TOPICAL REVIEW

Chemical modification of graphene for atomic-scale catalyst supports

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Abstract

One promising way to reduce the use of noble metal catalysts is to use extremely fine particle catalysts, such as subnanoclusters and single-atom catalysts. For practical use, suppression of diffusion and agglomeration of catalysts are needed. Heteroatom-doped graphene, which has high specific surface area, high chemical and mechanical stabilities, high electrical and thermal conductivities, and contains anchoring sites for catalysts, is promising catalyst support. Heteroatom-doped graphene can widely control the support effects. This review summarizes recent dopant structure characterization using spectroscopy and density functional theory calculations. The distribution of highly-dispersed metal catalysts and their diffusion properties are discussed. In addition, The effects of environmental conditions on catalyst dynamic behaviors are introduced. Finally, the outlook of heteroatom-doped graphene and new two-dimensional material supports is discussed.

1. Introduction

Noble metal catalysts have been widely used in clean energy fields, such as fuel cell electrodes [1–4], exhaust gas purification [5], hydrogen production [6–10], and so on. Most of these noble metals which have high catalytic activities are precious metals. The demand for precious metal catalysts is increasing due to the urgent need to realize a green and sustainable society. In addition, precious metals are commonly used in the battery field [11–13]. However, precious metals are scarce, expensive, and unevenly distributed on the Earth. Therefore, reducing the usage of noble metal catalysts is one of the most critical objectives for realizing a clean energy society.

One promising way to reduce the use of noble metal catalysts is to use extremely fine particle catalysts, such as subnanoclusters and single-atom catalysts (SACs). These catalysts are composed of tens of metal atoms or fewer. Therefore, specific surface area, i.e., the number of active sites per weight, is drastically increasing from bulk materials. In addition, extremely fine particles show different atomic and electronic structures with bulk metals thanks to their quantum size effects [14–16]. For instance, the discrete energy level, high surface energy, magnetization, and bond length change are crucial in catalytic fields. It was experimentally elucidated that the sizes of metal clusters strongly affect catalytic activities [16–19]. Therefore, controlling and keeping catalyst sizes, which require suppression of catalyst migration and agglomeration, are essential for long-life catalysts.

Most inhomogeneous SACs are embedded in the host materials. It has been widely studied the single atom catalyst embedded in molecules [20–23], graphene-related materials [24–37], ceramic materials [38–44], and metals [45–54]. The embedded SACs can suppress the diffusion and agglomeration of catalysts. The stable embedded SACs show high cycle and reuse properties [39, 47]. On the other hand, the embedded SACs are limited in the variation of coordinated elements, size, and structures. In the case of supported catalysts, not only the size of catalysts but ligand effects and ensemble effects through alloying can be utilized in more varied ways. However, the supported subnanoclusters and SACs generally show lower adsorption energy and diffusion barriers than embedded ones. In addition, fine catalyst particles have high surface energy, which results in the agglomeration and coarsening of catalysts [55]. The high surface energy also results in the Ostwald ripening of...
fine particles [56]. Therefore, suppression of detachment and diffusion of catalysts on support materials are necessary for designing new long-life supported catalysts.

The other important factor in determining catalytic activities is the support and ligand effect, which modifies the electronic and magnetic states of catalysts [47, 49, 57]. Decreasing the catalyst particle size, the support effects become more significant. In the case of large nanoparticle catalysts, support effects are localized as interfacial effects, which emerge only in the vicinity of interface regions between nanoparticle catalysts and support materials. Therefore, the reactant adsorption and chemical reaction mainly occur at interface sites [58, 59]. On the other hand, most of the component atoms in the subnanocluster catalysts and SACs are directly coordinated with the support materials, which results in the drastic modification of catalytic activities of the subnanocluster catalysts and SACs through the interaction with support materials.

Carbon materials have been widely used as catalyst supports. Graphene and carbon nanotube support have been widely studied to achieve a high specific surface area [60–66]. As catalytic electrodes, these carbon allotropes have strong sp²-frameworks and show promising properties, i.e., high chemical and mechanical durability, and high electronic and thermal conductivities. However, the surfaces of these materials are covered with delocalized π-electrons, which show weak adsorption and fast diffusion of adsorbates [67]. It was experimentally reported that the fine catalyst particles are mainly distributed on the edges of graphene [68]. These results indicate that catalyst diffusion easily occurs at the graphene basal plane. Therefore, improved catalyst stability and diffusion suppression at the graphene basal plane are essential to effectively utilize the high specific surface area of graphene and carbon nanotube supports, which are of utmost importance for their further spread.

This topical review discussed the support fabrication through heteroatom doping at graphene basal plane as catalyst anchor sites. Recent reports of the various dopants in graphene and their structures were briefly introduced. Catalyst adsorption and diffusion properties on heteroatom-doped graphene were also touched. Finally, the outlook of metal subnanoclusters and single metal atoms on heteroatom-doped graphene was pointed out.

2. Heteroatom dopants in graphene

The doping of light elements into graphene has been widely studied for a long time [69]. The dopants are mainly introduced into graphene through chemical vapor deposition (CVD), implantation using an ion beam [70], and annealing reduced graphene oxide in an atmosphere containing target elements. Most of the reported light-element doped graphene are B- [71–74], N- [75–99], and co-doped graphene [100–102], since boron (0.85 Å) and nitrogen atoms (0.75 Å) have similar single-bond covalent radii as carbon atoms (0.71 Å) [103]. We note that boron and nitrogen atoms have lower and higher electronegativity than carbon atoms. Therefore, boron and nitrogen atoms substituted in graphene lattice have a positive and negative charge, respectively. From these points, nitrogen atoms do not induce the lattice distortion in graphene, and are easy for substitutional doping. It was also revealed that larger and heavier element doping is more challenging than nitrogen using a first-principles calculation based on density functional theory (DFT) [74]. Figure 1 shows the calculated substitutional energy of the light-element doped graphene. The substitutional energy of dopant X $E_{\text{sub}}^X$ was defined as follows;

![Figure 1. Calculated substitutional energy of light-element doped graphene. Reprinted with permission from [67]. Copyright (2017) American Chemical Society.](image-url)
Where $E_{\text{gra}}^X$ is the total energy of X-doped graphene, and $\mu_X$ and $\mu_C$ are the chemical potential of dopants X and C. Smaller substitutional energy means easier substitution. As shown in figure 1, nitrogen and boron atoms, which have similar atomic radii to carbon atoms, are relatively easier for substitutional doping than elements in the next period. In contrast, the substitutional energy of oxygen atoms is close to those of larger elements. This trend is because three-coordinated oxygen atoms, where six valence electrons occupy the 2s and 2p orbitals, only bond to two coordinating carbon atoms, forming an unstable dangling bond on the other carbon atom. The large aluminum, silicon, phosphorus, and sulfur atoms form the protruding steric structure through doping to release internal stress.

From the viewpoint of dopant distributions, it is well-known that most experimentally observed nitrogen atoms in graphene are in the vicinity of vacancy and edge sites of graphene. There are four types of nitrogen dopants in graphene. Graphitic-, pyridinic-, pyrrolic-, and amino-type species are nitrogen in pristine graphene lattice, nitrogen in the hexagonal lattice at the edge sites of graphene or next to the atomic vacancy, nitrogen in the pentagonal lattice at the edge sites of graphene or adjacent to the atomic vacancy, and nitrogen adsorbed on graphene, respectively. A schematic image of three substitutional dopants is shown in figure 2.

Zhang and co-workers precisely studied the nitrogen doping sites using x-ray absorption near edge structure (XANES) and x-ray photoelectron spectroscopy (XPS). As shown in figure 3(a)–(e), XANES and XPS spectra clearly show that the ratio of nitrogen species depends on the annealing temperature. The N-doped graphene is formed by heat treatment of graphene oxide in NH$_3$ flow. In the case of annealing at 300 °C, amino-type nitrogen dopants (8.13%) form much more than pyridinic- (2.06%) and graphitic-type (0.74%). This trend is because amino-type structures require breaking only a single C-O bond, while pyridinic- and graphitic-type structures require to break two and three C-C bonds, respectively. Therefore, amino-type structures can be observed more in low temperature annealing. With increasing the annealing temperature, the amount of pyridinic- and graphitic-type nitrogen dopants also increase. However, amino-type nitrogen dopants decrease above 500 °C. This is because amino-type nitrogen dopants forms only a single C-N bond and easily desorbe from graphene sheet. On the other hand, pyridinic- and graphic-type nitrogen dopants are stable at high temperatures because they have two and three C-N bonds, respectively. These results indicate that pyridine- and graphic-type nitrogen dopants are relatively stable once formed but difficult to form because of the accompanying C-C bond breaking. Therefore, it can be concluded that the nitrogen dopants substituted in graphene lattice are difficult to be formed. The pyridinic-type nitrogen dopants were observed more than graphic-type nitrogen dopants. The pyridinic-type nitrogen dopants are formed through the following three reaction passes; (1) substitution of carbon atoms in a pristine graphene lattice with the concomitant introduction of carbon vacancies in adjacent sites, (2) substitution of carbon atoms adjacent to vacancies, (3) substitution of carbon atoms at edge sites of graphene. Stumbla and co-workers also studied the nitrogen dopant species using XANES and transmission electron microscopy (TEM) with electron-energy loss spectroscopy (EELS) [68]. EELS spectra in figure 3(f) also indicate that amino- and pyridinic-type nitrogen dopants are dominant.
From the viewpoint of the dopant positions from the edge, the edge sites are preferable for doping. Nitrogen dopants can be observed only at the edge sites in the classical molecular dynamics (MD) simulation of the annealing of graphene nanoflake in NH$_3$ and CH$_3$CN [105]. The dopant position dependence and flake size dependence on the formation energy of nitrogen substitutional dopants in graphene nanoflakes were also studied using DFT [106]. The edge preference of nitrogen doping is clearly shown in figure 4. We note that the graphene nanoflake considered in the previous study has hexagonal structures with hydrogen-terminated zigzag edges. The most stable structures are graphitic-type, which means hydrogen-terminated pyridinic-type at the edge sites. The formation energy of graphitic-type nitrogen dopants at the edge sites is about 1 eV lower than inside of graphene nanoflake. This trend is because the carbon atoms in graphene edges are more unstable than those in basal planes, since carbon atoms at the edge sites have only two C-C bonds. In addition, atomic relaxation may easily occur near graphene edges. In the case of the formation of the nitrogen dopants in the graphene basal plane, the formation energy of pyridinic-type nitrogen dopants (0.066 eV) is even larger than that

Figure 3. (a) N K-edge XANES spectra of NG-300, NG-500, NG-700, and NG-800. (b), (c), (d), and (e) high-resolution N 1s XPS of NG-300, NG-500, NG-700, and NG-900. (f) Normalized EEL spectra of N K edge acquired from N-doped graphene sheets with 50 ALD Pt cycles and two separate areas. The N K edge is divided by the π*(P1-P4) and σ*(P5) regions, where P1 and P4 are attributed to the individual N-dopants of pyridinic- and graphitic-type, respectively. (a)–(e) are reproduced from [77] with permission from the Royal Society of Chemistry. (f) is reprinted with permission from [68]. Copyright (2014) American Chemical Society.
of graphitic-type nitrogen dopants (0.375 eV), while flake size dependence is unobvious [107]. This is because the formation of pyridinic-type nitrogen dopants requires a single carbon atom vacancy adjacent to nitrogen dopants, as we mentioned, resulting in the carbon atom vacancy forming unstable dangling bonds in coordinating atoms. Therefore, it seems that most of the experimentally observed nitrogen dopants are located at edge sites as pyridinic-type structures. These trends agree with the experimental results where edge nitrogen dopants dominate for a long growth time of N-doped graphene [96]. This edge preference may be more significant for larger dopants, since, at the edge sites, the distortion and accompanying lattice relaxation lattice distortion by doping can more easily occur than in basal planes.

Hydrogen termination also affects the stability and electronic properties of doped graphene. As we mentioned, the unstable dangling bonds remain in the vicinity of pyridinic-type structures. These dangling bonds may be terminated with hydrogen atoms same as graphene edge atoms. Actually, at the pyridinic-type structures in the graphene basal plane, increasing nitrogen dopants, the formation energy of pyridinic-type nitrogen dopants become smaller, in contrast, larger in the graphitic-type structures [107]. This is because nitrogen atoms have one more electron than carbon atoms, which change the unstable dangling bonds, i.e., half-filled electron orbitals, to stable lone pair orbitals. We also note that the combination study of XPS and first-principles calculations elucidated the effect of structures, dopant sites, and hydrogen termination on core level shift, as shown in figure 5 [108]. In addition, hydrogen termination induces the core level shift of neighbor atoms. Therefore, the more precise measurement and analysis of these spectra may clarify the dopant circumstance in more detail.

To increase the support effect options and application of catalytic reactions, more elements need to be doped into graphene. Recently, the larger heteroatom dopants in graphene were also reported. The atomic structures of Al- [109], Si- [114, 110–113, 115], P- [116, 117], S- [118–121], and Ge-doped graphene [122] were experimentally characterized. High-angle annular dark field (HAADF) and middle-angle annular dark field (MAADF) scanning TEM (STEM) experiments, which are sensitive to atomic numbers, are powerful tools to characterize such heavy-element doped graphene. Atomically resolved HAADF- and MAADF-STEM experiments elucidated that silicon, phosphorus, sulfur, and germanium dopants in graphene can form graphitic-type structures [110, 116, 122], as shown in figure 6, while these dopants have much larger atomic radii than carbon atoms. We note that, especially in the cases of larger dopants, four-fold dopants at divacancy sites, as shown in figure 6, are energetically favorable because of less internal stress. It is well-known that such four-fold structures can accept even transition metals [123, 124]. From the viewpoints of anchoring sites, protruded graphitic-type larger dopants, which form the sp³ hybrid orbitals accompanying dangling bonds, are very promising. Larger dopants are often implanted in graphene lattices using ion beams. Direct implanting using ion bombardments not only shows the low efficiency of doping but introduces severe damage to graphene through the knock-on and cascade process, which results in the formation of holey graphene, amorphized graphene, and graphene nanoflakes [125–128]. These drastic structural modifications affect graphene stability and electronic properties. Therefore, to take advantage of the superior properties of graphene, for instance, high specific surface, high chemical and mechanical stability, and high electron conductivity, it is necessary to increase the amount of doping in the basal plane with gentler methods.
One of the promising candidates is vacancy-mediated doping, which is a two-step process with pretreatment to introduce atomic vacancies in the graphene basal plane. The formation energy of light-element dopants in graphene with a single atom vacancy becomes negative, which indicates that the doping process is exothermic\(^6\). Atomic vacancies can enhance heteroatom doping. Energy-controlled ion and particle bombardments are widely used for creating vacancies in carbon materials\(^{129-131}\). These bombardments introduce various structural defects, i.e., monovacancy, divacancy, trivacancy, and so on. MD simulation of Au atom collisions with graphene shows the possibility of controlling defects in graphene by adjusting bombardment conditions\(^{129}\). It is well-known that electron beam irradiation can also introduce vacancies in graphene lattices\(^{132-140}\). An electron microscope can form atomic vacancies in graphene and observe the structure at the same time. Electron beam irradiation position and current density can be easily adjusted. MD simulation of electron irradiation has also been performed to reveal the relationship between defect formation in graphene and electron irradiation conditions, which shows the possibility of controlling defects in graphene\(^{138}\). Therefore, the fabrication of graphene suitable for heteroatom doping may be possible with proper electron irradiation.

3. Single metal atoms and clusters on doped graphene

Catalyst metal atoms and clusters are conventionally deposited with the atomic layer deposition (ALD) technique, as shown in figure 7\(^6\). Recently, the atomically dispersed deposition using plasma sputtering, suppressing agglomeration, is also realized\(^{141}\). Metal atoms on graphene are revealed to be trapped in the edge of overlying graphene nanoflake or bonded with contaminations using HAADF-STEM, XPS, and DFT calculations\(^{142,143}\). DFT calculations elucidated that Pt atoms preferably adsorb at the zigzag edges\(^{144}\). In addition, as we mentioned, anchoring sites for metal atoms, i.e., dopant atoms, are mainly located at the
graphene edge. In figure 8, HAADF-STEM images of Pt decorated N-doped graphene [68]. Single Pt atoms and atomic clusters are adsorbed primarily at graphene edges. This trend is maintained up to 150 ALD cycles without the formation of nanoparticles. This result indicates that the nitrogen dopants, probably carbon atoms adjacent to nitrogen dopants [145, 146], work as the anchoring sites for adsorbates. Pt atoms on terrace sites seem trapped
at the vacancy and dopants. Such anchoring effects, accompanying prominent cycle properties, and superior catalytic activity of catalysts have been reported in various dopants and adsorbates [147–155].

DFT calculations also clearly show the anchoring effects of heteroatom dopants in graphene. The adsorption energy on X-doped graphene is conventionally obtained as follows;

\[ E_{ad}^X = E_{adsorbate/gra}^X - [E_{gra}^X + E_{adsorbate}], \]

where \( E_{adsorbate/gra}^X \), \( E_{gra}^X \), and \( E_{adsorbate} \) are the total energies of total adsorbed systems, isolated X-doped graphene, and adsorbates, respectively. The adsorption energy of a single atom on heteroatom-doped graphene is shown in figure 9 [156]. The heteroatom doping enhances the adsorption of a single Pt atom. Especially, O-, Si-, P-, and S-doped graphene significantly stabilize a single Pt atom. This is because these graphene have dangling bonds to form strong chemical bonds with adsorbates. As we mentioned, O-doped graphene has dangling bonds in adjacent carbon atoms. Silicon, phosphorus, and sulfur atoms in graphene have steric structures, resulting in the formation of sp\(^3\) hybrid orbitals accompanying dangling bonds perpendicular to the graphene plane. Therefore, these dopants show more significant effects than boron and nitrogen atoms. The importance of van der Waals (vdW) interactions was also revealed. Since graphene is chemically inert because of \( \pi \) electrons, vDW interactions play important roles in adsorption and adhesion. Conventional exchange-correlation functionals can not treat dispersion interactions accurately. Therefore, nonlocal correlation functionals are required for graphene-related materials [157–166]. In the cases of a single Pt atom adsorption on heteroatom-doped graphene, dispersion interactions strengthen the adsorption by about 0.3 eV, corresponding to more than 15% of adsorption energy on pristine graphene [156].

The diffusion of metal atoms is also suppressed by heteroatom doping. Figure 10 shows the diffusion barrier of a single Pt atom on heteroatom-doped graphene obtained from DFT calculations [156]. A single Pt atom on pristine graphene has a diffusion barrier of only 0.15 eV. The corresponding diffusion coefficient of a single Pt atom is in the order of \( 10^{-9} \) m\(^2\)/s. Therefore, atomically dispersed Pt atoms on pristine graphene can easily diffuse and agglomerate. B- and N-doped graphene show larger diffusion barriers than pristine graphene. However, the effects of B and N doping are less than 1 eV. On the other hand, O, Si, P, and S increase the diffusion barriers by more than 1 eV. As a result, the corresponding diffusion coefficients are reduced by more than 20 orders of magnitude, and the diffusion of a single platinum atom is strongly suppressed. Such anchoring effects originate not from the increase of potential barrier but the deepening adsorption potential well in the
vicinity of dopants. Figure 11 shows the HADDF-STEM images of the Pt nanocluster catalysts on S-doped and S-free carbon supports before and after sintering tests at 700 °C, 600 min [167]. The sizes of Pt catalysts are about 1 nm before sintering tests. In the sintering test, Pt catalysts on the desulfurized (<0.01 at% S) and commercial carbon support diffuse and agglomerate. The Pt catalysts agglomeration occurs, and their sizes reach 3 and 17 nm on the desulfurized and commercial carbon supports after the sintering test, respectively. This result clearly indicates that the nanocluster catalyst migration, agglomeration, and/or Ostwald ripening occur in the long-term thermal treatment. The catalyst size distribution also becomes considerably broader. On the other hand, Pt catalysts on S-doped carbon supports (~14 wt%) maintain their size through sintering tests. Even increasing Pt catalyst loading from 1 to 5 wt%, Pt catalyst coarsening does not occur. These results indicate that the S dopants suppress the Pt diffusion even in high-temperature conditions. Suppression of coarsening of metal nanocluster catalysts on S-doped carbon supports was observed in other metals, Rh, Rh, Os, and Ir. Therefore, the concept of long-life catalysts based on heteroatom-doped carbon supports can be applied to various catalysts. While these supports contain vacancies, desulfurized carbon supports are less effective for Pt coarsening suppression. Therefore, not only vacancies but S dopants also play an essential role in suppressing Pt diffusion. In addition, Pt catalyst coarsening occurs on N-doped carbon supports. These results indicate that the S dopants suppress Pt diffusion more than N dopants. The decrease of N dopants (3.01 to 1.44 at%) was also observed through sintering tests. Therefore, the dopant concentration and stability of dopants are also important for catalyst usage in severe conditions.

The effects of atmospheric gasses have to be addressed for practical use. The diffusion barriers of a single Pt atom with H and H₂ are also shown in figure 10 [156]. The adsorption of H and H₂ on a single Pt atom reduces the diffusion barriers on pristine graphene to less than 0.07 eV. Even in the cases of heteroatom-doped graphene supports, the hydrogen atmosphere enhances the Pt diffusion, except in several cases. In addition, the adsorption energy becomes smaller through hydrogen adsorption in all cases, which indicates that the hydrogen atmosphere also enhances the detachment of Pt catalysts. These results indicate that atmospheric gas adsorption strongly affects the metal catalyst detachment, migration, and agglomeration, i.e., a lifetime of catalysts. Experimentally observed Pt catalyst coarsening on the desulfurized and commercial carbon catalysts in figures 11 (f) and (h) may be enhanced by a hydrogen atmosphere. Such dynamic structural changes of materials in various atmospheric gasses were also experimentally reported using in situ TEM [168–173]. Liu and co-workers systematically studied the effect of various conditions on Pt cluster behaviors in zeolite crystallites and elucidated that not only agglomeration but redispersion of subnanometric Pt catalysts occur depending on atmospheric gasses and environmental temperature. Figure 12 shows a summary of the behaviors of subnanometric Pt catalysts under different reaction conditions [174]. Under the reductive condition, i.e., CO + O₂ and CO + H₂O, atomically dispersed Pt catalysts diffuse and agglomerate into Pt clusters at 100 °C–300 °C. Then, Pt catalysts atomically redisperse in CO + O₂ at 400 °C, while Pt catalysts continue to grow in CO + H₂O at higher temperatures. In oxidative atmosphere gasses, i.e., NO + H₂ and NO + CO, Pt clusters disintegrate into atomically dispersed Pt at 200 °C–400 °C. Then, atomically dispersed Pt catalysts agglomerate into clusters and small particles at 600 °C–800 °C. Formed Pt clusters and particles are stable even at 1000 °C. These results revealed that the behaviors of metal catalysts are very complex and strongly relate to atmospheric gasses and environmental temperatures. Therefore, to comprehend not only coarsening but redispersion of metal catalysts, Therefore, to understand redispersion as well as coarsening of metal catalysts, it is necessary to study both kinetics and equilibrium theory, including diffusion barriers on the support, adsorption energy of atmospheric gasses, and binding energy between catalysts.
4. Summary and outlook

We briefly reviewed the recent progress of heteroatom doping of graphene and metal catalysts behaviors on heteroatom-doped graphene. Thanks to the detailed characterization using XPS, XANES, and EELS, the atomic structures of heteroatom-doped graphene were elucidated. Pyridinic-type structures were often observed in substitutional doping, while graphitic-type structures were less contained. From the viewpoints of doping positions, DFT calculations and classical MD simulations clarified that dopants are preferably located at the edge sites. HAADF- and MAAADF-STEM revealed that heavier dopants can also be doped in the graphene basal plane, while the concentration of dopants is low. The more dopants in the graphene basal plane, the more anchor sites for highly-dispersed metal atoms and clusters, which results in more catalyst loading. Therefore, new synthetic procedures for a higher concentration of graphitic-type dopants without damage are required to realize broad applications utilizing the high specific surface area, high chemical and mechanical durability, and high electrical and thermal conductivity.

Dopants in graphene enhance the adsorption of a single metal atom and clusters. HAADF-STEM elucidated that highly-dispersed Pt atoms are preferably adsorbed at edge sites, where dopants in graphene are abundant. Diffusion barriers of a single Pt atom increase by dopants in graphene. The anchoring effects of dopants were also experimentally confirmed with HAADF-STEM. Sizes of Pt clusters on S-doped carbon supports keep through high-temperature heat treatment, while coarsening of Pt clusters occurs on desulfurized and commercial carbon supports. Sizes and distribution of Pt were systematically observed in various atmospheric gases and environmental temperatures. Not only agglomeration but redispersion occur depending on environmental conditions.

For practical applications, controlling support effects is essential to improve target functionalities. for instance, catalytic activities of bulk materials generally show ‘volcano’ relationships with the adsorption energy of reaction intermediates [3, 175]. However, DFT calculations elucidated that a single Pt atom and clusters on light-element doped graphene describe different volcano shapes from bulk catalysts [176]. Therefore, the catalytic activities of subnanometric catalysts cannot be estimated from the bulk database. Recently, new boron-based two-dimensional materials have been intensively studied [177–184]. These materials may be new options to control support effects. Recently, atomic-scale manipulation has been developed in the electron microscope [185]. This technique can help to fabricate precisely controlled heteroatom-doped graphene supports. Recent advances in atomic-scale vibrational spectroscopy [186, 187] and electromagnetic field measurements [188–192] are also promising tools to characterize newly developed support materials.

In addition, geometric differences between a single Pt atom and clusters on doped graphene and bulk materials should be reconsidered. A single Pt atom and clusters on doped graphene consist of a composite of small active metal sites, inert terrace area, and low-dimensional edge sites, which may also show catalytic activity. Therefore, reaction processes over a large area may have collective mechanisms, including chemical reactions on doped graphene sites and reactant spillover [45, 46, 193]. Direct in situ/operando measurements and DFT calculations are crucial to designing new atomic-scale catalysts supported on heteroatom-doped graphene.

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Data availability statement

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