Graphdiyne Based Atomic Catalyst: an Emerging Star for Energy Conversion

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Atomic catalysts(ACs) consisting of zero-valent metal atoms anchored on supporting materials have shown promising potentials in catalysis and energy conversion due to their higher atomic utilization, higher selectivity, activity and durability toward target reactions. However, traditional single-atom catalysts are mainly composed of clusters of metal atoms, which cannot effectively solve the problems of easy migration and aggregation of metal atoms. Besides, the traditional synthesis methods still lack breakthroughs in improving the stability and accurately controlling the chemical structure and charge distribution of metal atoms, which seriously limits the understanding of structure-activity relationship and catalytic mechanism in the catalytic reaction process at the atomic level. Graphdiyne(GDY) based ACs are stabilized by incomplete charge transfer between metal atoms and supporting materials, resolving the easy migration and aggregation of traditional single atomic catalysts, which have been regarded as the next generation of catalysts. This review will start with the overview of the synthesis methods for precisely anchoring of different zero-valent transition metal atoms(*e.g.*, Ni, Fe, Mo and Cu) and noble metal atoms(*e.g.*, Pd and Ru), followed by focusing on the recent advances in the researches of the ACs toward a series of important reactions for energy conversion technologies, including the electrochemical water splitting(EWS), nitrogen reduction reaction(NRR), oxygen reduction reaction(ORR) and others. Finally, the review concludes with a perspective highlighting the promises and challenges in the further development of ACs.

Keywords Graphdiyne; Atomic catalysis; Atomic catalyst; Energy conversion

1 Introduction

Singly-dispersed metal atoms have promising potentials in catalysis and energy conversion due to the high atomic utilization, high activity and high durability toward target reactions. Scientists have made many important contributions to the basic and applied research on single-atom catalysts[1—33]. In 2011, Zhang and co-workers[1] prepared Pt_1/FeO_x single-atom catalyst by loading platinum atoms on iron oxide substrates, exhibiting excellent catalytic performances in CO oxidation reaction. Afterwards, various types of single-atom catalysts were reported. For example, Bao and coworkers[13] reported the iron single-atom catalyst loaded on Si for the efficient synthesis of ethylene and aromatics from methane in the absence of oxygen. Li and Wu[33] reported Cu-SAS/N-C single-atom catalyst for oxygen reduction(ORR) performance. In recent years, large amounts of single-atom catalysts have been reported by loading transition metal atoms(*e.g.*, Fe[13,14,27,34], Co[15,28]) and noble atoms(*e.g.*, Pt[1,5,7—9,20—24], Pd[3,16—18,25], Rh[30,31], Ir[32], Ru[35], Au[6,10,11,19,26], Ag[4,12]) on different supporting materials. The survey entails that traditional single-atom catalysts are generally loaded on the supporting materials by forming metal alloys, clusters, oxygen vacancy[1,5—11,18,19,21,25], or engineered defects on traditional carbon materials[14—16,36—39]. Unfortunately, the traditional preparation methods of single-atom catalysts still lack breakthroughs in (i) improving the stability of metal atoms because of the agglomeration during the synthesis and/or reaction processes; (ii) synthesizing atomic catalysts with a determined valence of the metal atoms and the structure of the support materials; (iii) accurately controlling the chemical structure and charge transfer during the catalytic process, which seriously limits the understanding of structure-activity-relationship and catalytic mechanism at the atomic level.

Graphdiyne(GDY) is a novel two-dimensional carbon allotrope, in which each benzene ring(sp^2-C) is linked by six butadiyne linkages(—C≡C—C≡C—, sp-C). Since the first successful synthesis in 2010 by Prof. Li[40—44], GDY has rapidly attracted the wide attention of scientists from different disciplines in the world, and rapidly forms a new field, and has shown great potentials in various fields(*e.g.*, catalysis, energy conversion[45—67], energy storage[68—81], solar cells[82—89], etc.) due to its unique structure and fascinating properties(*e.g.*, alkyne-rich structure, natural pores, large π conjugation, natural direct band gaps, high conductivity and stability, etc.). Importantly, superior to the traditional carbon materials, such as graphene and carbon nanotubes, which contain only sp^2 hybridization, the unique sp/sp^2-cohybridization nature of GDY makes the π/π^* can rotate toward any direction perpendicular to —C≡C— and more possible to point toward metal atoms[90]. Benefiting from these unique advantages, GDY

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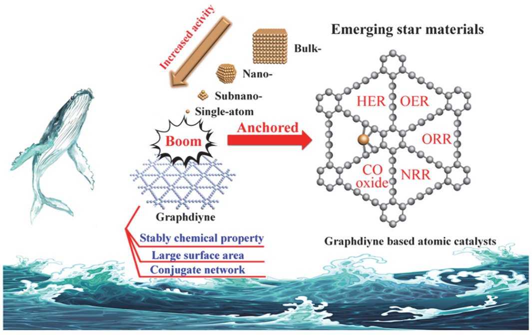

Fig.1 Preparation of GDY-based atomic catalysts and their potential applications

provides a new idea for the synthesis of atomic catalysts with a clear chemical structure, determined valence state and high stability.

In 2018, Li and coworkers[46] for the first time anchored zero-valent transition metal atoms on GDY(Fig.1), exhibiting excellent catalytic performances for hydrogen evolution reaction(HER) closed to Pt/C under acidic conditions. The electron-donating effects, the spatially confined effects of GDY, and the special incomplete charge transfer between metal atoms and GDY endow the catalyst with excellent catalytic activity and stability, resolving the easy migration and aggregation of traditional single-atom catalysts. This is the first reported zero-valent metal atom catalysts, and they named it atomic catalyst(AC). GDY-based AC is of great academic significance for researchers to clearly understand the anchoring process of single atoms on the support, the interaction of metal atoms with the support, the energy, electron transfer and conversion behaviors in the system, and the relationship between the catalytic performance and the above scientific issues. Its discovery will lead the rapid development of catalysis science. Following Prof. Li's pioneering work, a great number of theoretical and experimental efforts have been dedicated to the understanding of the properties and applications of GDY-based ACs. In this review, we start from the geometric and electronic structures of single metal atoms anchored on GDY. Then, we describe the methods for synthesizing GDY-based zero-valent ACs and the advanced characterization technologies for analyzing the structures of the GDY-based zero-valent ACs at the atomic level. We also summarize the important catalytic applications of the GDY-based ACs and structure-reactivity correlations of metal atoms anchored on GDY. In final, perspectives on the future developments in this field are given.

2 Synthesis of GDY-based Zero-valent Metal Atomic Catalysts

Downsizing the size of the bulk catalysts to atomic scale(single metal atoms) can maximally increase the atom-utilization efficiency and maximize the number of active sites, which is beneficial for improving the intrinsic catalytic activity. However, single atoms would easily migrate and aggregate on the surface of traditional supports like graphene during the preparation and/or catalysis processes due to their high surface free energy[91]. It is important to search appropriate supporting materials and effective methods for the dispersion and stabilisation of single metal atoms. As described above, the special chemical and electronic structures of GDY endow it with unique superiorities for anchoring single metal atoms.

Scientists have long been looking forward to the emergence of zero-valence transition metal atomic catalysts. Unfortunately, previously reported single metal atoms were suffered from undermined valence states(positive or mixed) and inaccurate chemical structures due to the complicated and harsh synthesis conditions. The zero-valence transition metal atomic catalyst is a great challenge in the field of catalysis and has not been synthesized, yet graphdiyne exhibited unique characteristics to overtake this challenge. Widespread triple carbon bonds could anchor metal atoms through the overlapping of *p-d* molecular orbitals. By utilizing the acetylene-rich and pore structure of GDY, and the interactions between GDY and metal atoms, and combining the spatial-confined effect of the porous structure, zero-valence atomic catalysts were successfully synthesized by our group[46] for the first time across the world, which has been widely regarded as the great breakthrough in the field of catalysis.

In 2018, our group[46] reported a novel one-step strategy for controllably anchoring zero-valence transition metal atoms (Ni and Fe) on the surface of GDY(Ni^0/GDY and Fe^0/GDY) through a simple electrochemical deposition[Fig.2(A)]. Typically, a piece of freshly-prepared GDY electrode was immersed in 0.5 mol/L H_2SO_4 solution containing Ni^{2+}(or Fe^{3+}) ions for the adsorption of metal atoms. This was followed by the electrochemical reduction treatment under galvanostatic conditions at a constant current density of 10 mA/cm^2 with finely tuned reduction current density and reduction time at room temperature. The resulted samples were carefully washed by 0.5 mol/L H_2SO_4, deionized water and 0.5 mol/L H_2SO_4, respectively. High-angle annular dark field(HAADF) imaging has been widely employed to study the configuration of single metal atoms. In normal observations, anchored metal atoms are brighter than the base owing to their higher atomic number. X-Ray absorption spectroscopy(XAS), which is one of the most powerful tools for depicting local structures, is usually used to analyse the chemical environment and the status of atoms. The XAS spectrum can be divided into X-ray absorption near edge structure(XANES) and extended X-ray absorption fine structure(EXAFS). XANES analysis is performed to characterize the geometric configuration and

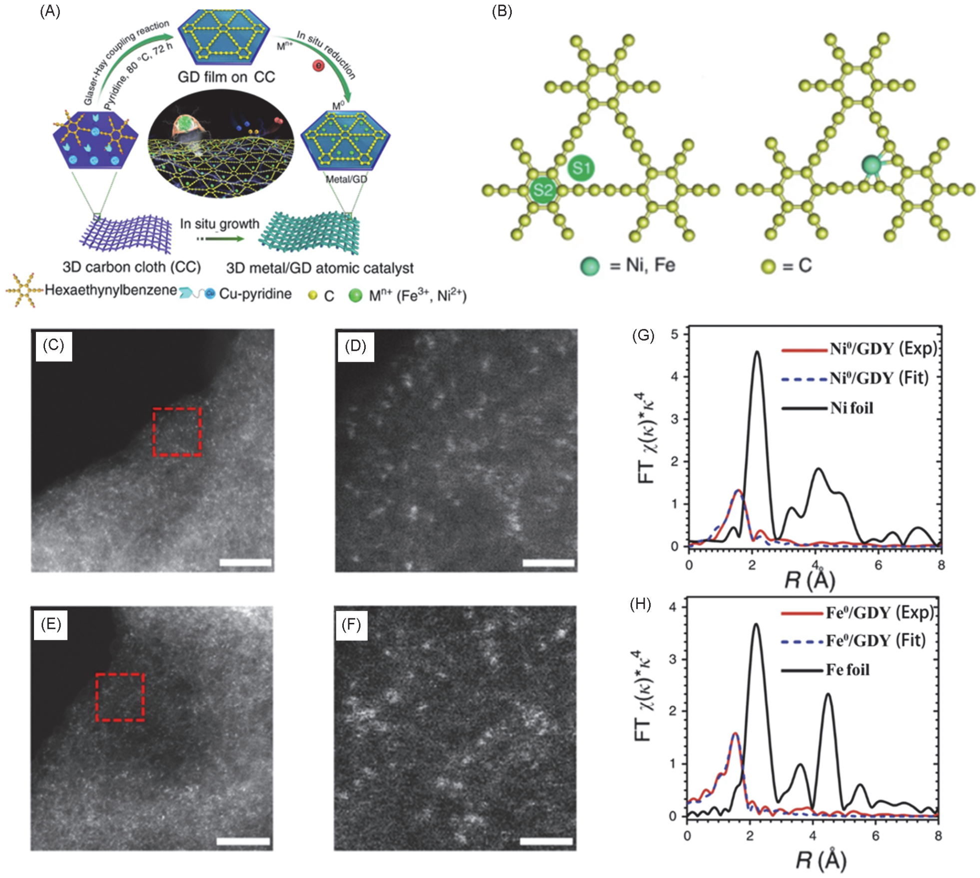

Fig.2 Diagram for anchoring of Ni^0/GDY and Fe^0/GDY(A), possible atomic adsorption sites(left) and the optimized configuration (right)(B), HAADF-STEM images of Ni^0/GDY(C, D), HAADF-STEM images of Fe^0/GDY(E, F), and *ex situ* EXAFS spectra of Ni^0/GDY(G) and Fe^0/GDY(H)

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electronic structure of metal atoms in the surrounding environment. And the coordination environment of atoms can be identified through EXAFS. As observed through HAADF-STEM, isolated Ni/Fe atoms(white dots) were dispersed at the atomic level on GDY. Subangstrom-resolution high-angle annular dark field-scanning transmission electron microscopy[HAADF-STEM, Fig.2(C)—(F)] and the extended X-ray absorption fine structure[EXAFS, Fig.2(G) and (H)] spectra confirmed that the metal atoms were isolatedly and uniformly anchored on GDY. Additional histogram analysis reveals that the size distributions for Ni and Fe are (0.123±0.04) nm and (0.102±0.033) nm, respectively, which are consistent with the typical sizes of single Ni and Fe atoms. The X-ray absorption near-edge structure(XANES) results and theoretical calculations were further employed to determine the valence states of the metal atoms. The derivative XANES spectra confirmed that the Ni and Fe anchored on GDY were at zero valences. In order to determine the structural stability of the GDY-based ACs, XANES and EXAFS spectra were measured after the hydrogen reduction(5% H_2/He) at different temperatures of 50, 100 and 150 °C for 30 min, respectively, and showed that the Ni and Fe atoms in Ni^0/GDY and Fe^0/GDY still were metallic states before and after hydrogen reduction. To gain a deeper insight into the states of Ni(Fe) atoms in Ni^0/GDY(Fe^0/GDY), theoretical studies were performed. The potential energy surface scanning results confirmed that the S1 site[Fig.2(B)] was more energetic favorable than the S2 site for the anchoring of metal atoms. Our results revealed that the metal-C bonding in GDY-based ACs was the orbital charge overlaps rather than the conventional covalent/ionic bond. The unique incomplete charge transfer between single metal atoms and GDY is beneficial for their stability, electrical conductivity and catalytic activity.

Recently, Hui *et al.*[64] successfully stabilized zero-valence copper atoms on GDY surface(Cu^0/GDY), which exhibited superior hydrogen evolution reaction(HER) performance to commercial 20%(mass ratio) Pt/C. The formation energy calculation results showed that the Cu atoms preferred to locate at the corner of the acetylenic ring. After anchoring the Cu on GDY[Fig.3(I)], the strong *p-d* coupling connected localized charge along nearly all edges of the acetylenic ring, resulting in the optimal charge exchange properties. The HOMO charge densities were concentrated within the Cu—C bonding area. C1—Cu—C1 and C2—Cu—C2 were

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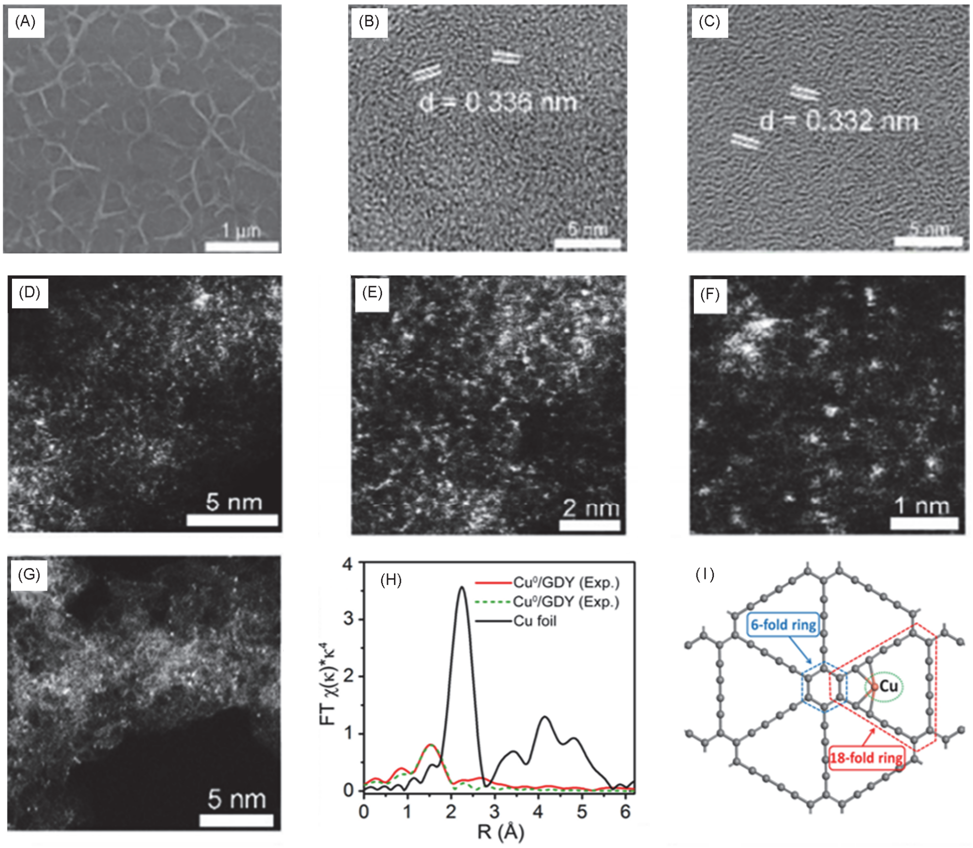

Fig.3 SEM image of GDY foam(A), TEM images of GDY(B) and Cu^0/GDY(C), HAADF-STEM images of Cu^0/GDY(D—G), *ex situ* EXAFS spectra of Cu^0/GDY and Cu foil(H), and schematic representation of Cu^0/GDY(I)

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demonstrated to be two potentially useful charge transfer channels for HER catalysis. Theoretical further revealed the fast charge exchange behavior and formation of the zero-valent single Cu atoms by strong *p-d* coupling induced charge compensation. These theoretical studies indicate that GDY should be an ideal support for anchoring Cu^0. Scanning electron microscopy(SEM) and transmission electron microscopy(TEM) confirmed the formation of GDY nanosheets array on carbon fiber[Fig.3(A) and (B)]. There were no observable changes in the morphology, indicating the robust nature of GDY. The high-resolution TEM images showed a smaller spacing distance of Cu^0/GDY(0.332 nm) than pristine GDY(0.336 nm), which might be due to the strong interactions between adjacent GDY layers[Fig.3(C)]. Atomic-resolution HAADF-STEM, SEM, TEM, HRTEM and EXAFS results further confirmed the high dispersion of isolated Cu^0 on the surface of GDY[Fig.3(D)—(H)]. Cu LMM auger spectra solidly demonstrated that the Cu atoms anchored on GDY were zero-valent. XPS valence band(VB) spectra revealed the higher conductivity of Cu^0/GDY than that of GDY. These advantages of Cu^0/GDY would be greatly useful for enhancing the catalytic activity.

Zero-valent palladium-based materials have been demonstrated to be the active centres in many reactions. However, no zero-valent Pd AC has been reported. Until very recently, our group[45] obtained the first zero-valence Pd AC(Pd^0/GDY) by using the *in-situ* reduction method. HAADF-STEM images[Fig.4(A)—(H)] and the EXAFS spectrum [Fig.4(I)] of Pd^0/GDY clearly showed the isolated and uniform dispersion of single Pd atoms on GDY. The XANES and pre-edge derivative of XANES spectra of Pd^0/GDY showed that the main peaks of Pd^0/GDY and Pd foil were located at the same energies, indicating the zero-valence of Pd atoms [Fig.4(J)]. Theoretical studies revealed that the single Pd atoms could anchor on GDY in two cases: (i) one Pd atom singly anchored at the corner of the acetylenic ring and (ii) three Pd atoms triply anchored at the corner of the acetylenic ring[Fig.4(K)]. Further investigation showed that the strong *p-d* charge transfer occurred to activate the *d* electrons from the Pd atom onto the C1 and C2 sites for H atom adsorption [Fig.4(L)], indicating the high HER catalytic activity for Pd^0/GDY.

As above-discussed, the emergency of GDY-based ACs is a great breakthrough for the controllable design and synthesis of atomic catalysts with accurate structures and determined valence states, getting rid of the complicated and harsh

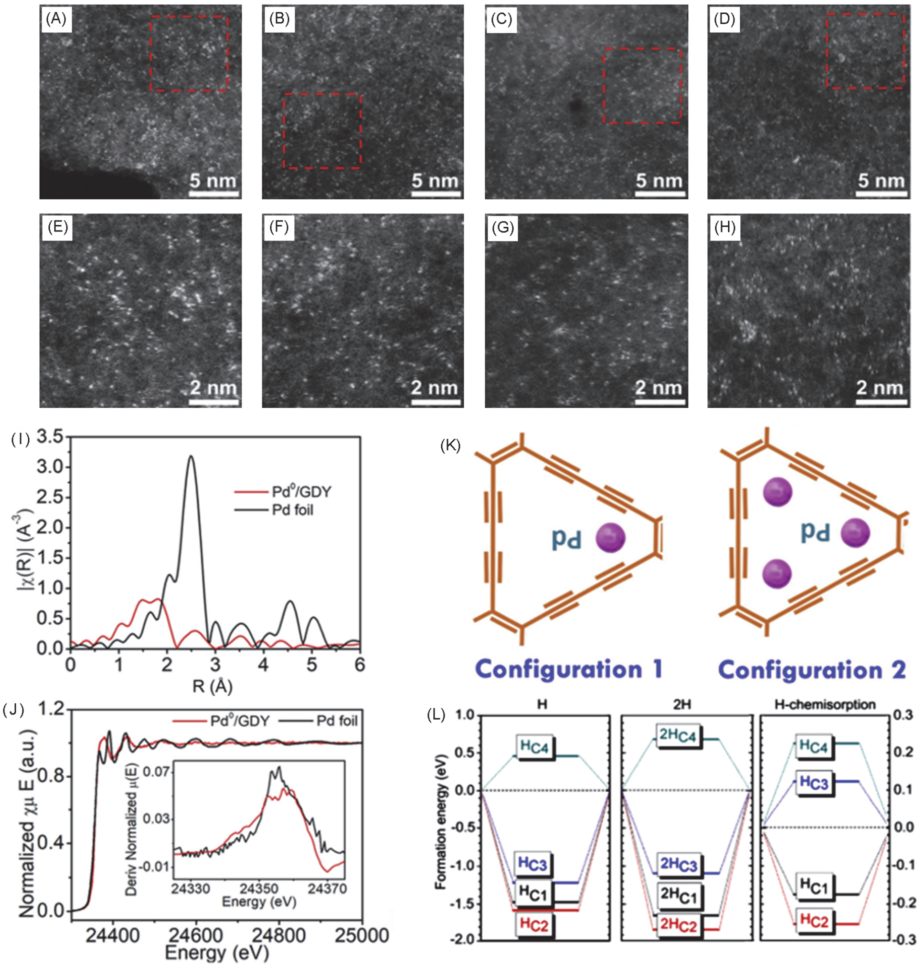

Fig.4 HAADF-STEM images of Pd^0/GDY(A—H), *ex situ* EXAFS spectra of Pd^0/GDY and Pd foil at the Pd *K*-edge(I), normalized Pd *K*-edge XANES spectra and fit curves(the inset) of Pd^0/GDY(J), structural configuration for singly(left) and triply(right) anchoring sites(K), and adsorption formation energies of H and 2H on four different C atom sites(L)

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preparation processes of traditional preparation methods[45—47,64].

3 Applications

Compared with the conventional single-atom catalysts, GDY-based zero-valent ACs feature accurate chemical/electronic structures, determined valence state, and incomplete charge transfer between metal atoms and supports, which affords an ideal model system for the fundamental and conceptual study of catalysis and the opportunity to explore the catalytic mechanism at the atomic level.

3.1 Electrochemical Water Splitting

Electrochemical water splitting(EWS), which contains two independent electrode reactions of HER at the cathode and the oxygen evolution reaction(OER) at the anode, has been considered as one of the most promising technologies for producing hydrogen(H_2). However, the low efficiency of energy conversion and slow reaction rates caused by the sluggish kinetics of EWS processes largely limit its practical applications. GDY-based ACs have been regarded as an ideal catalytic model system of catalysts because of their unique and fascinating properties(such as electronic state, high catalytic activity and selectivity) and have shown excellent catalytic performances in various reactions.

Our group[46] firstly anchored zero-valence transitional metal atoms(Ni^0 and Fe^0) on GDY for HER. Remarkably, Fe^0/GDY shows the best HER activity with the smallest onset overpotential of 9 mV and the overpotential of 66 mV at the current density of 10 mA/cm^2, which are better than most of the reported electrocatalysts and even Pt-based electrocatalysts[92]. In addition, the mass activities of Fe^0/GDY (80.0 A/mg$_{\text{metal}}$) and Ni^0/GDY(16.6 A/mg$_{\text{metal}}$) are 34.6 and 7.19 times greater than that of Pt/C(2.31 A/mg$_{\text{metal}}$) at an overpotential of 0.2 V, respectively. The upper limit numbers of the active sites for Ni^0/GDY(2.56×10^{16} sites/cm^2) and Fe^0/GDY

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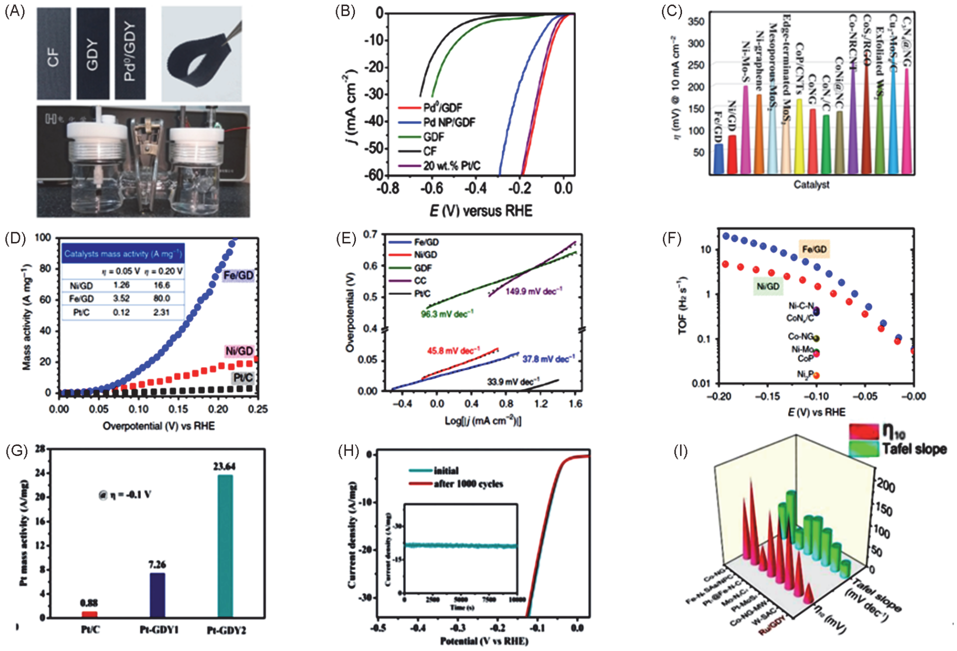
(2.38×10^{16} sites/cm^2) were larger than that of Pt(111)(1.5×10^{15} sites/cm^2)[93]. Fe^0/GDY and Ni^0/GDY all exhibited high turnover frequency(TOF) values. For example, at 100 mV, the TOF values of Fe^0/GDY(4.15 s^{-1}) and Ni^0/GDY(1.59 s^{-1}) are much higher than that of the reported electrocatalysts. In addition to the excellent catalytic activity, the Fe^0/GDY and Ni^0/GDY showed high stability over 60 and 116 h during the potential-constant electrolysis processes [Fig.5(A)—(F)]. XPS and HAADF-STEM characterizations confirmed the robust nature of the GDY-based ACs with no changes in the composition and no aggregations for single metal atoms during the long-term cycling operation.

In order to solve the problem of the high cost of noble metal-based catalysts, novel GDY-based noble metal atomic catalysts were designed and synthesized to maximize the catalyst utilization and overcome the limiting factors including their scarcity and high cost. Lu and coworkers[94] prepared GDY anchored by Pt atoms(Pt-GDY-1) *via* spontaneous chemical reduction arising between GDY and $[PtCl_4]^{2-}$. By modulating the coordination between C and Pt atoms(Pt-GDY-2), the optimal electrocatalysts with high HER performances were obtained, exhibiting higher mass activity(23.64 A/mg at 100 mV) than commercial Pt/C[Fig.5(G) and (H)]. Recently, our group[95] experimentally prepared the GDY-based ruthenium atomic catalysts for both HER and OER under acidic conditions for the first time. This was also the first bifunctional ACs, offering a new strategy for the design and synthesis of novel multifunctional catalysts[Fig.5(I)]. Such superior catalytic performances of GDY-based ACs could be ascribed to the special incomplete charge transfer between the anchored metal atoms and GDY, which significantly facilitated the efficient charge transfer between the active sites, increased the number of active centers, and improved the reaction selectivity, activity and long-term stability.



Catalysts mass activity (A mg⁻¹)	η = 0.05 V	η = 0.20 V
Ni/GD	1.26	16.6
Fe/GD	3.52	80.0
Pt/C	0.12	2.31

Fig.5 Photographs of Pd^0/GDY, GDY, CF and three-electrode system(A), LSV curves of Pd^0/GDY and other references(B), comparation among Ni/GDY, Fe/GDY and other catalysts, which have been reported(C), mass activities of Ni/GDY, Fe/GDY and Pt/C(D), Tafel slopes of Ni/GDY, Fe/GDY and other references(E), TOF values of Ni/GDY, Fe/GDY and other references(F), mass activities of Pt-GDY-1, Pt-GDY-2 and Pt/C(G), CV curves and IT curves of Pt-GDY-2(H), and Tafel slope and overpotential at 10 mA/cm^2 of Ru/GDY and other references(I)

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3.2 Electrochemical Ammonia Synthesis

Ammonia(NH_3), an important chemical material in agricultural and industrial production and an ideal H_2 carrier, plays a critical role in human production and life. Unfortunately, the industrial methods for ammonia synthesis were performed at high temperatures(400—600 °C) and under high pressures(20—40 MPa), which generally causes serious pollution and requires high energy to improve the reaction speed and increase the reaction conversion rate. Strategies for efficient ammonia synthesis at ambient temperatures and under ambient pressures are therefore of great significance. To this end, extensive efforts have been made to synthesize new catalysts with high selectivity and activity, such as noble metals[96,97], metal nitrides[98], metal oxide[99—104] and MOFs[105,106]. However, their ammonia yielding rates and Faradaic efficiency are still far from practical applications. Developing

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highly active and selective catalysts with excellent performance for ammonia synthesis is still a giant challenge.

Our group[47] successfully *in-situ* anchored zerovalent Mo atoms on GDY(Mo^0/GDY with the Mo loading of 7.5%, mass ratio) for electrochemical nitrogen reduction reaction(ECNRR) to produce ammonia. Our results found that zero-valent Mo atoms anchored on GDY network could serve as electron-rich sites to adjust the electron distribution of C and to fix N_2 for ECNRR observed from the bonding and antibonding orbitals near Fermi level. The strong orbital overlap between Mo$_{4d}$ and C$_{2p}$ dramatically affected the distribution of electron cloud from PODSs of Mo^0/GDY and accelerated the electron transfer to stabilize the Mo atoms in the process of ECNRR [Fig.6(A)—(D)]. Mo^0/GDY exhibits high selectivity and outstanding catalytic activity for electrochemical reduction of N_2 to NH_3 in neutral environments[NH_3 yield rate: 145.4 μg/(h·mg$_{\text{cat.}}$) and Faradaic efficiency: >21% in 0.1 mol/L Na_2SO_4]. At the same time, Mo^0/GDY possesses better ECNRR performance in 0.1 mol/L HCl with the Y_{NH_3} of 2.0 μg$_{NH_3}$/(h·mg$_{\text{cat.}}$) and FE of 15.6% at −0.1 V *vs.* SCE. Very recently, by using a simple self-reduction strategy, a new GDY-based AC consisting of zero-valence Pd atoms on GDY(Pd^0/GDY) was synthesized for the ammonia production. Outstandingly, the catalyst shows the highest average NH_3 yield of (4.45±0.30) mg$_{NH_3}$/(mg$_{Pd}$·h), larger than the previously reported ones, and 100% reaction selectivity in neutral media. And Pd-GDY exhibits almost no decreases in the NH_3 yield and Faradaic efficiency. Duan[107] reported the stereoconfinement-induced strategy for densely anchoring metal atoms(Rh, Ru and Co) on GDY for ECNRR performance under high pressures. Among the prepared catalysts, the Rh^0/GDY exhibited a record-high NH_3 yield up to 74.15 μg/(h·cm^2) and high Faraday efficiency of 20.36% at 55 atm. The driving force for the formation of end-on N_2* on Rh^0/GDY dramatically was increased under high pressure.

3.3 Other Catalysis

Under the inspiration of the excellent catalytic performance of GDY-based zero-valent metal atom catalyst, Liu and Zhang *et al*.[108] prepared the atomic Pd catalysts through anchoring Pd atoms on graphdiyne/graphene heterostructure(GDY/G), which was prepared by a vdW epitaxy method in the solution phase[Fig.6(E)]. The Pd loading was 0.855%(mass ratio). In the presence of $NaBH_4$, Pd$_1$/GDY/G could achieve highly active and selective catalysis of the reaction from 4-nitrophenol (4-NP) to 4-aminophenol(4-AP), with the rate constant of 0.953 min^{-1}, which was 44 times that of Pd/C. The turnover frequency(TOF) was 1762.17 min^{-1}. It was found that the conversion rate of 4-NP still had an over 99% retention after 10-time repeated cycles, suggesting the excellent long-time stability of Pd$_1$/GDY/G. In addition, density functional theory calculations showed that graphene in the GDY/G heterostructure played a key role in improving the catalytic

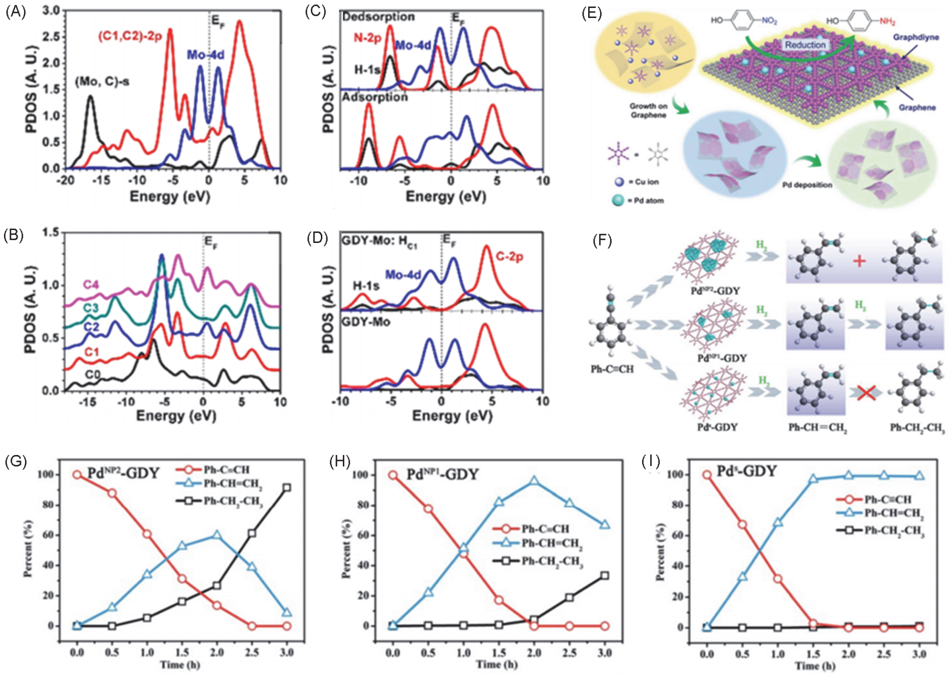

Fig.6 3D real spatial orbital contour plots for Mo^0/GDY(A)—(D), composite diagram of Pd$_1$/GDY/G(E), different hydrogenation processes of phenylacetylene over different Pd-GDY catalysts(F), and conversion and selectivity of Pd^{NP2}-GDY(G), Pd^{NP1}-GDY(H) and Pd^s-GDY(I) phenylacetylene over different Pd-GDY catalysts

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efficiency of the electron transfer process. More recently, Lu and coworkers[109] prepared the Pd$^{\rm s}$-GDY catalysts by simple wet-chemistry routes. It was observed that the Pd-GDY catalysts showed obvious size-dependent performances on the hydrogenation of phenylacetylene[Fig.6(F)—(I)]. The Pd$^{\rm s}$-GDY exhibited the highest catalytic activity, with TOF up to 6290 h^{-1} at 100% conversion with 99.3% selectivity in hydrogenation of phenylacetylene to styrene, compared to that of GDY-supported Pd nanoparticle(NP) catalysts, namely, Pd$^{\rm NP1}$-GDY(with 2 nm Pd NPs) and Pd$^{\rm NP2}$-GDY(with 12 nm Pd NPs). Their results revealed that Pd$^{\rm s}$-GDY had the weakest adsorption to styrene, which was responsible for its high performance. These reports demonstrated the application potential of graphdiyne-based metal atomic catalysts for organic reactions with desirable activity and selectivity.

4 Summary and Outlook

Since the first successful synthesis in 2010 by Li and coworkers[40], GDY has rapidly attracted the wide attention of scientists from different disciplines in the world, and rapidly forms a new field. By utilizing the unique electronic and chemical structures advantages of GDY, zero-valent single transition metal and noble metal atoms were successfully anchored on the surface of GDY, forming the atomic catalysts. Our research work represents a new concept of atomic catalysis, which is of great significance for a deeper understanding of the catalytic process. The emergency of the zero-valent atomic catalyst provides real insights into the strategies for developing new single-atom catalysts, expands the methodologies for the synthesis of single-atom synthesis, and provides an ideal model system and opportunity for us to explore the mechanisms of the interaction of metal atoms with supporting materials and the catalytic processes, and finally establish the correlations between the catalytic performance and the above issues.

Although some achievements have been made, studies on GDY-based atomic catalysts are still in their infancy and many challenges and chances still exist, such as (1) developing new theory and characterization methods suitable for characterizing the precise anchoring position of single metal atoms on the supporting materials; (2) exploring the mechanisms for the energy transfer and electron transport between the metal atoms and supporting materials; (3) understanding the fundamental chemical and electronic properties of GDY-based atomic catalysts will help to further expand the research of GDY in many different fields; (4) exploring the new properties, functions and applications of atomic catalysts in energy conversion.

The unique and outstanding properties of GDY-based ACs endow them with many superiorities from fundaments to applications. We believe that all challenges and shortcomings can be conquered and GDY-based ACs can be applied to more and more practical applications. We hope that this work could provide an in-depth understanding and a guidance for synthesis and practical applications of atomic catalysts.

Acknowledgements

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Conflicts of Interest

The authors declare no conflicts of interest.

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