

Cite this: *Nanoscale*, 2013, 5, 10765

Synthesis of graphene-supported noble metal hybrid nanostructures and their applications as advanced electrocatalysts for fuel cells

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Graphene (GN) is an emerging carbon material that may soon find practical applications. With its unusual properties, GN is an ideal platform for constructing a series of GN-based functional nanomaterials. Among them, GN/noble metal hybrids become one of the families of composite materials with extraordinary properties by combining the advantages of noble metal nanostructures and GN. The recent progress in the synthesis of GN/noble metal hybrids is presented first, such as *in situ* solution based methods, electrochemical deposition methods, self-assembly and other methods. Then, the applications of these novel GN/noble metal hybrids in fuel cells are summarized and discussed. Future research trends and challenges of design and synthesis of GN/noble metal hybrids are proposed.

Received 26th June 2013

Accepted 3rd September 2013

DOI: 10.1039/c3nr03280a

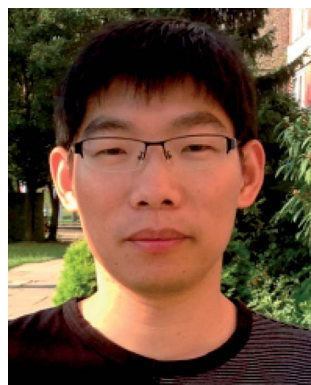
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1. Introduction

Noble metal nanomaterials with unique physical and chemical properties have received enormous attention not only for their fundamental scientific interest, but also for their many technological applications.^{1,2} Great contributions have been made in the synthesis of novel noble metal nanomaterials and their applications in catalysis, sensing, biomedical diagnosis and

therapy, energy storage and conversion, and so on.^{3,4} Recent advances revealed that rational control of the size, morphology and composition of noble metal nanostructures could provide attractive opportunities to enhance their functions and potential applications. For example, our group has synthesized a series of noble metal nanostructures with different morphologies and compositions, which were successfully investigated as advanced nanocatalysts in fuel cells and electrochemical sensing platforms.^{5–15} It can be noted that hybridization provides an effective strategy for enhancing the functionality of materials. Among them, noble metal nanomaterials (e.g., Pt, Au,

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Pd, and Ag) supported on carbon materials are one of the most widely used materials in electrochemical catalysis.^{6,9,16,17} To maximize further the activity of noble metal-derived catalysts and minimize the use of various noble metals, it is necessary to load noble metal nanostructures with high activity on the surface of supporting nanomaterials with low cost, high surface area, and good electrical conductivity, which not only maximize the availability of catalyst surface area for electron transfer but also provide better mass transport of reactants to the catalyst. To date, various carbon nanomaterials such as carbon nanotubes, carbon nanohorns and carbon black were incorporated into the hybrids to construct novel noble metal-based nanocomposites.^{18–20} Recently, graphene (GN) has received great interest and is regarded as a novel and promising support for the preparation of GN/noble metal hybrids.²¹

Graphene (GN), a two-dimensional single atomic planar sheet, has attracted tremendous and increasing attention in recent years since its discovery in 2004.²² This exciting new material has quickly sparked great interest across many disciplines because of its unique physicochemical properties: the quantum hall effect, high carrier mobility at room temperature, high Young's modulus, good optical transparency, high surface area (theoretically 2630 m² g^{−1} for single-layer GN), excellent thermal conductivity and electric conductivity, and strong mechanical strength.^{23,24} Great efforts have been made to develop GN-based nanomaterials and explore their applications in sensors,^{25–27} electronics and optoelectronics,^{28–30} electrochemical energy storage,^{31–33} efficient catalysts,^{34–36} *etc.* Up to now, a number of approaches to obtaining high-quality GN have been explored.^{22,37–39} The chemical reduction of GO has been evaluated as one of the most efficient methods for the low-cost, large-scale production of GN.^{40,41} In addition, due to abundant oxygen-containing functional groups within GO, such as hydroxyl, epoxide, carbonyl, carboxyl, *etc.*, GO possesses good solubility in solvents and provides fertile opportunities for the construction of GN-based hybrid nanocomposites and their potential applications.^{42,43} GN-based nanomaterials provide more potential to compete with the performance of their carbon nanotube-based counterparts because large-scale production with low cost and processing methods for high-quality GN has become available. Moreover, GN/noble metal hybrids have emerged as a new kind of nanocomposite which successfully integrates the unique properties of two classes of materials and exhibits some novel functions induced by the synergistic effects between GN and noble metal nanomaterials.^{44–46}

This review focuses on up-to-date research on the simple synthesis and electrochemical application of GN/noble metal hybrids in fuel cells. First, recent achievements in developing different simple approaches for the synthesis of diverse GN-supported noble metal nanostructures are summarized, such as an *in situ* solution based method, electrochemical methods, self-assembly based approaches, and so on (Fig. 1). Then, some exciting progress in the use of GN/noble metal hybrids for electrochemical application in fuel cells is also presented. Finally, we conclude with a look at the future challenges and prospects in the synthesis and application aspects of GN/noble metal hybrids.

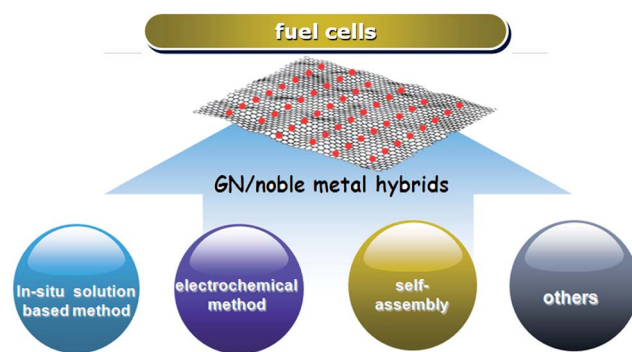


Fig. 1 The scheme of preparation of GN/noble metal hybrids and their electrochemical application in fuel cells.

2. Synthesis of GN/noble metal hybrids

2.1 *In situ* solution based method

The preparation of noble metal nanoparticles (NPs) is normally based on treating an appropriate metal salt in the presence of reducing agents and stabilizers. With regard to the synthesis of GN/noble metal hybrids, the binding sites within GN(GO) play a crucial role in anchoring the precursors of metal ions and forming the well-dispersed nanostructures on the surface of GN. As one of the most important precursors, GO with different kinds of oxygen-containing functional groups can be dispersed in water or polar organic solvents and was favorable for the synthesis of various GN/noble metal hybrids, which is advantageous over the carbon nanotube-based counterparts. Therefore, the most convenient way to prepare GN-loaded noble metal catalysts was based on simultaneous reduction of GO and metal precursors. For example, several groups have synthesized different GN/noble metal hybrids based on simultaneous reduction of GO and metal precursors in the presence of NaBH₄.^{47–55} Besides, other reducing agents such as ethylene glycol,^{56,57} formic acid⁵⁸ and ethanol⁵⁹ were also adopted to produce GN/noble metal hybrids. It should be noted that since most oxidized functional groups are removed during the reduction of GO, the resulting GN nanosheets are likely to aggregate due to the hydrophobic effect, which is unfavorable for the dispersion of the final products. Sometimes well-dispersed nanostructures on the GN are difficult to obtain due to insufficient binding sites within GO for anchoring the precursors of metal ions as well as the rapid reduction rate. Both of these are inevitably decrease the applied performances of GN/noble metal hybrids.

However, the merit of this method is that no additional stabilizing agents were added except for the GO and metal precursors. In this case, the as-made catalyst is very “clean” as a result of the surfactant free formation process, allowing it to express high performance in electrocatalysis. Recently, layer-by-layer films comprised of alternating GN and Au NPs layers were reported through vacuum filtration of a reduced GO solution.⁶⁰ Interestingly, they found that gold NPs can be easily formed by spontaneous reduction of gold ions in a gold salt solution on the GN films. After that, Tang *et al.* presented a novel and

general strategy to grow ultrafine Au clusters and other metal (Pt, Pd) clusters on the reduced graphene oxide (rGO) sheets using the same method.⁶⁴ As shown in Fig. 2A, a well-dispersed Au cluster size with an average diameter for Au clusters of 1.8 nm was well observed. The detailed formation mechanism of the Au/rGO hybrids was provided. First of all, positively charged Au(III) ions were absorbed on the surface of reduced GO *via* partial replacement. Most Au(III) ions will coordinate with the heteroatoms at the defects on the rGO sheets, which act as the initial nucleation site for Au clusters. Then rGO can act as the electron donors or the reductants for subsequent Au cluster growth on the rGO surface. It should be pointed out that the strong absorption and the moderate reduction of rGO sheets toward metal ions in the solution plays a key role in synthesizing the final product. Significantly, Pd(Pt) cluster/rGO hybrids were also successfully produced by mixing rGO sheets and metal precursors. As expected, GO could be also used as a reducing agent to reduce metal precursors. GN/GO supported Ag^{62–66} and Pd (Fig. 2B)^{44,67,68} nanohybrids were also reported in previous references. Similar to carbon nanotubes,⁶⁹ these phenomena are explained by the difference in the redox potentials of metal precursors and GO (0.48 V *vs.* SCE) or reduced GO (+0.38 V *vs.* SHE), which facilitates the reduction of noble metal ions. Due to the lack of oxygen-containing groups, GN cannot serve as a reducing agent to synthesize these GN/noble metal hybrids. However, an alternative approach, *i.e.* etching a copper/cobalt template with noble metal precursors, was also reported previously to prepare GN/Pd(Pt) hybrids.^{70–72}

As mentioned above, the size, shape and composition of noble metal nanostructures are important key parameters for their functions and potential applications. Under these circumstances, functionalization of GN/GO and the introduction of a directing/capping agent can not only be helpful to stabilize the obtained metal nanostructures, but can also avoid effectively the aggregation of the GN. Significantly, the noble metal catalysts with desired morphology and composition can be also easily controlled and synthesized on the GN-based platform. A typical example is that demonstrated by our group for the first time: a wet-chemical approach for the synthesis of high-quality 3D Pt-on-Pd bimetallic nanodendrites supported on GN. The obtained hybrid composite possessed several advantages, such as good dispersion of 3D Pt-on-Pd bimetallic nanodendrites onto the surface of GN (Fig. 3A–C).⁷³ The Pt

nanoparticle ensemble-on-GN hybrid nanosheet could be rapidly prepared through a one-step microwave-assisted heating procedure with the assistance of poly(methacrylic acid sodium salt) (Fig. 3D–F).⁷⁴ DNA was demonstrated to functionalize GN and further to guide the growth of ultrasmall Pd nanocrystals with an average size of 5 nm and uniform distribution on GN.⁷⁵ Lin's group synthesized functional GN as a general platform for *in situ* growth of Pt^{76,77} or AuPt⁷⁸ NPs using poly(diallyldimethylammonium chloride) (PDDA) as both a reducing agent and a stabilizer, which were demonstrated as promising electrocatalysts in fuel cells. Zhang *et al.* synthesized the fluorescent Au nanodots (with size ~ 2 nm)⁷⁹ and Au nanowires with alternating hexagonal close-packed (hcp) and face centered cubic (fcc) domains⁸⁰ using rGO/GO in the presence of 1-octadecanethiol and 1-amino-9-octadecene, respectively. Besides, they also synthesized square-like Au nanosheets with an hcp structure,⁸¹ which could result in an increase in its thickness and induced the hcp-to-fcc phase transformation on the GO surface.⁸² A series of GN/noble metal hybrids, such as GN/Ag,^{83,84} GN/Au,^{85,86} GN/PdAg nanorings,⁸⁷ GN/PtPd cubes⁸⁸ and GN/Au–Pd core-shell structures⁸⁹ were also reported previously. To extend the applications of these GN/noble metal hybrids, other compositions were introduced to construct GN-based ternary hybrid nanocomposites. In addition to the novel properties and a synergistic effect *via* a combination of different nanomaterials, the third composition is also beneficial to the formation of well-dispersed noble metal nanostructures on the surface of GO/GN. For example, we reported a simple, aqueous-phase route to the synthesis of two-dimensional GN/SnO₂/Pt ternary composite nanosheets. Functional 2D GN/SnO₂ was obtained through the reduction of GO using SnCl₂ in the presence of polyelectrolyte PDDA. GN/SnO₂/Pt ternary hybrid nanomaterials were generated by *in situ* reduction of negatively charged PtCl₆^{2–} precursors adsorbed on the positively charged surface of GSCN through electrostatic attraction.⁹⁰ An *in situ* reduction route to the synthesis of 2D GO/SiO₂ hybrid nanostructures consisting of Au NPs supported on the both sides of GO/SiO₂ was demonstrated *via* Sn²⁺ linkage and reduction.⁹¹ Liu

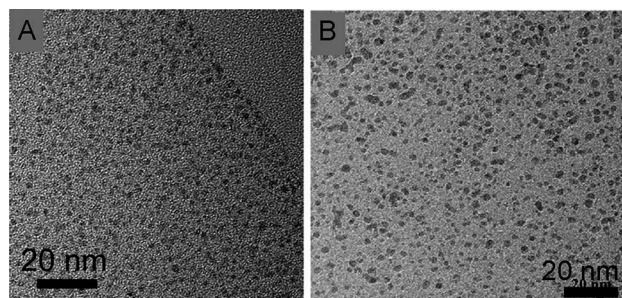


Fig. 2 TEM images of rGO/Au clusters (A) (from ref. 61 with permission) and GO/Pd hybrids (B) (from ref. 44 with permission).

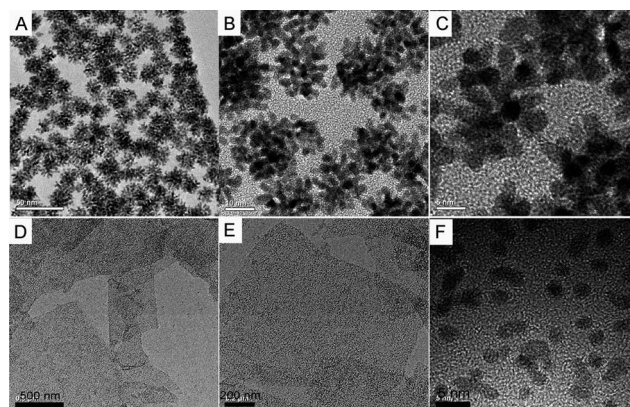


Fig. 3 TEM images of three-dimensional Pt-on-Pd bimetallic nanodendrites supported on GN (A–C) (from ref. 73 with permission) and Pt nanoparticle ensemble-on-GN hybrid (D–F) at different magnifications (from ref. 74 with permission).

et al. reported a new method to deposit indium tin oxide (ITO) and Pt NPs on GN and form stable metal–metal oxide–GN triple junctions for electrocatalytical applications. They found that ITO NPs on GN can help disperse Pt NPs and the supported Pt NPs are more stable at the Pt–ITO–GN triple junctions.⁹²

Compared to 2D GN nanosheets, 3D nanostructured GN provides a higher specific surface area and larger pore volume, and a multiple lattice-layered graphitic structure, which have been demonstrated successfully in various applications.^{93,94} Since catalyst supports with high specific surface area are highly desired, it is of great interest to fabricate the 3D nanostructured GN with increased specific surface area as a potential excellent catalyst support for noble metal nanostructures loading. Therefore, great efforts have been made to design 3D GN-based nanomaterials aiming to enlarge the specific surface area, control the pore size, layer stacking and distribution of GN and meanwhile act as supports to further enhance their applied performance. To date, the most popular method is direct synthesis of 3D GN/noble metal hybrids in the presence of GO and metal precursors. Thermal treatment has been proved to be an efficient approach to construct rationally 3D GN nanostructures.^{94,95} Significantly, GN/noble metal hybrids with 3D nanostructures could also be easily synthesized by virtue of the hydrothermal method. A typical example is a dual solvothermal process that was used to prepare ternary Pt/PdCu hollow nanocubes on 3D GN nanostructures, devised by Qu's group (Fig. 4A and B). 3D GN nanostructures with *in situ* formed hollow binary PdCu nanocubes were first fabricated *via* a one-pot solvothermal strategy. Then, the ternary Pt/PdCu nanoboxes were subsequently formed through the second solvothermal process.⁹⁶ Similarly, the same dual solvothermal approach was adopted to design ternary Pd₂/PtFe nanowires on 3D GN nanostructures (Fig. 4C and D).⁹⁷ Wang *et al.* found that the 3D assembly of GO into macroscopic porous structures could be achieved successfully with the assistance of noble-metal

nanocrystals (Au, Ag, Pd, Ir, Rh, Pt, *etc.*) under hydrothermal treatment.⁹⁸ Aside from hydrothermal approaches, ice templation of an aqueous suspension comprised of Nafion, GO, and chloroplatinic acid to form a microcellular porous network and the following mild reduction was also reported to produce 3D multifunctional GN-supported Pt NPs on a Nafion scaffold, combining electrical and ionic conductivity with porosity and catalytic activity.⁹⁹ The other method is that noble metal NPs were formed on the surface of the previously obtained 3D GN nanostructures. For example, Wang *et al.* demonstrated highly ordered multi-layered 3D GN structures decorated with Pd, Pt and Au NPs. The ability to control the morphology, distribution and size of the metal NPs on the 3D GN support upon changing the electro- and electroless-deposition conditions was stressed.¹⁰⁰ Li and colleague prepared GN/Pd hybrids using thermally treated 3D nanostructured GN as enhanced supporting material, which showed better electrocatalytic activity towards ethanol oxidation in alkaline media.¹⁰¹

2.2 Electrochemical deposition method

Electrochemical deposition has been considered to be an efficient method to produce various NPs (especially metal NPs), because it enables effective control over nucleation and growth of metal NPs. Moreover, this method is green, easy to carry out and the as-prepared nanomaterials are directly immobilized on the conducting substrate, facilitating further applications. Most researches have focused on the deposition of noble metal NPs and their alloys, these were usually used in heterogeneous catalysis, fuel cells and biosensors. It is worth noting that this method was not only applied for the synthesis of various noble metal nanostructures, but also adopted to prepare corresponding GN/noble metal hybrids.

Our group for the first time reported the electrochemical synthesis of GN from GO, greatly extending the synthesis of GN-based nanomaterials and their applications.¹⁰² Subsequently, there have been several works further researching the electrochemical reduction GO and investigating the obtained GN as electrode materials for various applications in electrochemistry.^{103,104} In combination with noble metal nanostructures, all these researches have inspired the synthesis and applications of GN/noble metal hybrids in different fields. In detail, there are two different ways to synthesize GN/noble metal hybrids based on electrochemical methods. As for indirect methods, either GO films first electrochemically reduced or GN were used as the substrate to construct further hybrid materials. Noble metals, *e.g.* Au,¹⁰⁵ Pt,^{106,107} Pd,^{108,109} bimetallic PtAu¹¹⁰ and PtPd^{111,112} NPs, were electrodeposited on the surface of GN to form GN-based composites. However, the fact that the obtained NPs electrodeposited on the surface of the GN with large size and poor dispersity made them unfavorable for electrochemical applications. Recently, Luo *et al.* illustrated that GN nanosheets could directly deposit onto a glassy carbon electrode through cyclic voltammetric reduction of a GO colloidal solution.¹¹³ Thereafter, alternative one-step electrochemical method to the synthesis of GN/noble metal hybrids (Au^{114,115} and Pd¹¹⁶) was also proposed under cathodic conditions (Fig. 5). It should be

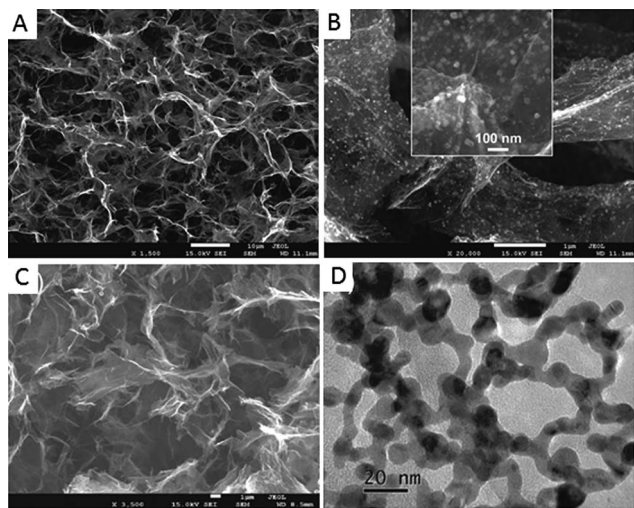


Fig. 4 SEM images of the Pt/PdCu nanocubes (A and B) (from ref. 96 with permission) and Pd₂/PtFe nanowires (from ref. 97 with permission) (C and D) on 3D GN nanostructures.

noted that the electrochemical reduction of GO and the formation of noble metal nanostructures takes place simultaneously. The resulting composite exhibited layered nanostructures consisting of alternating layers of well-dispersed metal NPs and GN sheets.¹¹⁴

2.3 Self-assembly between GN and noble metal nanostructures

Self-assembly is an important and effective strategy for nanofabrication that involves self-organizing the building blocks into functional structures by different driving forces. The most important driving force for self-assembly is the interaction between building blocks that range from atoms and small molecules to particles, macromolecules, and polymers. GN can be a promising building block in the hybridization with various noble metal NPs. Through electrostatic interaction, cationic materials (e.g. polyelectrolyte,^{117,118} ionic liquid¹¹⁹) were utilized to synthesize functional GN as the building block in the self-assembly of GN/noble metal hybrids to enhance the electrochemical catalytic ability and SERS signals. Our group synthesized GN-mesoporous silica-gold nanoparticle hybrids through a self-assembly approach and utilized this functional material as an enhanced electrochemical platform to detect sensitively DNA,¹²⁰ chiral D-vasopressin¹²¹ and adenosine triphosphate.¹²² Through electrostatic self-assembly, OD GN quantum dots (GQDs) located near AuNCs showed enhanced fluorescent intensities and improved photostabilities, which allowed specific visualization of the epidermal growth factor receptor on cancer cells.¹²³ Proteins are complex amphiphilic biopolymers, featuring hydrophobic and hydrophilic patches on their surfaces, which makes them well-known for the adhesiveness to solid surfaces. As shown in Fig. 6, Deng *et al.* demonstrated that GO can be readily reduced and decorated by BSA, resulting in an extremely versatile and highly efficient self-assembly platform to create GN/noble metal hybrids.¹²⁴ Qu's group synthesized GO/Au nanoclusters through the self-assembly between GO and protein stabilized Au nanoclusters, which showed excellent peroxidase-like activity over a broad pH range and had great potential for the next generation of mimetic enzyme systems.¹²⁵ Sun *et al.* found that mixing the hexane dispersion of FePt⁴⁵ and Pd¹²⁶ NPs and the DMF solution

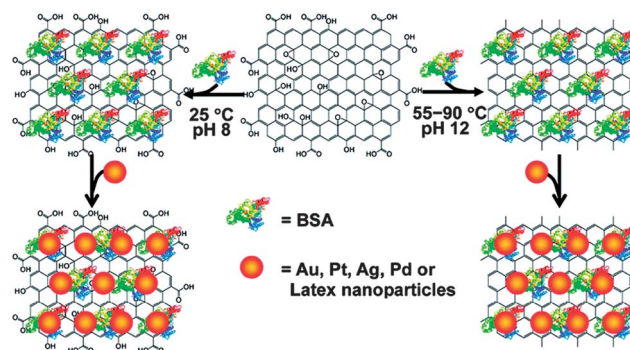


Fig. 6 Protein-based decoration and reduction of GO, leading to a general nanopatform for nanoparticle assembly (from ref. 124 with permission).

of GN sheets under sonication led to direct assembly of one layer of NPs on GN. GN was proved to be an ideal support to improve NP activity and durability for practical catalytic applications in fuel cells. Besides, 3D GN/noble metal hybrids film based on layer-by-layer assembly were also reported,^{119,127,128} which found wide applications in various fields. It should be noted that the main advantage of this self-assembly strategy stems from the highly desirable size- and shape-dependent nanostructures, free from GN modification, which greatly enhance their functionalities.

2.4 Other methods to synthesize GN/noble metal hybrids

Other methods, including physical vapor deposition,¹²⁹ heat-treatment,^{130,131} magnetron sputtering¹³² and laser synthesis¹³³ are also used to prepare noble metal GN/noble hybrids, as they can also provide excellent control over the size, shape and uniformity of the noble metal nanostructures. A typical example is the growth of metallic NPs formed on GN by physical vapor deposition, which has been investigated. A variety of noble metals with different morphologies was obtained. They found that GN-metal interaction is important for controlling nanoparticle and thin-film growth on GN.¹²⁹ Pt nanoclusters of varying thickness are deposited on porous GN nanoflakes using magnetron sputtering have been investigated as supports for catalytic Pt nanoclusters in direct methanol electro-oxidation, and their effects on the electrocatalytic activity for oxidizing methanol are systemically studied.¹³² Although GN/noble metal hybrids have been successfully synthesized through these methods, they still suffer from the need for special and expensive equipment and lack of large-scale production.

3. Electrochemical applications of GN/noble metal hybrids in fuel cells

The ever-increasing use of fossil fuels, coupled with the limited supply of these natural resources, has motivated the serious search for renewable and sustainable sources of energy. In various applications, proton exchange membrane fuel cells (PEMFCs) have become attractive competitors in transportation and electrical power generation, especially for mobile and portable applications due to their exciting performance.¹³⁴⁻¹³⁶

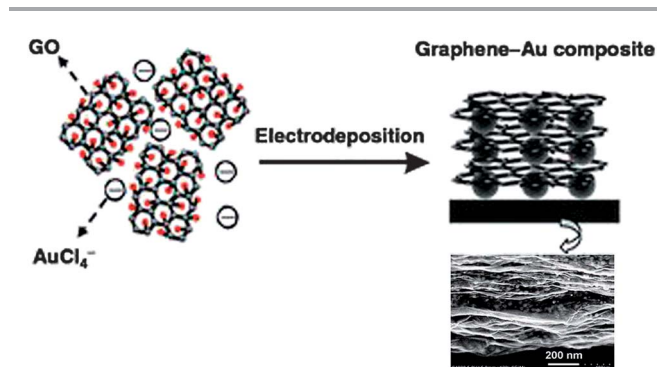


Fig. 5 The typical scheme of production of GN/Au nanocomposites and their SEM image (from ref. 114 with permission).

Despite their great potential as an efficient device to convert chemical energy into electric energy, PEMFCs do have their own serious limitations that prevent them from being scaled-up for commercial applications. Both the fuel oxidation reaction and the ORR need a catalyst to lower their electrochemical over-potentials and to obtain high voltage output, and Pt-based nanomaterials have been the universal choice of catalyst for both reactions. Therefore, developing advanced nanoelectrocatalysts and thus improving the performances of fuel cells is highly desirable and remains a great challenge. GN has been extensively used in electrochemistry because of its low price, suitable electrocatalytic activity for a variety of redox reactions, broad potential window, and relatively inert electrochemistry.¹³⁷ Combining the excellent electrocatalytic activities of noble metal nanostructures with the supporting effect of GN, GN/noble metal hybrids have emerged as a novel kind of nanocomposites and received great attention in electrocatalysis.

3.1 Anodic oxidation

GN-based nanomaterials are considered to be excellent electrocatalyst supports in fuel cells. In order to further maximize the activity of noble metal-derived catalysts and minimize the use of various noble metals, it is necessary to load noble metal nanostructures with high activity on the surface of supporting nanomaterials with low cost, high surface area, and good electrical conductivity, which not only maximize the availability of catalyst surface area for electron transfer but also provide better mass transport of reactants to the catalyst. Besides, according to density function theory (DFT) calculations, the binding between metal and GN would result in charge transfer across the metal–GN interface, changing the Fermi level of both the metal and GN, and thus enhancing their catalytic activity and stability.^{45,126,138} The most part of GN-supported noble metal catalysts has been evaluated for a potential application as anode materials in direct methanol fuel cells.^{47,71,73,130,131,139–143} For example, our group synthesized high-quality 3D Pt-on-Pd bimetallic nanodendrites supported on GN nanosheets (TP-BNGN), which represents a new type of GN/metal heterostructure. As shown in Fig. 7, TP-BNGN showed higher electrochemical surface area (ECSA) with respect to Pt and E-TEK Pt/C. At the same time, TP-BNGN also exhibited higher mass current density, better cyclic stability as well as higher tolerance to the poisoning species.⁷³ This good electrocatalytic activity was ascribed to the following factors: (i) the size of Pt nanobranches is comparable to commercial nanocatalysts; (ii) the bimetallic dendritic NPs could provide high ECSA, thus leading to high electrocatalytic activity; (iii) better dispersion of dendritic NPs on the GN nanosheets with high surface area should be also emphasized towards methanol oxidation. Cai *et al.* investigated the effects of structure, composition, and carbon support properties on the electrocatalytic activity of GN/PtNi nanocatalysts for the methanol oxidation.¹⁴¹ As shown in Fig. 8A, it is clear that the electrocatalytic activity including onset potential and peak current was evidently improved when alloyed with Ni. Moreover, the composition-dependent electroactivity was well observed and highest activity could be obtained

at a Pt/Ni molar ratio of 1 : 1 (curve c). Also, compared with SWCNT/PtNi and C/PtNi catalysts, the obtained GN/PtNi hybrids exhibited higher activity due to lower metal particle size (Fig. 8B). More importantly, the oxygen-containing functional groups of GN improve the electrocatalytic activity by removing accumulated carbonaceous species that are formed during the oxidation of methanol.¹⁴¹

In addition to methanol, the catalytic activity of GN/noble metal hybrids for the oxidation of ethanol^{96,101,108,111,140,144} and formic acid^{49,97,145,146} has also been investigated. To decrease the loss of electroactive sites during the electrochemical process induced by the strong planar stacking of GN, Qu's group developed the shape-defined ternary Pt/PdCu nanoboxes anchored onto 3D GN framework as a new complex catalyst system, which showed a higher activity for ethanol electro-oxidation.⁹⁶ Niu *et al.* prepared a GN/AuPd alloy nanostructure *via* facile self-assembly between ionic liquid-grafted GN and hollow alloy NPs. The resulting GN/AuPd alloy nanostructure exhibited striking electrocatalytic activities towards formic acid because of the very good electrical conductivity of GN and unique alloy nanostructures.¹⁴⁵

3.2 Oxygen reduction reaction (ORR)

ORR is the most studied and strongly determines the overall performances of fuel cells directly. To date, many contributions have addressed the activity of the ORR of GN/noble metal hybrids.¹⁴⁷ Similarly to anode catalysts, GN loaded noble metal catalysts were verified to remarkably enhance the electrocatalytic activity and durability for ORR in fuel cells. 2D GN was proved to be the most promising candidate for a catalyst support in ORR and many research groups have developed various GN/noble metal hybrids and successfully used them as advanced catalysts in fuel cells.^{45,46,61,66,76,87,119,148–151} Significantly, GN supports have exhibited superior ORR characteristics and more robust performance compared to those of CNTs and carbon black supported counterparts, indicating their potential application for catalyst support in ORR.^{76,151} For instance, our group succeeded in constructing a hybrid 3D nanocomposite film by alternatively assembling the GN-IL and Pt NPs. The newly prepared 3D nanomaterials containing GN-IL and Pt NPs showed high electrocatalytic activity toward ORR. Furthermore, the electrocatalytic activity of the films could be further tailored by simply choosing different cycles in the LBL process.¹¹⁹ GN supported Au clusters with an average diameter of 1.8 nm were also synthesized. Owing to the small size effect, the clean surface of Au the clusters and the synergetic coupling effect between Au clusters and GN, the GN/Au clusters hybrids exhibited excellent electrocatalytic performance toward ORR, which has a comparable onset potential to commercial Pt/C catalyst, but superior methanol tolerance and enhanced electrocatalytic stability.⁶¹ To further enhance the ORR activity, GN/PtM alloy NPs as ORR catalysts have been also explored.^{45,152,153} As shown in Fig. 9A, Sun *et al.* assembled FePt NPs on the GN surface *via* a facile solution-phase self-assembly method.⁴⁵ Obviously, GN/FePt NPs exhibited better electrocatalytic activity toward ORR than C/FePt and C/Pt NPs at the same Pt loading

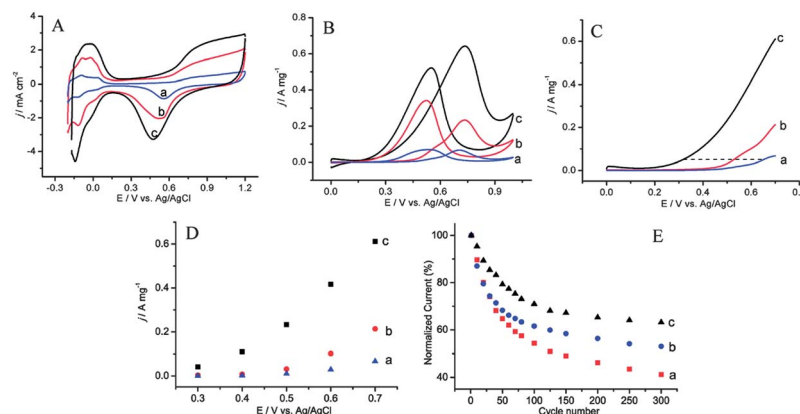


Fig. 7 (A) CVs of PB (trace a), E-TEK catalyst (trace b), and TP-BNGN (trace c) modified glassy carbon electrodes in a N_2 -sparged 0.5 M H_2SO_4 solution at the scan rate of 20 mV s^{-1} . CVs (B) and linear sweep voltammetry (C) of PB (trace a), E-TEK catalyst (trace b), and TP-BNGN (trace c) modified glassy carbon electrodes in a 0.5 M H_2SO_4 solution containing 1 M methanol at the scan rate of 50 mV s^{-1} . (D) Potential-dependent current density of methanol electrooxidation on the PB catalyst (a), E-TEK catalyst (b), and TP-BNGN (c). (E) Electrocatalytic cycling stability of E-TEK catalyst (curve a), PB (curve b), and TP-BNGN (curve c) (from ref. 73 with permission).

(Fig. 9B and C). The excellent stability was also featured by the fact that there is nearly no activity change in the ORR polarization curve after 10 000 potential sweeps (Fig. 9D).

GN/noble metal hybrid based multicomponent hybrids have received considerable interest, which not only avoid the stacking of GN but also provide functional electrocatalysts for ORR. For instance, ORR stability of the Pt NPs could be further improved by attaching Pt to ITO NPs on GN because of the forming metal-metal oxide-GN triple junctions (Fig. 10).⁹² Both experimental work and periodic density functional theory (DFT) calculations show that the supported Pt NPs are more stable at the Pt-ITO-GN triple junctions. Furthermore, DFT calculations suggest that the defects and functional groups on GN also play an important role in stabilizing the catalysts. Besides, nanocomposites prepared by well-mixing carbon black (CB) with Pt-loaded GN could efficiently prevent the stacking of GN and promote diffusion of oxygen molecules through the GN nanosheets and enhancing the ORR electrocatalytic activity. It is suggested that the unique 2D profile of the GN functioned as a barrier, preventing leaching of Pt into the electrolyte, and the CB in the vicinity acted as active sites to recapture/renew the dissolved Pt species. The accelerated durability test demonstrates that the hybrid supporting material

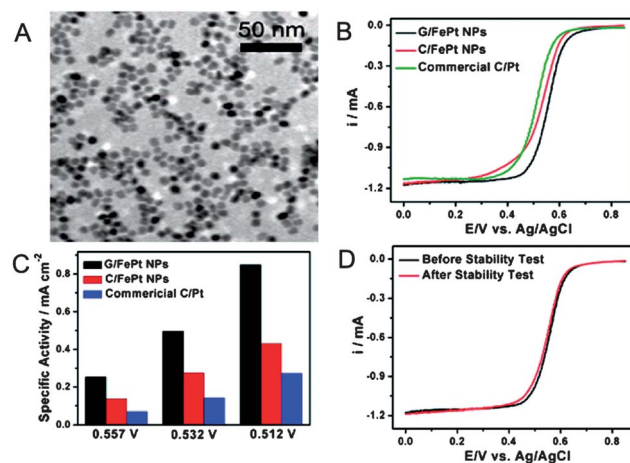


Fig. 9 (A) TEM images of GN/ FePt_{78} NPs. (B) Polarization curves for ORR in O_2 -saturated 0.1 M HClO_4 solution at 295 K. The potential scan rate was 10 mV s^{-1} and the electrode rotation speed was 1600 rpm. (C) ORR specific activities of the GN/ FePt_{78} , C/ FePt_{78} , and commercial C/Pt catalysts, with Pt loading amounts of 14.3, 14.6, and 8 μg , respectively. (D) ORR polarization curves of the GN/ FePt_{78} NPs before and after 10 000 potential sweeps between 0.4 and 0.8 V (from ref. 45 with permission).

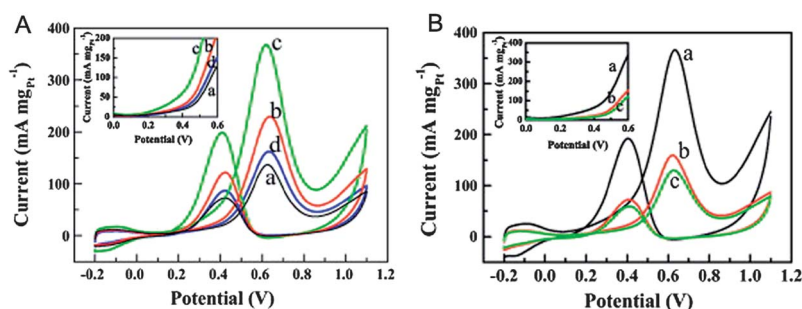


Fig. 8 (A) The voltammetric responses of the oxidation of 0.5 M methanol at the GN/Pt (a) and the GN/PtNi electrode with a Pt/Ni molar ratios of 1 : 0.5 (b), 1 : 1 (c), and 1 : 2 (d) in a 0.5 M H_2SO_4 solution. (B) The voltammetric responses of the oxidation of 0.5 M methanol in a 0.5 M H_2SO_4 aqueous solution at the PtNi catalyst with a Pt/Ni molar ratio of 1 : 1 supported on GN (a), SWNTs (b), and XC-72 carbon (c). The scan rate was 50 mV s^{-1} (from ref. 141 with permission).

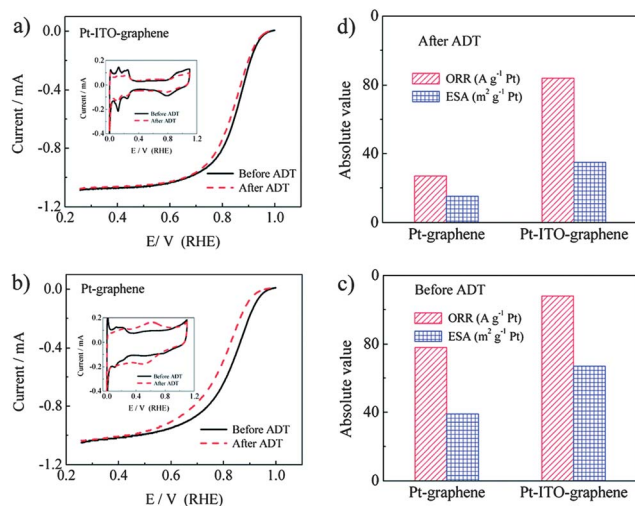


Fig. 10 Linear sweep voltammetry polarization curves of oxygen reduction on Pt-ITO-GN (A) and Pt-GN (B) in O₂-saturated 0.1 M HClO₄ (5 mV s⁻¹, 1600 rpm). Inset: cyclic voltammograms on Pt-ITO-GN and Pt-GN in N₂-saturated 0.1 M HClO₄ (50 mV s⁻¹). (C and D) Electrochemically active surface area and ORR kinetic currents before and after 22 h accelerated degradation test (ADT) (from ref. 92 with permission).

can dramatically enhance the durability of the catalyst and retain the electrochemical surface area of Pt.⁴⁶ Besides, GN-Pt NPs impregnated with the ionic liquid¹⁵⁰ and PdAg nanorings supported on GN⁸⁷ were also reported, both of which exhibited enhanced electrocatalytic activity and excellent methanol tolerance for ORR.

4. Conclusions and perspectives

As a new and very promising class of functional materials, GN/noble metal hybrids are one of the families of composite materials with extraordinary properties obtained by combining the advantages of noble metal nanostructures and GN. Recent achievements in developing different simple approaches for the synthesis of diverse GN-supported noble metal nanostructures are summarized, such as *in situ* solution based methods, electrochemical methods, self-assembly based approaches, and so on. In the meantime, this review highlights the electrochemical application of GN/noble metal hybrids in fuel cells. Although great contributions were made in the synthesis and electrochemical applications of GN/noble metal hybrids, there are still some challenges: (1) well-defined noble metal nanostructures, with small size, abundant morphological characteristics and good dispersion on the GN surface are greatly desirable for applications. (2) The mechanism for the controlled growth of specific noble metal architectures on the GO/GN surface is still be elusive and needs to be deeply explored. (3) Maintaining the good dispersion of 2D GN and making full use of properties of GN should be considered simultaneously to optimize the high performance of GN/noble metal hybrids. (4) Multicomponent composites involving GN/noble metal hybrids need to be rationally and systematically designed to extend their potential applications. The nature of interfacial interactions between the active

metal phase and the support materials should be well tuned and optimized, which is considered to be the key factor to achieve high performance. Further experimental research and theoretical calculation are still necessary to understand clearly the detailed mechanisms. Despite being in the infancy of their research, it is easy to foresee that GN/noble metal hybrids may find promising potential applications in various fields, such as electrochemical energy storage, electrochemical sensors, and so on.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (no. 20935003 and 21075116) and 973 Project (no. 2011CB911002 and 2010CB933603).

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