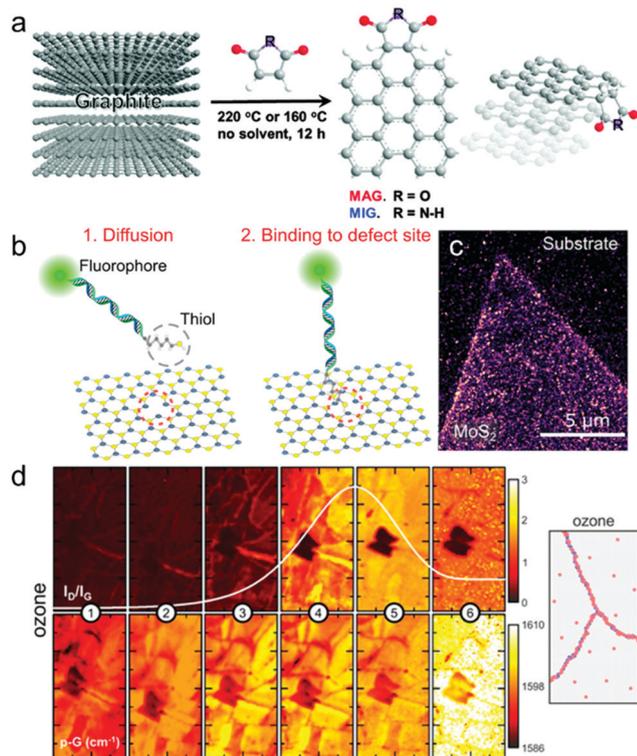


Fig. 2 (a) Schematic drawing of edge functionalization and delamination of graphite edge by Diels–Alder reaction with maleimide (reprinted with permission from ref. 131 Copyright 2014 Chemical Communications). (b) Schematic drawing of selective chemisorption of a thiol group to S vacancy site of MoS₂. (c) Fluorescent microscope image of fluorophore attached to MoS₂ vacancy site (reprinted with permission from ref. 136 Copyright 2021 ACS Nano). (d) (left) G peak position Raman map of ozone functionalized graphene near grain boundary, for six different oxidation steps. (right) Schematic of defect (red) accumulated at grain boundary (reprinted with permission from ref. 156 Copyright 2015 *2D Mater.*).

Consequently, many studies have attempted to improve or modify the properties of GBs, including the addition of metal nanoparticles^{152,153} or nanowires¹⁵⁴ to them.

GBs are susceptible to chemical reactions, including functionalization and chemical etching, because of their high chemical potential.¹⁵⁵ Fig. 2(d) clearly shows that ozone exposure produces highly localized oxygen functionalization at the GB.¹⁵⁶ This mechanism can be applied to the functionalization of GB for visual observation.^{157,158} Several theoretical studies predict the possibility of emerging electronic,^{151,156,159} magnetic,¹⁶⁰ and mechanical^{161,162} properties by functionalizing GB. To our knowledge, however, experimental results regarding the additional properties are not yet reported.

2.4 Basal plane

This section covers the functionalization of the intrinsic basal plane of 2D materials without any defects. However, most molecules used for functionalization may include other active groups on the other side of the molecule, which increases the variety of structures and properties, including the physical properties and applications of functionalized 2D materials.

Therefore, this section will focus on reactions between the 2D basal plane and the bonding part of the functional molecules to avoid unnecessary complexity.

Chemically stable 2D material surfaces and molecules can react with additional energy inputs, such as plasma, electric fields, and photon irradiation. On the other hand, when 2D materials or reacting molecules are chemically unstable and reactive enough, defects or other sites with high chemical potentials are not mandatory.

Functionalization of carbon nanotube (CNT)^{163–165} and fullerene (C₆₀)^{166–169} by attacking the C–C bond at the carbon ring has a long history of research, and most of them are currently utilized to functionalize graphene with a few exceptions, such as reactions with some metal complexes.^{170–172} Most of the defect-free covalent functionalization of graphene can be categorized into two types—that is, cycloaddition and free-radical addition.

2.4.1 Cycloaddition. Cycloaddition is a chemical reaction that adds a new ring to the graphene surface. The number of atoms in the newly formed ring is between 3 and 6, the ring being composed of carbon, nitrogen, and/or oxygen. Fig. 3 shows a simple schematic of the possible cycloaddition reactions for graphene. There is a total of 12 cycloadditions, three 2 + 1 reactions (Bingel reaction, carbene addition, and nitrene addition), one 2 + 2 reaction, six 2 + 3 reactions (pyrazoline adduct, Prato reaction, pyrrole adduct, isoxazoline adduct, zwitterion-mediated, and oxolane adduct), and two 2 + 4 reactions (Diels–Alder reaction by both dienophile and diene).

The Bingel reaction produces three carbon atom rings, using bromo-substituted malonate.^{173,174} Bingel reactions occur with either carbonate catalyst (Na₂CO₃, K₂CO₃, or NaHCO₃)¹⁷⁴ or external energy by heating or microwave.¹⁷³

The carbene intermediate reaction produces a ring of three carbon atoms. Catalyst,¹⁷⁵ heat, or ultraviolet light (UV)¹⁷⁶ activates carbene intermediate from diazirine or chloroform.¹⁷⁵

The reaction with nitrene and graphene produces a ring of two carbon atoms and one nitrogen atom. Molecules with azide groups are popular for generating nitrene intermediates, with thermal (approximately 90 °C) or photochemical activation (UV exposure).^{177–180}

The 2 + 2 cycloaddition reaction between graphene and aryne (benzyne)^{181,182} produces four carbon atoms ring. Intermediate aryne is formed chemically,¹⁸¹ by UV,¹⁸³ or by microwave-assistance.¹⁸²

Reaction with nitrilimines, a 1,3-dipolar cycloaddition, produces a pyrazoline structure with two nitrogen atoms and three carbon atoms. Owing to its high threshold energy, the reaction demands either days of heating at high temperatures or hours of microwave irradiation.¹⁸⁴

The Prato reaction is also the 1,3-dipolar cycloaddition,^{185,186} creating a pyrrolidine structure with one nitrogen atom and four carbon atoms. Azomethine ylide is commonly used as a precursor,¹⁸⁵ but other derivatives, such as sarcosine, can also be used.¹⁸⁶

The reaction with oxazolone produces a pyrrole structure, a ring of one nitrogen atom, and four carbon atoms, with one N–C double bond. The reaction requires a sealed container in solvent-free condition.^{187,188}

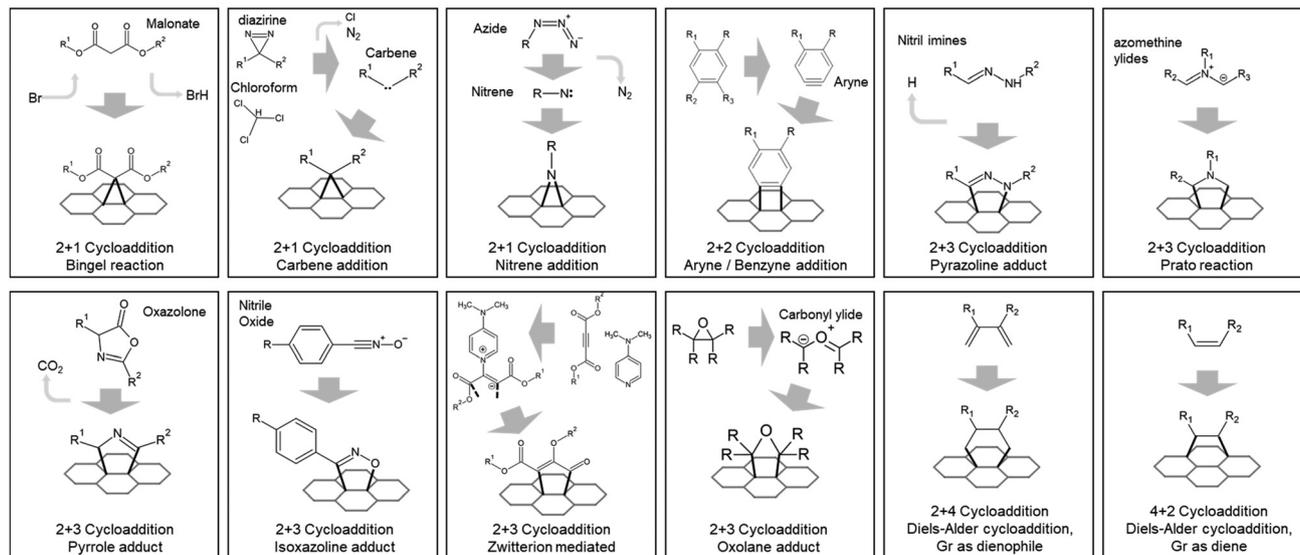


Fig. 3 Reaction diagrams of cycloaddition reactions to defect-free, intrinsic graphene surface.

The 1,3-dipolar cycloaddition reaction with nitrile oxide produces an isoxazoline structure, a five-atom ring with one oxygen atom, one nitrogen atom, and three carbon atoms. Similar to cycloaddition by nitrilimine, it requires a high temperature (170 °C) or external assistance such as microwave irradiation to overcome its high activation energy.¹⁸⁹

The zwitterion-mediated cycloaddition reaction produces a carbon monocyclic five-atom ring. 4-dimethylaminopyridine and acetylene dicarboxylate react with each other to produce reactive zwitterion intermediates and functionalized graphene.¹⁹⁰

The cycloaddition reaction with carbonyl ylide—formed by the epoxide ring-opening process—produces an oxolane structure, a five-atom ring with one oxygen atom, and four carbon atoms. This reaction occurs between graphene and tetracyanoethylene oxide under moderate heating conditions (140 °C–160 °C).^{191,192}

Diels–Alder cycloaddition is a commonly used reaction in graphene chemistry because of its wide reaction temperature range, broad solvent selection, and relatively short reaction time. This method produces a ring with six carbon atoms *via* the reaction between dienophile and diene. In graphene functionalization, graphene can act as both dienophile^{193–197} and diene,^{131,194,196,198} depending on the molecule it reacts to.

2.4.2 Free radical addition. Free-radical addition is a functionalization method that involves the reaction between 2D materials and molecules with unpaired electrons. Fig. 4 shows a simple list of possible functionalization reactions by free radicals.

Free-radical halogenation is one of the simplest functionalization methods for 2D materials. Halogen radicals Dissociating diatomic halogen gas or organic halides produces free halogen radicals. External energy is required to generate radicals such as plasma,^{199–203} UV,^{204–206} electrochemical,^{207,208} e-beam,²⁰⁹ gamma-ray,²¹⁰ microwave,²¹¹ laser,²¹² and thermal heating.^{213–216} Some molecules (*e.g.*, XeF₂) are unstable enough to produce

halogen radicals and react with graphene without external energy.^{199,201,217–220}

Birch reduction is a hydrogenation method for graphene, using alkali metals (Li, Na, or K) as an electron source. Alcohol or water is usually used as a hydrogen source, with ammonia as the solvent to dissolve metal.^{221–225}

Azo compounds are well-known initiators for free-radical polymerization. Under low-temperature heating in an organic solvent, they decompose to radicals, releasing nitrogen gas.²²⁶

Xanthate is another common molecule involved in radical reactions. With a peroxide initiator, xanthate breaks the C–S bond and releases a radical group. Reaction with xanthate derivatives is beneficial for controlling the reaction because of (1) controlled reaction activation timing by radical initiator triggering, and (2) self-regulating consistent functionalization reaction by reversible radical generation from the degenerative exchange behavior of the xanthate group.²²⁷ It also has several other attractive features, such as the broad availability of functional groups, solvents, and reacting concentration.²²⁸

The radical reaction by diazonium salt is one of the most popular functionalization methods—not only for graphene but also for other 2D materials—because of its generous reaction requirement.²²⁹ Diazonium salt can spontaneously become radical when exposed to low heat or accelerated electrochemically^{230–233} under both dry and solution conditions. Aryl diazonium,^{230,231,234–236} azide molecules,^{237,238} and others^{232,233,239,240} can be applied to this method.

Peroxide is a well-known for radical initiator and photoinitiator. Due to its low stability, peroxide can decompose in many ways, including low heat, light, and UV exposure. Benzoyl peroxide is often used for patterned functionalization by light-initiated decomposition.^{228,241,242}

The thiol–ene reaction is a C–S bond-forming reaction between the thiol group and C=C bond, with the help of a radical initiator or catalyst. Although several methods can

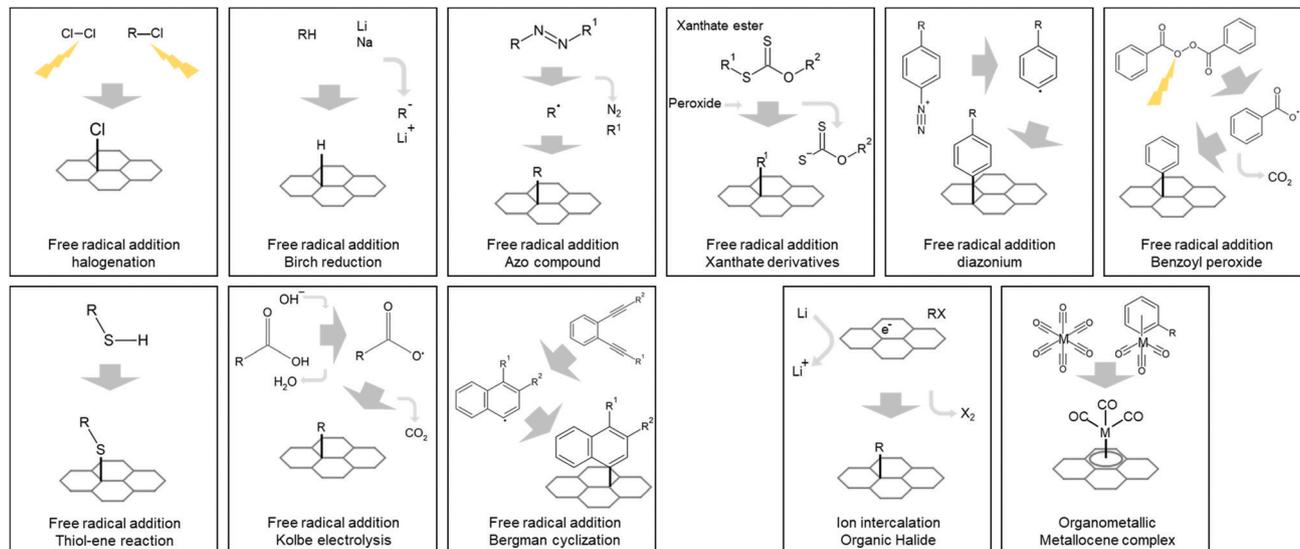


Fig. 4 Reaction diagrams of 9 radical functionalization reactions and two uncategorized functionalization reactions to defect-free, intrinsic graphene surface.

remove hydrogen from the thiol group and produce thiyl radical-catalysts, heat, light, and the radical initiator – method using azo compound azobisisobutyronitrile (AIBN) as a thermal radical initiator has been reported as major method for functionalizing graphene. Since AIBN decomposes to radicals at a low temperature of approximately 40 °C, thiol-ene functionalization methods with AIBN require mild reaction conditions, usually around 70 °C in the organic solvent.^{243–247}

The Kolbe electrolysis reaction (not the Kolbe–Schmitt reaction) is an electrochemical decarboxylation reaction. Radical formation from carboxyl group dissociation under hydroxyl ions and electric potential ($\text{RCOOH} + \text{OH}^- \rightarrow \text{R}^* + \text{H}_2\text{O} + \text{CO}_2 + \text{e}^-$).²⁴⁸

Functionalization by Bergman cyclization—also called the Masamune–Bergman reaction—uses a radical intermediate generated from the cyclization of enediyne. Few Bergman cyclization reactions use low temperatures, such as 150 °C,²⁴⁹ but the most cases require the high cyclization temperature (up to 200 °C), limiting the selection of a solvent.

2.4.3 Other addition reactions. Some other addition functionalization processes do not belong to cycloaddition or free-radical addition.

Similar to the Birch reduction methods, negatively charged 2D material—a common byproduct of metal ion intercalated liquid exfoliation—can act as a radical and take halogen atoms from organic halides.^{250–254} Moreover, modulating the metal ion ratio during the intercalation process allows the control of functionalization density.²⁵⁴

Several metal atoms—such as Fe, Cr, Mo, and W—can bond with five or six carbon atom rings by a haptic covalent bond (hexahapto(η^6)-metal bond) to form metallocene complexes (sandwich or half-sandwich compounds). In the same way, these organometallic complexes—such as $\text{Cr}(\text{CO})_6$ and (η^6 -benzene) $\text{Cr}(\text{CO})_3$ —can bond to carbon rings at the graphene surface.^{255–257} Metal complexes other than Cr, like Mo and W, have also been also tried.^{258,259} Functionalization by the

η^6 -metal bond is beneficial for mild modification because it does not fully convert C–C hybridized bond.

2.4.4 Reactions for other 2D materials. The many of above-mentioned functionalization can also be applied to other 2D materials. Several free-radical addition reactions—diazonium,^{260–262} azo compounds,²⁶³ and nitrene intermediate²⁶⁴—have been used for BP functionalization. Fig. 5(a) shows one example of diazonium functionalization of BP surface.²⁶⁰ Besides free radical reactions, the chemical instability of BP makes several other reactions affordable, such as reaction with polymers,^{265–269} alkyl halide,²⁷⁰ and metal ligands.^{271–273} Furthermore, BP is reactive even at ambient conditions, and starts to decompose just by being exposed to ambient air²⁷⁴ and moisture.²⁷⁵ Consequently, increasing its environmental

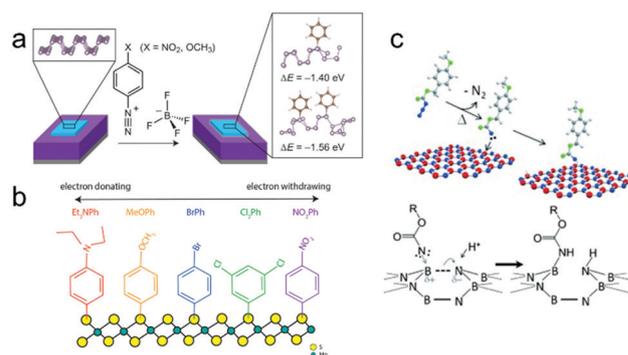


Fig. 5 (a) Reaction between BP surface and diazonium derivative and DFT calculated structure of the following distortion (reprinted with permission from ref. 260 Copyright 2016 nature chemistry). (b) Schematic drawing of various functional groups attached to MoS_2 arranged in order of doping (reprinted with permission from ref. 280 Copyright 2017 Journal of American Chemical Society). (c) Schematic illustration of reaction mechanism between nitrene and hBN (reprinted with permission from ref. 287 Copyright 2012 Chem. – Eur. J.).

stability is one of the primary goals for functionalizing BP.^{260,263,264,273,274,276,277}

Diazonium functionalization was also applied to TMDC.^{278–280} Fig. 5(b) shows diazonium-functionalized MoS₂ with different attached groups to control the doping levels of MoS₂ from p-type to n-type.²⁸⁰ Other functionalization methods using organic halide with ion intercalation^{281–284} and Michael addition reactions using maleimide²⁸⁵ have also been reported for functionalization of TMDC.

Although hBN is less likely to be functionalized owing to its high chemical stability, some radical reactions like carbene intermediate²⁸⁶ and nitrene intermediate²⁸⁷ can react with hBN (Fig. 5(c)).

Halogenation of 2D materials other than graphene requires much more consideration because they readily disintegrate when exposed to halogenation gases such as XeF₂.²¹⁷ However, halogenating BP or hBN without disintegrating is possible by several different approaches, such as using a stable fluorine source (polymer^{288,289} or ammonium fluoride^{290–293}) or controlling the reaction speed (temperature,²⁹⁴ electric potential,²⁹⁵ or ion beam irradiation²⁹⁶).

2.5 Local strain

2D materials with ripples, wrinkles, Moiré patterns, or 2D materials that are transferred onto the substrate with nanoparticles or patterned structures, has disturbed strain field in it, and local strain field is known to change the local chemical potential.^{201,234,297} As a result, functional groups are more likely to attach to the strained area^{201,234,298,299} (Fig. 6(a)).

The Moiré structure is a repeated pattern observed in stacked 2D materials with misalignment or 2D material on a crystalline substrate, which gives periodic strain and potential wave.^{300–302} The size and form of the Moiré pattern are

determined by the lattice constant difference or twisted angle of the stacked materials.³⁰³ Despite that Moiré pattern gives relatively small strain, several studies have revealed that the chemical bonding onto 2D material surfaces is favorable along with the Moiré pattern.^{198,304–306} Fig. 6(b and c) show a clear example of selective bonding between monolayer graphene on the Ir(111) surface and iron phthalocyanine (FePc) molecules.¹⁹⁸

2.6 Functional group

Intrinsically or intentionally formed functional groups on 2D material surfaces are great locations for chemical reactions and further functionalization due to their high chemical potential.

However, as pointed at Section 2.4, practically limitless numbers of molecules can become functional group of 2D materials, thus it is almost impossible to cover every related reaction that substitute or add other molecules to existing group. Therefore, for clarity and simplicity, we will discuss simple and common groups for 2D materials, such as epoxide, ketone, hydroxyl, carboxylic,³⁰⁷ hydrogen, and halogen. Fig. 7 and 8 show simplified schematic diagrams of the substitution and addition reactions.

2.6.1 Carboxylic group. The carboxylic group (–COOH) is commonly found at the edges and surfaces of GO.³⁰⁷

The acyl chloride group (–COCl) is well-known as an intermediate step to introduce several other groups. It can be synthesized from the carboxylic group through reaction with SOCl₂,^{308–314} COCl₂,³¹⁵ or PCl₃.³¹⁶ Several conversion processes are applied to acyl chloride, such as alcohol to an ester (–COOR),³¹² amine to amide (Schotten–Baumann reaction),^{308,317–320} phosphorous acid to phosphonate,³¹⁶ and the ring-closing reaction of amine (R–(COCl)₂ + R'–NH₂ → pyrrole-R).^{315,317,321,322}

There are two known carboxylic to ester conversion processes—that is, the Fischer esterification reaction with alcohol/hydroxyl initiated by carbodiimide/acid condition,^{323–325} and Williamson ether synthesis by alkyl halide.^{326,327} Carbodiimide is also used as a coupling agent for conversion reactions, from carboxyl to thioester (–COSR)^{328,329} and the amide (–CONR) group.^{330–337}

Carboxyl reacts with thiol/thiourea to produce a thioester structure.

The reaction with an amino group and a carboxyl group produces an amide. Amino groups require a coupling agent such as hydroxybenzotriazole³³⁰ to react with carboxyl and make amides, while some reactive molecules such as hydrazine³²⁷ and isocyanate³³⁸ can react without a coupling agent. The fabricated primary amide group can be exchanged to the amine by the Hofmann rearrangement reaction (–CONH₂ → –NH₂).³²⁰

Friedel–Crafts acylation is a reaction that produces a ketone bond between the carboxyl group and the aromatic ring, with AlCl₃ as a catalyst. This reaction is used when attach ferrocene to GO.³³⁹

Several other conversion reactions occur in the carboxyl group. For example, the hydroxymethyl group (–CH₂OH) can be produced by LiAlH₄,³⁴⁰ and the Hunsdiecker reaction (–COOH + MX → –X) can exchange carboxyl to a halogen atom.^{341,342}

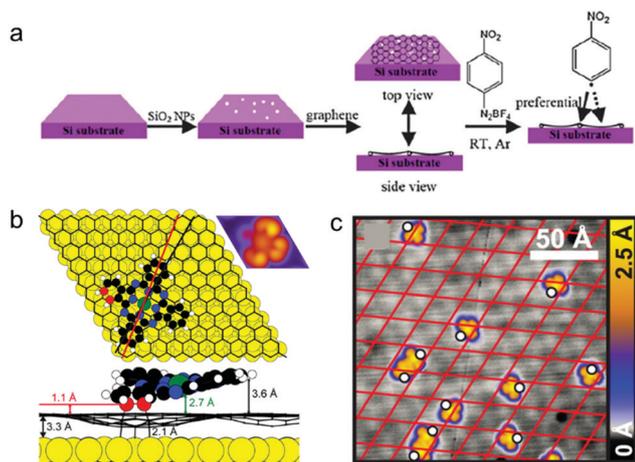


Fig. 6 (a) Schematic drawing of diazonium radical functionalization on locally strained graphene (reprinted with permission from ref. 234 Copyright 2012 Chemical Communications). (b) DFT calculated structure of Iron phthalocyanine (FePc) on graphene/Ir(111) surface, bonded onto Moiré position. (c) STM topograph image of FePc on Iron phthalocyanine (FePc) on graphene/Ir(111) surface, arranged with Moiré pattern (reprinted with permission from ref. 198 Copyright 2015 *J. Am. Chem. Soc.*).

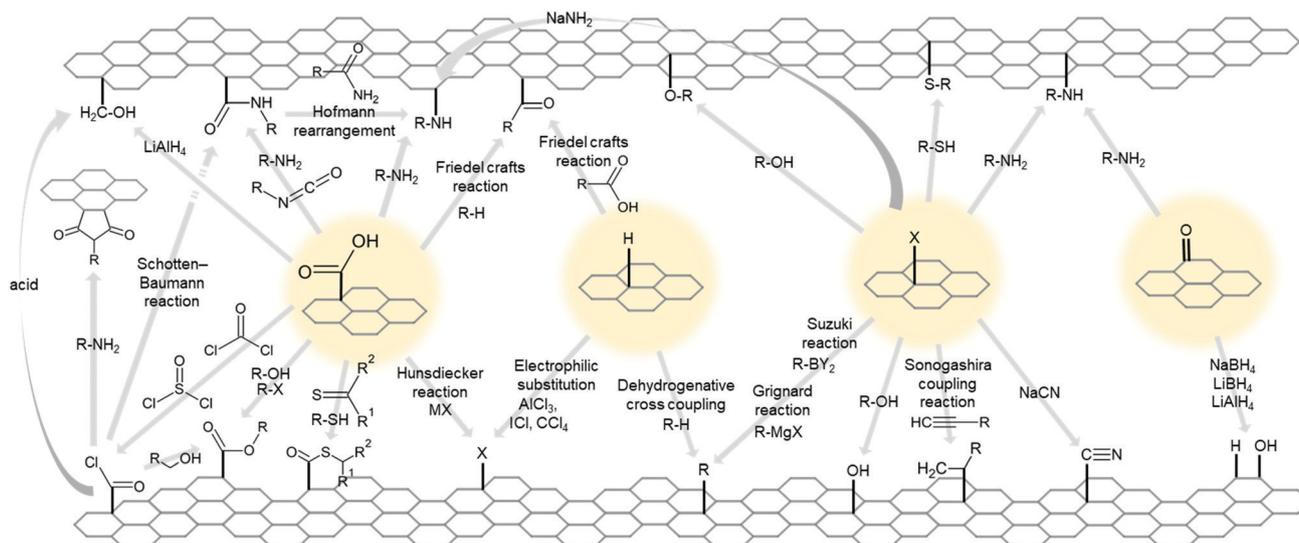


Fig. 7 Schematic diagram of possible reactions for functional groups, carboxylic ($-\text{COOH}$), hydrogen ($-\text{H}$), halogen ($-\text{X}$), and ketone ($=\text{O}$). X is for halogen, and M is for metal.

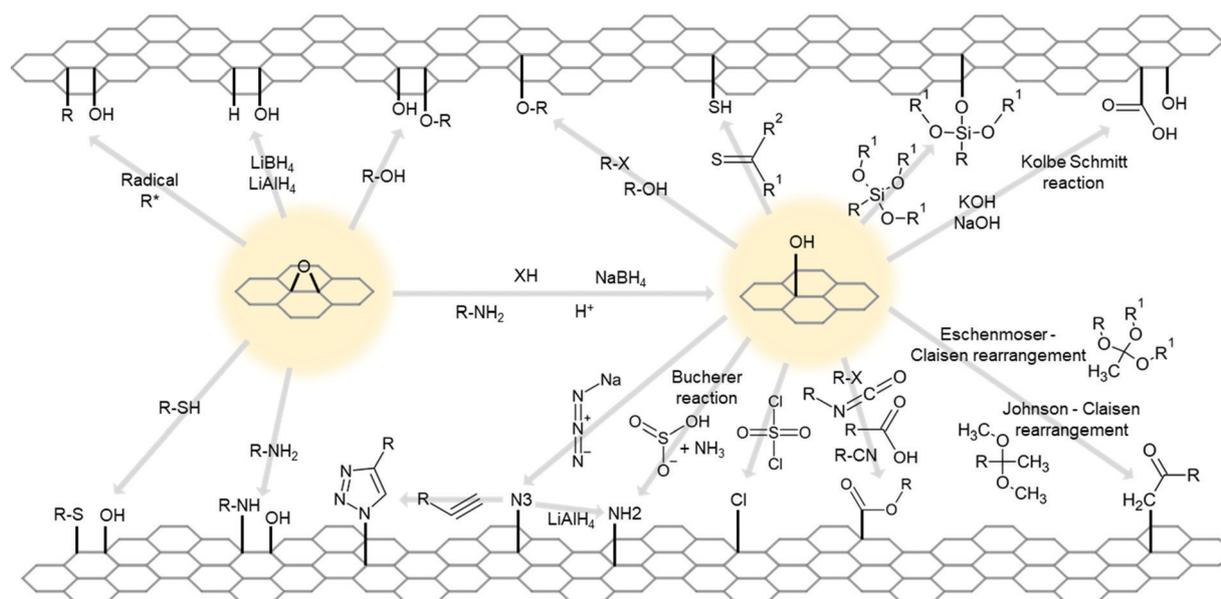


Fig. 8 Schematic diagram of possible reactions for functional groups, hydroxyl ($-\text{OH}$) and epoxide ($-\text{O}-$). X stands for halogen.

2.6.2 Hydrogen. Hydrogen atoms on hydrogenated graphene—usually synthesized by annealing or plasma processes—can be substituted with halogen, alkyl groups, and ketone bonds.

Electrophilic substitution reactions can halogenate hydrogenated graphene. For example, AlCl_3 , ICl , or CCl_4 ³⁴³ were used to synthesize chlorinated graphene. Likewise, bromosuccinimide³⁴⁴ was used to synthesize brominated graphene.

Alkyl groups can be grafted with ketone bonds by Friedel-Crafts acylation, where graphene acts as an aromatic ring.³⁴⁵ Alkyl group also can directly bond to the hydrogenated graphene surface in the presence of a proper oxidant through a dehydrogenative cross-coupling reaction.³⁴⁶

2.6.3 Halogen. The halogen exchange reaction has attracted much attention because the reaction process is simple and does not cause severe damage to the graphene surface. Among them, fluorinated graphene is the most widely studied for functionalization by halogen exchange processes. Currently reported halogen exchange reactions on graphene surface are reaction with thiol ($-\text{S}-\text{R}$ /thioethers),^{347,348} NaNH_2 ($-\text{NH}_2$, $-\text{NR}$ /primary and secondary amine),^{348–353} cyanide ($-\text{CN}$ /cyano group),³⁵⁴ and alcohol ($-\text{OH}$ /hydroxyl).^{355,356}

The Sonogashira coupling reaction,³⁵⁷ Grignard reaction, and Suzuki coupling reaction displace halogen atom to an alkyl group. The Grignard reaction uses an alkyl metal halide to

exchange halogens with other groups. It has been applied to fluorinated^{358,359} and chlorinated graphene.^{360,361} The Suzuki coupling reaction (or Suzuki Miyamura reaction) is a halogen exchange reaction ($-X \rightarrow -R$) in the presence of a palladium complex catalyst. It has been used to brominated graphene.^{362,363}

Atom transfer radical polymerization is another promising application for halogen-functionalized 2D materials. Halogen atoms at the surface of 2D materials or the end of a functional group can be used as an initiator for atom transfer radical polymerization, such as polymer functionalization of 2D materials and continuous polymerization by the halogen exchange process.^{313,364–366}

2.6.4 Epoxide group. The epoxide group ($-O-$) is another frequent group on GO surfaces. Several epoxide ring-opening reactions can introduce a variety of functional groups with additional hydroxyl groups. Radical ($-O- + R^* \rightarrow -OH + -R$),³⁶⁷ amine ($-O- + R-NH_2 \rightarrow -NH-R + -OH$),^{368–370} thiol ($-O- + R-SH \rightarrow -S-R + -OH$),^{371,372} and lithium hydride ($-OH + -H$)³⁴⁰ have been employed in the epoxide ring-opening reaction. If the epoxide group reacts with molecules that supply an additional electron—such as HBr ,³⁷³ sodium borohydride,^{340,374} hydrazine,³⁷⁵ and acid³⁷⁶—a direct conversion reaction to a single hydroxyl group rather than a ring-opening reaction is possible.

2.6.5 Hydroxyl group. The hydroxyl group might be the most abundant group on both surfaces of GO and at the edge of other 2D materials, especially when 2D materials are exposed to ambient air or water.

When sodium azide reacts with a hydroxyl group, it exchanges the hydroxyl group with the azido group ($-N_3$).^{377–379} Due to the high reactivity of the azido group, it can readily react with other molecules. For example, $LiAlH_4$ ³⁷⁹ converts the azido group into an amine group, and the azide-alkyne Huisgen cycloaddition reaction produces a triazole group (a ring with three nitrogen atoms and two carbon atoms).^{379,380}

Organic halides,^{342,366,375} alcohol,³⁸¹ and carboxylic³⁷³ can form an epoxide bond with the hydroxyl group through a dehydration reaction.

Hydrogen exchange reaction replaces hydrogen atom at the hydroxyl group to bond with other molecules such as cyanide (Pinner reaction)^{338,382,383} and siloxane (silanization reaction).^{384–389} Many silanization cases allow each siloxane group to interconnect to create a dense network of siloxane molecules or composites.

Similar with epoxide bond formation reactions, ester bond formation is possible through the Claisen rearrangement reaction. Two slightly different Claisen rearrangement reactions—that is, the Eschenmoser–Claisen rearrangement³⁹⁰ and Jonson–Claisen rearrangement³⁹¹—convert hydroxyl groups to ester bonds with functional molecules.

The Kolbe–Schmitt reaction, reaction by alkaline metal hydroxide and CO_2 ($-OH \rightarrow -OH + -COOH$), attaches another carboxyl group adjacent to the hydroxyl group on the graphene surface.³⁹²

There are some substitution reactions for the hydroxyl groups. Specifically, SO_2Cl_2 produces chlorine ($-Cl$),³¹¹ thiourea

produces sulfhydryl ($-SH$),³⁹³ and hydrazine³²⁷ produces amide. Conversion onto amine ($-NH_2$) is performed by both the Bucherer-like reaction³⁹⁴ and amine.^{395,396}

2.6.6 Other groups. The ketone groups ($=O$) are rarer than the other groups on the graphene surface. Similar to the epoxide group, the ketone group can be exchanged with a hydroxyl group ($-OH + -H$) by reacting with $NaBH_4$, $LiBH_4$, or $LiAlH_4$.³⁴⁰ Moreover, hydrazine converts ketone to amide ($=N-NH_2$).³⁹⁷ $NaBH_4$, $LiBH_4$, and $LiAlH_4$ can also react to another uncommon group, converting aldehyde group ($-COH$) to hydroxymethyl group ($-CH_2OH$).³⁴⁰

Oxygen-containing groups on graphene surfaces can bond with metal complexes, such as Pd ,³⁹⁸ Co ,³⁹⁹ and Pt ,^{400,401} but specific reacting groups have not been identified.

2D material edges usually contain $-H$ or hydroxyl groups. Therefore, if the surface is sufficiently free of defects and no group is attached, these intrinsic groups can be used as targets for edge-selective functionalization.^{315,343,402}

2.7 Intrinsic dangling bonds

Not all 2D materials are vdW layered materials. Many ‘bulk’ materials, which form atomic bonds to all three dimension directions and no vdW gap, can form a 2D structure by well-controlled synthesis or exfoliation methods.^{403–405} Several metal oxides (In, Sn, Ti, Zn, W, Co, Ce, Gd, Eu), metal chalcogenides (MX, M = Cd, Zn, Pb, In, Cr, Cu, X = S, Se, Te), metals (Au, Rh, Pd, Ru, Te, Se, Ge), are known to form non-vdW 2D structure. Unlike layered vdW materials, those non vdW 2D materials have intrinsic active sites and dangling bonds, making those materials great candidates for catalyst and energy storage applications.^{406–409}

The surface of non-vdW 2D materials is usually $-H$ or $-OH$ group terminated from the ambient environment, or metal ion terminated from the exfoliation or synthesis process. However, research about non-vdW 2D materials is still in early stage, and surface passivation/encapsulation is currently in main interest, further functionalization is not widely reported yet.

Metal–organic framework nanosheet (MON) is another 2D structured material group, which is the porous compound that is composed of periodically interconnected organic ligand and metal ion/cluster.^{410–414} Similar to other non-vdW 2D materials, MON has intrinsic active sites at both metal and organic ligand, which make MON suitable material for various applications such as sensor and catalyst.^{415–418} Plus, owing to its unique porous structure, filter, absorbent, or molecular separation also attract much interest as a promising application.^{412,414,415,419}

Various groups can attach to active sites of MON during or post-synthesis. Currently, functionalizing MON is mainly aiming for several applications such as increasing/modifying catalytic activity, pore functionalization to modulate molecular selectivity for filtration, or increasing exfoliation yield after synthesis using functionalized ligand as synthesis precursor.⁴²⁰

2.8 Outlook

Functionalizing molecule reacts with every possible active site in 2D materials. That is, most functionalization reactions

introduced in basal plane sections will react with defect sites also, even though the reaction works on clean crystal surfaces and does not require defect sites. Therefore, in many cases, the functionalization location depends on many parameters such as kind/status of 2D materials and functional group, rather than choice specific location exclusively. For example, for the mass-produced liquid dispersed 2D materials, the edge should be considered as a prominent functionalization location, and the local strain-dependent reaction would be neglected.

Functionalizing reaction to an existing group is beneficial in this manner, because functionalization density, uniformity, and location can be controlled. Beginning the functionalization process by attaching a simple group makes many problems easier, including avoiding unwanted groups or locations. For the molecules that cannot bond directly with 2D materials, application of another functionalization step is applicable.

Among all functionalizing reactions, the free radical reaction would be the most versatile choice. They are less selective than other reactions, but work with almost every 2D materials, with or without defect, and accept many other functionalization techniques beyond solution chemistry, including various initiation methods.

3. Functionalization techniques

Among the various functionalization techniques for 2D materials, the solution process is mandatory for most techniques, regardless of which chemical reaction is performed in the solution. For example, most chemical reactions described in Section 2 are solution-phase chemical reactions.

Therefore, in this section, we will discuss specific techniques for functionalizing 2D materials besides that solution-phase chemical processes.

3.1 Plasma

Plasma is a simple method for activating molecules into free radicals, and modifying 2D materials by plasma treatment is widely studied.^{421,422} Plasma modifies 2D materials *via* two major routes. First, highly reactive ionized molecules react more easily with the 2D material surface. Second, ions accelerate to the target surface during the plasma process, providing additional energy to activate the reaction, or create defects by knock-off surface atoms.^{30,423} Collision energy and movement of ions in the plasma chamber can be controlled by modulating the chamber design and working conditions.⁴²⁴ Various methods have been studied to avoid damage to the material by ion bombardment, including a remote plasma technique that generates plasma separately from the sample^{425,426} or by covering samples with a metal mesh.⁴²⁷

Light-weight diatomic molecules, hydrogen,^{199,202} oxygen,^{426,428,429} or halogen^{200,430,431} are commonly used in plasma functionalization technique because large molecules tend to dissociate, making it difficult to control the reaction result (Fig. 9(a)).

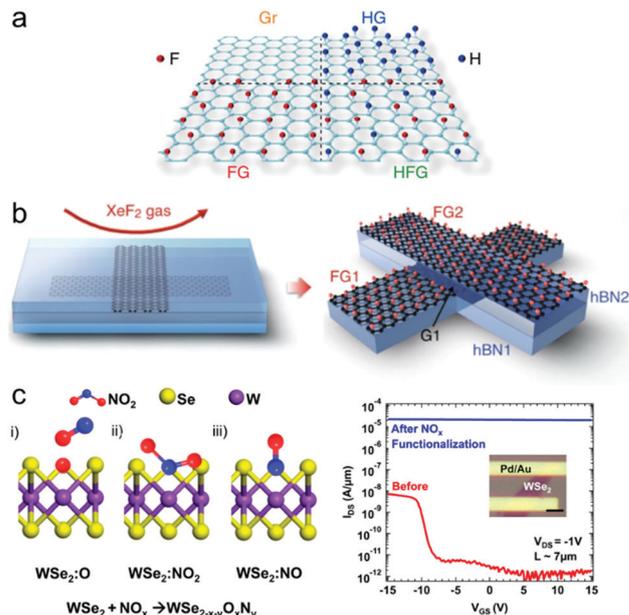


Fig. 9 (a) Patterned graphene surface functionalization by plasma hydrogenation and fluorination by XeF₂ (reprinted with permission from ref. 199 Copyright 2019 Advanced Materials). (b) Etching and functionalization process of graphene/hBN heterostructure by XeF₂. hBN layers are etched away while graphene is fluorinated (reprinted with permission from ref. 217 Copyright 2018 nature communications). (c) Three possible reaction configurations between Se vacancy of WSe₂ and NO₂ gas (left) and transfer curve before/after NO₂ treatment (right) (reprinted with permission from ref. 135 Copyright 2014 ACS Nano).

3.2 Gas exposure

If the gas or 2D material surface is chemically reactive, a simple gas exposure can functionalize the 2D material without further treatment.

Graphene fluorination by XeF₂ is a well-known example of functionalization by reactive gas.^{199,201,217–220} In addition, using reactive XeF₂ gas can do more than functionalize graphene. Son *et al.*²¹⁷ fabricated an electronic device while etching off the hBN layer adjacent to the graphene layer, as shown in Fig. 9(b), to use graphene as an atomic-level etching block while successfully functionalizing graphene into fluorinated graphene using XeF₂ exposure.

As discussed in Section 2, 2D material surfaces become reactive with vacancies or other defects, and reactive surfaces can bond with relatively chemically stable gas molecules. Fig. 9(c) shows an example of gas functionalization by surface vacancy defects, the chemical bond between NO₂ gas molecules, and WSe₂ at selenium vacancy.¹³⁵

For less stable materials such as BP, oxygen or moisture acts as 'reactive gas' for functionalization, even without surface defects.^{274,275}

3.3 Heating

Many functionalization processes, especially solution reaction processes, require a specific temperature range for the reaction. The reaction temperatures are determined by several

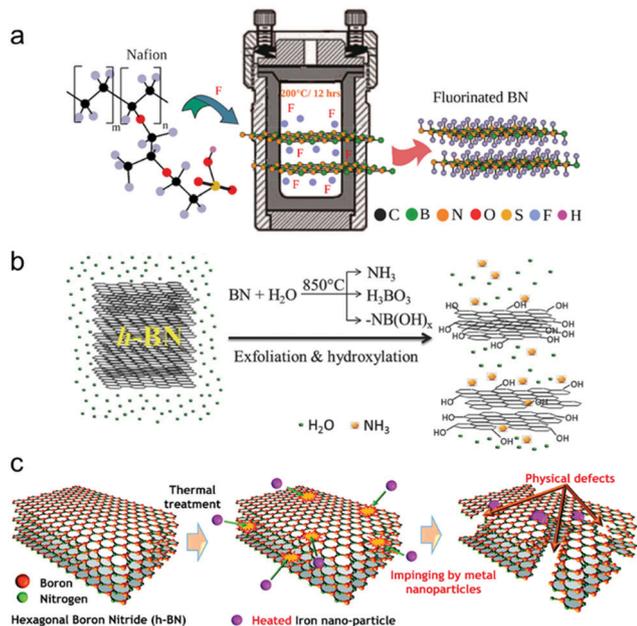


Fig. 10 (a) Schematic image of hydrothermal fluorination of hBN method (reprinted with permission from ref. 289 Copyright 2017 Science Advances). (b) Schematic drawing of high-temperature steam-assisted hydroxylation and exfoliation process of hBN (reprinted with permission from ref. 432 Copyright 2015 Advanced Materials). (c) schematic drawing of defect engineering of hBN by high-temperature annealing with iron nanoparticles (reprinted with permission from ref. 433 Copyright 2016 RSC Adv.).

aspects—that is, the threshold energy for the reaction, the boiling temperature of the solvent, the material thermal stability, and reaction speed.

Some functionalization methods require a much higher temperature than the boiling point of most solvents ($>300\text{ }^\circ\text{C}$)—that is, sufficiently high that the thermal stability of 2D materials becomes an important issue. Fig. 10(b) shows a schematic diagram for one of the high-temperature functionalization processes, steam-mediated hydroxylation of hBN.^{213,432} Likewise, high temperature treatment can generate physical defects. For example, thermal treatment with iron nanoparticles cracks and expose defects to hBN⁴³³ (Fig. 10(c)).

Some functional groups—especially halogens on the graphene surface—can be attached or detached simply by heating.²⁰⁶ For example, fluorinated graphene can be converted into hydroxylated graphene by heating with mixed alkali powder in air at $180\text{ }^\circ\text{C}$.³⁵⁵

3.4 Hydrothermal synthesis

Hydrothermal (water-based solution) or solvothermal (non-water solution) synthesis is a reaction method that uses high temperatures and pressures in a confined container with a non-reacting wall surface. High temperatures and pressures allow many reactions possible that are barely occur under other conditions. Another advantage of using the hydrothermal reaction method is the possibility of continuous reactor design⁴³⁴ with continuous precursor supply and the removal of by-products. Hydrothermal functionalization has been reported

for various 2D materials and functional groups—that is, graphene (amine,^{370,394,435} fluorine,^{436,437} and bromine⁴³⁸), MoS_2 (carboxyl⁴³⁹ and thiol ligands⁴⁴⁰), hBN (hydroxyl^{441–444} and fluorine^{289,290,292}), and BP (hydroxyl⁴⁴⁵). Fig. 10(a) shows one example of hydrothermal synthesis process for fluorinated hBN, using polymer Nafion as a fluorine source.

3.5 Laser

Laser irradiation is a simple method for applying high energy into confined spaces using high-intensity collimated light through photothermal²¹² or photochemical effects. For instance, the laser can increase the local temperature to generate defects or cracks, or even disintegrate 2D materials. Fig. 11(a) shows a schematic of the functionalization mechanism—the reaction between the defected TMDC surfaces and the dissociated solvent molecule—by laser irradiation.⁴⁴⁶

Laser is also an excellent tool for initiating photochemical reactions, mainly when used for patterned functionalization. Radical reactions using photoinitiators, commonly azo compounds and peroxides, can be activated by light illumination.^{241,242} Fig. 11(b) shows a schematic of the functionalization process using peroxide by patterned laser irradiation on graphene.²⁴¹

3.6 UV light

Depending on the wavelength of the light, UV light can break the bonds of several molecules to create reactive radicals. Owing to the high photon energy of UV light, UV irradiation is widely used in chemical reactions to activate them or generate radicals.

For example, several cycloaddition reactions can be activated by UV irradiation.^{176,177,183,197} One photo-induced cycloaddition example is shown in Fig. 11(c). In this research, Diels–Alder cycloaddition onto fluorinated graphene is activated by 320 nm UV, which isomerizes molecules into diene.¹⁹⁷

Furthermore, depending on the wavelength of the light, UV light can break the bonds of several molecules to create reactive radicals. Several UV-activated radical functionalization cases involving azide,¹⁷⁸ ozone,^{157,447–449} and halogen^{204–206} have been reported.

UV ozone is a popular method for light oxidation. Owing to its relatively low reactivity, UV-ozone oxidation has been used in several studies to functionalize or etch GBs selectively, to visualize GBs optically.^{157,158} Another popular application of soft functionalization by UV-ozone is to improve the layer uniformity of the deposited film.^{448,449} Uniform chemical potential at 2D material surfaces restricts thin film growth by atomic layer deposition (ALD). Consequently, surface functionalization of 2D materials is a promising method to improve the adhesion between 2D material surfaces and deposited material without severely damaging the electrical properties. Fig. 11(d) shows a clear example of improved film quality on MoS_2 by UV-ozone treatment before the ALD.⁴⁴⁸ In Fig. 11(d), the deposited Al_2O_3 film shows a significant difference in

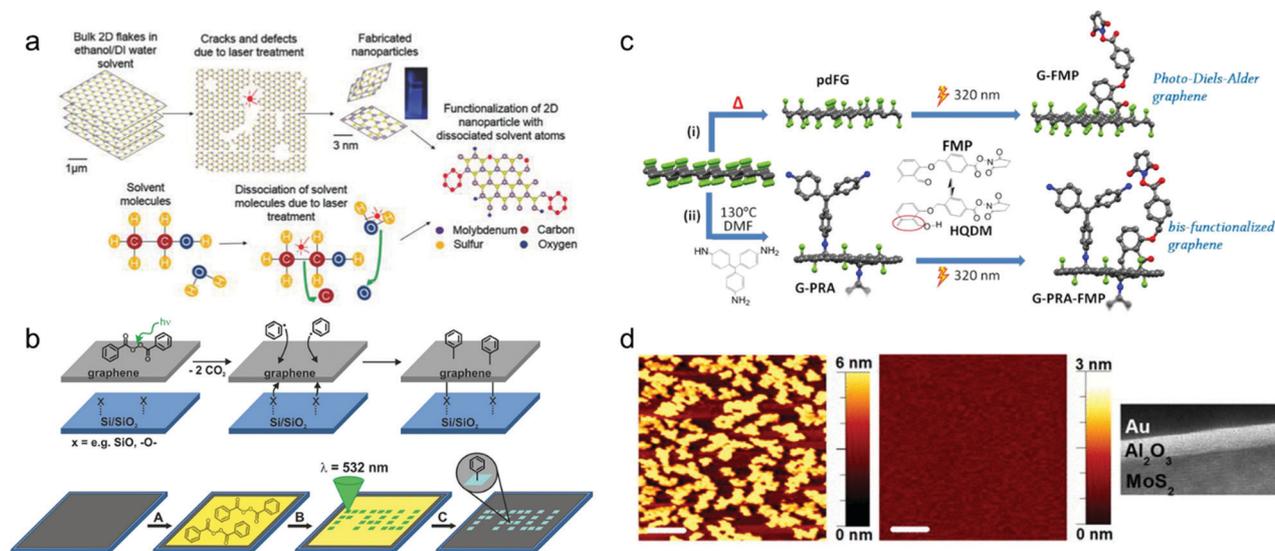


Fig. 11 (a) Schematic illustration of laser-induced functionalization of 2D materials for defect generation (top) and dissociation of the solvent molecule (bottom) (reprinted with permission from ref. 446 Copyright 2018 Advanced Optical Materials). (b) Schematic drawing for the mechanism of laser-induced patterned functionalization of graphene using peroxide molecule (reprinted with permission from ref. 241 Copyright 2020 Angewandte Chemie International Edition). (c) schematic drawing of a process for UV-initiated functionalization of fluorinated graphene (reprinted with permission from ref. 197 Copyright 2019 Carbon). (d) AFM images of ALD grown Al₂O₃ on MoS₂ (left), UV-ozone-functionalized MoS₂ (center) and cross section HRTEM image of Al₂O₃ deposited on functionalized MoS₂ (reprinted with permission from ref. 448 Copyright 2014 *Appl. Phys. Lett.*).

roughness between with and without UV-ozone treatment, even with the same amount of deposition.

3.7 Liquid exfoliation

Liquid dispersion of 2D materials is a widely studied topic^{23–25,450,451} as it is critical because many functionalization methods are solution-based processes or include solution steps. Among the liquid exfoliation methods, mechanical methods such as sonication and jet milling are known to breaking apart 2D materials into tiny pieces along with delamination.^{23–25,450} 2D materials are functionalized as soon as a new defect or edge sites are exposed during the liquid process unless an inert organic solvent is selected for the purpose. For example, 2D materials are hydroxyl-functionalized when exfoliated in water.^{119,120,395,452}

Liquid exfoliation through chemical intercalation methods is preferable to mechanical methods for the larger flake size and defect generation. However, it still introduces defects and other modifications, including phase transition.^{453,454} Conversely, liquid chemical exfoliation is mandatory for some functionalization techniques. As discussed in Section 2.4, metal ion intercalation-induced liquid exfoliation induces electric charging of 2D materials, which is critical for several functionalization reactions.^{221–225,250–254,455} In these functionalization processes, modulating the metal intercalation process controls functionalization activation and density.^{254,455}

3.8 Ball mill

The conventional ball-mill method has been widely applied to 2D materials for its simplicity and effectiveness.^{24,98,450,456} However, ball milling also introduces many defects and

exposed edges with delamination, similar to liquid-phase mechanical exfoliation methods.^{121,456}

Functionalization by ball-mill exfoliation is similar to that by liquid exfoliation for functionalization by defect generation. However, the versatility of environmental control during the process and additional energy supply for the chemical reaction from the ball's kinetic energy makes the ball-mill method a more versatile tool for functionalization.^{456,457} As shown in Fig. 12(a), performing the ball-mill process under the desired gas or liquid environment functionalizes 2D materials with selected groups. Various groups and elements, such as S,^{458,459} N,¹²⁵ O,^{124,458} OH,^{460–462} carboxyl,⁴⁶³ halogen,^{122,123,130,293} NH₂,¹²⁶ polymer,²⁶⁹ and C₆₀,²⁷⁶ have been used to functionalize 2D materials. Moreover, a ball mill with some additives such as acid, base, or salt, can accelerate exfoliation, breakage, and hydroxyl functionalization of 2D materials, even for chemically stable materials such as hBN^{464–470} and graphene.⁴⁷¹

3.9 Other techniques

There are few reports for functionalization using other techniques.

Bian *et al.*¹⁹³ reported a pressure-induced Diels–Alder cycloaddition reaction to functionalize graphene and patterned polymer chain growth on the surface (Fig. 12(b)).

Many functionalization processes can be activated or assisted by microwave irradiation. Microwaves activate reactions in two ways—that is, by heating or supplying energy directly to reacting molecules.^{173,182,184,189,206,211,472,473} Microwave heating works more efficiently than other conventional heating methods because it supplies thermal energy directly to the required location. Moreover, it is more effective for

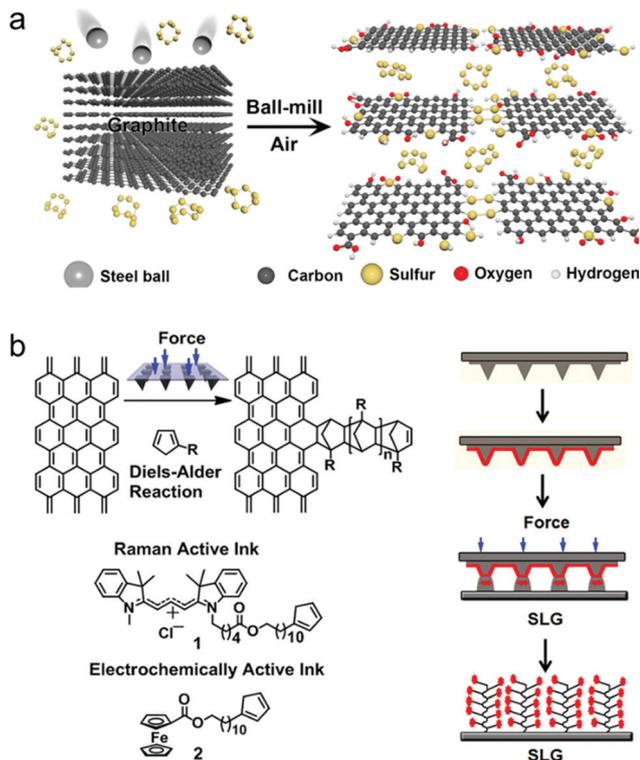


Fig. 12 (a) Schematic illustration of edge functionalization process of graphene by ball milling (reprinted with permission from ref. 458 Copyright 2014 ACS Nano). (b) Molecular structure of Diels–Alder cycloaddition reaction for mechanical force accelerated graphene functionalization (left) and schematic drawing for patterned functionalization process (right) (reprinted with permission from ref. 193 Copyright 2013 *J. Am. Chem. Soc.*).

non-water solvents or no-solvent conditions, in which microwave energy is not absorbed by the solvent. For example, just a few seconds of microwave irradiation can increase the temperature of graphite with liquid halogen under cryogenic conditions by more than 800 °C, producing exfoliated and halogenated graphene.²¹¹

High energy ion irradiation can also be used for functionalization. Entani *et al.*²⁹⁶ reported that 2.4 MeV Cu ion irradiation could successfully fluorinate hBN covered by LiF layer.

3.10 Outlook

Some functionalization techniques (*e.g.*, hydrothermal reaction, liquid exfoliation, ball mill) are practical when focusing on the productivity. Functionalization by liquid exfoliation or ball mill produces 2D material liquid dispersion simultaneously with functionalization, removing the demand for a separate functionalization step.

Other techniques are fitted for flake or film structured 2D materials on the chip. Most of them functionalize 2D materials by supplying energy for the initiation of the reaction, which also can damage 2D materials not only activate functionalizing reaction. Therefore, minimizing damage on 2D materials becomes one of the most critical factors for choosing a technique.

Specifically, two points are mainly considered; the benefit from functionalization would be large enough for taking a risk of damage, or damage from functionalization can be

minimized. An example of a high benefit would be patterned functionalization, or when the technique for a specific functional group is limited (*e.g.*, halogenation or hydrogenation). Otherwise, the remote plasma technique, or using low energy photon laser, just above to excite photoinitiator, is attempting to lower damage to 2D materials.

4. Direct synthesis of functionalized 2D materials

Although CVD is the most popular method for synthesizing high-quality 2D materials,^{143,144} there are several other synthesis methods,^{144,474,475} many of which support the possibility of the direct synthesis of functionalized 2D materials without a separate functionalization process.

4.1 Laser

Graphene^{476–480} and TMDCs^{481–483} can be synthesized by laser irradiation by local high-temperature heating from the photo-thermal effect. When the laser power is sufficiently strong to carbonize the precursor before it reacts with oxygen in the air and burns, the carbon-containing material thermally carbonizes and becomes laser-induced graphene (LIG).^{484–486} LIG has abundant oxygen, hydroxyl, and carboxyl functional groups on its surface and edge sites. The density of the functional group in LIG decreases as the laser power increases. Polymers are often selected as precursors for synthesis of LIG because of their uniform and controllable chemical composition, but other carbon-containing materials such as paper, wood, and fabric, can also be synthesized to LIG.^{487,488}

4.2 Nanotube unzipping

Nanoribbons can be synthesized by unzipping nanotubes, such as CNTs^{489–491} or hBN nanotubes.⁴⁹² Furthermore, several unzipping methods leave the functionalized group at the edge of the synthesized nanoribbon. A prominent example is a carboxyl and hydroxyl edge-functionalized graphene nanoribbon (GNR), synthesized by intercalation-assisted unzipping with KNO₃ and KMnO₄ (Fig. 13(a)).^{493–495}

As explained in the liquid exfoliation section, the unzipping process exposes non-passivated new edge sites, which bond with the surrounding molecules to be functionalized. The hBN nanoribbons fabricated by sonication unzipping are alkyl-chain functionalized if sonicated with alcohol,⁴⁹⁶ and NH₂ functionalized when sonicated with ammonia.⁴⁹⁷

4.3 Hydrothermal synthesis

Hydrothermal (solvothermal) synthesis has been widely studied for the synthesis of 2D materials.^{434,498,499} Like liquid exfoliated 2D materials, the hydrothermal method synthesizes O or OH group-functionalized 2D materials from water as a solvent in the synthesis process.⁵⁰⁰ Groups other than OH are also possible, with wisely chosen additives for the reaction. For example, synthesis of amino-functionalized graphene⁵⁰¹ and

polymer-functionalized MoS₂ with polyethylene glycol (PEG)^{502–504} and polyvinylpyrrolidone (PVP),⁵⁰⁵ are reported.

Hydrothermal synthesis is more suitable for synthesizing small particles than large and thin sheets. Functionalized 2D material quantum dots (QDs) are commonly synthesized using the hydrothermal process.⁵⁰⁶ The primary purpose for *in situ* functionalization for QD synthesis is to improve dispersion in solution and stability.^{440,507–511}

4.4 Solution synthesis

Synthesis of 2D materials by solution chemistry to synthesize functionalized GNR,^{512–517} graphene,^{518–522} and TMDC^{523–525} using various molecules as precursors has been studied for a long time. During the synthesis of functionalized 2D materials, functional groups at the edge can be designed to modify the material properties and limit the size of the product.⁵²⁵

Carefully designed precursors and reactions can produce high-quality functionalized 2D materials with well-defined geometries (Fig. 13(b)). Complex geometry restricts the reaction and bonding mechanism between precursors, making the functional group and geometry of the product controllable.⁵²⁶ By contrast, simple primary precursors synthesize 2D materials with more defects and smaller sizes, such as QD⁵²⁷ (Fig. 13(c)).

4.5 Outlook

Nanotube unzipping and solution synthesis with large, complex precursors can produce highly crystalline 2D materials with low defect density.

However, other synthesis techniques in this section produce low crystallinity 2D materials. Therefore, in many cases, the synthesis of functionalized 2D materials is one of two cases; functionalized unavoidably during the synthesis process (LIG, unzip) or designed to assist the synthesis process (hydrothermal, solution).

5. Characterization

Many of the techniques that are used for characterizing 2D materials also gave information about the functionalization states of 2D materials. This section will cover general techniques to characterize groups, density, and location of functionalization on 2D materials. Techniques designed for specific applications (gas absorption, liquid dispersion stability, HER, and others) will not be discussed.

5.1 Optical spectroscopy

Optical spectroscopy is one of the most widely used technique for characterizing 2D materials for its simplicity. Among the known optical spectroscopy methods, Raman spectroscopy, photoluminescence (PL), Fourier-transform infrared spectroscopy (FT-IR), and Ultraviolet-visible spectroscopy (UV-vis) are favored for characterizing the functionalization state of 2D materials.

Raman spectroscopy is simple, non-destructive measurement technique. It is considered as one of the most fundamental characterization techniques for the research of 2D materials. Raman scattering signal is sensitive to various modifications, such as strain,¹⁵ doping,⁵²⁸ and defect.³¹ For this reason, almost every 2D material functionalization studies use Raman spectroscopy in various forms, including spatial mapping, tip-enhanced Raman spectroscopy,^{529,530} polarized Raman spectroscopy,⁵³¹ and so forth.

PL also is a well-known technique for showing the band-related properties of 2D materials, which is easily influenced by the functionalization state. Although it can only be applied to materials with a bandgap less than 3 eV like TMDCs, and does not give a direct form of information for the band structure as Ultraviolet photoelectron spectroscopy (UPS) does,¹⁸⁴ this simple method is widely used for characterizing the band structure of materials, including modified charge density and new band state.^{20,28,532,533}

Other optical spectroscopy techniques including UV-vis^{312,362,511,534} and FT-IR^{286,323,379,455,511,535} are absorption spectroscopy methods that allow the chemical analysis of functionalized 2D materials. Those are usually utilized to track the functionalization and chemical reactions with organic molecules during and after the functionalization process. Both FT-IR and UV-vis share similar limitations. That is, the bonding status between functional groups cannot be measured, and a large quantity of 2D materials are required to be dispersed in solid powder or liquid medium for the analysis.

5.2 High energy spectroscopy

High energy spectroscopy,⁵³⁶ such as X-ray photoelectron spectroscopy (XPS),^{189,232,393,537} electron energy loss

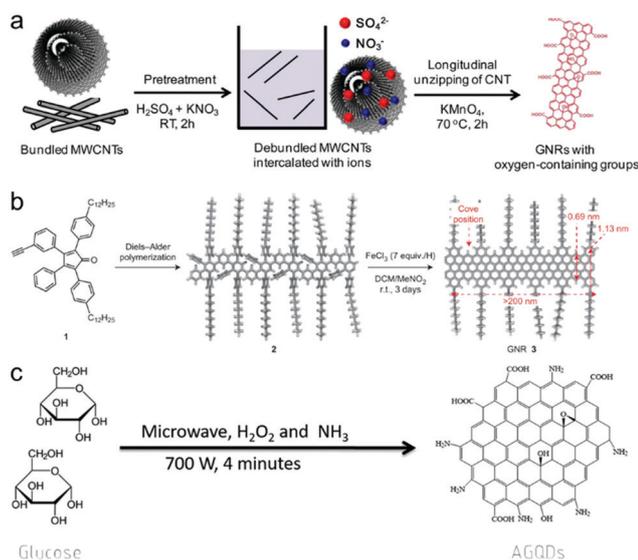


Fig. 13 (a) Schematic drawing of carboxyl functionalized GNR procedure by ion intercalation assisted CNT unzipping (reprinted with permission from ref. 493 Copyright 2015 ACS Applied Materials & Interfaces) (b) Schematic drawing of a synthesis route for alkyl functionalized GNR via polymerization (reprinted with permission from ref. 526 Copyright 2014 Nature Chemistry). (c) Schematic drawing for reaction route to microwave-assisted solution synthesis method for amine-functionalized graphene quantum dot (reprinted with permission from ref. 527 Copyright 2019 C. R. Chim.).

spectroscopy (EELS),^{286,538} energy-dispersive X-ray spectroscopy (EDS or EDX),²⁸⁶ and Auger electron spectroscopy (AES),¹⁹² are direct methods to analyze element composition of 2D materials using high energy beam radiation (*e.g.*, photon, electron, or ion).

Because they give the most straightforward results about chemical compositions of target sample, high energy spectroscopy methods are widely used for characterizing the functionalization of 2D materials, even with several limitations – expensive equipment, difficult sample preparation step, difficult/impossible to measure light element (H or Li), and risk of damaging the sample.

Different spectroscopy techniques are favored for different 2D materials and functional groups. XPS is more suitable when the sample has various functional groups (*e.g.*, GO) or a large organic functional group because it can detect the bonding status of the element. EDX or EELS can be a better option when high spatial resolution is required. Since EDX and EELS are attachable measurement options of electron microscopy, scanning electron microscope (SEM) and transmission electron microscope (TEM), they share similar requirements and limitations of SEM/TEM. Likewise, a sample with a single element functional group (*e.g.*, halogenated graphene) would give the best result from EDX and EELS since a high-energy electron beam easily damages large organic molecules.

5.3 Scanning probe microscopy

Scanning probe microscopy (SPM) techniques are a substantial option for characterizing the surface property of functionalized 2D materials.

Observing the topography of an individual functional group might give the most straightforward image data about functionalization. However, it is applied to limited cases only, because of its tricky measurement and sample preparation.^{128,304} Roughness,²³⁰ which can be derived from relatively simple atomic force microscopy (AFM), may give indirect information about functionalization density.

Besides topography, from various measuring modes of AFM, one can distinguish changed 2D materials surfaces properties after functionalization. Friction measurement^{199,389} would be the easiest method that clearly shows the functionalization state. Although AFM friction cannot give quantitative results about the exact type of functional group itself, it can clearly distinguish the area with different functional groups or bare surfaces. Kelvin probe force microscopy (KPFM)⁶¹ also shows a clear contrast between different functionalization groups, in addition to Fermi level shift, without the risk of damaging the sample surface.

5.4 Others

Thermogravimetric analysis (TGA)^{185,187,189,228,232,247,252,323,362,379,472,524} is a convenient tool for getting brief information about the chemical bonding states of functional groups, especially for large organic functional groups. It also can be coupled with mass spectroscopy to get more information about functional groups by measuring the exact mass of dissociated byproducts.

Mass spectroscopy, both coupled with TGA and time-of-flight secondary ion mass spectrometry (TOF-SIMS),^{199,286,336,364} is another direct element analysis technique. Unlike XPS or EDX, they can detect hydrogen or other light elements, becoming almost the sole technique for characterizing hydrogenated 2D materials.

In addition, unlike TGA and TGA-coupled mass spectroscopy, TOF-SIMS does not require a large amount of sample and ion beam irradiation is controllable, allowing element analysis with space distribution, which is greatly beneficial, especially for atomic thickness 2D materials.

5.5 Outlook

Characterization methods for functionalized 2D materials can be selected considering several factors.

For a sample of flake or film structured 2D materials, which can be supported by chip or TEM grid, Raman, PL, EDX, AFM, and EELS are possible options. When the film is large enough, XPS can also be chosen. FT-IR, UV-vis, and TGA generally require a large quantity of sample and TGA can be selected when the sample damage is not a critical issue.

The functional group is also an important factor. XPS, UV-vis, FT-IR, and TGA are widely selected when 2D materials are functionalized with large organic molecules, especially the chemistry of the functional group itself is important, and 2D materials act as supporting substrates. By comparison, when the specific element of the functional group has to be detected, such as from single or few atom groups (*e.g.*, halogenated graphene), EDX, EELS, XPS, and mass spectroscopy can be the proper option.

When the precise chemistry of the functional group is already known by previous studies or from other measurements, fast, approximate measurement may be enough for characterization. In this case, Raman or AFM can be the simplest and fastest option.

Raman, PL, AFM, EDX, and EELS provide characterization with the spatial distribution, which is highly demanding for many 2D material studies. Other methods, such as FT-IR or XPS may also support spatial analysis, but it is limited in resolution (FT-IR) or requires a difficult setup (XPS).

6. Conclusions

In this review, we discussed the currently reported covalent functionalization processes for 2D materials. Applying additional functionality to 2D materials by chemical modification has been a popular topic from the early stages of research. Furthermore, because of the continuous discovery of new 2D materials and increased demand for them, the importance of proper functionalization techniques for 2D materials continues to grow.

In conventional 3D materials, surface functionalization only changes its surface properties, and bulk properties are considered to remain intact. Consequently, surface functionalization adaptation for bulk materials is limited to particular

applications, such as control surface reactions and biocompatibility. However, for 2D materials with a large surface-to-volume ratio, importance of surface modification by functionalization greatly increases, because it directly affects their properties.

Proper functionalization is critical for eliciting the potential of 2D materials, even including finding new 2D materials or synthesizing high-quality 2D materials. Apparently, an appropriate method should be carefully selected to expedite proper functionalization and improve product quality with high yield and low cost.

An enormous variety of molecules can be used to functionalize 2D materials using direct or group exchange methods. This versatility widens applications of 2D materials by controlling the doping level, forming a composite with polymer/nanoparticle/other 2D layers, and bonding with other biomolecules. However, 2D materials and their functionalization methods for the industry are still a long way off, with several limitations that need to be solved.

(1) It is difficult to control the exact bonding sites of the functional group. The molecules react simultaneously at different sites. For example, vacancy-targeted functionalization reactions also occur at the edge or at other defect locations, and many group exchange reactions occur with several different groups or locations. Even for the reactions designed for specific types of locations, only the density or distribution of functional groups can be controlled for most functionalization methods.

(2) Several functionalization methods result in unwanted defects, thereby lowering the quality of the end-product. For this reason, the energy supply during functionalization processes and defect generation must be well controlled so as not to damage the 2D materials to minimize material quality deterioration. Even non-defect-mediated pure chemical reactions under mild conditions cause reactive chemicals and byproducts during the process, which can attack and damage 2D materials. Moreover, even when the functionalization process does not cause unwanted defects, it inevitably disturbs other physical properties, such as electron mobility or mechanical strength.

(3) Many functionalization methods have been studied only for specific reaction conditions, materials, or material configurations (e.g., liquid dispersion, exfoliated flakes, or bulk). Although every 2D material shares some physical properties, such as clean surfaces and layered structures, but they differ in chemistry and reactivity, making it almost impossible to develop a universal 2D material functionalization process.

Currently, more research is required to solve or at least mitigate all the aforementioned problems. Every new 2D material functionalization research will add a step to fulfill the list of possible functionalization processes for every 2D material. Even though the process of completing this list is tedious, step-by-step efforts without a direct outcome, each step will bring the impractical dream of 'perfect 2D functionalization methods' a little closer to reality.

Moreover, research for completing the list will be more than just developing convenient experimental procedures or industrial applications. We believe that researching the functionalization of

2D materials will benefit the entire field of 2D materials, lead to a better understanding of the chemistry of 2D materials and eventually open new research areas full of unexplored territory.

Author contributions

Jae Hwan Jeong did every investigation and writing of this paper. Sojung Kang and Gwan-Hyoung Lee did review and editing. Namwon Kim and Rakesh Joshi review this work. Whole writing is done under Gwan-Hyoung Lee's supervise.

Conflicts of interest

There are no conflicts to declare.

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