

## Porous graphene: Properties, preparation, and potential applications

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Graphene has recently emerged as an important and exciting material. Inspired by its outstanding properties, many researchers have extensively studied graphene-related materials both experimentally and theoretically. Porous graphene is a collection of graphene-related materials with nanopores in the plane. Porous graphene exhibits properties distinct from those of graphene, and it has widespread potential applications in various fields such as gas separation, hydrogen storage, DNA sequencing, and supercapacitors. In this review, we summarize recent progress in studies of the properties, preparation, and potential applications of porous graphene, and show that porous graphene is a promising material with great potential for future development.

**graphene, porous graphene, electronic structure, gas separation, DNA sequencing**

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Graphene, a densely packed two-dimensional (2D) sheet of  $sp^2$ -hybridized carbon atoms, has become important in the field of materials science, attracting both theoretical and experimental interest, as a result of its exceptional properties and potential applications. Although studies of graphite with fewer layers had been carried out before [1,2], a single layer of graphene was first successfully observed under the microscope by Geim and coworkers [3] in 2004 through reverse exfoliation of graphite. Since then, investigations into this novel material have increased significantly. Graphene can be prepared using mechanical exfoliation and many other methods. For instance, graphene has been obtained by epitaxial growth on insulating substrates such as SiC [4] and  $SiO_2$  [5], and on metal substrates such as Ir(111) [6] and Ni(111) [7]. Chemical vapor deposition [8] and thermal oxidation of graphite [9] have made the preparation of large-area graphene feasible. The most intriguing aspect of graphene is its extraordinary properties. Graphene, which is constructed by strong  $sp^2$  covalent bonds, is believed to be the strongest material ever measured [10]. Experiments

have revealed that graphene exhibits a high ambipolar electric-field effect at room temperature, better conductivity than any other known material [3], and many other novel properties, including room-temperature quantum Hall effects, mass-less Dirac electrons near the K point, and high mobility of carriers ( $10^6$  m  $s^{-1}$ , close to the speed of light) [11–13]. All these properties distinguish graphene from ordinary materials, and make graphene an ideal candidate for the manufacture of electronic devices. To develop a full understanding of its nature and realize the full potential of graphene, extensive investigations have proceeded in various directions. For instance, the electronic and magnetic properties of graphene can be modified by hydrogenation [14] and doping [15].

Another research area, porous graphene, has also attracted increasing attention recently. Porous graphene is a collection of graphene-related materials with nanopores in the plane. Depending on the production techniques used, the pore size ranges from atomic precision to nanoscale. As a result of the nanopores in the graphene plane, porous graphene exhibits properties distinct from those of pristine graphene, leading to its potential applications in numerous

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fields such as energy storage [16], gas purification [17,18], and DNA sequencing [19,20]. In this review, we will summarize recent progress on research into the properties, preparation, and potential applications of porous graphene.

## 1 Properties of porous graphene

### 1.1 Structural properties of porous graphene

Depending on the production technique, the structure of porous graphene varies with respect to pore size and distribution.

Recently, 2D polyphenylene, a porous graphene with single-atom-wide pores and sub-nanometer periodicity, has been successfully fabricated, as shown by the scanning tunneling microscopy (STM) image in Figure 1(a) [21]. The resulting porous graphene can be understood as pristine graphene with one hexagon missing per  $3 \times 3$  unit cell. First-principles computations indicate that the pore width is  $\sim 2.48$  Å [22]. Although similar 2D polymer networks can also be found elsewhere [23–25], this is the one most closely related to graphene.

By electron beam irradiation of transmission electron microscopy (TEM), Fischbein et al. [26] introduced nanopores into graphene sheets, demonstrating that closely packed nanopore arrays could be achieved. Subsequent studies showed that drilling holes using TEM was a robust and well-reproducible procedure [27]. The pore diameters range from 2 to 40 nm in multilayer and monolayer graphenes, as shown in Figure 1(b) and (c). Despite the local damage around the pore, the crystallinity of the monolayer surrounding the hole was preserved.

### 1.2 Electronic properties of porous graphene

The electronic properties of 2D polyphenylene-type porous graphene have been investigated using both density functional theory (DFT) [16,22] and crystal orbital methods [28]. The computations all revealed that this porous graphene is a semiconductor with a direct band gap. However, the values of the band gap vary widely in different computations. The crystal orbital method gives a band gap of 3.7 eV, whereas two DFT computations give values of 3.2 eV [16] and

2.48 eV [22]. It is well known that DFT usually underestimates the band gap, and hybrid functionals such as HSE06 (a functional developed by Heyd, Scuseria, and Ernzerhof) should give more accurate results [16]. As shown in Figure 2, the band gap of 3.2 eV may be close to the real value. Porous graphene is particularly attractive since many efforts have been made to open a gap in the band structure of graphene for practical applications [29–33]. Unfortunately, the band gap is rather large in polyphenylene-type porous graphene. For a porous graphene with large nanopores in the plane, the electronic conductivity should decrease as a result of destruction of the integrity of the conjugated  $sp^2$  carbon network.

## 2 Preparation of porous graphene

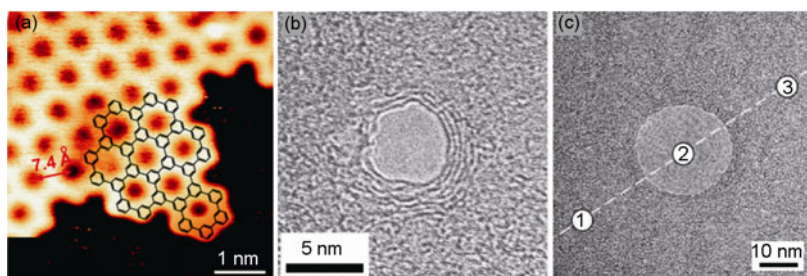
Porous graphene can be prepared using chemical or physical methods, as summarized below. Different methods provide porous graphene with different structural properties.

### 2.1 Surface-assisted aryl-aryl coupling of cyclohexa-*m*-phenylene (CHP)

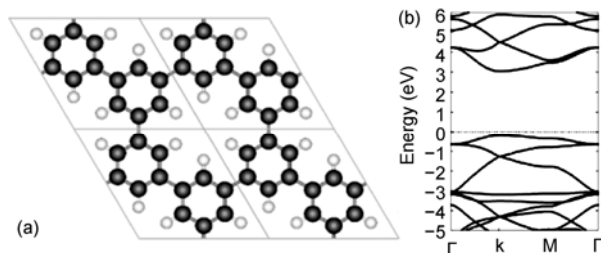
The porous graphene obtained by this method is a new 2D porous hydrocarbon network; it can be regarded as graphene with phenyl rings periodically missing. The bottom-up surface-promoted aryl-aryl coupling reaction gives a covalently linked hydrocarbon super-honeycomb network with high precision and high resolution [21].

In this experiment, CHP was deposited at room temperature from resistively heated quartz crucibles held at 745 K onto an Ag(111) crystal surface, which was cleaned beforehand by  $Ar^+$  sputtering and annealing at 725 K for 15 min. After annealing the substrate for 5 min to 575 K, the surface-assisted coupling reaction began, and finally resulted in fully developed 2D polyphenylene networks at temperatures above 575 K. The mechanism is illustrated in Figure 3.

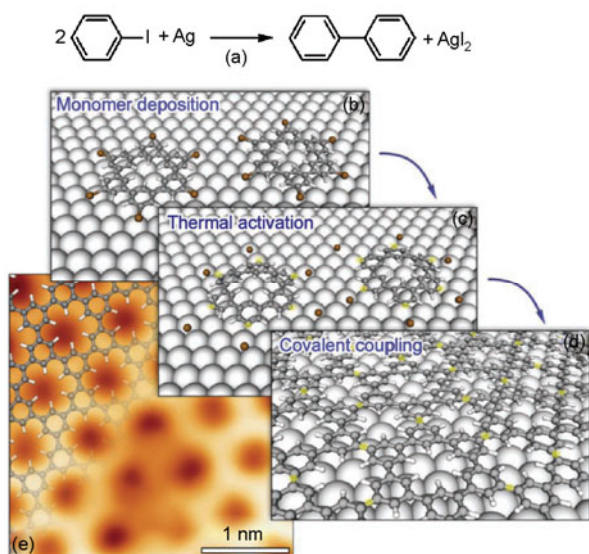
Further investigations [34] clarified the effect of the substrate on the morphology of the porous graphene. On Cu(111), the networks were dominated by dendritic structures with single-molecule-wide branches, and a mixture of branches and small domains of compact network clusters



**Figure 1** Structures of porous graphenes: (a) STM image of 2D polyphenylene-type porous graphene [21]; TEM images of nanopores drilled into (b) multilayer graphene and (c) monolayer graphene [27].



**Figure 2** (a) Optimized geometry for 2D porous graphene (dark atoms C and light atoms H). (b) Computed band structures based on HSE06 exchange correlation functional [16]. The dotted line at zero indicates the Fermi level.



**Figure 3** (a) Ag-promoted aryl-aryl coupling of iodobenzene to biphenyl; (b)–(d) mechanism of surface-promoted aryl-aryl coupling of CHP to fabricate porous graphene; and (e) STM images of porous graphene supported on an Ag(111) surface after the polymerization process at 805 K [17]. Color code: carbon, gray; hydrogen, white; iodine, brown.

was observed on an Au(111) surface, whereas highly ordered and dense polyphenylene networks emerged only on an Ag(111) surface.

## 2.2 Electron beam irradiation of suspended graphene

Electron beam irradiation of suspended graphene sheets [26] is a typical way of producing porous graphene. Using focused electron beam irradiation in a TEM apparatus, nanopores and other nanoscale patterns of arbitrary design can be introduced into graphene sheets. It has also been demonstrated that the resulting structures were maintained over time, and significant long-range distortions of the graphene sheets did not occur, even if there was extensive removal of carbon; this confirms the stability of porous graphene obtained in this way.

In this method, graphene sheets are deposited on a ~50-nm-thick suspended SiN<sub>x</sub> membrane substrate, on which

arrays of ~1-μm<sup>2</sup> holes have been made in advance. Then, by sequentially increasing the TEM magnification, condensing the imaging electron beam to its minimum diameter, ~1 nm, and moving the beam position with the condenser deflectors, arbitrary patterns are created.

## 2.3 Helium ion bombardment of suspended graphene

Bell et al. [35] reported that it was possible to precisely cut and pattern graphene with helium ions using a modified helium ion microscope for lithography. With computer-controlled alignment, patterning, and exposure, graphene on Si/SiO<sub>2</sub> substrates can be tailored according to a design. It was also pointed out that little obvious damage to or doping of the sample would occur once suitable beam doses were determined, whereas extensive deterioration and ionic contamination would arise under the same acceleration voltage in the case of a gallium ion beam, as a result of its higher atomic mass.

Apparently, porous graphene synthesized using chemical methods exhibits orderly pore distribution and atomic precision, whereas the pore size of porous graphene prepared via physical approaches is tunable from nanometer to sub-nanometer by changing the ion and electron doses and acceleration voltage, depending on the subsequent applications.

In addition to the methods mentioned above, there are other potential ways of preparing porous graphene, such as atomic force microscope local oxidation nanolithography [36] and crystallographic etching with catalytic metal nanoparticles [37,38]. Further investigations are needed to develop economical syntheses of well-ordered large-area porous graphene.

## 3 Potential applications of porous graphene

Porous graphene, as a result of its distinct structural and electronic properties, is being increasingly investigated because of its potential applications in many fields such as gas purification, DNA sequencing, hydrogen storage, and supercapacitors. These will be discussed below.

### 3.1 Gas separation and purification

Whether for industrial purposes or scientific investigations, pure gases, such as helium and hydrogen, are in great demand. Compared with traditional methods of gas separation such as cryogenic distillation and pressure-swing adsorption, membrane separation of gases has lower energy costs, uses smaller plants, and has less mechanical complexity [39]. The separation of different gases can be achieved on the basis of differences in their diffusion rates.

For traditional strategies of membrane separation, many kinds of membranes have been developed, including metal,

zeolite, and polymer membranes [40–42], with thicknesses ranging from 10 to  $10^3$  nm. Since the membrane permeability is inversely proportional to its thickness [43], these traditional membranes seem inferior to graphene, which is only one-atom thick. However, a perfect graphene is impermeable even to the smallest gas atom, helium, since the densely packed honeycomb crystal lattice is strong enough to prevent atoms and molecules from passing through it [44,45]. To explore its potentially high permeability, it is therefore necessary to introduce pores into the graphene planes.

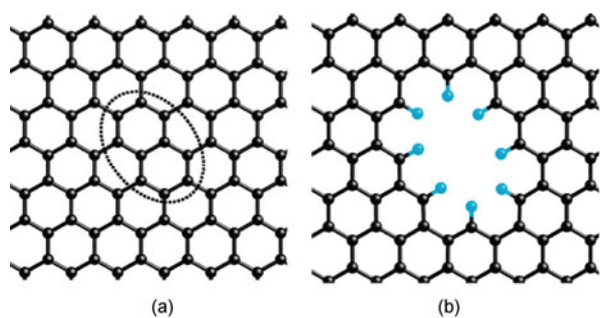
Theoretical investigations have progressed further than experiments on the application of porous graphene for gas purification. Although there has as yet been no report of experimental success, theoretical investigations based on first-principles computations have been conducted to explore the use of porous graphene for gas separation.

Jiang et al. [18] first proposed the use of porous graphene as a one-atom-thin, highly efficient, and highly selective membrane for gas separation, by designing pores in graphene, as shown in Figure 4.

The pore in Figure 4(b) is approximately rectangular in shape, with dimensions of  $2.5 \text{ \AA} \times 3.8 \text{ \AA}$  for all-hydrogen passivation. The computed diffusion barriers through the pore are 0.22 and 1.6 eV for  $\text{H}_2$  and  $\text{CH}_4$ , respectively. We can estimate the selectivity of  $\text{H}_2$  relative to  $\text{CH}_4$  using the Arrhenius equation:

$$S_{\text{H}_2/\text{CH}_4} = \frac{r_{\text{H}_2}}{r_{\text{CH}_4}} = \frac{A_{\text{H}_2} e^{-E_{\text{H}_2}/RT}}{A_{\text{CH}_4} e^{-E_{\text{CH}_4}/RT}},$$

where  $r$  is the diffusion rate,  $A$  is the interaction (diffusion) prefactor, and  $E$  is the diffusion barrier. Assuming that the prefactors here are the same, the equation yields a high selectivity,  $10^{23}$ , for  $\text{H}_2/\text{CH}_4$  at room temperature ( $T = 300 \text{ K}$ ). Based on molecular dynamics stimulations, the permeance of  $\text{H}_2$  at 600 K under a pressure of  $10^5 \text{ Pa}$  across the membrane is as high as  $1 \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ , whereas a 30-nm-thick silica membrane has a permeance of  $2 \times 10^{-7} \text{--} 3 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  at 673 K [46]. This result is encouraging; however, the controlled formation of designed pores in



**Figure 4** (a) Pristine graphene sheet. The carbon atoms in the dotted circle are removed. (b) An all-hydrogen passivated pore in graphene [18]. Color code: C, black; H, grey.

graphene planes seems impossible at present.

Bieri et al. [21] successfully synthesized 2D polyphenylene-type porous graphene. This novel structure, with one-atom thickness, periodically distributed pores, and uniform pore size, has attracted much attention with respect to its application to gas purification. On the basis of DFT computations, Li et al. [22] compared the diffusion barriers for  $\text{H}_2$  (Figure 5),  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$ ; they are 0.61, 2.21, 2.35, and 5.19 eV, respectively. The selectivities of  $\text{H}_2/\text{CO}_2$ ,  $\text{H}_2/\text{CO}$ , and  $\text{H}_2/\text{CH}_4$ , calculated using the Arrhenius equation, are  $10^{26}$ ,  $10^{29}$ , and  $10^{76}$ , respectively, at 300 K.

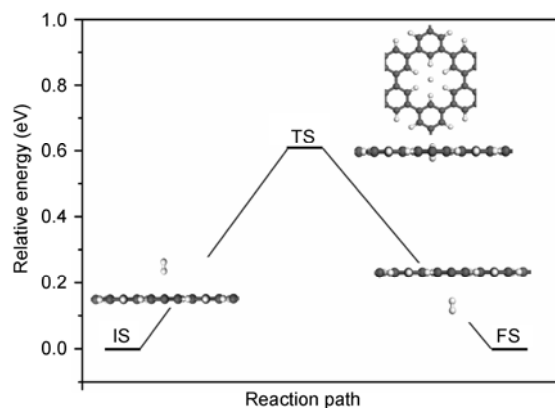
From a more practical standpoint, however, the theoretical models in the above studies are too simple to be accessible experimentally. Blankenburg et al. [17] proposed a more feasible model by designing a single layer of porous graphene supported on  $\text{Al}_2\text{O}_3$ , giving high selectivities of  $2 \times 10^{23}$  and  $7 \times 10^{16}$  for  $\text{H}_2/\text{N}_2$  and  $\text{H}_2/\text{CO}_2$ , respectively.

More recently, via atomistic Monte Carlo simulations, Schrier proposed that 2D polyphenylene and fluoropolyphenylene surfaces can be used to adsorb gases selectively since the nanoporosity and fluorination can tune the binding strength of gas adsorption; this can be applied to  $\text{CO}_2$  sequestration, biogas upgrading,  $\text{SO}_2$  pollution control, and air dehumidification [47]. More recently, porous graphene has been proposed for isotopic separations [48,49].

All the above computations show that porous graphene is an ideal material for gas separation and purification in the future; experimental explorations to achieve large-area 2D polyphenylene-type porous graphene are needed.

### 3.2 DNA sequencing

Solid-state [50,51] and biological nanopores [52] are emerging as powerful tools for next-generation DNA sequencing. Compared with the traditionally used Sanger method [53], which was the key to sequencing the human genome [54], nanopore technology may increase the speed,



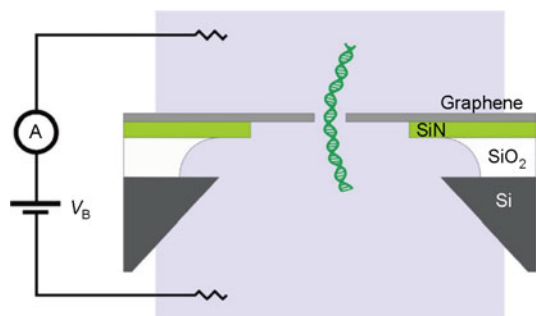
**Figure 5** Energy profiles for  $\text{H}_2$  passing through a pore in polyphenylene. The insets are the corresponding configurations of the initial state (IS), transition state (TS), and final state (FS). For the TS, both the top and side views are given [22]. Color code: C, black; H, white.

reduce the cost, and achieve higher resolution of DNA sequencing. Previous studies demonstrated that single-stranded RNA and DNA molecules could be driven through a nanosized channel under an electric field [52], and the four DNA bases, or nucleotides, hindered the ion current to different extents in the nanopore, causing different drops in the measured current [55]. These pioneering basic investigations lay a firm foundation for nanopore-related DNA sequencing. Now nanopore materials are being developed to detect the electrical signal flux during the translocation of DNA molecules, identify the four different types of nucleotide, and finally achieve single-base resolution of DNA sequencing.

Many porous membrane materials such as  $\text{SiO}_2$  [56],  $\text{Al}_2\text{O}_3$  [57], and  $\text{Si}_3\text{N}_4$  [58] have been fabricated to explore their possible use for DNA sequencing. However, the major barricade to achieving high resolution is the finite length of the channel through the pore, which makes it difficult to distinguish the different current signals of the four nucleotides. In order to leave no more than one nucleotide within the interaction range of the electrodes when the target DNA is passing through the pore, the optimum thickness of the membrane is expected to be the single-nucleotide size of  $\sim 1$  nm.

Porous graphene has therefore been proposed as an ideal material for DNA sequencing. Apart from its atomic thickness, graphene is an excellent electrical conductor and capable of enduring large trans-membrane pressures [44,45]. Theoretical investigations have proved the feasibility of its use [20], and experiments are also making progress. Almost simultaneously, two groups separately achieved the translocation of a single DNA molecule through porous graphene experimentally [27,59], as illustrated in Figure 6. Schneider et al. [27] demonstrated that characteristic temporary conductance changes were observed in the ionic current through the nanopore when an individual DNA molecule was translocated through the pore.

Besides the observed different current signals, Merchant et al. [59] also studied the influence of substrate on the translocation of DNA molecules, discovering that atomic-layer deposition of  $\text{TiO}_2$  on both sides of the graphene



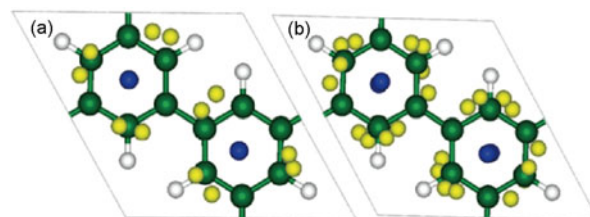
**Figure 6** Graphene nanopore device for DNA sequencing. A bias voltage,  $V_B$ , is applied between the reservoirs to drive DNA through the nanopore [59].

membrane consistently reduced the nanopore noise level and improved the mechanical robustness of the device compared with  $\text{SiN}$ -coated porous graphene. The lower noise level was attributed to the improved hydrophilicity of the  $\text{TiO}_2$  surface [60] and its superior bonding to graphitic materials [61]. More recently, theoretical investigations have implied that edge-hydrogenation of porous graphene would bring several advantages and provide better performances for DNA sequencing, including enhanced interaction between nucleotides and graphene electrodes, and reduced signal-to-noise ratios [62].

Note that the fraction of detectable DNA translocation through porous graphene is smaller than supposed, despite its atomic thickness [59]. As with traditional porous membranes, other issues, such as control of the DNA translocation rate, signal overlap between adjacent nucleobases, and the lack of well-defined interactions between nanopores and nucleobases [63], need in-depth consideration to make porous graphene practical for DNA sequencing.

### 3.3 Hydrogen storage

Hydrogen attracts great attention in the field of renewable energy and is expected to be a major power source in the future because of its abundance, cleanness, and high energy density. However, the biggest challenge in making industrial use of hydrogen practical is finding materials able to store hydrogen safely and efficiently. Graphene is expected to store hydrogen at a high volumetric density since hydrogen molecules can be adsorbed on both sides of the graphene. However, it is obvious that there are only weak van der Waals interactions between graphene and hydrogen molecules; this has been confirmed by Arellano et al. [64], who computed the binding energy to be smaller than 0.1 eV, and similar phenomena were also observed for carbon and BN nanotubes [65]. The introduction of heteroatoms, especially metal atoms, is proposed as a possible way of enhancing the interactions between  $\text{H}_2$  and substrates [66–70]. Porous graphene may be helpful in avoiding the metal clustering problem [71]. Du et al. [16] explored hydrogen storage in Li-decorated porous graphene using first-principles computations, and predicted that metal-decorated porous graphene is a promising hydrogen storage material (Figure 7).



**Figure 7** Top views of the optimized geometries for (a) 6 and (b) 12 hydrogen molecules adsorbed on two- and four-Li-decorated porous graphenes. Green, white, blue, and yellow balls represent C, H, Li, and physisorbed hydrogen molecules, respectively [16].

Reunchan et al. [72] extended the choice of metal atoms to alkaline-earth metals and transition metals (TMs). By computing the interactions of  $H_2$  with porous graphene decorated with various metals, they demonstrated two types of interaction with  $H_2$ . Alkali metal and alkaline-earth metal atoms become ionized as a result of charge transfer to the porous graphene, resulting in static multipole Coulombic interactions. In the case of TM atoms, the interaction with  $H_2$  is the relatively strong Kubas type: the hybridization of TM d and  $H_2$   $\sigma$  and  $\sigma^*$  states. It is believed that Ca-decorated porous graphene is the most favorable candidate for hydrogen storage since it could bind  $H_2$  with an adsorption energy of  $\sim 0.23$  eV, and the maximum capacity was estimated to be  $\sim 9$  wt%.

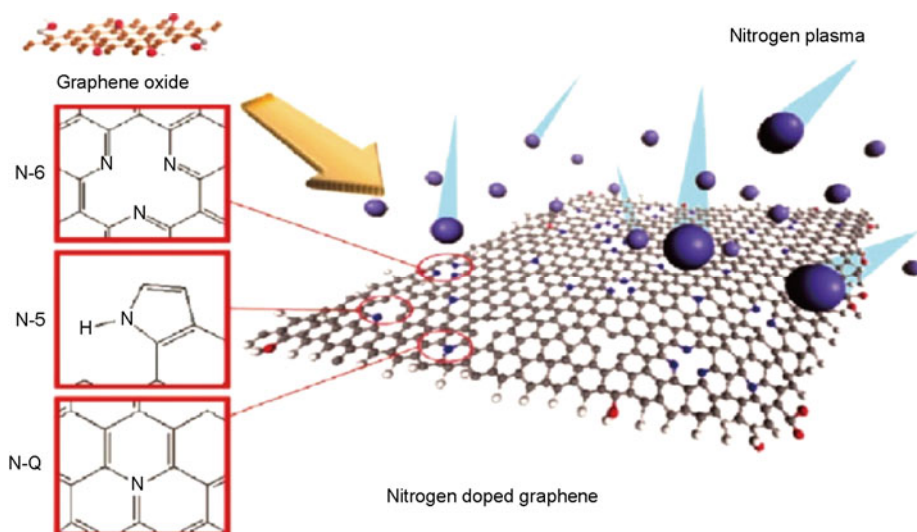
However, in metal-decorated graphenes, metal atoms are vulnerable to other active components of air, such as oxygen, and the presence of oxygen would interfere with hydrogen storage if oxygen is chemically adsorbed on the metal atoms in advance [73]. Despite interesting ideas and proposals, hydrogen storage is still a major challenge.

### 3.4 Supercapacitors

Supercapacitors are electrochemical power devices used for energy storage. Compared with the commonly known Li-ion batteries, supercapacitor can be fully charged in seconds and achieve a much higher power delivery ( $10 \text{ kW kg}^{-1}$ ). Moreover, supercapacitors are able to sustain millions of more cycles than batteries can, and maintain a longer application lifetime. Typically, there are two types of supercapacitor, according to their charge storage mechanisms. The most commonly used devices at present, mainly based on carbon materials such as porous carbon materials [74,75] and carbon nanotubes [76,77], are known as electrochemical double-layer capacitors, and they store charge electrostatically by reversible accumulation of ions at the elec-

trode/electrolyte interface. Another type, pseudo-capacitors, adopts TM oxides or conducting polymers as electrode materials, using fast and reversible surface or near-surface reactions for charge storage. Although the specific pseudo-capacitance generally exceeds that of carbon materials with a double-layer charge storage mechanism, pseudo-capacitors suffer from lack of stability during cycling.

Graphene has been proposed as a competitive material for supercapacitors because of its excellent chemical stability [78], high electrical conductivity [3], and large specific surface area [79]. So far, several groups [80–83] have reported progress on graphene-based supercapacitors. More recently, Jeong et al. [84] have demonstrated a high-performance supercapacitor using nitrogen-doped graphene as the electrode material, produced by a nitrogen plasma process. N-doped graphene presented a specific capacitance of more than  $250 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$ ; more than 95% of the initial capacitance was retained after over 10000 cycles and 70% remained even over a time period of  $\sim 3$  months. The reason for its excellent performance lies in its novel structure; several local N-configurations were observed using scanning photoemission microscopy, and these configurations may result in some pseudo-capacitance. The N-configurations in Figure 8 have been recognized computationally by Li et al. [85]. The presence of nitrogen atoms in graphene at edges and in basal planes also influences the local electronic structures, enhancing binding with ions in solution [86]. As a result, more ions can be accommodated on the electrode surface for a given electrode surface area. It has also been pointed out that the N-6 configuration in the basal planes played a major role in improving the capacitance because of the large difference between its binding energy and that of its pristine graphene counterpart. Note that the N-6 configuration can be regarded as pores in porous graphene saturated with nitrogen atoms; this encourages investigations of porous graphene as supercapacitors.



**Figure 8** Illustration of the plasma doping process. In the plasma process, as a result of physical momentum, nitrogen atoms replace the existing carbon atoms. Inset: possible nitrogen configurations resulting from the doping treatment [84].

## 4 Conclusion and future prospects

We have summarized recent studies of the properties, preparation, and potential applications of porous graphene. Porous graphene can be obtained by electron and helium ion beam irradiation as well as by surface-assisted aryl-aryl coupling of phenylene. Because of its unique structural and electronic properties, porous graphene attracts great attention in fields such as gas purification, DNA sequencing, hydrogen storage, and supercapacitors.

However, experimental investigations of this novel material are much needed, together with computational studies, for progress to be made. Future studies should focus on the following issues. First, it is essential to explore economical methods for the synthesis of porous graphene since the costs of the methods mentioned above are prohibitive for its commercial production. Second, the synthesis of large-area porous graphene is still a great challenge, and this is a prerequisite for the experimental investigation of its chemical and physical properties, such as mechanical and thermal stability, as well as its use in gas separation. Third, more potential applications of porous graphene need to be explored. For example, since the band gap of 2D polyphenylene-type porous graphene lies in the range of ultraviolet light, it may be possible to combine porous graphene with photocatalysts and solar cell materials such as TiO<sub>2</sub>. Finally, the potential of porous graphene as catalyst substrates and Li-ion battery materials, which in the case of graphene has attracted great interest, remains unexplored [87–90]. We are fully convinced that as increasing numbers of investigations are carried out, porous graphene will bring more surprises in the future.

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- Affoune A. Experimental evidence of a single nano-graphene. *Chem Phys Lett*, 2001, 348: 17–20
- Lu X, Yu M, Huang H, et al. Tailoring graphite with the goal of achieving single sheets. *Nanotechnology*, 1999, 10: 269–272
- Novoselov K S, Geim A K, Morozov S V, et al. Electric field effect in atomically thin carbon films. *Science*, 2004, 306: 666–669
- Berger C, Song Z, Li T, et al. Ultrathin epitaxial graphite: 2D electron gas properties and a route toward graphene-based nanoelectronics. *J Phys Chem B*, 2004, 108: 19912–19916
- Ishigami M, Chen J H, Cullen W G, et al. Atomic structure of graphene on SiO<sub>2</sub>. *Nano Lett*, 2007, 7: 1643–1648
- Pletikosić I, Kralj M, Pervan P, et al. Dirac cones and minigaps for graphene on Ir(111). *Phys Rev Lett*, 2009, 102: 056808
- Lahiri J, Miller T, Adamska L, et al. Graphene growth on Ni(111) by transformation of a surface carbide. *Nano Lett*, 2011, 11: 518–522
- Reina A, Jia X, Ho J, et al. Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano Lett*, 2009, 9: 30–35
- Eda G, Fanchini G, Chhowalla M. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nat Nanotechnol*, 2008, 3: 270–274
- Lee C, Wei X, Kysar J W, et al. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, 2008, 321: 385–388
- Zhang Y, Tan Y W, Stormer H L, et al. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature*, 2005, 438: 201–204
- Novoselov K S, Geim A K, Morozov S V, et al. Two-dimensional gas of massless Dirac fermions in graphene. *Nature*, 2005, 438: 197–200
- Morozov S, Novoselov K, Katsnelson M, et al. Giant intrinsic carrier mobilities in graphene and its bilayer. *Phys Rev Lett*, 2008, 100: 016602
- Ryu S, Han M Y, Maultzsch J, et al. Reversible basal plane hydrogenation of graphene. *Nano Lett*, 2008, 8: 4597–4602
- Xu B, Lu Y H, Feng Y P, et al. Density functional theory study of BN-doped graphene superlattice: Role of geometrical shape and size. *J Appl Phys*, 2010, 108: 073711
- Du A, Zhu Z, Smith S C. Multifunctional porous graphene for nanoelectronics and hydrogen storage: New properties revealed by first principle calculations. *J Am Chem Soc*, 2010, 132: 2876–2877
- Blankenburg S, Bieri M, Fasel R, et al. Porous graphene as an atmospheric nanofilter. *Small*, 2010, 6: 2266–2271
- Jiang D, Cooper V R, Dai S. Porous graphene as the ultimate membrane for gas separation. *Nano Lett*, 2009, 9: 4019–4024
- Premkumar T, Geckeler K E. Graphene-DNA hybrid materials: Assembly, applications, and prospects. *Prog Polym Sci*, 2012, doi: 10.1016/j.progpolymsci.2011.08.003
- Postma H W C. Rapid sequencing of individual DNA molecules in graphene nanogaps. *Nano Lett*, 2010, 10: 420–425
- Bieri M, Treier M, Cai J, et al. Porous graphenes: Two-dimensional polymer synthesis with atomic precision. *Chem Commun*, 2009, 45: 6919–6921
- Li Y, Zhou Z, Shen P, et al. Two-dimensional polyphenylene: Experimentally available porous graphene as a hydrogen purification membrane. *Chem Commun*, 2010, 46: 3672–3674
- Treier M, Pignedoli C A, Laino T, et al. Surface-assisted cyclodehydrogenation provides a synthetic route towards easily processable and chemically tailored nanographenes. *Nat Chem*, 2011, 3: 61–67
- Schmitz C H, Ikonov J, Sokolowski M. Two-dimensional polyamide networks with a broad pore size distribution on the Ag(111) surface. *J Phys Chem C*, 2011, 115: 7270–7278
- Ourdjini O, Pawlak R, Abel M, et al. Substrate-mediated ordering and defect analysis of a surface covalent organic framework. *Phys Rev B*, 2011, 84: 125421
- Fischbein M D, Drndić M. Electron beam nanosculpting of suspended graphene sheets. *Appl Phys Lett*, 2008, 93: 113107
- Schneider G F, Kowalczyk S W, Calado V E, et al. DNA translocation through graphene nanopores. *Nano Lett*, 2010, 10: 3163–3167
- Hatanaka M. Band structures of porous graphenes. *Chem Phys Lett*, 2010, 488: 187–192
- Li Y, Zhou Z, Shen P W, et al. Structural and electronic properties of graphene nanoribbons. *J Phys Chem C*, 2009, 113: 15043–15046
- Zhou J, Wang Q, Sun Q, et al. Ferromagnetism in semihydrogenated graphene sheet. *Nano Lett*, 2009, 9: 3867–3870
- Nourbakhsh A, Cantoro M, Vosch T, et al. Bandgap opening in oxygen plasma-treated graphene. *Nanotechnology*, 2010, 21: 435203
- Zhou S Y, Gweon G H, Fedorov A V, et al. Substrate-induced bandgap opening in epitaxial graphene. *Nat Mater*, 2007, 6: 770–775
- Chang H, Cheng J, Liu X, et al. Facile synthesis of wide-bandgap fluorinated graphene semiconductors. *Chem-Eur J*, 2011, 17: 8896–8903
- Bieri M, Nguyen M T, Gröning O, et al. Two-dimensional polymer formation on surfaces: Insight into the roles of precursor mobility and reactivity. *J Am Chem Soc*, 2010, 132: 16669–16676
- Bell D C, Lemme M C, Stern L A, et al. Precision cutting and patterning of graphene with helium ions. *Nanotechnology*, 2009, 20: 455301
- Weng L, Zhang L, Chen Y P, et al. Atomic force microscope local oxidation nanolithography of graphene. *Appl Phys Lett*, 2008, 93: 093107
- Datta S S, Strachan D R, Khamis S M, et al. Crystallographic etching of few-layer graphene. *Nano Lett*, 2008, 8: 1912–1915

- 38 Ci L, Xu Z, Wang L, et al. Controlled nanocutting of graphene. *Nano Res*, 2008, 1: 116–122
- 39 Freemantle M. Membranes for gas separation. *Chem Eng News*, 2005, 83: 49–57
- 40 Dong J, Lin Y S, Kanezashi M, et al. Microporous inorganic membranes for high temperature hydrogen purification. *J Appl Phys*, 2008, 104: 121301
- 41 Adhikari S, Fernando S. Hydrogen membrane separation techniques. *Ind Eng Chem Res*, 2006, 45: 875–881
- 42 Phair J W, Donelson R. Developments and design of novel (non-palladium-based) metal membranes for hydrogen separation. *Ind Eng Chem Res*, 2006, 45: 5657–5674
- 43 Oyama S, Lee D, Hacarlioglu P, et al. Theory of hydrogen permeability in nonporous silica membranes. *J Membrane Sci*, 2004, 244: 45–53
- 44 Leenaerts O, Partoens B, Peeters F M. Graphene: A perfect nanoballoon. *Appl Phys Lett*, 2008, 93: 193107
- 45 Bunch J S, Verbridge S S, Alden J S, et al. Impermeable atomic membranes from graphene sheets. *Nano Lett*, 2008, 8: 2458–2462
- 46 de Vos R M, Verweij H. High-selectivity, high-flux silica membranes for gas separation. *Science*, 1998, 279: 1710–1711
- 47 Schrier J. Fluorinated and nanoporous graphene materials as sorbents for gas separations. *ACS Appl Mater Interfaces*, 2011, 3: 4451–4458
- 48 Schrier J, McClain J. Thermally-driven isotope separation across nanoporous graphene. *Chem Phys Lett*, 2012, 521: 118–124
- 49 Hauser A W, Schwerdtfeger P. Nanoporous graphene membranes for efficient  $^3\text{He}/^4\text{He}$  separation. *J Phys Chem Lett*, 2012, 3: 209–213
- 50 Dekker C. Solid-state nanopores. *Nat Nanotechnol*, 2007, 2: 209–215
- 51 Healy K, Schiedt B, Morrison A P. Solid-state nanopore technologies for nanopore-based DNA analysis. *Nanomedicine*, 2007, 2: 875–897
- 52 Kasianowicz J J. Characterization of individual polynucleotide molecules using a membrane channel. *Proc Natl Acad Sci USA*, 1996, 93: 13770–13773
- 53 Sanger F. DNA sequencing with chain-terminating inhibitors. *Proc Natl Acad Sci USA*, 1977, 74: 5463–5467
- 54 Venter J C, Adams M D, Myers E W, et al. The sequence of the human genome. *Science*, 2001, 291: 1304–1351
- 55 Clarke J, Wu H C, Jayasinghe L, et al. Continuous base identification for single-molecule nanopore DNA sequencing. *Nat Nanotechnol*, 2009, 4: 265–270
- 56 Storm A J, Chen J H, Ling X S, et al. Fabrication of solid-state nanopores with single-nanometre precision. *Nat Mater*, 2003, 2: 537–540
- 57 Venkatesan B M, Shah A B, Zuo J M, et al. DNA sensing using nanocrystalline surface-enhanced  $\text{Al}_2\text{O}_3$  nanopore sensors. *Adv Funct Mater*, 2010, 20: 1266–1275
- 58 Li J, Stein D, McMullan C, et al. Ion-beam sculpting at nanometre length scales. *Nature*, 2001, 412: 166–169
- 59 Merchant C A, Healy K, Wanunu M, et al. DNA translocation through graphene nanopores. *Nano Lett*, 2010, 10: 2915–2921
- 60 Smeets R, Keyser U, Wu M, et al. Nanobubbles in solid-state nanopores. *Phys Rev Lett*, 2006, 97: 088101
- 61 Zhang Y, Dai H. Formation of metal nanowires on suspended single-walled carbon nanotubes. *Appl Phys Lett*, 2000, 77: 3015–3017
- 62 He Y, Scheicher R H, Grigoriev A, et al. Enhanced DNA sequencing performance through edge-hydrogenation of graphene electrodes. *Adv Funct Mater*, 2011, 21: 2674–2679
- 63 Branton D, Deamer D W, Marziali A, et al. The potential and challenges of nanopore sequencing. *Nat Biotechnol*, 2008, 26: 1146–1153
- 64 Arellano J S J, Molina L M, Rubio A, et al. Density functional study of adsorption of molecular hydrogen on graphene layers. *J Chem Phys*, 2000, 112: 8114–8119
- 65 Zhou Z, Zhao J, Chen Z, et al. Comparative study of hydrogen adsorption on carbon and BN nanotubes. *J Phys Chem B*, 2006, 110: 13363–13369
- 66 Yildirim T, Ciraci S. Titanium-decorated carbon nanotubes as a potential high-capacity hydrogen storage medium. *Phys Rev Lett*, 2005, 94: 175501
- 67 Zhao Y F, Kim Y H, Dillon A C, et al. Hydrogen storage in novel organometallic buckyballs. *Phys Rev Lett*, 2005, 94: 155504
- 68 Zhang C, Zhang R, Wang Z X, et al. Ti-substituted boranes as hydrogen storage materials: A computational quest for the ideal combination of stable electronic structure and optimal hydrogen uptake. *Chem-Eur J*, 2009, 15: 5910–5919
- 69 Zhou Z, Gao X, Yan J, et al. Doping effects of B and N on hydrogen adsorption in single-walled carbon nanotubes through density functional calculations. *Carbon*, 2006, 44: 939–947
- 70 Li M, Li Y, Zhou Z, et al. Ca-coated boron fullerenes and nanotubes as superior hydrogen storage materials. *Nano Lett*, 2009, 9: 1944–1948
- 71 Sun Q, Wang Q, Jena P, et al. Clustering of Ti on a  $\text{C}_{60}$  surface and its effect on hydrogen storage. *J Am Chem Soc*, 2005, 127: 14582–14583
- 72 Reunchan P, Jhi S H. Metal-dispersed porous graphene for hydrogen storage. *Appl Phys Lett*, 2011, 98: 093103
- 73 Sigal A, Rojas M, Leiva E. Is hydrogen storage possible in metal-oped graphite 2D systems in conditions found on earth? *Phys Rev Lett*, 2011, 107: 1–4
- 74 Vixguterl C, Frackowiak E, Jurewicz K, et al. Electrochemical energy storage in ordered porous carbon materials. *Carbon*, 2005, 43: 1293–1302
- 75 Fuertes A B, Pico F, Rojo J M. Influence of pore structure on electric double-layer capacitance of template mesoporous carbons. *J Power Sources*, 2004, 133: 329–336
- 76 Yoon B. Electrical properties of electrical double layer capacitors with integrated carbon nanotube electrodes. *Chem Phys Lett*, 2004, 388: 170–174
- 77 Pushparaj V L, Shaijumon M M, Kumar A, et al. Flexible energy storage devices based on nanocomposite paper. *Proc Natl Acad Sci USA*, 2007, 104: 13574–13577
- 78 Geim A K, Novoselov K S. The rise of graphene. *Nat Mater*, 2007, 6: 183–191
- 79 Stankovich S, Dikin D A, Piner R D, et al. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*, 2007, 45: 1558–1565
- 80 Wang Y, Shi Z, Huang Y, et al. Supercapacitor devices based on graphene materials. *J Phys Chem C*, 2009, 113: 13103–13107
- 81 Liu C, Yu Z, Neff D, et al. Graphene-based supercapacitor with an ultrahigh energy density. *Nano Lett*, 2010, 10: 4863–4868
- 82 Zhang L L, Zhou R, Zhao X S. Graphene-based materials as supercapacitor electrodes. *J Mater Chem*, 2010, 20: 5983–5992
- 83 Yu A, Roes I, Davies A, et al. Ultrathin, transparent, and flexible graphene films for supercapacitor application. *Appl Phys Lett*, 2010, 96: 253105
- 84 Jeong H M, Lee J W, Shin W H, et al. Nitrogen-doped graphene for high-performance ultracapacitors and the importance of nitrogen-oped sites at basal planes. *Nano Lett*, 2011, 11: 2472–2477
- 85 Li Y, Zhou Z, Shen P, et al. Spin gapless semiconductor-metal-half-metal properties in nitrogen-doped zigzag graphene nanoribbons. *ACS Nano*, 2009, 3: 1952–1958
- 86 Imran Jafri R, Rajalakshmi N, Ramaprabhu S. Nitrogen doped graphene nanoplatelets as catalyst support for oxygen reduction reaction in proton exchange membrane fuel cell. *J Mater Chem*, 2010, 20: 7114–7117
- 87 Yoo E, Kim J, Hosono E, et al. Large reversible Li storage of graphene nanosheet families for use in rechargeable lithium ion batteries. *Nano Lett*, 2008, 8: 2277–2282
- 88 Su L W, Jing Y, Zhou Z. Li ion battery Materials with core-shell nanostructures. *Nanoscale*, 2011, 3: 3967–3983
- 89 Lu Y H, Zhou M, Zhang C, et al. Metal-embedded graphene: A possible catalyst with high activity. *J Phys Chem C*, 2009, 113: 20156–20160
- 90 Li Y, Zhou Z, Yu G, et al. CO catalytic oxidation on iron-embedded graphene: Computational quest for low-cost nanocatalysts. *J Phys Chem C*, 2010, 114: 6250–6254