



SPECIAL TOPIC: Single-atom Catalysts

Graphene-supported metal single-atom catalysts: a concise review

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ABSTRACT Single-atom catalysts (SACs) have become an emerging frontier trend in the field of heterogeneous catalysis due to their high activity, selectivity and stability. SACs could greatly increase the availabilities of the active metal atoms in many catalytic reactions by reducing the size to single atom scale. Graphene-supported metal SACs have also drawn considerable attention due to the unique lattice structure and physicochemical properties of graphene, resulting in superior activity and selectivity for several chemical reactions. In this paper, we review recent progress in the fabrications, advanced characterization tools and advantages of graphene-supported metal SACs, focusing on their applications in catalytic reactions such as CO oxidation, the oxidation of benzene to phenol, hydrogen evolution reaction, methanol oxidation reaction, oxygen reduction reaction, hydrogenation and photoelectrocatalysis. We also propose the development of SACs towards industrialization in the future.

Keywords: single-atom catalysts, graphene substrate, advanced characterization methods, catalytic reaction

INTRODUCTION

It is necessary for a heterogeneous catalysis reaction to undergo three processes: first, the reactants must be chemically adsorbed on the catalyst surface; second, the reactants are transformed; and finally the products need to desorb from the catalyst surface. Therefore, the solid-supporting catalytic substrate plays a very important role in the processes. Although the metal loadings on traditional heterogeneous catalysts are high, the majority of active metal species are buried below the surface of the nanoparticles. The low catalytic efficiency can hardly satisfy the demands of industrialization [1,2]. Therefore, it

is crucial to reduce the size of precious metal catalysts to promote the catalytic efficiency. When the size of the precious metal catalysts is reduced to the sub-nanometer level, the precious metals on the catalyst surface are isolated from each other, which can significantly improve the catalytic efficiency [3,4]. Single-atom catalysts (SACs) have been playing important roles in the field of catalysis since they were proposed [5–9]. Qiao *et al.* [5] prepared the Pt/FeO_x catalysts by anchoring single Pt atoms on the surface of FeO_x and proposed the concept of SACs for the first time. The catalysts with high activity and stability significantly increased the utilization of precious metal atoms. Sahoo *et al.* [10] proved that non-precious metal SACs could also achieve enhanced C–H bond methane activation by using theoretical calculations.

Graphene, as the thinnest two-dimensional (2D) carbon material with one atom thickness (0.334 nm) [11–14], has been widely used in many fields. Its unique and stable lattice structure results in excellent thermal conductivity [15,16], electrical conductivity [17–20], large specific surface area [21–23] and facile chemical modification [24–26]. Graphene has also been reported to be an excellent support for SACs due to its remarkable properties [27–34]. Liang *et al.* [35] compounded bi-functional Co₃O₄/reduced graphene oxide (RGO) catalysts with excellent durability and activity. Li *et al.* [36] fabricated MoS₂ nanoparticles supported on RGO by a selective solvothermal method, which presented excellent electrocatalytic performance in the hydrogen evolution reaction (HER).

However, the deposition of single metal atoms on the graphene surface remains challenging. Firstly, the interaction between metal atoms and the graphene surface is

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weak, which leads to instability during catalytic reactions [9]. Secondly, it is difficult to obtain graphene-supported SACs. Finally, reducing the size of metal catalysts definitely results in significant aggregation, causing deactivation of the catalysts during catalytic reactions [37]. In this review, we introduced diverse preparation methods and advantages of graphene-supported metal SACs aimed at solving the above-mentioned challenges. We also summarized their applications in CO oxidation [5,38–40], oxidation of benzene to phenol [41], HER [42,43], methanol oxidation reaction (MOR) [44–46], oxygen reduction reaction (ORR) [47–50], hydrogenation [32,51] and photoelectrocatalysis [52–55]. At last, we focused on the prospect and future developments of graphene-supported metal SACs.

SELECTION OF SUBSTRATES

Metal substrates and metal oxide substrates

With the decreasing size of active metals, the metal catalysts can achieve enhanced catalytic activity while bringing large surface free energy [8], which is an important reason for the instability of conventional metal-supported SACs (Fig. 1). Therefore, the choice of substrate is the key to the synthesis of stable SACs. The substrates of supported catalysts can be divided into traditional metal substrate, metal oxide substrate and new 2D material substrate. Many outstanding active metals of SACs, such as Pt [56,57], Au [58], Pd [59], Fe [60–62], Co [63–65], Ni [66] and Cr [67], have exhibited extraordinary activity in many catalytic reactions. There are also some common metal-oxide supporting substrates of SACs, such as FeO_x [5], TiO_2 [68], ZrO_2 [69] and ZnO [70]. Metal SACs can be synthesized by general methods, such as mass-selected soft-landing technique [71], coprecipitation [72], successive reduction [73] and solid phase melting method [74], etc.

Zhang *et al.* [73] prepared single Au atoms supported on Pd (Au/Pd catalysts) by the successive reduction method. Their results showed that the catalytic efficiency of Au/Pd catalysts was 17 times higher than the Au nanoparticle catalysts, which indicated excellent catalytic performance of Au/Pd catalysts. The metal/metal catalysts (single metal atoms anchored to the surface of metal supporting substrate) and metal/metal-oxide catalysts (single metal atoms anchored to the surface of metal-oxide supporting substrate) exhibited high activity, good chemical selectivity and durability. However, there are still obvious defects in the metal and metal-oxides as catalytic substrates. As substrates, the catalytic efficiency of or-

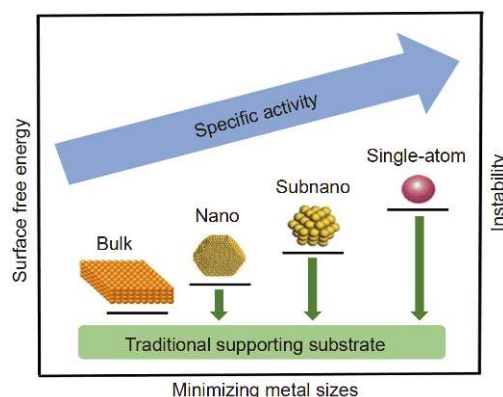


Figure 1 Schematic diagram illustrating the relationships of surface free energy, instability and specific activity per metal atom on traditional supporting substrate with metal size.

dinary metals is lower than precious metals. Otherwise, there are also some shortcomings of catalysts such as high cost, low light-off temperature and easy-sintering at high temperature, which prove problematic for the application on industrial scale. Thus, we should explore high-efficiency, low-temperature and non-metal SAC substrates.

2D material substrates

Graphene has become the emerging non-metal substrate of SACs due to its unique 2D structure, good mechanical properties and conductivity [54,75–82]. The honeycomb-like sheet of graphene will provide more active sites, and the porous structure will effectively reduce the agglomeration of metal atoms [30,83]. Sahoo *et al.* [84] calculated the possibility of depositing single transition metal (TM) atoms, such as Cr, Mn, Fe, Co, and Cu atoms, on the surface of graphene by density functional theory (DFT). The results showed that the single-atom TM/graphene catalysts exhibited a high activity in the methane activation reaction. Graphene as a support has been proven to be stable during different catalytic reactions, such as CO oxidation and hydrogenation, due to superior chemical compatibility and surface-modification chemistry [32,40]. At present, the main methods for preparation of graphene-supported metal SACs include atomic layer deposition (ALD) [30], focused electron beam irradiation [85], ethylene glycol (EG) reduction [50], high-energy ball milling [41] and arc discharge method [86], etc.

Graphene substrate

Wang *et al.* [87] obtained single Si atoms supported on graphene (Si/graphene catalysts) by a chemical vapor deposition (CVD) method. Single Si atoms, as a catalytic wedge in the form of energetic electrons, were observed

by high-resolution transmission electron microscopy (HRTEM) (Fig. 2a). The C atom of graphene was gradually replaced by Si atom to form a stable structure. Fig. 2b demonstrates the catalytic mechanism of the single Si ad-atom on the surface and edges of graphene. The experimental results showed that Si/graphene catalysts with dynamic, stability and high selectivity provided the possibility for developing stable molecular devices at the atomic scale.

Liu *et al.* [39] reported the Pt/graphene catalysts by simulating single Pt atoms embedded into graphene lattice *via* first principles and DFT calculations. The calculation showed that the binding energy was up to -0.71 eV, which enhanced the stability of the catalysts. Diffusion and agglomeration of embedded Pt atoms were thus effectively avoided. When the regenerative energy barrier of Pt atoms reached 0.46 eV, the energy barriers for the formation and dissociation of the peroxide-like intermediate were only 0.33 and 0.15 eV, respectively, which also showed the superior activity of Pt-embedded graphene catalysts in low temperature CO oxidation reaction.

Zhao *et al.* [34] observed single Fe atoms at the graphene edges by *in situ* atomically resolved TEM and

discovered anomalous diffusion. The carbon atoms were directly substituted by or merged with single Fe atoms. High catalytic performance of single Fe atoms was consistent with the result of theoretical calculations (molecular dynamic simulations and DFT), which could contribute to the basis for the sp^2 carbon growth of graphene-supported metal SACs.

Nitrogen-doped graphene substrate

Fei *et al.* [43] synthesized single Co atoms supported on nitrogen-doped graphene (Co/N-graphene catalysts) with graphene oxide (prepared by modified Hummers method) in the Ar/NH₃ atmosphere for 1 h (Fig. 3a). The Co/N-graphene catalysts exhibited high activity, stability and low overpotentials (30 mV), which was due to the coordinating role of nitrogen atoms in the substrate center (Fig. 3b–d).

Zhang *et al.* [40] synthesized single Pt atoms supported on nitrogen-doped graphene (Pt/N-graphene catalysts) with high stability and activity in CO oxidation. The stability of single Pt atoms could be improved by suitable doping. They had much higher stability, activity and lower energy barrier (0.16 eV) through tri-molecular

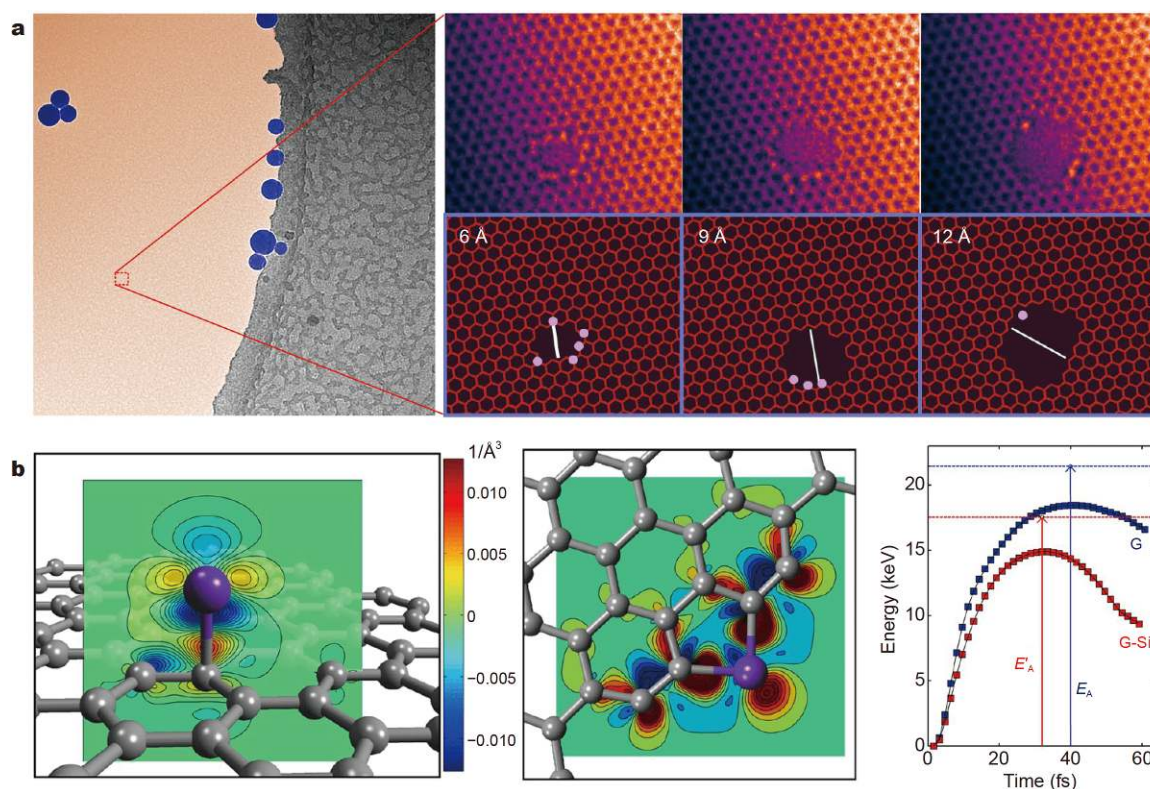


Figure 2 (a) HRTEM images of silicon/graphene sample, (b) catalytic principles of the single Si ad-atom. Reprinted with permission from Ref. [87], Copyright 2016, American Chemical Society.

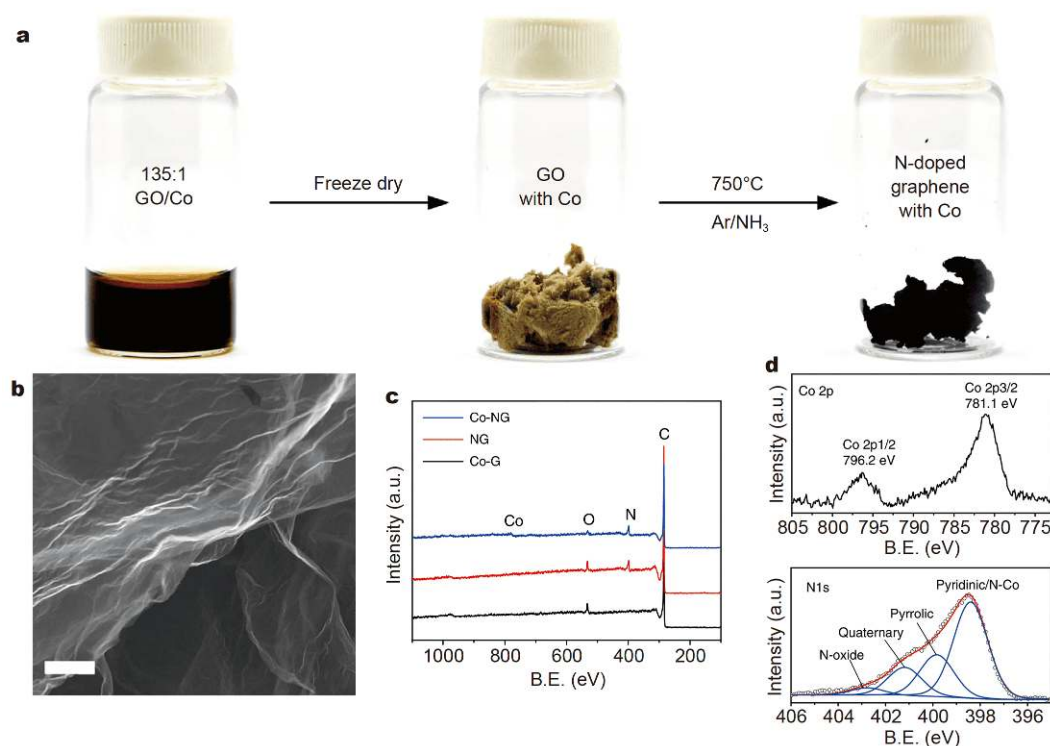


Figure 3 Preparation, morphology and compositional characterizations of the Co-NG. (a) Preparation process of the Co-NG catalyst, (b) SEM image, (c) XPS spectra (NG represents N-graphene), (d) HR XPS Co 2p and N 1s spectra. Reprinted with permission from Ref. [43], Copyright 2015, Nature Publishing Group.

Eley-Rideal mechanism, which was obviously better than Langmuir-Hinshelwood or Eley-Rideal mechanisms for CO oxidation.

Single Ni atoms supported on nitrogen-doped graphene (Ni/N-graphene catalysts) were prepared with N-graphene as catalytic substrate by Yang *et al.* [88], with the process of zirconia ball grinding, pyrolysis, freeze-drying and reheating under an argon atmosphere. The Ni/N-graphene catalysts could retain 98% of original catalytic performance after CO₂ reduction for 100 h.

Graphene is the nucleation center of single metal atoms to exert the maximum catalytic activity in chemical reactions. The large specific surface area can provide plenty of effective active sites for single metal atoms. Nevertheless, efficient and cost-effective preparation methods of graphene-supported metal SACs are critical.

PREPARATION METHODS OF GRAPHENE-SUPPORTED METAL SACs

ALD

For ALD, single atom layer is coated to the target surface through a reactor. The film deposition quality of tradi-

tional CVD is related to several factors, such as deposition time, temperature and gas flow. Compared with conventional CVD method, ALD is a novel technique depositing a thin film by different precursors. It has many advantages in terms of film formation uniformity, quality and number of layers, which can be mainly used in the fields of semiconductor [89–91] and nanotechnology [92–94]. In recent years, ALD has been frequently applied in the field of catalysis. This technique can precisely control the morphology, size, density and loading of single metal atoms, sub-nanoclusters and nanoparticles.

Sun *et al.* [30] prepared single Pt atoms supported on graphene nanosheets (Pt/GNS catalysts) by the ALD technique. Fig. 4a shows the schematic of Pt ALD on graphene surface. The isolated and well-grown single Pt atoms were uniformly deposited on the graphene surface as confirmed by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). By changing the number and conditions of ALD cycles, the morphology, size, density and loading of single Pt atoms could be efficiently controlled. When the numbers of ALD cycles reached 50, the methanol oxidation peak current density for 50ALD Pt/GNS catalysts was

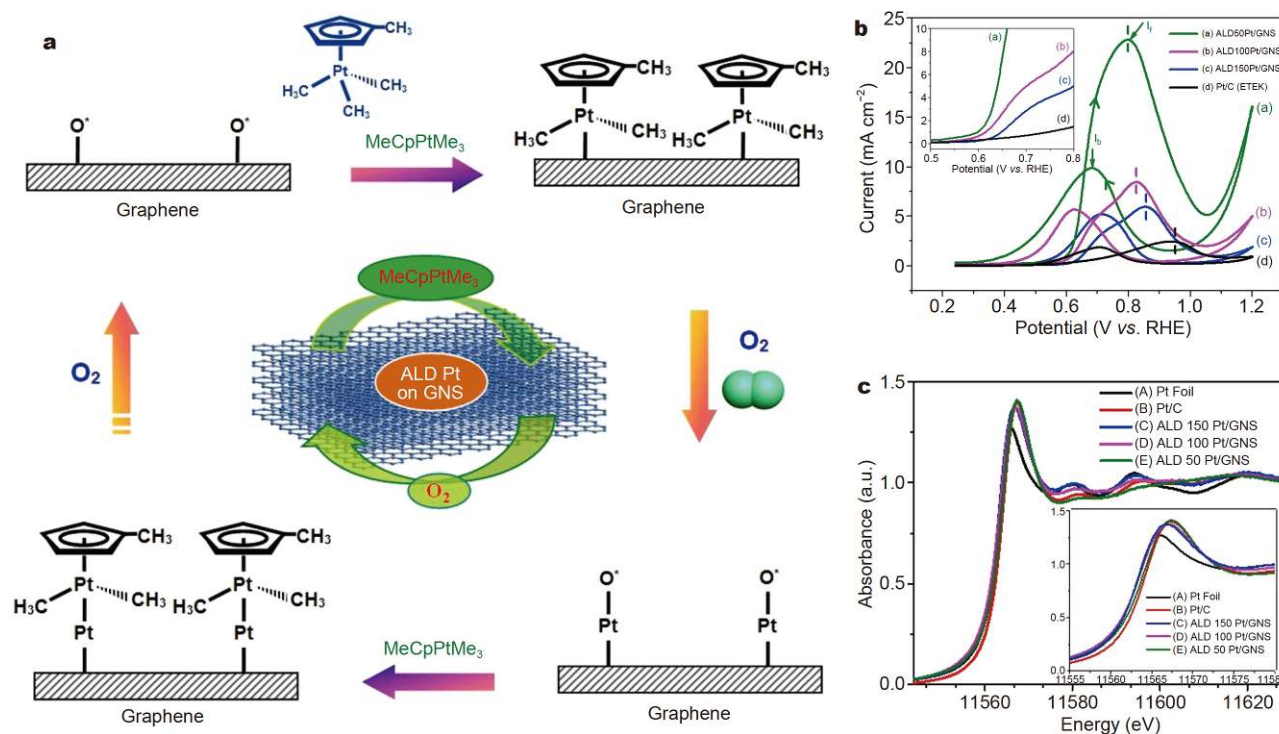


Figure 4 (a) Schematic diagrams of Pt ALD principle, (b) CV curves of methanol oxidation, (c) XANES spectra at Pt L₃ edge. Reprinted with permission from Ref. [30], Copyright 2013, Nature Publishing Group.

22.9 mA cm⁻² by adopting cyclic voltammetry (CV) and X-ray absorption fine structure (XAFS) in MOR, which was 2.7 and 9.5 times that of 100ALD Pt/GNS and Pt/C catalysts, respectively (Fig. 4b, c). The excellent catalytic performance of Pt/GNS catalysts attributed to the isolated single Pt atoms and unique structure of graphene. It indicated that Pt/GNS catalysts had an excellent CO tolerance and adsorption rates. Above all, compared with commercial Pt/C catalysts, the Pt/GNS catalysts exhibited superior activity and durability in MOR and CO oxidation reaction.

Yan *et al.* [82] compounded stable dimeric Pt₂/graphene catalysts, with nucleation center with single Pt₁ atoms deposited on graphene substrate, by ALD (Fig. 5a). The single Pt atoms had an optimum nucleation condition due to the unique properties and large specific area of graphene. Meanwhile, the dimeric Pt₂/graphene catalysts exhibited 2800 mol_{H₂} mol_{Pt}⁻¹ min⁻¹ at room temperature, which was 45-fold higher than Pt/graphene catalysts in hydrolytic dehydrogenation of ammonia borane (Fig. 5b).

Yan *et al.* [32] prepared Pd₁/graphene catalysts through depositing single Pd atoms on the graphene surface by ALD. The catalysts exhibited 100% butene selectivity and

95% conversion rate by aberration-corrected HAADF-STEM and XAFS, which demonstrated excellent durability in the continuous selective hydrogenation of 1,3-butadiene reaction for 100 h without any change in activity and selectivity. Therefore, the Pd₁/graphene catalysts presented excellent application prospects in the selective 1,3-butadiene hydrogenation reaction.

Stambula *et al.* [48] compounded Pt/N-graphene catalysts by depositing single Pt atoms on N-graphene surface *via* ALD, which exhibited outstanding catalytic performance. It provided a direction for the synthesis of large specific surface area catalysts in the proton exchange membrane fuel cell (PEMFC).

Focused electron beam irradiation

Robertson *et al.* [85] fabricated single atom Fe/graphene catalysts by irradiating graphene surface with the focused electron beam irradiation. The dopant single Fe atoms, embedded to graphene lattice, have caused the displacement of carbon atoms, which was important for designing the Fe/graphene catalysts with theoretical results.

EG reduction

EG reduction is a method for preparing metal/substrate

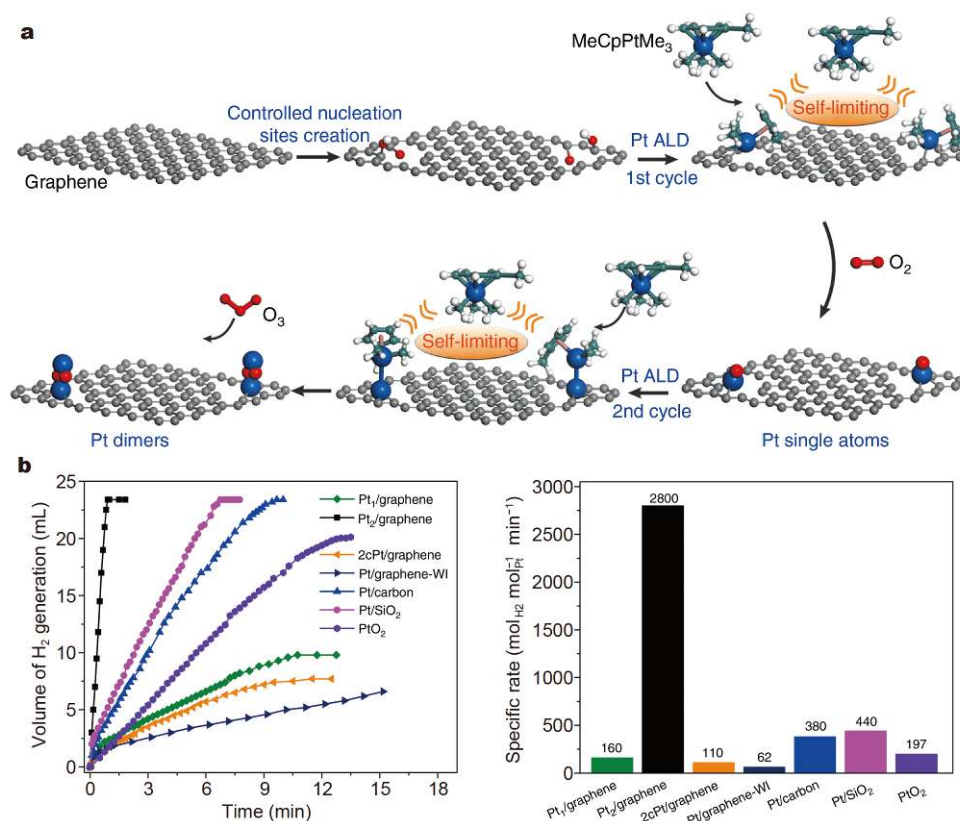


Figure 5 (a) Schematic diagrams of dimeric Pt₂/graphene catalysts, (b) catalytic activities of diverse Pt catalysts. Reprinted with permission from Ref. [82]. Copyright 2017, Springer Nature.

electrocatalysts [95,96]. Shao *et al.* [95] deposited Pt nanoparticles on the poly(diallyldimethylammonium chloride) (PDDA) coated with graphene nanoplatelets (GNPs) by the ethylene glycol reduction method. The preparation processes included the following steps: first, GNPs were uniformly dispersed in the PDDA aqueous solution; second, PDDA-functionalized GNPs were added into the EG solution and stirred for 1 h; and finally, the products were washed with deionized water and vacuum dried at 90°C for 3 h. Compared with the traditional Pt nanoparticles supported on carbon nanotubes (Pt/CNT catalysts) or Pt/C catalysts, the Pt nanoparticles supported on graphene nanoplatelets (Pt/GNPs catalysts) exhibited excellent catalytic performance for oxygen reduction in fuel cells (Fig. 6).

High-energy ball milling

Deng *et al.* [41] prepared graphene-embedded FeN₄ (FeN₄/GN, GN represents nanosheet) catalysts with FePc and GN composites. The catalysts exhibited an excellent catalytic performance (conversion of 23.4% and yield of 18.7%) in the direct catalytic oxidation of benzene to

phenol, and the conversion still maintained 8.3% at 0°C for 24 h.

Arc discharge

Zhang *et al.* [86] prepared single Nb atoms supported on graphite (Nb/graphite catalysts) by controlling the distance between niobium rod and carbon rod, and finally niobium atoms and carbon atoms were deposited at the same time. The experiment revealed that Nb/graphite catalysts enhanced the overall conductivity and prevented the agglomeration of single atoms. Theoretical calculations indicated that the Nb/graphite catalysts showed high activity and high stability in cathodic ORR.

CHARACTERIZATION METHODS

The advanced, accurate and efficient characterizations of SACs have attracted great attention in recent years. The main characterization methods of SACs include HAADF-STEM and XAFS.

XAFS spectroscopy

XAFS is an emerging technique developed with syn-

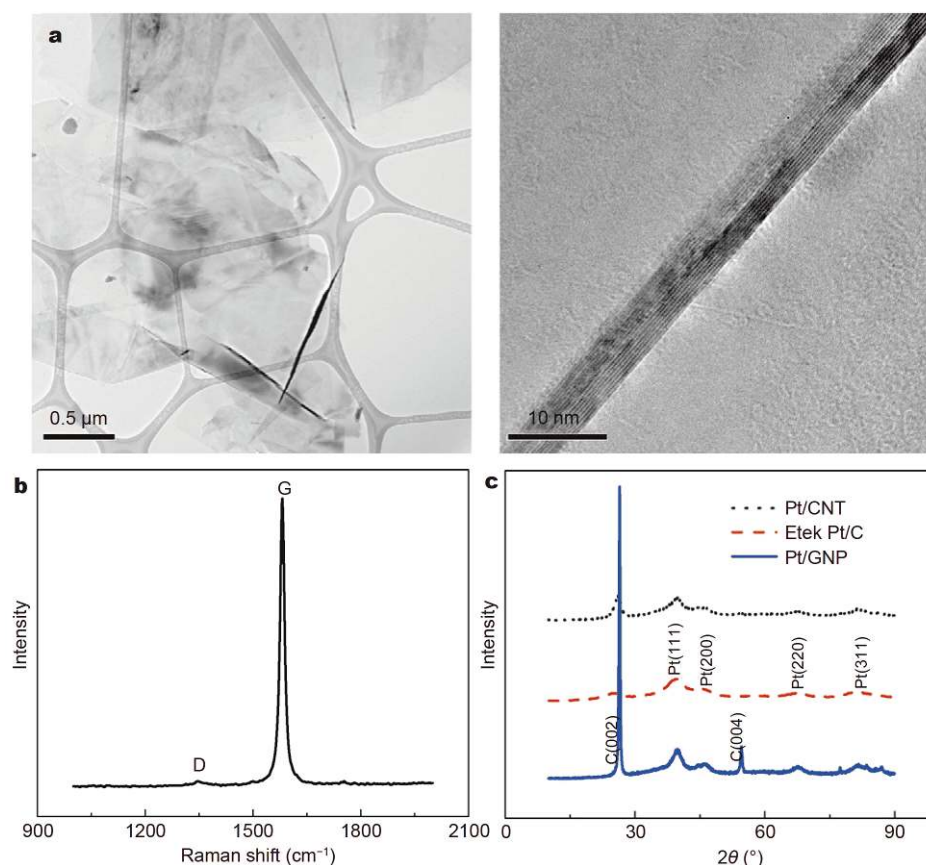


Figure 6 TEM images (a), Raman spectrum (b) and XRD patterns (c) of graphene nanoplatelets. Reprinted with permission from Ref. [95], Copyright 2010, Elsevier.

chrotron radiation, which is an important method for studying the localized atomic structure and electronic structure of materials.

As shown in Fig. 7 [97], the XAFS spectrometer consists of two parts, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The energy range of EXAFS is about 50–100 eV, which is derived from the single-scattering effect of the inner-shell photoelectrons excited by X-rays. XANES contains energy ranges of less than 10 eV and over 50 eV, which are mainly derived from the multiple scattering effects of inner-shell photoelectrons excited by X-rays.

Sun *et al.* [30] prepared single atom Pt/graphene catalysts. It was difficult to find the Pt crystal phase by conventional XRD techniques due to the low Pt loading. Whereas, the single Pt atoms could be characterized by XAFS. The L₃-edge white-line intensity of single Pt atoms on the graphene surface was slightly different from that of Pt/carbon black. The L₃-edge white-line intensity de-

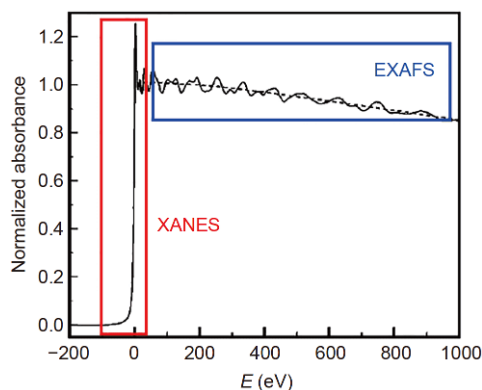


Figure 7 Pt L₃-edge XAFS spectrum for platinum foil. Reprinted with permission from Ref. [97], Copyright 2000, Springer.

creased while the ALD deposition layer increased (50ALDPt/GNS > 100ALDPt/GNS > 150ALDPt/GNS > Pt/C), in accord with the same order of CO tolerance and MOR. Therefore, the interfacial bonding force of Pt/GNS was stronger than that of Pt/C; meanwhile, the decrease

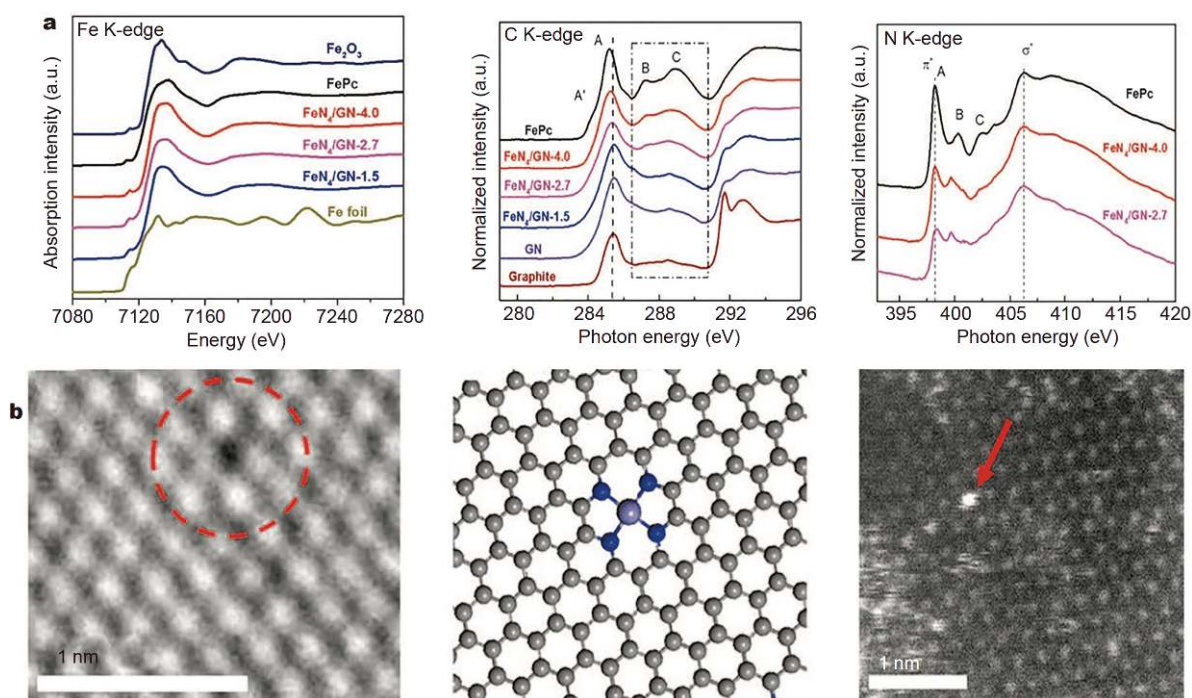


Figure 8 (a) Coordination structure and valence state of FeN_4/GN catalysts, (b) morphology analysis of FeN_4/GN catalyst. Reprinted with permission from Ref. [41], Copyright 2015, American Association for the Advancement of Science.

of deposition times could effectively increase the white-line intensity.

Yan *et al.* [32] observed the isolated single Pd atoms dispersed on graphene by XANES and XAFS. The XANES spectra of the Pd K-edge indicated that the isolated Pd atoms on graphene surface may be zero valence or +2 valence states. The EXAFS spectra of the Pd K-edge indicated that the coordination environment around the Pd atom exhibited a highly distorted structure, which showed accurate quantitative XAFS contributing to the characterization of the deposited single atoms on graphene.

Deng *et al.* [41] revealed the coordination structure and valence state of single Fe atoms in the FeN_4/GN catalysts by XAFS (Fig. 8a). The near-edge structure of FeN_4/GN catalysts was similar to that of original FePc by the Fe K-edge of XANES. The number of C=N bonding decreased significantly, which indicated that the FeN_4 structure remained stable (Fig. 8b).

Aberration-corrected HAADF-STEM

The HAADF-STEM can improve the resolution to the sub-angstrom level and eliminate the spherical phase difference in the transmission system. The single atoms or clusters can be observed as a light spot by HAADF, so

that the chemical composition information of the atomic resolution can be obtained [98].

As shown in Fig. 9, in the range of θ_3 , the signals are primarily transmitted electron beams and scattering electrons. In the range of θ_2 , the received signals are Bragg scattering electrons. If the received signals are primarily incoherent scattering electrons with high-angle in the θ_1 range, the HAADF image can be obtained. The light spot in the image always correlates to the column of atoms [99]. Therefore, HAADF-STEM plays a decisive role in materials science, chemistry, physics and other fields.

Yan's group [32] discovered the single atom $\text{Pd}_1/\text{graphene}$ catalysts with high activity, superior selectivity of butene and stability under continuous reaction. They demonstrated by HAADF-STEM that the isolated single Pd atoms were randomly deposited on the graphene surface (Fig. 10a). Single Pd atoms presented a special steric effect when the annealing temperature was 1050°C , which was a crucial reason for excellent catalytic performance of $\text{Pd}_1/\text{graphene}$ catalysts (Fig. 10c).

Stambula *et al.* [48] observed isolated single Pt atoms and clusters on N-graphene surface by HAADF-STEM. Single Pt atoms were mainly stacked on the graphene edges. Only a small number of single Pt atoms were

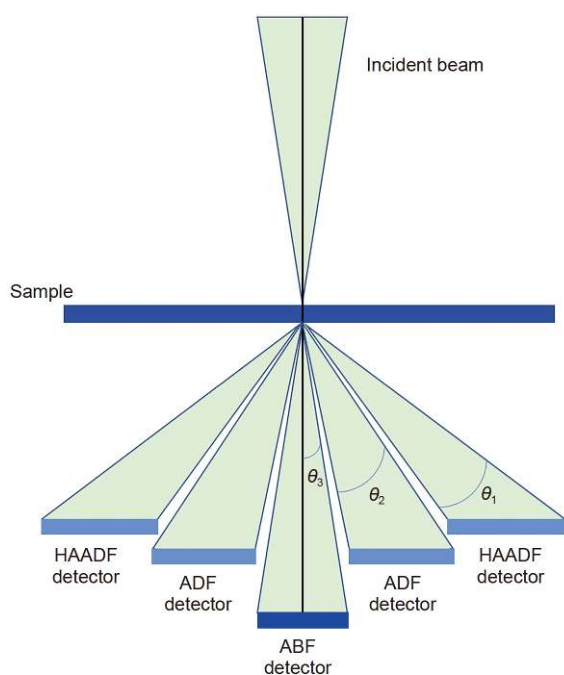


Figure 9 STEM detector distribution diagram.

distributed in the center of graphene surface. It was proved that the Pt element stacked on N-graphene existed as single atoms or clusters through HAADF-STEM.

ADVANTAGES OF GRAPHENE-SUPPORTED METAL SACs

High activity

The catalytic efficiency of metal solid-supported catalysts will increase in order of magnitude when the size reaches to single atom scale. Qiao *et al.* [5] prepared single atom Pt_1/FeO_x catalysts with 2–3 orders of magnitude higher catalytic performance than conventional catalysts. In recent years, the preparation techniques of high-quality graphene have been improved, which is frequently used as solid-support catalytic substrate. On account of the large specific area (approx. $2630 \text{ m}^2 \text{ g}^{-1}$), graphene can reduce the surface free energy and prevent agglomeration of single atoms. Yang *et al.* [88] also synthesized single atom Ni/N-graphene catalysts, in which single Ni atoms were adopted as active metals. Fig. 11a, b show the scanning electron microscopy (SEM), atomic force microscopy (AFM) and TEM images of single atom Ni/N-graphene catalysts. The exchange current density and turnover frequency (TOF) were an order of magnitude higher than the traditional catalysts (Fig. 11c, d). The high CO_2 reduction activity resulted from the large specific surface area of the graphene substrate, which led to the distribution of the single atom Ni on the surface of graphene and the formation of Ni-C bonds, and finally the

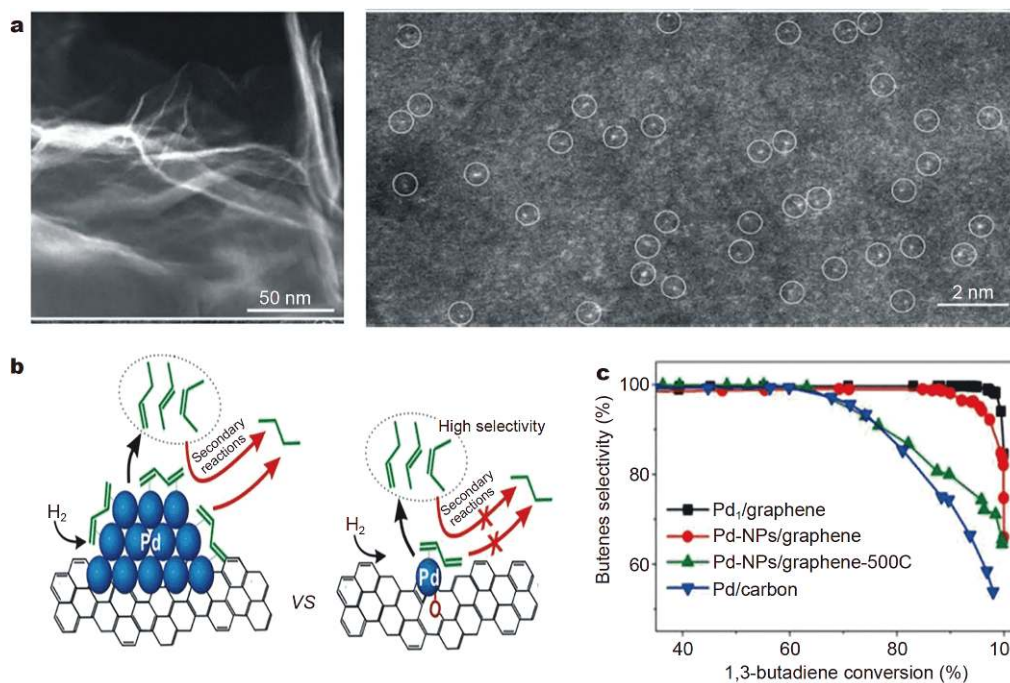


Figure 10 (a) HAADF-STEM images of $\text{Pd}_1/\text{graphene}$, (b) schematic diagrams of butene selectivity on $\text{Pd}_1/\text{graphene}$ catalyst, (c) catalytic capabilities of various samples. Reprinted with permission from Ref. [32], Copyright 2015, American Chemical Society.

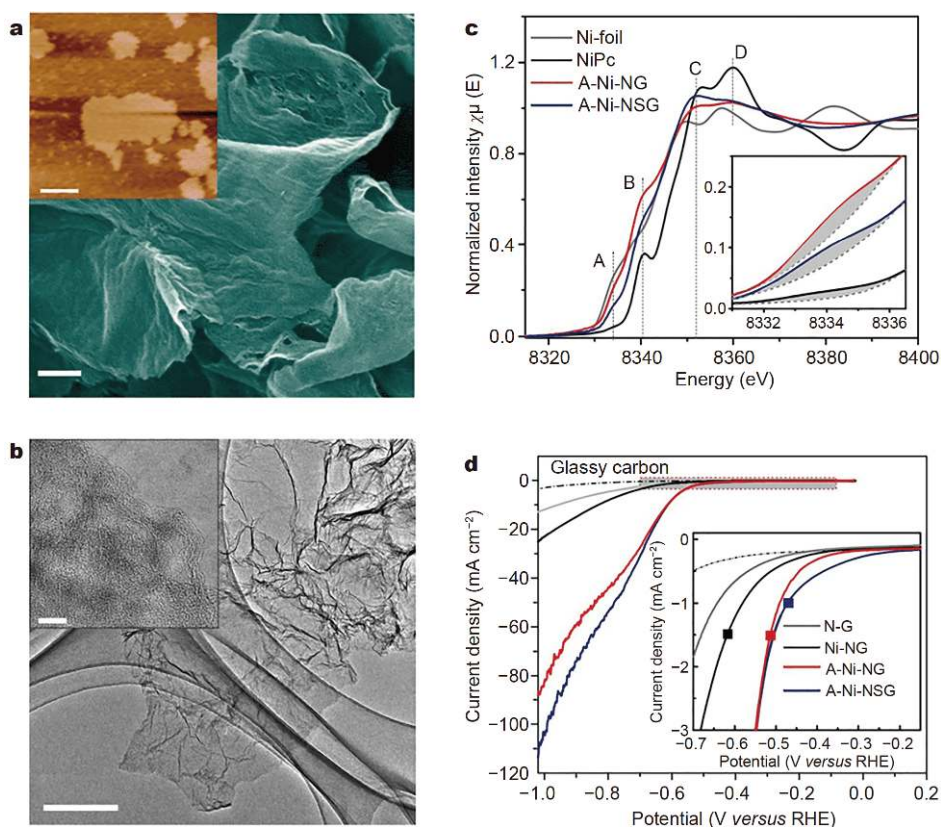


Figure 11 (a) SEM and AFM images of single atom Ni-graphene catalyst, (b) TEM image of Ni-graphene catalyst, (c) electronic states of Ni atom in the Ni-graphene catalysts, (d) CO₂ reduction in aqueous solution. Reprinted with permission from Ref. [88], Copyright 2018, Springer Nature.

redistribution of electrons in the Ni 3d orbital. Ta *et al.* [31] compounded the single Cr atoms supported on graphene (Cr/graphene catalysts). Graphene substrates with a single atomic layer thickness played a decisive role and can accurately characterize single atomic Cr under TEM. The current density of the SACs was several orders of magnitude higher than that of commercial catalysts. Compared with commercial Pt/C catalysts, Sun *et al.* [30] prepared the single atom Pt/graphene catalysts with excellent performance in MOR and CO oxidation, which was attributed to the distinctive properties of graphene substrate (high surface area, high conductivity and unique surface structure), and ultimately improved utilization efficiency of single Pt atoms.

High stability

For traditional industrial catalysts, the stability and catalytic activity will reduce in chemical reaction for hundreds of hours, resulting in the deactivation of the catalysts. However, the SACs cannot be easily agglomerated and inactivated due to the low-loading of single metal atoms and unique graphene structure. Deng *et al.*

[41] synthesized single Fe atoms supported on graphene, which revealed high stability in the catalytic reaction of benzene to phenol. The conversion yield of phenol still reached 8.3% over 24 h. Due to its unique structure and electronic properties, graphene is a good carrier to limit metallic coordinatively unsaturated iron atoms in the matrix. Yang *et al.* [88] fabricated the single atom Ni/N-graphene catalysts (forming Ni–C bonds), which could retain up to 98% activity in the CO formation current density after a 100 h continuous reaction. Yan *et al.* [32] prepared single atom Pd₁/graphene catalysts that revealed superior stability in hydrogenation reaction of 1,3-butadiene, which exhibited 100% butene selectivity at 95% conversion rate over 100 h. The unique structure of graphene ensured a highly distorted coordination around Pd atoms, and formed Pd–C coordination and Pd–O coordination. Fei *et al.* [43] synthesized single atom Co/N-graphene catalysts. The Co/N-graphene catalysts exhibited good stability according to the current density of the cathodic polarization curve for 1000 cycles, which was attributed to the high catalyst loading, tolerance of harsh reactions and acceleration of electron transfer of gra-

phene substrate and Co–C path.

High selectivity

The noble metal atomic radii of SACs are in the range of 1–1.5 Å; meanwhile, the minimum size and low loading determine the isolated catalytic active sites. Zhao *et al.* [100] prepared metal–organic framework-derived catalysts with improved ORR selectivity. Wang *et al.* [87] predicted that single Si atoms would exhibit superior activity and ultra-high selectivity based on DFT calculations. High-selectivity single atom Si/graphene catalysts could open micropores on the graphene surface and maintain the integrity of graphene, which could contribute to novel electronic and spintronic properties of graphene nanostructures and the better design for preparation of SACs. Yan *et al.* [32] introduced single atom Pd₁/graphene that exhibited 100% selectivity of 1,3-butadiene and 70% selectivity of 1-butene, which provided a new possibility for improving the selectivity of hydrogenation reaction.

Graphene-supported metal SACs have exhibited excellent catalytic performance in many catalytic reactions. The isolated and efficient single metal atoms anchored on the graphene sheet present a stable structure. Meanwhile, graphene-supported metal SACs have exhibited high selectivity in ORR reactions and revealed excellent toxic tolerance and stability in CO oxidation reactions. Graphene-supported metal SACs will provide a new direction to design novel and more efficient catalysts for green catalysis.

APPLICATIONS OF GRAPHENE-SUPPORTED METAL SACs

CO oxidation reaction

A majority of CO is derived from fossil fuel combustion emissions, vehicle exhaust emissions and chemical industry exhaust gas, which seriously influence our environment. High-efficiency oxidation of CO at low temperature is the most direct, inexpensive and simple method to effectively reduce CO pollution. Qiao *et al.* [5] firstly obtained Pt₁/FeO_x catalysts that exhibited high activity in CO oxidation. The theoretical binding energy of adsorbed CO on a single Pt atom was 1.27 eV, which was much lower than the calculated value of Pt cluster. In the CO_{ad} + O–O_{ad} → CO₂ + O_{ad} reaction process, the active barrier calculation was 0.49 eV. When the second CO molecule was adsorbed on the Pt atom, the active barrier was 0.79 eV according to the CO_{ad} + O_{ad} → CO₂ + O_{vac} reaction process. Therefore, the low barriers ensured

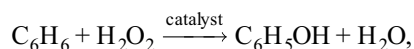
the thermodynamic and kinetic reaction equilibrium of Pt₁/FeO_x catalysts. From then on, graphene-supported metal SACs have made an important progress in CO removal.

Wu *et al.* [38] calculated the stability and CO oxidation behavior of single Fe atom catalysts. In the Eley-Rideal mechanism, CO oxidation involves the following two reactions: O_{2(ad)} + CO_(gas) → O_(ad) + O_(ad) + CO_(gas) → O_(ad) + CO_{2(gas)}, CO_(gas) + O_(ad) → CO_{2(gas)}. Compared with traditional catalysts, the energy barrier of novel single Fe atom catalysts was only 0.21 eV by the theoretical calculation, which was due to Fe–C bonds, leading to the high activity and stability of the single Fe atom catalysts in CO oxidation.

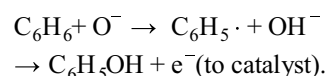
Liu *et al.* [39] obtained the Pt-embedded/graphene catalysts on graphene substrate, which exhibited high catalytic efficiency of CO oxidation at low temperature due to the breaking of the O–O bond and the formation of new C–O bonds (Fig. 12). Zhang *et al.* [40] prepared the Pt/N-graphene catalysts (forming Pt–C bond), which also showed excellent activity and stability in CO oxidation at low temperature through 2CO + O₂ → OCO–OCO → 2CO₂ mechanism.

Oxidation of benzene to phenol

Phenol, as an important organic petrochemical raw material, is widely used in the fields of synthetic rubber [101,102] and petroleum refining [103,104]. Industrial synthetic phenol is confronted with several problems, such as long reaction time, heavy pollution and high cost [105,106]. The oxidizing agents include H₂O₂ and N₂O. The equation for the heterogeneous catalysis system of the H₂O₂ is listed below:



and the equations for the N₂O system are as follows [107]:

$$\text{N}_2\text{O} + \text{e}^- (\text{from catalyst}) \rightarrow \text{N}_2 + \text{O}^-;$$


Both catalytic processes are environment-friendly. However, direct oxidation of benzene to phenol in industry requires highly active catalysts and long reaction path. Deng *et al.* [41] compounded the FeN₄/GN catalysts by depositing single Fe atoms on graphene. The results proved direct catalytic oxidation of benzene to phenol with high efficiency due to Fe=O intermediate. The conversion and yield could reach 23.4% and 18.7% at room temperature, respectively. Furthermore, the conversion could still maintain 8.3% after 24 h, which was

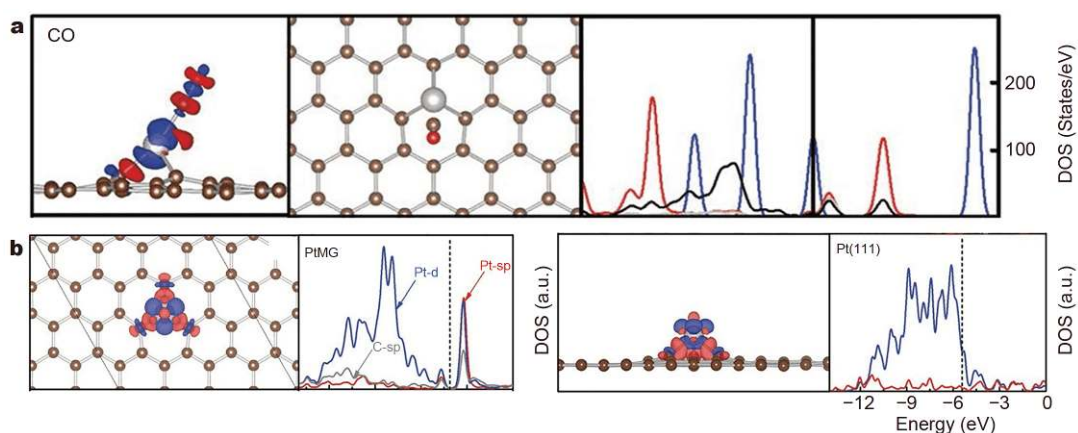


Figure 12 (a) The plausible theoretical calculation results for CO adsorption on PtMG, (b) the contour plot of PtMG, DOS of PtMG and Pt (111) surface. Reprinted with permission from Ref. [39], Copyright 2014, Royal Society of Chemistry.

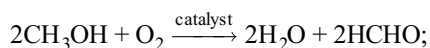
superior to traditional catalysts (homogeneous precious metal catalysts). Graphene-supported metal SACs are expected to solve the problems absolutely of benzene to phenol at room temperature.

HER

Hydrogen is an energy carrier with high energy density and superior heat release properties which render it attractive as a clean and carbon-free fuel [108–110]. Water electrolysis plants in industry require highly active and stable catalysts, which is relatively difficult in HER ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) by large scale. Yan *et al.* [82] fabricated single atom Pt_2 /graphene catalysts (forming Pt–C, Pt–Pt and Pt–O bonds). The specific rate of dimeric Pt_2 /graphene catalysts was 45-fold higher than Pt nanoparticle/graphene catalysts in hydrolytic dehydrogenation of ammonia borane. Fei *et al.* [43] prepared single atom Co/N-graphene catalysts (forming Co–C path), which exhibited superior catalytic performance in water electrolysis plant of hydrogen. The catalysts maintained a high activity even for low over potential (30 mV). Single atom Co/N-graphene catalysts with high adaptability of HER have the potential to replace expensive Pt catalysts in the future.

MOR

Formaldehyde is widely used in chemical industry, such as for wood, textile and aczoiling applications [111]. The commonly used method for the preparation of formaldehyde is direct oxidation with precious metal catalysts such as Pt



however, the catalytic efficiency is very limited [112]. Yoo

et al. [44] synthesized the Pt/GNS electrocatalysts which exhibited extraordinary activity for MOR (existing Pt–C bonds). Fig. 13a, c show the TEM image, histogram and HAADF-STEM image of Pt/GNS. Fig. 13b shows the current-potential curves for MOR on Pt/carbon black, Pt/GNS and Pt/Ru-carbon black, which indicates excellent catalytic activity for MOR on Pt/GNS. Li *et al.* [45] obtained the Pt/chemically converted graphene (Pt/CCG) catalysts by depositing Pt nanoparticles on RGO. The electrochemically active specific area was $36.27 \text{ m}^2 \text{ g}^{-1}$, superior to single Pt atoms supported on multi-walled carbon nanotubes catalysts for $34.43 \text{ m}^2 \text{ g}^{-1}$. The Pt/CCG catalysts exhibited good durability in MOR due to functional groups like –COOH and –OH groups. Zhao *et al.* [46] reported the Pd/polypyrrole-graphene (Pd/PPy-graphene) catalysts by depositing Pd nanoparticle on PPy-functionalized graphene, which showed a catalytic performance superior to traditional catalysts in the MOR.

ORR

Fuel cell is a new-generation efficient and green device in the 21st century [113–115]. The ORR reaction occurs when oxygen is reduced at the cathode of the fuel cell. The half-cell reaction is as follows: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$; $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$.

The chemical formula demonstrates the overall process of the ORR of the catalyst surface, including the ORR to directly generate H_2O through an ideal four-electron pathway, or the formation of H_2O_2 intermediate through an undesirable two-electron pathway. However, the high cost of the traditional Pt catalysts limits large-scale industrial applications [56,116,117]. Lefèvre *et al.* [47] produced microporous carbon-supported iron-based

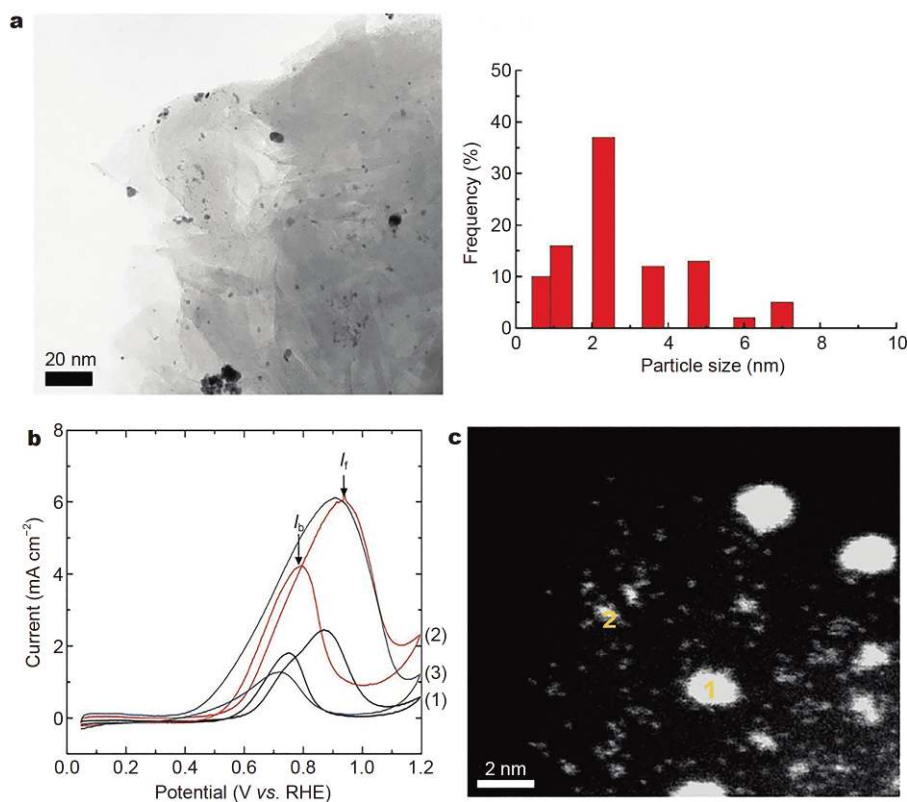


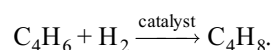
Figure 13 (a) TEM images and histogram of Pt/GNS; (b) current-potential curves for MOR on (1) Pt/carbon black, (2) Pt/GNS and (3) Pt/Ru-carbon black; (c) HAADF-STEM image of Pt/GNS. Reprinted with permission from Ref. [44], Copyright 2009, American Chemical Society.

catalysts, whose cathode current density could be comparable to that of platinum. This work provided a new direction of iron-based catalysts for ORR in polymer electrolyte membrane fuel cells. Wan *et al.* [118] established the connection between electrocatalysis and SAC. Compared with conventional 2D planar catalysts, the newly designed non-planar coordinated single atom cobalt had lower energy levels in 3d orbital. The as-prepared single atom cobalt sites extremely improved the catalytic activity and selectivity in the ORR, which could be applied in the field of electrocatalysis. Graphene-supported SACs could not only present enhanced stability and durability for ORR, but also exhibit good oxygen adsorption and activation. Stambula *et al.* [48] prepared Pt/N-graphene catalysts by depositing single Pt atoms on N-graphene surface (forming Pt–C bond). These catalysts prevented agglomeration due to the large number of Pt active sites. Compared with carbon black supported Pt nanoparticles, Pt/N-graphene catalysts could achieve enhanced catalytic efficiency in ORR and solve the problems in industrialization of PEMFC. Shao *et al.* [95] prepared Pt/PDDA-GNPs catalysts with outstanding catalytic per-

formance (existing Pt–C interaction). The catalytic efficiency of the Pt/PDDA-GNPs catalysts was 3-fold improved compared with Pt/C catalysts, which could gradually replace traditional catalysts on an industrial scale.

Hydrogenation

Selective hydrogenation of acetylene gas is an important step to purify olefin and obtain butadiene. The activity of precious metal Pd catalysts is degraded under high conversion conditions. Yan *et al.* [32] prepared Pd₁/graphene catalysts by depositing single Pd atoms on graphene surface (forming Pd–C coordination and Pd–O coordination). The Pd₁/graphene catalysts exhibited 100% butene selectivity and 95% conversion rate than conventional catalysts in selective hydrogenation of 1,3-butadiene



Nie *et al.* [51] fabricated Pd nanoparticles supported on N-doped RGO (Pd/N-RGO catalysts) by depositing Pd nanoparticle on N-RGO surface (forming C=C and C–N

bonds). The characterization exhibited high activity and selectivity of Pd/N-RGO catalysts in hydrogenation of phenol to cyclohexanone



Above all, it is indicated that graphene-supported metal SACs will play an important role in selective hydrogenation reactions.

Photoelectrocatalysis

In recent years, CO_2 concentration in the atmosphere constantly increases because of the large amount of fossil energy consumption, thus photoelectrocatalysis of CO_2 reduction has become an important research direction. Cheng *et al.* [55] combined the Pt-modified RGO (Pt-RGO) and Pt-modified TiO_2 nanotubes (Pt-TNT) with cathode and photoanode catalysts (existing C–O, C=O and O=C–O bonds). The liquid product generation rate (CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, HCOOH , and CH_3COOH) of approximately $600 \text{ nmol h}^{-1} \text{ cm}^{-2}$ and carbon atom conversion rate of $1130 \text{ nmol h}^{-1} \text{ cm}^{-2}$ were demonstrated ($\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$; $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$; $\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$; $\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$), which were much higher than those of Pt-modified carbon nanotubes and platinum carbon as cathode catalysts. This type of hybrid catalysts would effectively relieve global warming and develop a low-carbon economy.

So far, the research of graphene-supported metal SACs is still in the laboratory stage, and the performance is mainly focused on traditional chemical reactions such as CO oxidation. The dual advantages of SACs on graphene substrate should be exerted, and further large-scale industrial application should be applied to energy issues such as fuel cells to solve environmental problems in the future.

CONCLUSION

SACs have become an emerging trend in the field of heterogeneous catalysis in the past few years. The graphene-supported metal SACs, which combine the advantages of 2D graphene and single atom active sites, have promoted the development of SACs in the catalytic field as the medium between heterogeneous catalysis and homogeneous catalysis. Graphene-supported metal SACs could exhibit excellent catalytic ability in the fields of CO oxidation, oxidation of benzene to phenol, HER, MOR, ORR, hydrogenation and photoelectrocatalysis. With the development of techniques for preparation of high-quality graphene and SACs, graphene-supported metal SACs

may realize large-scale fabrication and industrial applications in the future, which can achieve highly efficient and green catalysis. However, as a new field, there are still some challenges in SACs. Intrinsic theoretical understanding of the origination of the high catalytic performance is still in infancy. Graphene-supported metal SACs can be fabricated *via* ALD technology, yet there are still many challenges, such as low output, large energy consumption and low control accuracy. Therefore, scientists need to continuously improve scalable preparation techniques to achieve their industrial application in the near future. In conclusion, graphene-supported metal SACs have demonstrated potential in many reactions. The market prospect of graphene-supported SACs will be broad with the effort of researchers.

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石墨烯基金属单原子催化剂: 综述

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摘要 单原子催化剂具有较高的活性、选择性和稳定性, 已成为多相催化领域的一个新兴前沿趋势. 通过将催化反应中活性金属原子的尺寸减小到单原子尺度, 单原子催化剂可以大幅提高活性金属原子在众多催化反应中的有效性. 石墨烯基金属单原子催化剂也因其独特的晶格结构和物理化学性质而备受关注, 使其在一些化学反应中表现出了优异的活性和选择性. 本文综述了近年来石墨烯基金属单原子催化剂的制备方法、先进表征手段及优点, 重点介绍了其在一氧化碳氧化、苯氧化制苯酚、析氢反应、甲醇氧化反应、氧还原反应、加氢及光电催化等方面的应用. 最后, 我们对石墨烯基金属单原子催化剂未来的产业化发展提出了建议.