Recent developments in superhydrophobic graphene and graphene-related materials: from preparation to potential applications†

Jian-Nan Wang,a Yong-Lai Zhang,*a Yan Liu,b Wanhua Zheng,c Luke P. Leea and Hong-Bo Sun*ab

In the past decade, graphene has revealed a cornucopia of both fundamental science and potential applications due to its exceptional electrical, mechanical, thermal, and optical properties. Recently, increasing effort has been devoted to exploiting its new features, for example, wetting properties. Benefiting from its inherent material properties, graphene shows great potential for the fabrication of superhydrophobic surfaces, which could be potentially used for various anti-water applications. In this review, we summarize the recent developments in superhydrophobic graphene and graphene-related materials. Preparation strategies using pure graphene, graphene oxide, and graphene/polymer hybrids are presented and their potential applications are discussed. Finally, our own perspective of this dynamic field, including both current challenges and future demands, has been discussed. It is anticipated that the cooperation of the numerous merits of graphene and superhydrophobicity will lead to new opportunities for high-performance multifunctional devices.

Wetting behaviors of solid substrates have long been investigated under the continued stimulation of broad applications, both in daily life and commercial production. Generally, the surface wettability is mainly governed by the physical architecture and the chemical composition, so solid surfaces with extreme hydrophobicity can be rationally created by combining hierarchical roughness and low-surface-energy materials. According to this line, superhydrophobic graphene surfaces have been successfully obtained in recent years. To construct binary micro/nanostructures from planar graphene, a series of technologies have been employed, such as self-assembly, electrospinning, freeze-drying, and structured graphene surfaces with various two-dimensional or stereo configurations have been realized, remarkably increasing the surface roughness. Additionally, graphene and its related materials can work as nice building blocks to construct complicated layered assemblies, for instance through layer-by-layer assembly, and the organized structures may contribute to control of their surface topology. On the other hand, to generate low-surface-energy coatings, several kinds of strategies have been generally used, for example direct utilization of low-surface-energy materials, modification of low-surface-energy layers on the prepared rough surface using molecular grafting, and post removal of surface hydrophilic functional groups. In view of the processing capability and the modification flexibility both brought by the abundant oxygen-containing groups (OCGs), chemically exfoliated graphene oxide (GO) has been firstly chosen as a preferred starting material to achieve superhydrophobic graphene surfaces. With the rapid progress of graphene science,
high quality graphene could be acquired by multiple means, such as chemical vapor deposition (CVD), laser treatment, and is even commercially available in different sizes and states, which enriches the possible approaches to super-nonwetting graphene surfaces. Gradually, investigations on the dewetting properties of graphene and graphene-related materials have emerged as an active research field, which is evidenced by the ever growing body of published literature. In the process of summarizing the pertinent research, we found that superhydrophobic graphene surfaces inspired by creatures in nature have attracted a great deal of curiosity from scientists from different realms including chemistry, physics, biology, electronics, and tissue engineering. It has been revealed that the cooperation of graphene and superhydrophobicity will promote the development of non-wetting research and provide opportunities to develop novel graphene-based devices.

In this review, we focus on recent developments in superhydrophobic graphene and graphene-related materials. The article starts with a brief presentation of the wettability of graphene and graphene oxide. Then, a comprehensive review of the preparation methods is summarized in the second section, grouped by material categories. In the following part, potential applications of these functional surfaces are presented one by one. Finally, a brief discussion of the current state and future challenges in this area is provided in our own perspective.

Fundamentals of superhydrophobic materials

Basic principle for the construction of superhydrophobic surfaces

Superhydrophobic surfaces are solid surfaces that are extremely difficult to wet; the contact angle (CA) of a water droplet on such a surface is larger than 150°, and roll-off angle/contact angle hysteresis is less than 10°. For an absolutely flat surface, wettability is determined by the surface free energy of the solid, which can be described by Young’s equation (Fig. 1a).39

\[
\cos \theta_y = \frac{\gamma_{sv} - \gamma_{sd}}{\gamma_{sv}},
\]

where \(\gamma_{sv}, \gamma_{sd}\) and \(\gamma_{sv}\) are the surface free energies of solid–gas, solid–liquid and liquid–gas interfaces involved in the system, respectively. According to this equation, a solid material with a low surface energy is necessary to achieve a high CA. But this is not the only factor. For a real surface that is usually rough, topological roughness plays a crucial role in the wetting behavior of solid surfaces. To explain the relationship between surface roughness and wettability, two classical empirical models, the Wenzel regime and the Cassie–Baxter regime, have been extracted from various experimental data. In Wenzel’s model,40 it is assumed that liquid completely fills the grooves of the rough surface (Fig. 1b), so the relationship can be explained by the following equation.

\[
\cos \theta_w = r \cos \theta_y,
\]

where \(r\) is the surface roughness factor, defined as the ratio of the true surface contact area to the projection area, \(\theta_w\) is the contact angle of a water droplet on the rough surface.

Hong-Bo Sun received his B.S. and Ph.D. degrees from Jilin University, China, in 1992 and 1996, respectively. He worked as a postdoctoral researcher in the University of Tokushima, Japan, from 1996 to 2000, and then as an assistant professor in Department of Applied Physics, Osaka University, Japan. In 2005, he was promoted to full professor (Changjiang Scholar) at Jilin University, China. His research interests have been focused on ultrafast optoelectronics, particularly on laser nanofabrication and ultrafast spectroscopy. So far, he has published over 200 scientific papers, which have been cited by SCI journals more than 7000 times.

Yong-Lai Zhang received his B.S. (2004) and Ph.D. (2009) from Jilin University, China. In 2008, he worked at the Fritz-Haber-Institut of the Max-Planck-Gesellschaft as an exchange PhD student. After receiving his Ph.D, he joined the faculty in the State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University. In 2011, he worked as a research professor in Yonsei University, Korea. After that, he was awarded a “Hong Kong Scholar” postdoctoral fellowship and worked at the Center of Super Diamond and Advanced Films (COSDAF), City University of Hong Kong. His research interests include laser nanofabrication of biomimetic surfaces, graphene-based microdevices and Lab-on-a-Chip systems.
apparent contact angle in the Wenzel model, and $\theta_0$ is the contact angle for a liquid droplet on an ideal flat surface. The surface roughness could amplify the original wetting nature of the surface, either hydrophobic or hydrophilic.

In contrast, for Cassie’s case, the liquid is assumed to sit on top of the surface protrusions with air pockets trapped below (Fig. 1c). The effect of the solid–air composite interface on the CA of the surface can be derived using the following equation:

$$\cos \theta_{\text{CB}} = f_1 \cos \theta_1 + f_2 \cos \theta_2,$$

where $\theta_{\text{CB}}$ is the apparent contact angle in the Cassie-Baxter model, $f_1$ and $f_2$ are the fractional areas of the solid and air of the surface, respectively, $\theta_1$ and $\theta_2$ are the CAs for the flat solid surface and air, respectively. And we have $f_1 + f_2 = 1$, $\theta_2 = 180^\circ$ as air is considered a completely non-wetting material. Then eqn (3) can be derived as:

$$\cos \theta_{\text{CB}} = f_1 (\cos \theta_1 + 1) - 1$$

Therefore, a high CA may be achieved by increasing the surface roughness or introducing more buried air bubbles.

The above theories have been successfully adopted to explain the underlying mechanism of the famous “lotus effect”. It has been found that both the hierarchical micro-nanostructures (randomly distributed micropapillae and fine branch-like nanostructures) and the epicuticular wax materials (low surface energy coating) are responsible for the self-cleaning property, in agreement with the above theories.

Surface wettability of graphene and graphene oxides

Surface wettability of graphene sheets plays a vital role in determining their compatibility with the desired environment. So a deep understanding of the wettability of graphene and its related materials is fundamentally important for the development of graphene-based devices. Recently, several experimental and simulation studies have been focused on the surface properties and wettability of graphene films. Based on density functional theory, Leenaerts et al. indicated that graphene is strongly hydrophobic. They concluded that the binding energies between water molecules are larger than the associated adsorption energies on the graphene surface, such that water molecules form clusters on the graphene sheet. Quantum molecular dynamics simulations afford fundamental insight into the wetting behavior of waternanodroplets on a free-standing single-layer graphene sheet, and also allow incorporation of the polarization interaction, main-body effect and hydrogen-bond interactions into the prediction of wettability. The simulation results show that the graphene sheet has a CA of $87^\circ$. Compared with the theoretical results, graphene grown by CVD gives a CA of $89.4^\circ$. Besides, Shin et al. reported that epitaxial graphene has a static contact angle (CA) of $92^\circ$ and is slightly hydrophobic regardless of its thickness, close to that of highly ordered pyrolytic graphite ($91^\circ$), while graphene reduced by hydrazine has a CA of $127^\circ$ and a small interfacial energy with water. Proved both theoretically and experimentally, graphene has a natural hydrophobicity, which is essential knowledge for understanding the wetting behavior of water on the surface of such a material.

In addition to pristine graphene, another important graphene-related material that has been widely used for the fabrication of graphene-based devices is GO. GO is prepared by chemical exfoliation of natural graphite, and could be considered as a derivative of graphene with oxygen functional groups on its basal planes and edges. Due to the presence of OCGs, GO could be well dispersed in polar solvents such as water. Its ease of synthesis and solution processing capability make GO a promising precursor for the preparation of superhydrophobic graphene surfaces. The wettability of the GO film is influenced by the OCG content on the surface. With various levels of oxidation, GO films exhibit different wetting properties. For instance, a GO film has a CA of $67.4^\circ$ compared to that of $30.7^\circ$. Invariably, GO shows hydrophilicity owing to the chemical nature of the groups, such as carboxyl, hydroxyl and epoxy. To further increase its hydrophobicity, proper reduction treatments (e.g., hydrazine reduction, thermal annealing, photoreduction) would be implemented. Drastic or partial removal of the hydrophilic OCGs would lower its surface energy, giving rise to much higher water CAs of the reduced GO (rGO).

Preparation methods

Superhydrophobic surfaces prepared from GO

The presence of abundant OCGs endows the GO sheets with tractable solution-processing ability and the possibility of further functionalization, therefore many graphene-based superhydrophobic materials have been fabricated using GO as starting materials. Following the basic principle, artificial superhydrophobic surfaces have been successfully prepared by combining rough surface structures and low-surface-energy material functionalization. In the following section, some typical approaches to superhydrophobic GO have been summarized.

Surface functionalization. Surface functionalization, which can alter the surface characteristics, is an effective way to obtain a water-repellent surface, and the ease of imparting superhydrophobicity to various surfaces greatly extends the usefulness of such functional surfaces. As a starting material, GO is naturally hydrophilic, since most of the functionalized OCGs are hydrophilic. So in order to drastically change its surface wettability, post-functionalization of GO sheets with hydrophobic groups seems a simple but effective method. As a typical example, Xue et al. obtained a superhydrophobic GO surface by functionalization of GO with polyhedral oligomeric silsesquioxane (POSS), a unique cage-like molecular structure with eight isobutyl groups surrounding the cubic core. The amine-POSS can be covalently grafted onto GO sheets via amide formation, and chemical functionalization could be simply proved by the phenomenon that POSS-modified GO moved from the water phase to the CHCl$_3$ phase, as shown in...
Fig. 2. (a) Surface modification of GO with POSS, photographs of the original GO in water and the synthesized POSS-graphene in CHCl3, (b) SEM image of the POSS-grafted GO film, the inset shows a water droplet with CA ∼111.2°. (c) SEM image of a rough POSS-graphene film prepared from POSS-graphene particles, with a corresponding water CA of 157°. Reproduced with permission.47 Copyright 2012, American Chemical Society.

Fig. 3. SEM images of a graphene film deposited on an Al substrate: (a) with pure acetone as the solvent (Graphene-A film), (b) with pure water as the solvent (Graphene-W film). (c) Tunable control of the CA of a graphene film on an Al substrate by using a water–acetone mixture as the solvent. Increasing the water proportion in the mixture results in more hydrophilic behavior, whereas higher acetone content yields a more hydrophobic response. (d) Contact angles of the chemically treated and untreated graphene aerogel surface vary with concentration. (e) SEM image of the FDTDs modified graphene aerogel. Reproduced with permission.50,52 Copyright 2010, Wiley-VCH and 2011, American Chemical Society, respectively.

Fig. 2a. The grafting leads to the introduction of hydrophobic moieties of isobutyl groups, and the grafted graphene (POSS-graphene) becomes hydrophobic with a water CA of 111.2° (Fig. 2b). To further increase the hydrophobicity, the POSS-graphene was ground into particles and redispersed in ethanol, and the regenerated film exhibited hierarchical asperity and an enhanced CA of 157° (Fig. 2c).

Generally, functionalization of GO sheets with large groups would physically separate the graphene layers from each other. As a result, the obtained GO hybrid becomes soluble in various solvents. Such solution-processing capability will facilitate the structuring process, making it possible to prepare superhydrophobic graphene through various routes.

The variety of OCGs on the GO sheets makes the molecular functionalization flexible. Starting from the nucleophilic substitution between epoxy groups on GO sheets and the amine group of ODA, Lin et al. also prepared superhydrophobic GO films by octadecylamine (ODA) bonding.46 The hydrophobic nature of ODA significantly lowers the surface energy of grafted GO. A rough ODA-grafted GO film could easily be prepared by a simple filtration process. The obtained surface exhibited a high CA of 163.2° and a low hysteresis of 3.1°. Through functionalizing GO with phenylisocyanate (C6H5NCO), Wang et al. changed hydrophilic GO into hydrophobic nanosheets via solvothermal synthesis.48 Besides, (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane (HFTMS) was also employed as a surface reactive molecule to create a superhydrophobic GO surface.49

Solvent modification. Owing to the large specific surface area and the presence of OCGs, GO can adsorb large amounts of solvent molecules when dispersed in solvents. Even after the formation of graphene films, the adsorbed molecules may also affect its surface energy, and change its wettability significantly. Recently, thermally reduced GO with tunable wettability has been obtained by solvent adjustment.50 SEM images of graphene films deposited on an aluminum substrate using pure water as the solvent (graphene-W film) and using pure acetone as the solvent (graphene-A film) were shown in Fig. 3a and b, respectively. As compared to the naked substrate, the graphene-coated samples show one to two orders of magnitude in the average surface roughness due to the irregular stacking of graphene sheets. Interestingly, totally different wetting performances were observed for the graphene-W film, which was complete wetting, and the graphene-A film, which showed a water CA of ∼160°. The opposite effect was ascribed to the fact that the chemisorption of acetone on the defective graphene introduces a hydrophobic carbon–oxygen bond, while immersion in water leads to the formation of a hydrophilic carbon–oxygen bond. Additionally, the surface roughness amplified the wettability according to Wenzel’s theory. Based on these results, the graphene films can be tailored from superhydrophilic to superhydrophobic with a water CA changing from 0° to 160° by using acetone–water mixed solvents with different proportions (Fig. 3c). Zhang et al. also observed the solvent-dependent hydrophobic phenomenon in diverse pure organic reagents, as they prepared highly
hydrophobic films from chemically reduced GO via suction filtration.\textsuperscript{54} In their work, graphene was dispersed in different pure organic solvents (methanol, ethanol, dimethylformamide, toluene, decanol, and so on) at the same centrifugal speeds; although there is no clear difference observed among the surface morphologies of the graphene films, they showed different water CAs. Among them, films treated with ethanol and isopropanol exhibit static CAs close to or exceeding 140°, and all films showed CAs above 90°. Interestingly, the film showed a reversible transition from hydrophobicity to hydrophilicity under the alternation of ultraviolet irradiation and air storage, deriving from the adsorption and desorption of oxygen molecules on the surface of the nanosheets. The solvent modification is a simple, low-cost and flexible method for controllable modulation of the surface chemical compositions of graphene, providing an effective approach to tune the wettability of graphene in a large range, from superhydrophobicity to superhydrophilicity.

Freeze-drying. The freeze-drying technique has been widely used to generate porous structures. Recently, in the preparation of superhydrophobic graphene, the freeze-drying technique has been successfully adopted as a simple and inexpensive method for building rough graphene surfaces. For instance, Lin et al. fabricated a serial of graphene aerogels using the freeze-drying technique, and all of them exhibited a water CA larger than 150°, even reaching 160° (Fig. 3d).\textsuperscript{52} By freeze-drying the GO aqueous dispersion, a GO aerogel has been successfully prepared. The surface roughness could be varied using a GO solution with concentrations increasing from 3 to 15 mg ml\textsuperscript{-1}, which directly leads to variation of the water CA (Fig. 3d). In this case, the tradeoff between aerogel density and structural porosity could be taken into account. The graphene aerogels become superhydrophobic when the OCGs were thermally removed at high temperature. In this work, both the formation of the porous structure and the removal of OCGs contribute to the hydrophobic nature of the resultant graphene aerogel (Fig. 3e). To further strengthen the hydrophobicity of the samples, 1H,1H-2H,2H perfluorodecyl-trichlorosilane (FDTS) was applied to the surface, which further decreases their surface energy.

Template method. In addition to the above-mentioned methods for constructing a rough graphene surface by irregular stacking, hierarchical graphene structures could also be made in a controlled manner. Lee et al. reported the preparation of superhydrophobic and transparent graphene films that consist of hollow graphene spheres using amine-functionalized silica particles (NH\textsubscript{2}-SiO\textsubscript{2}) as a template.\textsuperscript{53} The electrostatic interactions between the negatively charged groups (–COOH, –O\textsubscript{2}–, –OH) of GO and positively charged groups (–NH\textsubscript{2}) of NH\textsubscript{2}-SiO\textsubscript{2} have been adopted as a driving force to induce such an assembly. The GO layer coated on the surface of the SiO\textsubscript{2} particles was thermally reduced and the silica cores were etched away in a HF solution, in this way a structured graphene film was successfully prepared. To further lower the surface energy, the structure was treated with a silane surface, and the CA of the surface increased to 157°, reaching the superhydrophobic range. Moreover, the transmittance spectrum showed that the hollow graphene structured surface shows possibilities for transparent devices for flexible electronics, since the transmittance of modified graphene spheres on the PET film is around 72.7 ± 1.19% at 550 nm.

Biomimetic laser processing. Recently, photo-induced deoxygenization of GO has become an appealing GO reduction strategy, considering the controllable reduction degree and flexible patterning.\textsuperscript{54–56} Inspired from natural butterfly wings that exhibit both superhydrophobicity and beautiful structural color due to the presence of an ordered photonic crystal structure, graphene surfaces with superhydrophobicity and iridescence have been demonstrated by photo-reduction.\textsuperscript{57,58} Two beam laser interference was used for the synchronous construction of a periodic structure and modulation of the surface chemistry (Fig. 4a). Typically, periodic distribution of laser intensity would lead to the formation of grating structures, while the strong laser–matter interaction would result in partial ablation of the GO film and the drastic removal of OCGs from the surface. The one-step procedure endowed the graphene surface with both hierarchical roughness and decreased surface energy; both these effects contribute to the formation of a superhydrophobic surface. As shown in Fig. 4b, the tested water CA could reach 153° for a graphene film with a period of 2 μm. Considering the fact that the residual oxygen content was subject to the laser intensity, the surface wettability would be further tuned by the laser power.\textsuperscript{57} Moreover, the surface topology can be adjusted by the grating period, and
thus the incident angle of the two laser beams provided another way to tune the wettability.\textsuperscript{28} What is more, the laser intensity distribution could also be tuned by multi-exposure of two beam laser interference. 2D micro-pillar arrays were fabricated by dual laser interference with 90° rotation (Fig. 4c), and the CA of the prepared film is 155°; this would effectively avoid the anisotropic superhydrophobicity. Interestingly, the prepared graphene films with periodic structures took on a wonderful iridescence, as observed by the naked eye.

**Superhydrophobic surfaces prepared from graphene**

Generally, GO featured tractable water processing capability and the flexibility for functionalization, so various superhydrophobic graphene products have been successfully developed using GO as the starting material. However, despite various reduction protocols having been employed to restore the sp² region of GO, the residual OCGs and the generated defects dramatically alter the structure of the carbon plane, making the rGO a substantially different material. Nowadays, with the rapid progress of graphene preparation strategies, graphene can be produced by micro-mechanical exfoliation of highly ordered pyrolytic graphite (HOPG),\textsuperscript{59,60} chemical vapor deposition (CVD),\textsuperscript{61–65} epitaxial growth\textsuperscript{66,67} and solvent exfoliation.\textsuperscript{68–70} As a result, superhydrophobic graphene has been successfully developed based on real graphene.

**CVD growth on structured templates.** The CVD method becomes a promising strategy to produce graphene, since it enables the preparation of a single layer or a few layers of graphene of high-quality (e.g. large area, low number of defects, and high carrier mobility). However, the CVD graphene films were usually flat. Despite being compatible with device fabrication, for instance, with the help of a substrate transfer technique, the flat surface set obstacles for wettability control. To introduce structure into the prepared samples, a template assisted CVD growth method has been inventively proposed.\textsuperscript{44,71–73} Dong \textit{et al.} demonstrated superhydrophobic graphene films by microwave plasma CVD (MPCVD) using a patterned Si substrate.\textsuperscript{71} In their research, vertically aligned few-layer graphene nanosheets were first prepared on the usual planar Si substrate. Though a rough surface with sharp edges were obtained, the water CA was 132.9°, even when the surface was modified with ODA the CA slightly increased to 133.7°. To achieve highly nonwetting performance, graphene sheets were grown on a Si substrate with micropillar arrays. SEM images in Fig. 5a and b show that graphene sheets were evenly distributed on the substrate, including the sides and bottom of the pillars. With a composite structure consisting of a microtexture inherited from the substrate and a nanostructure originating from the sharp edges, the graphene surface obtained a CA of 149.8°. After ODA treatment, a water droplet on the graphene surface presented a quasi-spherical shape (Fig. 5c) and the measured CA increased to 152.0°. As shown in the optical microscope image (Fig. 5d), there is air trapped between the droplet and the silicon pillars, and therefore an ideal Cassie’s mode was used to derive the theoretical CA in this case. A similar strategy was employed to create a superhydrophobic flower-like graphene surface grown on Si nanocone arrays by hot filament CVD (HFCVD).\textsuperscript{72}

Additionally, 3D hollow molds, such as foamed nickel, could also be used to prepare structured graphene.\textsuperscript{44,73} Graphene could directly grow on Ni templates by CVD technique.\textsuperscript{73} After chemical etching of the metal sacrificial scaffold, a free-standing graphene foam was produced. The imparted porous network and subsequent Teflon coating led to the unique superhydrophobicity. Moreover, the graphene foam exhibited superior elasticity and mechanically robustness, as confirmed by the complete rebounding of the impacting droplet. Conveniently, the structure of the graphene foam could be flexibly tuned by selecting appropriate templates. To further increase the surface roughness, carbon nanotubes can then be grown onto the graphene/Ni scaffold by a two-step CVD.\textsuperscript{44} After the removal of the nickel template, a superhydrophobic carbon foam was prepared free of surface modification. The superhydrophobic graphene foam holds great promise for various functional applications such as non-wetting electrodes and oil/water separation.

**Dip coating.** Using a structured carrier, dip coating is a rapid and active alternative to establish superhydrophobic graphene, as reported by Nguyen \textit{et al.}\textsuperscript{74} A common sponge was employed as a frame for graphene coating. Benefiting from the mechanical flexibility of graphene and strong van der Waals forces between the nanosheets and the sponge, graphene was physically adhered to the sponge surface. Through a repeated dipping-drying process, controllable amounts of graphene could be loaded onto the porous skeleton. The
hydrophobic coating made the powerful water-absorbing medium waterproof. As the graphene loading increased to 7.3% (defined as the weight ratio of anchored graphene to the sponge), the graphene sponge obtained a saturated water CA of about 162°. When it was forcibly immersed in the water, the graphene sponge was wrapped in an air layer and exhibited a mirror-like appearance; when released, it floated on the water surface and remained dry due to its dewetting-induced buoyancy and low density. To avoid the detachment of graphene and ensure the stability of the superhydrophobicity, a dimethylsiloxane (PDMS) protective layer was made on the surface, which is thin enough not to erase the roughness formed by the protrusions of the nanosheets. The as-treated sponge can go through the squeezing test, indicating the mechanical stiffness and the possibility for recycling use. It was observed that the CAs of the graphene sponges were still larger than 150° after having floated on aqueous solutions with different pH values (2–14) for days, and thus the as-prepared superhydrophobic foam can be applied in corrosive environments with a long working period.

**Crumpling and unfolding.** The crumpling–unfolding process offers another simple and effective route towards the formation of surface roughness. Zang *et al.* developed a large-area functional graphene with wrinkle structures by harnessing the elongation of the supporting substrate.75 The fabricating scheme was schematically illustrated in Fig. 6a. With the help of a PDMS stamp, CVD grown few-layer graphene was transferred to a pre-stretched elastomer whose length is three times its original size (pre-strained by 200%). Then the substrate was relaxed along two directions and reset to its initial size. In this way, the adhered graphene contracted to the same degree, and hierarchical roughness formed. As shown in Fig. 6b and c, the graphene film developed wrinkles and delaminated buckles when the substrate was relaxed in one direction, and then grew crumples (Fig. 6d) as the substrate is relaxed biaxially. These self-organized structures can also spread out and become relatively flat (Fig. 6e), once the relaxed substrate was stretched back. In this way, the crumpling and unfolding of the graphene film can be irreversibly tuned. The microscopic procedure triggered by the stress can be reproduced by the atomistic simulation (Fig. 6f), from which a single crumple with ridges and vertices, as well as the corresponding stress distribution, can be clearly observed. If the substrate simultaneously relaxed in the two directions, a different irregular pattern would appear on the graphene surface. As the rough structure of the wrinkled graphene is crucial for water-repellency, the wettability of the surface can be tailored by tuning the relaxing type (e.g., uniaxially or biaxially) and pre-strain level (e.g., 100% or 250%). It is worth mentioning that the graphene film can maintain its integrity over multiple crumpling–unfolding cycles (>50) with only a few unconnected cracks.

**Doping.** The arc discharge technique has been used for the preparation of graphene since 2009.76–79 It is a simple and efficient approach to prepare few-layer graphene nanosheets. Besides, this technique is very suitable for graphene doping and modification.76,79 As mentioned previously, both the surface roughness and the chemical composition influence the surface wettability. Recently, in addition to the creation of a rough graphene structure, as discussed in previous sections, efforts have been devoted to tailoring the surface chemistry of graphene for the purpose of tuning its wetting behavior. As a typical example, Shen *et al.* prepared superhydrophobic fluoride-doped graphene using the direct current arc discharge method.80 In their synthesis, a hollow graphite rod filled with graphite fluoride was used as the anode instead of a conventional pure graphite rod. During the discharge process, the graphite fluoride evaporated and the dissociative F atoms and/or ions would react with carbon, so that F-doped graphene was grown gradually. Observation of the morphology showed that the F-doped graphene are multi-layers and there are wrinkles or ripples on the edges of the nanosheets. According to the XPS spectra, the content of the fluorine in the prepared graphene was 10 wt% and doped F atoms had an ionic character.

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**Fig. 6** (a) Schematic illustration of the strategy for the crumpled graphene induced from the pre-stretched substrate. SEM images of patterns developed on the graphene sheet: (b) wrinkles form and (c) delaminated buckles as the substrate is uniaxially relaxed, (d) crumples as the substrate is biaxially relaxed, (e) unfolded pattern as the substrate is biaxially stretched back. (f) Atomistic modeling results (of from left to right) crumpling of single-layer graphene under uniaxial compression, biaxial compression, and the Mises stress distribution. Reproduced with permission.75 Copyright 2013, Nature Publishing Group.
With the difference in surface chemical composition, F-doped graphene showed a CA of 158°.

Superhydrophobic surfaces prepared from graphene-based hybrids

The hybridization of graphene has received significant attention in the sense that the synergistic effect of components leads to the improvement of performance in multiple facets and the creation of new functionalities. In addition to the fabrication of superhydrophobic surfaces using solo graphene and its related materials, guest materials, for instance polymers, have been mixed with graphene, forming various hybrids for the development of superhydrophobic coatings. The introduction of other materials may provide possibilities for controlling both the surface morphology and the surface free energy, which facilitates the fabrication of superhydrophobic surfaces.

Solubility modulation. Solubility modulation, which can induce precipitation and crystallization, is a simple method to control the morphology of various materials. By solvent replacement, Zhang et al. established a polymer/graphene hybrid surface composed of a uniformly packed microsphere structure, which exhibited an average water CA of 151.6 ± 1.4° (Fig. 7a).81 In their work, N,N-dimethylformamide (DMF) has been selected as a solvent to dissolve poly (vinylidene fluoride-hexafluoropropylene) (PVDF-HFP), and graphene sheets could suspend stably in the solution by ultrasonication. Then water used as a non-solvent was adsorbed by the suspension. After solvent leaching in water and freeze-drying, DMF was removed and a porous material was obtained. Fig. 7b showed the formation mechanism of the PVDF-HFP/graphene microsphere. Upon contact with the poor solvent, the polymer tended to separate from the liquid and immobilize on the graphene nanosheets. The entanglements of the graphene sheets intercalated with the crystallized PVDF-HFP chains finally induced the formation of microparticles, and the surface of these particles were covered with irregular spikes and nets on the nanometer scale (Fig. 7c and d). Thus a multi-level surface structure was regarded as a critical feature of superhydrophobic surfaces. Besides, several other superhydrophobic polymer/graphene surfaces were constructed through solvent replacement,82–85 demonstrating the versatility of this approach. Generally, in these studies, graphene nanosheets, having a large surface area, provided abundant immobilization sites for the precipitated polymer and facilitated their crystallization. The polymer–graphene attachment can be further strengthened by multiple forces between the carbon surface and polymer chains such as hydrophobic affinity,81,82 π–π interaction,83,84 and dispersive, polar and hydrogen-bond interactions.85 In addition to the change in surface morphology and wettability of graphene, the polymer may bring other developments. For example, the deposited polymer on the carbon surfaces may work as a spacer, preventing graphene nanosheets from re-aggregation and improving their dispersion stability.84 In return, graphene may enhance the thermal stability of the polymer, as the release of volatile components was limited by the nanosheets.83,84

Self-assembly. As a potent nanofabrication method, self-assembly enables flexible construction of stereoscopic topology from nanoscale structure units.37 Recently, it has been demonstrated that soft 2D graphene materials can be assembled into robust 3D interconnected networks with the aid of nanoparticles, building a novel superhydrophobic graphene based material.86 Typically, GO was mixed with FeSO4 and kept at 90 °C for 6 hours, then a black hydrogel containing about 95.8 wt% water was naturally formed. The formation mechanism can be explained as the fact that Fe2+ ions tended to move towards GO sheets due to electrostatic attraction and then oxidized into Fe3+, while GO sheets were reduced into Fe3O4. Moreover, this method was demonstrated to form a robust 3D interconnected networks driven by the π–π stacking interaction between graphene sheets, using the anchored iron oxide nanoparticles as a powerful support. Additionally, the as-formed hydrogel exhibited a strong adsorption of heavy ions such as Cr(vi) and Pb(ii), which may arise from the synergistic effects of the electrostatic interaction, ion exchange, and surface complexion. After freeze-drying, the hybrid hydrogel becomes a superhydrophobic graphene aerogel. Interestingly, the iron oxide component of the graphene hybrid hydrogel can be controlled by the pH values from α-FeOOH to Fe3O4. Magnetic investigations revealed that the graphene/Fe3O4 aerogel showed ferromagnetism, which can produce strong magnetic signals at a small magnetic field. Moreover, this method was workable to induce the self-assembly of reduced graphene sheets with other metal oxides such as MnO2 and CeO2, assisted with Mn2+ and Ce3+, respectively. This method provides a facile way for building multifunctional and manifold graphene derivatives.
**Structural reconformation.** Due to the presence of OCGs and its water-processing capability, GO could be mixed with various functional polymers, providing the possibility for fabricating diverse hybrid structures. Recently, Choi et al. demonstrated the fabrication of superhydrophobic graphene/Nafion hybrid films through conformational rearrangement.\(^{87}\) As shown in Fig. 8 (top panel), Nafion, a fluorinated polymer, was blended with GO, then chemical reduction in hydrazine solution was implemented. The rGO can be uniformly coated with Nafion, driven by the hydrophobic interaction between the conjugated graphene sheets and the polymer backbone. What is more, the hydrophilic sulfonic groups of Nafion imparted high dispersion and long-term stability over 2 months to the rGO/Nafion (denoted as CMGN) hybrid. To obtain thin films, the hybrid solution was then vacuum filtrated. SEM images (Fig. 8, bottom panel) showed that a rough surface with a petal-like microstructure gradually emerged as the ratio of Nafion components increased. The roughness contributed to the structural reorientation of the hybrid sheets, that is, the favorable interactions between graphene and Nafion cause the conformational rearrangement of the Nafion and the wrinkling and protrusion of sheet edges. With the change of surface morphology, the CAs of the films increased from \(~97^\circ\) to \(~161^\circ\), indicating a tunable wettability with respect to the hybrid composition. It is worth mentioning that the electronic properties of graphene were carefully retained in the hybrid, as the coating of individual graphene sheets by Nafion was on the molecular level, and the supramolecular interactions caused close packing of the graphene sheets.\(^{88,89}\)

**Electrospinning.** Electrospinning is a straightforward and cost-effective method to provide surface roughness, and it has been widely adopted for the fabrication of superhydrophobic surfaces. Recently, superhydrophobic graphene nanocomposite fibers were fabricated in one step by electrospinning.\(^{90}\) In this work, graphene nanoparticles worked as an additive to enhance the surface roughness when added to the polymeric solution. Without the particles, pure electrospun poly (vinyl chloride) (PVC) fibers showed a water CA below \(140^\circ\). In comparison, the PVC hybrid polymer electrospun in the presence of graphene nanoflakes achieved a high CA of \(151.5^\circ\), even \(166.3^\circ\), presenting a realization of superhydrophobicity. Considering the small amount (1 wt%) needed to introduce sufficient hydrophobic character, graphene can be utilized as an effective superhydrophobic medium.

**Potential applications**

The combination of superhydrophobicity with graphene has triggered a number of new functionalities and uses. From the material point of view, graphene features high carrier mobility, good conductivity, transparency, excellent mechanical strength, and biocompatibility; while from the point of view of unique dewetting properties, additional functionalities, such as self-cleaning, anti-fogging, and oil/water separation could well be imparted to graphene and graphene-based devices. Currently, despite the fact that the fabrication strategies for superhydrophobic graphene surfaces have been well developed, functional applications are still limited to laboratory tests. In this regard, we briefly summarized a series of typical applications in this section.

**Water treatment**

As remediation of accidents, the cleanup of leaked chemicals or oil is a global environmental issue. Generally, porous materials that have high porosity and high surface areas show great potential for cleaning up oil/chemicals, however these materials usually show poor selectivity towards the target oil, and are thus easily saturated with water. To address this issue, nanoporous polydivinylbenzene (PDVB) with superhydrophobicity has been successfully developed for the high-capacity and high selectivity adsorption of organic compounds. Recently, graphene based materials with both superhydrophobic and superoleophilic properties\(^{44,74,91}\) emerge as a promising candidate for the selective absorption of oil and organic solvents without absorption of water. Fig. 9a showed the complete removal of gasoline labeled with Sudan III from the water using a graphene aerogel.\(^{86}\) The oil-saturated samples can be easily regenerated after drying in an oven at \(100^\circ\)C for 30 minutes. Notably, the graphene hybrid aerogel retained a high adsorption capacity after eight absorbing–drying periods for gasoline (Fig. 9b), the excellent recyclability was a promising feature for the adsorbent. In addition to gasoline, a variety of oil and solvents such as cyclohexane, toluene, paraffin oil, vegetable oil and phenoxin can be taken up (Fig. 9c). As another example, a superhydrophobic graphene sponge also show eminent absorption capacities ranging from 54 to 165 times their weight for a wide range of solvents.\(^{74}\) The sponges could also be renewed by a simple distillation or squeezing process, showing superior mechanical strength. In addition, the light weight, chemical inertness, low cost and environmental friendliness make the graphene sponge a powerful candidate for practical applications.

Moreover, graphene-based hydrogel was reported to show high adsorption rates of heavy ions, which are extremely toxic.
in water resources of heavy ions. The calculated maximum adsorption capacities for Cr(VI) and Pb(II) were 139.2 and 373.8 mg g$^{-1}$, respectively, which are much higher than active carbon for Cr(VI) (69 mg g$^{-1}$). Therefore, functional graphene-based materials are regarded as ideal choices for water purification.

**Wettability switching**

The manipulation of surface wettability is of great importance in many research areas such as cell culture, microfluidics, and water transportation. To this end, graphene surfaces with tunable wettability may exactly meet the needs of various applications requiring functional coatings. Several strategies have been proposed to investigate the wettability control of graphene.$^{50,51,57,58}$ Typically, Rafiee et al. reported a simple route, which can dramatically alter the graphene surface from super-hydrophilic to super-hydrophobic using a solvent modification method, as introduced in the previous section.$^{50}$ In their work, by combining water and acetone in a suitable proportion as the solvent, a graphene film with the desired wetting behavior would be achieved.

Besides, reversible wettability control of the hydrophobic graphene surface has also been realized through ultraviolet light irradiation, as reported by Zhang et al.$^{51}$ When the graphene film was exposed to ultraviolet light for 12 h, the film shown presented a water CA of 40°; when stored in air for 12 h, the film displayed a high water CA of 140°. The interesting phenomenon was bound up with the adsorption of oxygen molecules, which may result in the production of hydrophilic groups on the graphene surface. The observed tunable wettability could be reproduced for more than five cycles.

**Transparent coatings and electrodes**

Transparency is an essential requirement for many optical devices, such as windshields, OLEDs, and photovoltaic cells. To enhance light transmission and prevent moisture permeation, contaminant-proof or self-cleaning properties are also useful or even necessary for them. In this regard, transparent and superhydrophobic graphene films seem to be an ideal candidate for optical and optoelectronic materials.$^{53,75,87,90}$ Lee et al. demonstrated a simple route towards a transparent and flexible superhydrophobic graphene film, which exhibits a water CA of 157° and an optical transmittance of 72.7%.$^{53}$ Combined with high conductivity, functional graphene film shows great potential for transparent electrodes.$^{71,90}$ By tailoring the surface roughness, graphene surfaces with variable transmittance, resistance and wettability were obtained.$^{71}$ The prepared graphene film manifested high toughness and deformability compared with the usual electrode material of gold. The combination of stretchability, tunability and transparency will endow graphene electrodes with various potential uses.

**Smart actuator**

Man-made actuators are helpful in many applications such as energy harvesters and artificial intelligence. Crumpled superhydrophobic graphene has exhibited attractive potential for use in artificial muscles.$^{75}$ When a voltage of 3000 V was applied between the graphene films, the elastomer among them developed an electric field and deformed under the induced Maxwell stress. The pre-crumpled graphene films were unfolded as the elastomer stretched over 100%, and the transmission changed between 40–60%. The response was fast and the laminate would return to the unfolded state upon withdrawing the voltage (Fig. 10a). The procedure mimicked the behavior of an artificial actuator with tunable transparency. The stretchable graphene ensured the multiple manipulation of the actuator without fracture. This work presents a smart graphene device with a dedicated design and sheds light on the possible uses of graphene-based systems.

**Other applications**

Due to the ability to transfer charge and resist water, a conductive superhydrophobic graphene surface may also find broad applications in electronics. For instance, it could serve as a functional protective layer for electrostatic discharge and EMI shielding,$^{83,84,92}$ to improve the operating safety and signal stability of electronic devices; it may also prevent electronic failures caused by water contact. In the light of these capabilities, graphene based materials with unique superhydrophobicity would hold great promise for practical use. Recently, Fang et al. reported a graphene/polymer hybrid film with a high conductivity of 6560 S m$^{-1}$ and a total EMI shielding effectiveness value of 43.7 dB cm$^{-1}$ g$^{-1}$, which is 4 times greater than that of traditional metal shielding materials.$^{84}$ Besides, superhydrophobic graphene could be employed as functional papers$^{93}$ and advanced textiles,$^{94}$ which may be promising for wearable electronics.
In addition to the potential electronic applications, many superhydrophobic graphene surfaces are highly adhesive, which is responsible for water transportation and cell culture, revealing great potential in tissue engineering.\textsuperscript{49,57,72} Moreover, due to the water repellency and good dispersion in polymer solutions, polymer/graphene hybrids are considered as good candidates for catalyst support.\textsuperscript{81} Instead of a black appearance, superhydrophobic surface with periodic microstructures exhibit brilliant iridescence (Fig. 10b).\textsuperscript{58} Thus the colorful superhydrophobic graphene shows potential for embellishment coatings. Additionally, hydrophobic graphene could also be used as a functional coating for depth filters.\textsuperscript{95} A droplet coated with superhydrophobic graphene particles may serve as a miniaturized reactor standing on either hydrophobic or hydrophilic surfaces.\textsuperscript{47} Currently, the research topic “superhydrophobic graphene” is still in its infancy. Nevertheless, we still deem that, with the progress of superhydrophobic graphene and its related materials, it may find more and more promising applications, both for fundamental research and for practical usage.

### Conclusions and outlook

Due to its outstanding physical/chemical properties, graphene has been intensively investigated by diverse disciplines; in the past decade, it has been considered as a rising star over the horizon of materials science.\textsuperscript{96} Moreover, as numerous well-controlled structures have been triumphantly constructed from graphene-related materials, the development of this family has been vigorously propelled.\textsuperscript{18} In recent years, to investigate and utilize the surface property of graphene, different routes have been proposed to fabricate superhydrophobic graphene surfaces by controlling the surface roughness and chemical composition of graphene. In this review, we discussed the fabrication methods and potential applications of superhydrophobic graphene and related materials. In the beginning, owing to the ease of functionalization and the tractable water-processing capability, GO solution is regarded as a reservoir for the fabrication of various graphene-based non-wetting surfaces. Later, with the rapid progress of graphene production methods, superhydrophobic graphene has been successfully prepared based on pristine graphene. For instance, CVD provides an effective method for the fabrication of functional graphene surfaces. In addition to the superhydrophobic surfaces fabricated by solo graphene or graphene-related materials, with the aid of polymer and inorganic nanoparticles, manifest graphene derivatives can also be developed by hybridization. All of these graphene-based superhydrophobic materials exhibit great potential in a wide range of applications, such as water treatment, wettability switching, transparent electrodes and smart actuators. To make an overview of the state-of-the-art of this dynamic field, we summarized the recent developments of superhydrophobic graphene and its related materials in Table 1. Despite its short history, graphene has become a promising newcomer in superhydrophobicity research. Compared with conventional materials such as metals (including semimetals and metal alloys), oxides, and polymers, graphene and its related materials exhibit many superior features. To make a full comparison, some representative properties of these superhydrophobic materials have been briefly summarized in Table S1 (see ESI†).

Currently, as the research of superhydrophobic graphene is still at an early stage, there are still many challenges that need to be addressed. For example, a majority of the fabrication methods are limited to laboratory research and not suitable for large scale production. Besides, most of the superhydrophobic graphene films generally face the problem of poor mechanical stability. Mechanical durability is crucial to fulfill the need of real-world applications.\textsuperscript{97} The third challenge is how to make full use of the superhydrophobic graphene and its related materials. Besides its hydrophobic nature, graphene has various merits, including mechanical strength, optical transparency, high conductivity, large specific surface area, flexibility, and so on. It could be expected that the combination of these superior properties of graphene and superhydrophobicity would lead to novel functions in the field of electronic devices, optoelectronics, microfluidics and tissue engineering. Overall, we believe that an exciting future for superhydrophobic graphene surfaces will be witnessed, since multidisciplinary scientists and engineers have been contributing to the understanding and the design of such surfaces.
Table 1 Summary of the methods of fabricating superhydrophobic graphene and their potential applications

<table>
<thead>
<tr>
<th>Category</th>
<th>Method</th>
<th>Material</th>
<th>Potential application</th>
<th>Ref.</th>
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<sup>a</sup> ODA, octadecylamine. <sup>b</sup> HFTMS, (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane. <sup>c</sup> POSS, polyhedral oligomeric silsesquioxane. <sup>d</sup> FDTS, 1H,1H,2H,2H perfluorodecyl-trichlorosilane. <sup>e</sup> PVDF, polyvinylidene fluoride. <sup>f</sup> PVDF-HFP, poly(vinylidene fluoride-hexafluoropropylene). <sup>g</sup> P3HT, poly(3-hexyl thiophene). <sup>h</sup> MEH-PPV, poly[2-methoxy-5-(2’-ethyl-hexyloxy)-1,4-phenylene vinylene]. <sup>i</sup> PC, polycarbonate. <sup>j</sup> PVC, polyvinyl chloride. <sup>k</sup> CNTs, carbon nanotubes.

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