Understanding the Enhanced Catalytic Performance of Ultrafine Transition Metal Nanoparticles - Graphene Composites

Xin Liu^{†,‡}, Changgong Meng[†], Yu Han^{‡}*

[†] School of Chemistry, Dalian University of Technology, Dalian, 116024, P. R. China

[‡] Physical Sciences and Engineering Division, Advanced Membranes and Porous Materials Center, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia E-mail: yu.han@kaust.edu.sa

ABSTRACT

Catalysis, as the key to minimize the energy requirement and environmental impact of today's chemical industry, plays a vital role in many fields directly related to our daily life and economy, including energy generation, environment control, manufacture of chemicals, medicine synthesis and etc. Rational design and fabrication of highly efficient catalysts have become the ultimate goal of today's catalysis research. For the purpose of handling and product separation, heterogeneous catalysts are highly preferred for industrial applications and a large part of which are the composites of transition metal nanoparticles (TM NPs). With the fast development of nano-science and nano-technology and assisted with theoretical investigations, basic understanding on tailoring the electronic structure of these nano-composites has been gained, mainly by precise control of the composition, morphology, interfacial structure and electronic states. With the rise of graphene, chemical routes to prepare graphene were developed and various graphene based composites were fabricated. Transition metal nanoparticle- reduced graphene oxide (TM-rGO) composites have attracted considerable attention, because of their intriguing catalytic performance which have been extensively explored for energy- and environment- related applications to date. This review summarizes our recent experimental and theoretical efforts on understanding the superior catalytic performance of subnanosized TM NPs -rGO composites.

Tailoring catalysts and catalytic processes have long been the ‘Holy Grail’ of catalytic chemistry. The key elementary steps of catalytic reactions, such as the adsorption of reactants, the diffusion of intermediates and the desorption of products, all involve bond formation and dissociation and are associated with electron transfer among the catalyst and the adsorbed reaction species. According to the frontier molecular orbital theory, the strength of the bonding of reactants onto catalyst surfaces is closely related to the symmetry and occupation of the orbitals of reactants, and is strongly correlated with the difference in the energy levels of the reactants and those of the catalyst. Norskov and coworkers extended this idea to periodic transition metal systems and introduced the d-band center theory based on a large body of experimental and theoretical results, which emphasizes that the density of TM-d states around the Fermi level is an important factor affecting catalytic reactions.¹ To this end, controlled modulation of the spatial and energy distribution of the catalyst states would be a feasible way to lower the energy barriers and facilitate the adsorption and subsequent bonding evolution between reactants over the catalyst on the specific reaction paths to achieve high reactivity and so as the product selectivity.

The conventional methods to influence and adjust the electronic structure of a catalyst are to develop interactions and charge transfer among the primary catalytic composition with various additives. Alloying and doping are typical methods of this type. Alloying among TM elements will develop d-d bonding and shift the TM valence states to the desired energy levels to facilitate the adsorption and evolution of the reactants. For composites of TMs, the interactions at the TM-substrate interface can also induce charge transfer that in turn alter the electronic structure of the TM NPs to exhibit superior catalytic performance as compared with the mother materials.

With the emerging and development of ultra-vacuum and imaging technologies, people come to realize that the anisotropy in atomic stacking and interaction with surrounding atoms can significantly change the distribution of valence electrons of TM atoms, so that even different faces of the same TM crystal can exhibit dramatically different reactivity and stability. The crystal faces that a TM NP will present are mainly determined by the surface free energy, and is directly related to the environment in which the NP is synthesized and utilized. For supported TM NP, the interaction at the TM-substrate interface also contributes to the surface free energy and functions as a variant in determine the morphology and so as the reactivity of TM NP composites.²

The size of the deposited TM NPs has long been recognized as a determinant for the catalytic performance. For decades, quantum-size effects (QSE) have dominated the study of nanoscience, especially the structural stability and electronic properties of nanomaterials.³⁻⁹ The physics of the QSE is rather straightforward, namely, the finite size of a system causes a quantization of the kinetic energy, which manifests itself as distinct peaks in the density of states (DOS) or discrete quantized states. The formation and the existence of the quantized states, known as quantum well states on atomically flat metal ultrathin films at different thicknesses, have been identified and probed by using photoemission spectroscopy,¹⁰ density functional theory calculations,¹¹⁻¹² and scanning tunneling spectroscopy.¹³ Due to QSE, the energy levels of those quantized states is dependent on the finite size of the NPs, may lead to different matching between the catalyst states and the reactants. However, due to the localized nature of TM-d states, the electronic structure of TM NPs converge much faster to the bulk as compared with NPs of sp-metals and the impact of QSE on the electronic structure of TM NPs would be less significant as exemplified by the DFT calculation on CO adsorption on Pt NP of various size. The

undercoordinated TM atoms standing at the edges, corners or TM-substrate interface of NPs would act as reaction centers and the wide observed size effect in catalytic performance of composites of TM NPs can be associated with the amount of exposed reaction centers.¹⁴ In most composites of TM NPs for catalytic applications, the mass-averaged catalytic efficiency of TM is still low as compared with those of the homogeneous counterparts, because merely the surface sites are catalytic active and they contribute only a small percentage to the total usage of TM. Given the high price and limited resources of TMs, improving the mass-averaged catalytic efficiency in heterogeneous TM-based catalysts while keeping or even prompting the catalytic performance is of great significance and highly desired. Downsizing the TM NPs to sub-nano scale or single atoms that are catalytic active would be a feasible way to achieve a higher density of active sites for catalytic reactions and to improve the mass-averaged catalytic performance of TMs.¹⁵

The support also plays a critical role in the catalytic performance of a heterogeneous catalyst.¹⁶ Without surface states or defects, the Fermi level of a typical semiconductor/insulator lies inside the band gap and the density of states around the Fermi level is zero. The TM NPs deposited will be less influenced by the support and demonstrated the intrinsic characteristics of a 0-Dimensional structure. On other support materials, if the matching between spatial and energy distribution of the TM NP states and those of the support is poor, the interaction at the TM-support interface would not be plausible. But barriers will be formed at the TM-support interface and the TM-environment interface and the states of the TM NP will be modulated by these barriers and get quantized. Therefore, varying the size of NPs may, to some extent, adjust the energy level of the quantized states and promote the reactivity.^{12, 17} In fact, there are always surface states, heteroatoms, dangling bonds or defects on the surface of the support. If plausible

interaction can be formed at the TM-support interface, the TM atoms at the interface will be further hybridized and even interfacial alloying can be induced. This may induce further reorganization the charge distribution and bonding scheme within the NP. Alloying is an important effect in heterogeneous catalysis that can not only alter the electronic structure of the NPs, but also the atomic stacking at the interface as the size of atoms always vary with elements.¹⁸⁻²⁰ As the atomic stacking is confined and distorted at the interface to satisfy the requirement for epitaxial growth, the accumulation and release of the tension at the interface would also affect the morphology and electronic structure of the NPs and the adsorption and evolution of reactants on them. When the size of TM NPs goes down, the impact of NP support interfacial interaction would become more apparent. Depending on the interfacial structure,²¹⁻²³ the bonding between TM atoms and the support,²³⁻²⁵ this interaction would introduce strains at the interface, cause the energy and spatial redistribution of the TM states and thus change the performance of the resulting catalysts.²⁶⁻²⁷ The interfacial interaction may also help to effectively stabilize the tiny TM NPs or atoms and prohibit them from sintering under realistic reaction conditions, which are the key challenges for implementation of monodispersed ultrafine TM catalysts for practical applications.²⁸⁻²⁹ In this sense, a careful screening of the metal support interactions would be necessary to rationalize the design of mono-dispersed ultrafine TM NPs or single TM atoms as efficient catalyst for a specific reaction.

As a unique two-dimensional carbon material, graphene has been predicted to be an excellent support for dispersion of transition metal nanoparticle (TM NP) catalysts, due to its large surface area, outstanding electronic and thermal conductivity, as well as the high mechanical strength and potentially low production cost.³⁰⁻³² The graphene samples used as support materials for catalytic applications are commonly synthesized by oxidative exfoliation of graphite, followed

by reduction and the product is called rGO.³³ Depending on the conditions of exfoliation and subsequent reduction,³⁴ the reported surface area of rGO is 600–900 m² g⁻¹, which is already comparable with or even higher than that of bundle of carbon nanotube (CNT) grown by chemical vapour deposition³⁵ or mesoporous carbon³⁶ and can be further increased by introduction of various defects.³⁷

Unlike pristine graphene, where the TM atoms diffuse fast resulting in the renowned problem of particle aggregation and sintering, rGO has abundant types of defects, such as vacancies, stacking faults, domain boundaries, etc, that will act as anchor points for the nucleation and growth of TM NPs.^{34, 38-45} With the help of high resolution transmission electron microscope (TEM), Gomez-Navarro et al. identified the presence of various types of defects in rGO samples synthesized with Hummers method,³³ including clustered pentagons and heptagons, vacancies, edges and contaminations.⁴⁶ Theoretically, Wang *et al.* also showed that electron beam irradiation can serve as a useful tool to modify the defect morphology in a controllable manner and to tailor the physical properties of defective graphene as well as rGO.⁴⁷ The existence of these defects and their interconversion provide a solution to enhance the TM NP-support interaction and to tune the reactivity of the fabricated composites.^{38, 48}

Fig. 1. Structures of PG (a), SV (b), DV (c), 5577 (d), 555 777 (e), 555 567 777 (f) and their density of states (DOS) curves (g). The charge densities of defective states at the Fermi level in (g) are shown in purple in (b)–(f) with an isovalue of ± 0.003 a.u. (Reproduced from ref. 21 with kind permission from The Royal Society of Chemistry.)

As recent TEM experiments identified the presence of various types of defects in rGO including point defects,⁴⁶ and further IR, Raman and temperature programmed desorption (TPD) and theoretical results verified that on the final TM-rGO composites most of the oxygen containing groups and surface contaminations on rGO were removed chemically to a large extent during the reduction, the activation of the composites or the thermal treatments,^{49–51} pristine graphene (PG), single vacancy (SV), double vacancy (DV) and several haeckelite structures, namely 5577, 555777 and 55556777 defects (Fig. 1), were selected as the typical local structures to mimic the electronic basic of the rGO support. The calculated stability of these defects follows the order of $555777 > 55556777 > DV > 5577$, while that of SV is similar to DV. The high energies (typically at the level of 10 eV) required for the conversion among them suggest that

these defects would be stable in conventional reaction environments. There are sharp spikes within 0.5 eV from the Fermi level on the DOS curves of all these defects (Fig. 1g). The charge densities of these states were extracted (Fig. 1b–f) which further prove that these spikes are the defect states localized on the carbon atoms at the defect sites. As the other defects must be derived from SV whose stability is similar to that of DV, SV is typical for analyze the rGO-TM interaction. Previously, these defects were studied in CNT systems, where the changes in electron transport and electronic properties were discussed. Defects like these have also been predicted to alter the electronic properties of graphene and modify the chemical reactivity toward adsorbates.⁵²⁻⁵⁵ In this sense, these defects would provide reactive anchoring points to bind strongly with TM NPs and the interfacial interactions will further tune the electronic structure of the formed composites.

Ru and Ru alloy NPs deposited on carbon materials have drawn considerable attention for their outstanding catalytic performance. Ru NPs supported on active carbon showed high catalytic activity in hydrogenation of lactic acid, arene and ketone, and hydrolysis of NaBH_4 .⁵⁶⁻⁵⁸ Ru NPs embedded in ordered mesoporous carbon material also demonstrated a higher activity in Fischer–Tropsch synthesis,⁵⁹ hydrogenation of glucose,⁶⁰ and partial hydrogenation of dinitrobenzene into nitroanilines,⁵⁸ Finely dispersed Ru NPs on rGO also show superior catalytic performance in hydrogenation of arenes and ketone as compared with those deposited on mesoporous carbon.⁶¹⁻⁶² To address the superior catalytic performance of these finely dispersed Ru NPs and especially the Ru NPs deposited on rGO. We systematically investigated the electronic structure of Ru NPs supported on various local structures on rGO.(Fig. 2) We showed that Ru NPs prefer to nucleate at these localized defect structures on rGO, which act as strong trapping sites for Ru NPs. The binding of Ru NPs to rGO, which is dependent on these local defect structures and correlates

with the interfacial charge transfer, determines the electronic structure and reactivity of the composites.²¹

Fig 2. The correlations between charge transfer (Δq_B) and the Ru-C interfacial interaction (E_b) (a), between weight-averaged d-band center (ϵ_d) of the composite and E_b (b), between the adsorption of oxygen (E_{ad}) and ϵ_d , and between E_{ad} and E_b (d). The ϵ_d , in (c) is aligned with the vacuum levels, please see ref 21 for details. (Reproduced from Ref. 21 with kind permission from The Royal Society of Chemistry.)

Taking SV as typical defects with H, O and CO adsorption as probes, we also investigated the electronic structure of Ru NPs stabilized on N and B functionalized on rGO. Doping the defective with B would further increase the binding energy to -7.52 eV. The strong interaction results in the averaged *d*-band center of the deposited Ru nanoparticle being upshifted toward the Fermi level from -1.41 eV to -1.10 eV.²³ According to the d-band theory of Noskov *et al*, the

electronic structure change like this would result in superior catalytic performance in hydrogenation, oxygen reduction reaction and hydrogen evolution reaction.

Fig 3. The position of C atoms around the deposited Ru NP (a), and the potential energy of Ru atoms placed around the Ru NP (b). The dashed line in (a) shows the position of the basal plane of the graphene substrate, and the dashed line in (b) indicates the total energy of the co-adsorption system composed by a Ru NP at the vacancy defect and a Ru atom far apart, according to which the energies of the 2 systems were aligned. The filled squares correspond to the SV substrate, and the empty ones correspond to the PG substrate. (Reproduced from Ref. 22 with kind permission from The Royal Society of Chemistry.)

It is worth of noting that, accompanying the formation of Ru–C bonds, the interfacial C atoms are also displaced out of the graphene plane by 1.37 Å and the degree of this displacement decreases gradually (Fig. 3). A local curvature can be introduced to monitor this distortion, where the Ru NP is located at the convex surface of the curved graphene. Curvature on graphene nanoribbon are known able to differentiate the reactivity of graphene, and the larger the curvature, the higher the reactivity.⁴⁴ The correlation between the out-of-plane displacement of C

atoms and the total energy of the co-adsorption system on SV is well illustrated in Fig. 3. According to the difference in total energy, the diffusion of the Ru atom to the Ru NP at the vacancy site is thermodynamically preferred, but the reverse process is not. As the Ru atomic diffusion goes through a similar transition state on PG and SV, according to the Brønsted–Evans–Polanyi (BEP) correlation between the diffusion barrier and the binding energy of the products, the diffusion barrier will increase with the binding energy.⁶³ In Fig. 3b, the gain in total energy due to the local curvature around the vacant site is ~3.5 eV, which implies that the diffusion barrier of Ru atoms will also increase accordingly. Therefore, the diffusion of Ru atoms will be slowed down around the deposited Ru particles and the trapped Ru atoms will finally merge into the Ru NP at SV. In this sense, the Ru atomic diffusion from the vacancy site is also a kinetically inhibited process. According to Fig. 3, one can roughly consider the SV on the graphene substrate as a potential well on the energy surface for Ru diffusion (Fig. 3b). When a Ru atom reaches the well, it will be trapped as a part of the particle and can no longer move away. Thus, the particle growth by an Ostwald ripening mechanism will be prohibited by the Ru nanoparticle–rGO substrate interaction, and the defective sites would be more effective to stabilize the Ru NPs. Both the vacancy defects and the formed interfacial structure contribute to this special property of the Ru NP/rGO composites.²²

Catalytic hydrogenation is undoubtedly the best-recognized and most commonly applied method of reduction of unsaturated compounds and has been a basic step in the synthesis of many organic chemicals. The hydrogenation of arene is of particular importance in the petroleum industry and for environmental protection.⁶⁴ As the simplest aromatic compound, benzene is often used as a model system for the hydrogenation of arenes.⁶⁵ We investigated the impact of carbon substrate–Ru nanoparticle interaction on the benzene and hydrogen adsorption that is

directly related to the performance of catalytic hydrogenation of benzene.²² The stability of the Ru NP is enhanced on the rGO substrate due to the hybridization between the dsp states of the Ru NP with the sp^2 dangling bonds at the defect sites. The strong interfacial interaction results in the shift of the averaged d-band center of the deposited Ru nanoparticle, from -1.41 eV for a freestanding Ru NP, to -1.17 eV for the Ru/Graphene composites, and to -1.54 eV on MCF-C. Accordingly, the adsorption energies of benzene are increased from -2.53 eV for the Ru/MCF-C composites, to -2.62 eV on a freestanding Ru NP, to -2.74 eV on the Ru/rGO composites. (Fig. 4a) A similar change in hydrogen adsorption is also observed, and all these can be correlated to the shift of the d-band center of the NP. Thus, Ru NP/rGO composites are expected to exhibit both high stability and superior catalytic performance in hydrogenation of arenes as compared with the Ru/MCF composites. Further studies are necessary to fabricate and direct test the catalytic activity of the Ru/graphene composites to determine whether there is a volcano-type relationship between benzene hydrogenation activity and adsorption energy.

Fig. 4. (a) Density-of-states curves and contour plot of the differential charge densities of (b) Ru/rGO and (c) Ru/AC with their structures. (d) The Temperature-programmed desorption (TPD) of toluene from the Ru/rGO and Ru/MCF-C catalysts. HAADF-STEM images of the fresh Ru/rGO catalyst (e) and after its use in six consecutive toluene-hydrogenation reaction runs(f). In (b) and (c), the charge-accumulation regions and the charge-depletion regions are denoted in red and blue, respectively. (Reproduced from Ref. 25.with kind permission from Wiley-VCH Verlag GmbH& Co. KGaA, Weinheim.)

Based on the predicted outstanding catalytic performance of Ru/rGO composites, we investigated the hydrogenation of toluene and benzene on them combining experimental and theoretical efforts. We have developed a simple method to prepare fine- and well-dispersed Ru NPs on rGO to verify the theoretical findings. We used ethylene glycol(EG) for the co-reduction of both EO from revised Hummer's method and ruthenium chloride hydrate for fabrication of Ru/rGO. We also attempted to use PG, which was prepared from Ni foam by using a CVD method⁶⁶ as a support material for the deposition of Ru NPs, but found under identical preparation conditions, the Ru NPs only formed in solution rather than on the PG surface, as determined by TEM characterization. Elemental analysis confirmed that the content of Ru that was deposited onto PG was negligible (<0.1 %). These results are in accord with the prediction that PG is not suitable for supporting metal NPs owing to its high chemical stability. The temperature-programmed desorption (TPD) results showed that the desorption temperature of toluene from Ru/rGO was about 80 °C higher than that from Ru/MCF-C (Fig. 4d), thus confirming the calculations described enhanced reactivity of Ru/rGO. According to the BEP relationship,⁶³ the Ru/rGO catalyst would show a lower reaction barrier and, thus, higher activity for the hydrogenation of toluene. When used as a catalyst for arene-hydrogenation reactions, the

obtained Ru/rGO composite exhibited excellent catalytic activity, with a performance that exceeded that of Ru NPs with comparable sizes but supported on amorphous carbon materials as rendered by the TOF for benzene and toluene hydrogenation as 3.8 and $2.6 \times 10^4 \text{ h}^{-1}$, respectively. Furthermore, the change in size and morphology distribution of Ru NPs after 6 runs (Fig. 4e and f) is negligible, showing the outstanding stability of these composites for arene hydrogenation where the interfacial interaction may play a role. These results verified our theoretical predictions based on first-principles calculations, and revealed the important effect of the support material on stabilizing metal NPs and on modulating their catalytic activity through interfacial interactions.²⁵

Fuel cells are considered as an important Eco-friendly power source nowadays with high energy conversion efficiency and low pollution. The sluggish kinetic rates of both the oxidation reaction at the anode and the oxygen reduction reaction (ORR) at the cathode are the main challenges that hinder the energy conversion efficiency of fuel cells. A considerable effort has been focused on developing new electrocatalytic materials with both high catalytic activity and durability.⁶⁷⁻⁶⁸ Pd is regarded as the most Pt-like metal and recent investigations have validated that the ORR activity can be effectively enhanced by the synergistic effect between Pd and transition metals,⁶⁹⁻⁷¹ the modified electronic structure of the Pd d-band,⁷² and the decrease in O adsorption strength on the Pd catalysts.⁷³⁻⁷⁴

We investigated the impact of graphene substrate-Pd nanoparticle interaction on the O, OH, and OOH adsorption on Pd/graphene nanocomposites that is directly related to the electrocatalytic performance of these composites in oxygen reduction reaction.²⁴ The calculated binding energy of a Pd NP on a SV is as high as -6.10 eV , owing to the hybridization between

the d sp states of the Pd particles with the sp^2 dangling bonds at the defect sites. The strong interaction results in the averaged d-band center of the deposited Pd NPs shifted away from the E_F from -1.02 to -1.45 eV. Doping the SV with B or N will further tune the average d-band center and also the activity of composite toward O, OH, and OOH adsorption. The adsorption energies of O, OH, and OOH are reduced from -4.82 , -4.38 , and -3.52 eV on Pd/PG to -4.57 , -2.66 , and -1.39 eV on Pd/SV composites, showing that a defective graphene substrate will not only stabilize the Pd NPs but also reduce the O-containing species poisoning the ORR active sites.⁷⁵

Fig. 5 (a) Calculated O adsorption energies (E_{ad}) and binding energy (E_b) of MPd₁₂/SV composites plotted versus shift of d-band center ($\Delta\epsilon_d$). (b) Calculated O adsorption energies (E_{ad}) over MPd₁₂ and MPd₁₂/SVG composites plotted versus d-band center with respect to vacuum (ϵ_d). The dashed line is to guide the eye. (Reproduced from Ref 77 with kind permission from The American Chemical Society.)

Previously, the adsorption of O-containing species has been shown to be proportional with the adsorption of O.⁷⁶ We used adsorption of O atom as a probe and took MPd₁₂ (M = Fe, Co, Ni, Cu, Zn) NPs as model catalysts to investigate the joint effect of both rGO substrate and alloying on

the catalytic performance of these composites in ORR. We found that the alloying effect can enhance the stability of Pd NPs, and the reactivity of free-standing NPs is already comparable to that of Pt(111). Both the interfacial interaction and the alloying effect contribute to the additional stability of the nanocomposites, tune the averaged d-band center of the deposited TM NPs, and strongly interfere the adsorption of O. The calculated adsorption energy of O on these composites correlated well with the shift of the average d-band center of these NPs. As the adsorption of these O-containing species is weakened on these composites, the ORR kinetics hindered by strong adsorption of these species will also be promoted. These composites are thus expected to exhibit both high stability and superior catalytic performance in oxygen reduction reaction.⁷⁷

Fabrication of a suitable catalysts for a specific chemical process, with desired catalytic activity, selectivity and stability, is one of the key challenges in today's catalysis research. We are trying to understand the intriguing catalytic performance of TM-rGO composites from various aspects. There are many factors that influence the catalytic performance of these composites, such as the electronic structure of the graphitic support, the atomic structure and interaction at the graphene-metal interface, the alloying effect and the morphology of the TM NPs, and etc, some of which have been addressed but most remain unknown. There are tremendous opportunities ahead for both the design and fabrication of novel and efficient TM-rGO composite catalysts and their potential applications in energy and environmental related fields. The research on the TM-rGO composites will continue thrilling over coming decades.

AUTHOR INFORMATION

Corresponding Author

Prof. Yu Han, Physical Sciences and Engineering Division, Advanced Membranes and Porous Materials Center, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia E-mail: yu.han@kaust.edu.sa

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

This work was supported by faculty baseline funds and the academic excellence alliance program from King Abdullah University of Science and Technology. X. L. would also thank NSFC (21373036 and 21103015) and the Fundamental Research Funds for the Central Universities (DUT14LK09 and DUT15LK18) for financial support. Y. H. would also thanks Dalian University of Technology for the Seasky Professorship.

REFERENCES

1. Ruban, A.; Hammer, B.; Stoltze, P.; Skriver, H. L.; Norskov, J. K., Surface electronic structure and reactivity of transition and noble metals. *J. Mol. Catal. A-Chem.* **1997**, *115*, 421-429.
2. Norskov, J. K.; Bligaard, T.; Hvolbaek, B.; Abild-Pedersen, F.; Chorkendorff, I.; Christensen, C. H., The nature of the active site in heterogeneous metal catalysis. *Chem. Soc. Rev.* **2008**, *37*, 2163-2171.
3. Knight, W. D.; Clemenger, K.; Deheer, W. A.; Saunders, W. A.; Chou, M. Y.; Cohen, M. L., ELECTRONIC SHELL STRUCTURE AND ABUNDANCES OF SODIUM CLUSTERS. *Phys. Rev. Lett.* **1984**, *52*, 2141-2143.
4. Su, W. B.; Chang, S. H.; Jian, W. B.; Chang, C. S.; Chen, L. J.; Tsong, T. T., Correlation between quantized electronic states and oscillatory thickness relaxations of 2D Pb islands on Si(111)-(7 x 7) surfaces. *Phys. Rev. Lett.* **2001**, *86*, 5116-5119.
5. Yeh, V.; Berbil-Bautista, L.; Wang, C. Z.; Ho, K. M.; Tringides, M. C., Role of the metal/semiconductor interface in quantum size effects: Pb/Si(111). *Phys. Rev. Lett.* **2000**, *85*, 5158-5161.

6. Binggeli, N.; Altarelli, M., Surface reactivity and quantum-size effects on the electronic density decay length of ultrathin metal films. *Phys. Rev. Lett.* **2006**, *96*.
7. Paggel, J. J.; Miller, T.; Chiang, T. C., Quantum-well states as Fabry-Perot modes in a thin-film electron interferometer. *Science* **1999**, *283*, 1709-1711.
8. Guo, Y., et al., Superconductivity modulated by quantum size effects. *Science* **2004**, *306*, 1915-1917.
9. Chan, T. L.; Wang, C.; Hupalo, M.; Tringides, M.; Ho, K., Quantum size effect on the diffusion barriers and growth morphology of Pb/Si(111). *Phys. Rev. Lett.* **2006**, *96*.
10. Zhang, Y. F.; Jia, J. F.; Han, T. Z.; Tang, Z.; Shen, Q. T.; Guo, Y.; Qiu, Z. Q.; Xue, Q. K., Band structure and oscillatory electron-phonon coupling of Pb thin films determined by atomic-layer-resolved quantum-well states. *Phys. Rev. Lett.* **2005**, *95*.
11. Wei, C. M.; Chou, M. Y., Theory of quantum size effects in thin Pb(111) films. *Phys. Rev. B* **2002**, *66*.
12. Liu, X.; Zhang, S. B.; Ma, X. C.; Jia, J. F.; Xue, Q. K.; Bao, X. H.; Li, W. X., Wavevector-dependent quantum-size effect in electron decay length at Pb thin film surfaces. *Appl. Phys. Lett.* **2008**, *93*, 093105.
13. Ma, X. C.; Jiang, P.; Qi, Y.; Jia, J. F.; Yang, Y.; Duan, W. H.; Li, W. X.; Bao, X.; Zhang, S. B.; Xue, Q. K., Experimental observation of quantum oscillation of surface chemical reactivities. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 9204-9208.
14. Li, L.; Larsen, A. H.; Romero, N. A.; Morozov, V. A.; Glinsvad, C.; Abild-Pedersen, F.; Greeley, J.; Jacobsen, K. W.; Norskov, J. K., Investigation of Catalytic Finite-Size-Effects of Platinum Metal Clusters. *J. Phys. Chem. Lett.* **2013**, *4*, 222-226.
15. Yang, X. F.; Wang, A. Q.; Qiao, B. T.; Li, J.; Liu, J. Y.; Zhang, T., Single-Atom Catalysts: A New Frontier in Heterogeneous Catalysis. *Accounts of Chemical Research* **2013**, *46*, 1740-1748.
16. Khodakov, A.; Olthof, B.; Bell, A. T.; Iglesia, E., Structure and catalytic properties of supported vanadium oxides: Support effects on oxidative dehydrogenation reactions. *J. Catal.* **1999**, *181*, 205-216.
17. Chiang, T. C., Photoemission studies of quantum well states in thin films. *Surf. Sci. Rep.* **2000**, *39*, 181-235.
18. Chen, M. S.; Kumar, D.; Yi, C. W.; Goodman, D. W., The promotional effect of gold in catalysis by palladium-gold. *Science* **2005**, *310*, 291-293.
19. Stamenkovic, V. R.; Fowler, B.; Mun, B. S.; Wang, G. F.; Ross, P. N.; Lucas, C. A.; Markovic, N. M., Improved oxygen reduction activity on Pt₃Ni(111) via increased surface site availability. *Science* **2007**, *315*, 493-497.
20. Fu, Q., et al., Interface-Confined Ferrous Centers for Catalytic Oxidation. *Science* **2010**, *328*, 1141-1144.
21. Liu, X.; Sui, Y.; Meng, C.; Han, Y., Tuning the Reactivity of Ru Nanoparticles by Defect Engineering of the Reduced Graphene Oxide Support. *RSC Adv.* **2014**, *4*, 22230-22240.
22. Liu, X.; Meng, C. G.; Han, Y., Substrate-mediated enhanced activity of Ru nanoparticles in catalytic hydrogenation of benzene. *Nanoscale* **2012**, *4*, 2288-2295.
23. Liu, X.; Yao, K. X.; Meng, C. G.; Han, Y., Graphene substrate-mediated catalytic performance enhancement of Ru nanoparticles: a first-principles study. *Dalton Trans.* **2012**, *41*, 1289-1296.

24. Liu, X.; Li, L.; Meng, C. G.; Han, Y., Palladium Nanoparticles/Defective Graphene Composites as Oxygen Reduction Electrocatalysts: A First-Principles Study. *J. Phys. Chem. C* **2012**, *116*, 2710-2719.
25. Yao, K. X.; Liu, X.; Li, Z.; Li, C. C.; Zeng, H. C.; Han, Y., Preparation of a Ru-Nanoparticles/Defective-Graphene Composite as a Highly Efficient Arene-Hydrogenation Catalyst. *ChemCatChem* **2012**, *4*, 1938-1942.
26. Chen, M. S.; Goodman, D. W., Catalytically active gold on ordered titania supports. *Chem. Soc. Rev.* **2008**, *37*, 1860-1870.
27. Yao, Y. X.; Liu, X.; Fu, Q.; Li, W. X.; Tan, D. L.; Bao, X. H., Unique reactivity of confined metal atoms on a silicon substrate. *ChemPhysChem* **2008**, *9*, 975-979.
28. Uzun, A.; Ortalan, V.; Hao, Y. L.; Browning, N. D.; Gates, B. C., Nanoclusters of Gold on a High-Area Support: Almost Uniform Nanoclusters Imaged by Scanning Transmission Electron Microscopy. *ACS Nano* **2009**, *3*, 3691-3695.
29. Uzun, A.; Ortalan, V.; Browning, N. D.; Gates, B. C., A site-isolated mononuclear iridium complex catalyst supported on MgO: Characterization by spectroscopy and aberration-corrected scanning transmission electron microscopy. *J. Catal.* **2010**, *269*, 318-328.
30. Geim, A. K.; Novoselov, K. S., The rise of graphene. *Nat. Mater.* **2007**, *6*, 183-191.
31. Geim, A. K., Graphene: Status and Prospects. *Science* **2009**, *324*, 1530-1534.
32. Inagaki, M.; Kim, Y. A.; Endo, M., Graphene: preparation and structural perfection. *J. Mater. Chem.* **2011**, *21*, 3280-3294.
33. Hummers, W. S.; Offeman, R. E., Preparation of graphitic oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339-1340.
34. Zhu, Y. W.; Murali, S.; Cai, W. W.; Li, X. S.; Suk, J. W.; Potts, J. R.; Ruoff, R. S., Graphene and Graphene Oxide: Synthesis, Properties, and Applications. *Adv. Mater.* **2010**, *22*, 3906-3924.
35. Bacsa, R. R.; Laurent, C.; Peigney, A.; Bacsa, W. S.; Vaugien, T.; Rousset, A., High specific surface area carbon nanotubes from catalytic chemical vapor deposition process. *Chem. Phys. Lett.* **2000**, *323*, 566-571.
36. Han, Y.; Lee, S. S.; Ying, J. Y., High specific surface area carbon nanotubes from catalytic chemical vapor deposition process. *Chem. Mat.* **2007**, *19*, 2992-2998.
37. Chae, H. K.; Siberio-Perez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M., A route to high surface area, porosity and inclusion of large molecules in crystals. *Nature* **2004**, *427*, 523-527.
38. Banhart, F.; Kotakoski, J.; Krasheninnikov, A. V., Structural Defects in Graphene. *ACS Nano* **2011**, *5*, 26-41.
39. Krasheninnikov, A. V.; Lehtinen, P. O.; Foster, A. S.; Pyykko, P.; Nieminen, R. M., Embedding Transition-Metal Atoms in Graphene: Structure, Bonding, and Magnetism. *Phys. Rev. Lett.* **2009**, *102*, 126807.
40. Kim, G.; Jhi, S. H.; Park, N.; Louie, S. G.; Cohen, M. L., Optimization of metal dispersion in doped graphitic materials for hydrogen storage. *Phys. Rev. B* **2008**, *78*.
41. Sadek, A. Z.; Moafi, A.; Lau, D. M.; McCulloch, D. G.; Zheng, C.; Hu, Z.; Wlodarski, W.; Kalantar-zadeh, K.; Ieee, Highly Dispersed Gold Nanoparticles on Nitrogen Doped Carbon Nanotubes for Hydrogen Sensing. In *2010 Ieee Sensors*, Ieee: New York, 2010; pp 386-390.
42. Schäffel, F.; Wilson, M.; Bachmatiuk, A.; Rummeli, M. H.; Queitsch, U.; Rellinghaus, B.; Briggs, G. A. D.; Warner, J. H., Atomic Resolution Imaging of the Edges of Catalytically Etched Suspended Few-Layer Graphene. *ACS Nano* **2011**, *5*, 1975-1983.

43. Bao, W. Z.; Miao, F.; Chen, Z.; Zhang, H.; Jang, W. Y.; Dames, C.; Lau, C. N., Controlled ripple texturing of suspended graphene and ultrathin graphite membranes. *Nat. Nanotechnol.* **2009**, *4*, 562-566.
44. Gao, X. F.; Wang, Y.; Liu, X.; Chan, T. L.; Irle, S.; Zhao, Y. L.; Zhang, S. B. B., Regioselectivity control of graphene functionalization by ripples. *Phys. Chem. Chem. Phys.* **2011**, *13*, 19449-19453.
45. Wu, S. X.; He, Q. Y.; Zhou, C. M.; Qi, X. Y.; Huang, X.; Yin, Z. Y.; Yang, Y. H.; Zhang, H., Synthesis of Fe₃O₄ and Pt nanoparticles on reduced graphene oxide and their use as a recyclable catalyst. *Nanoscale* **2012**, *4*, 2478-2483.
46. Gomez-Navarro, C.; Meyer, J. C.; Sundaram, R. S.; Chuvilin, A.; Kurasch, S.; Burghard, M.; Kern, K.; Kaiser, U., Atomic Structure of Reduced Graphene Oxide. *Nano Lett.* **2010**, *10*, 1144-1148.
47. Wang, Z. G.; Zhou, Y. G.; Bang, J.; Prange, M. P.; Zhang, S. B.; Gao, F., Modification of Defect Structures in Graphene by Electron Irradiation: Ab Initio Molecular Dynamics Simulations. *J. Phys. Chem. C* **2012**, *116*, 16070-16079.
48. Hashimoto, A.; Suenaga, K.; Gloter, A.; Urita, K.; Iijima, S., Direct evidence for atomic defects in graphene layers. *Nature* **2004**, *430*, 870-873.
49. Scheuermann, G. M.; Rumi, L.; Steurer, P.; Bannwarth, W.; Mulhaupt, R., Palladium Nanoparticles on Graphite Oxide and Its Functionalized Graphene Derivatives as Highly Active Catalysts for the Suzuki-Miyaura Coupling Reaction. *J. Am. Chem. Soc.* **2009**, *131*, 8262-8270.
50. Xu, C.; Wang, X.; Zhu, J. W., Graphene-Metal Particle Nanocomposites. *J. Phys. Chem. C* **2008**, *112*, 19841-19845.
51. Gao, X. F.; Jang, J.; Nagase, S., Hydrazine and Thermal Reduction of Graphene Oxide: Reaction Mechanisms, Product Structures, and Reaction Design. *J. Phys. Chem. C* **2010**, *114*, 832-842.
52. Amorim, R. G.; Fazzio, A.; Antonelli, A.; Novaes, F. D.; da Silva, A. J. R., Divacancies in graphene and carbon nanotubes. *Nano Lett.* **2007**, *7*, 2459-2462.
53. Kotakoski, J.; Krasheninnikov, A. V.; Kaiser, U.; Meyer, J. C., From Point Defects in Graphene to Two-Dimensional Amorphous Carbon. *Phys. Rev. Lett.* **2011**, *106*, 105505.
54. Ghosh, D.; Periyasamy, G.; Pati, S. K., Adsorption of HF Pollutant on Single Vacant 2D Nanosheets: Ab Initio Molecular Dynamics Study. *J. Phys. Chem. C* **2013**, *117*, 21700-21705.
55. Denis, P. A.; Iribarne, F., Comparative Study of Defect Reactivity in Graphene. *J. Phys. Chem. C* **2013**, *117*, 19048-19055.
56. Primo, A.; Concepcion, P.; Corma, A., Synergy between the metal nanoparticles and the support for the hydrogenation of functionalized carboxylic acids to diols on Ru/TiO₂. *Chem. Commun.* **2011**, *47*, 3613-3615.
57. Crisafulli, C.; Scire, S.; Salanitri, M.; Zito, R.; Calamia, S., Hydrogen production through NaBH₄ hydrolysis over supported Ru catalysts: An insight on the effect of the support and the ruthenium precursor. *Int. J. Hydrog. Energy* **2011**, *36*, 3817-3826.
58. Su, F. B.; Lee, F. Y.; Lv, L.; Liu, J. J.; Tian, X. N.; Zhao, X. S., Sandwiched ruthenium/carbon nanostructures for highly active heterogeneous hydrogenation. *Adv. Funct. Mater.* **2007**, *17*, 1926-1931.
59. Chen, W.; Zuckerman, N. B.; Kang, X. W.; Ghosh, D.; Konopelski, J. P.; Chen, S. W., Alkyne-Protected Ruthenium Nanoparticles. *J. Phys. Chem. C* **2010**, *114*, 18146-18152.

60. Liu, J. J.; Bai, P.; Zhao, X. S., Ruthenium nanoparticles embedded in mesoporous carbon microfibers: preparation, characterization and catalytic properties in the hydrogenation of D-glucose. *Phys. Chem. Chem. Phys.* **2011**, *13*, 3758-3763.
61. Yao, K. X.; Liu, X.; Li, Z.; Li, C. C.; Zeng, H. C.; Han, Y., Preparation of Ru Nanoparticles/Defective Graphene Composite as a Highly Efficient Arene Hydrogenation Catalyst. *ChemCatChem* **2012**, *4*, 1938-1942.
62. Gopiraman, M.; Ganesh Babu, S.; Khatri, Z.; Kai, W.; Kim, Y. A.; Endo, M.; Karvembu, R.; Kim, I. S., Dry Synthesis of Easily Tunable Nano Ruthenium Supported on Graphene: Novel Nanocatalysts for Aerial Oxidation of Alcohols and Transfer Hydrogenation of Ketones. *J. Phys. Chem. C* **2013**, *117*, 23582-23596.
63. Cheng, J.; Hu, P.; Ellis, P.; French, S.; Kelly, G.; Lok, C. M., Bronsted-Evans-Polanyi relation of multistep reactions and volcano curve in heterogeneous catalysis. *J. Phys. Chem. C* **2008**, *112*, 1308-1311.
64. Cooper, B. H.; Donnis, B. B. L., Aromatic saturation of distillates: An overview. *Appl. Catal. A-Gen.* **1996**, *137*, 203-223.
65. Nagahara, H.; Ono, M.; Konishi, M.; Fukuoka, Y., Partial hydrogenation of benzene to cyclohexene. *Appl. Surf. Sci.* **1997**, *121*, 448-451.
66. Chen, Z.; Ren, W.; Gao, L.; Liu, B.; Pei, S.; Cheng, H.-M., Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition. *Nat. Mater.* **2011**, *10*, 424-428.
67. Chen, Z.; Higgins, D.; Yu, A.; Zhang, L.; Zhang, J., A review on non-precious metal electrocatalysts for PEM fuel cells. *Energy Environ. Sci.* **2011**, *4*, 3167-3192.
68. Zhao, X.; Yin, M.; Ma, L.; Liang, L.; Liu, C.; Liao, J.; Lu, T.; Xing, W., Recent advances in catalysts for direct methanol fuel cells. *Energy Environ. Sci.* **2011**, *4*, 2736-2753.
69. Fernandez, J. L.; Raghuvver, V.; Manthiram, A.; Bard, A. J., Pd-Ti and Pd-Co-Au electrocatalysts as a replacement for platinum for oxygen reduction in proton exchange membrane fuel cells. *J. Am. Chem. Soc.* **2005**, *127*, 13100-13101.
70. Fernandez, J. L.; Walsh, D. A.; Bard, A. J., Thermodynamic guidelines for the design of bimetallic catalysts for oxygen electroreduction and rapid screening by scanning electrochemical microscopy. M-Co (M : Pd, Ag, Au). *J. Am. Chem. Soc.* **2005**, *127*, 357-365.
71. Li, H. Q.; Sun, G. Q.; Li, N.; Sun, S. G.; Su, D. S.; Xin, Q., Design and preparation of highly active Pt-Pd/C catalyst for the oxygen reduction reaction. *J. Phys. Chem. C* **2007**, *111*, 5605-5617.
72. Fouda-Onana, F.; Savadogo, O., Study of O(2) and OH adsorption energies on Pd-Cu alloys surface with a quantum chemistry approach. *Electrochim. Acta* **2009**, *54*, 1769-1776.
73. Suo, Y. G.; Zhuang, L.; Lu, J. T., First-principles considerations in the design of Pd-alloy catalysts for oxygen reduction. *Angew. Chem.-Int. Edit.* **2007**, *46*, 2862-2864.
74. Zhang, S.; Shao, Y. Y.; Liao, H. G.; Liu, J.; Aksay, I. A.; Yin, G. P.; Lin, Y. H., Graphene Decorated with PtAu Alloy Nanoparticles: Facile Synthesis and Promising Application for Formic Acid Oxidation. *Chem. Mat.* **2011**, *23*, 1079-1081.
75. Liu, X.; Li, L.; Meng, C.; Han, Y., Palladium Nanoparticles/Defective Graphene Composites as Oxygen Reduction Electrocatalysts: A First-principles Study. *J. Phys. Chem. C* **2012**, *116*, 2710-2719.
76. Abild-Pedersen, F.; Greeley, J.; Studt, F.; Rossmeisl, J.; Munter, T. R.; Moses, P. G.; Skulason, E.; Bligaard, T.; Norskov, J. K., Scaling properties of adsorption energies for hydrogen-containing molecules on transition-metal surfaces. *Phys. Rev. Lett.* **2007**, *99*, 016105.

77. Liu, X.; Meng, C.; Han, Y., Defective Graphene Supported MPd₁₂ (M = Fe, Co, Ni, Cu, Zn, Pd) Nanoparticles as Potential Oxygen Reduction Electrocatalysts: A First-Principles Study. *J. Phys. Chem. C* **2013**, *117*, 1350-1357.