Precisely regulating the electronic structures of metal active species is highly desirable for electrocatalysis. However, carbon with inert surface provide weak metal–support interaction, which is insufficient to modulate the electronic structures of metal nanoparticles. Herein, we propose a new method to control the electrocatalytic behavior of supported metal nanoparticles by dispersing single metal atoms on an O-doped graphene. Ideal atomic metal species are firstly computationally screened. We then verify this concept by deposition of Ru nanoparticles onto an O-doped graphene decorated with single metal atoms (e.g., Fe, Co, and Ni) for hydrogen evolution reaction (HER). Consistent with theoretical predictions, such hybrid catalysts show outstanding HER performance, much superior to other reported electrocatalysts such as the state-of-the-art Pt/C. This work offers a new strategy for modulating the activity and stability of metal nanoparticles for electrocatalysis processes.

**Abstract:** Precisely regulating the electronic structures of metal active species is highly desirable for electrocatalysis. However, carbon with inert surface provide weak metal–support interaction, which is insufficient to modulate the electronic structures of metal nanoparticles. Herein, we propose a new method to control the electrocatalytic behavior of supported metal nanoparticles by dispersing single metal atoms on an O-doped graphene. Ideal atomic metal species are firstly computationally screened. We then verify this concept by deposition of Ru nanoparticles onto an O-doped graphene decorated with single metal atoms (e.g., Fe, Co, and Ni) for hydrogen evolution reaction (HER). Consistent with theoretical predictions, such hybrid catalysts show outstanding HER performance, much superior to other reported electrocatalysts such as the state-of-the-art Pt/C. This work offers a new strategy for modulating the activity and stability of metal nanoparticles for electrocatalysis processes.

**Introduction**

Precise tailoring and controlling of the electronic structure of a catalyst have long been pursued for achieving outstanding catalytic performance.[1] Conventionally, manipulation of catalysts’ surface electronic states can be realized by particle size/shape tuning, hetero-element doping, organic ligands microenvironment engineering, and substrate interaction.[2] To date, oxide materials have been considered as favorable substrates to support metal nanoparticles, due to their strong electronic metal–support interaction (EMSI).[3] which enables the modulation of the electronic structure and catalytic property of metal nanoparticles. On the other hand, carbon materials as substrates possess superior electrical conductivity and high chemical stability.[4] However, carbon materials with a relatively inert surface can only provide weak EMSI with metal nanoparticles, which is often insufficient to effectively steer the electronic structures of the loaded metal nanoparticles.

To address this challenge, several strategies have been proposed for optimizing the EMSI of carbon-based electrocatalysts. For instance, doping carbon substrates with non-metal elements can induce the redistribution of electrons or the spin state of the $sp^2$ conjugated carbon matrix, thus tailoring the valence orbital energy of the active sites on carbon surface.[5] Besides, carbon surface functionalization using oxygen-containing groups can also introduce extra electronic states near the Fermi level, which alters its surface reactivity.[6] The enhanced EMSI results in strong orbital hybridization between metal nanoparticles and carbon surface, which is beneficial for electron transfer at their interface.

Distinct from non-metal dopants or functional groups for surface modification, metallic dopants carry more versatile electronic states, which can be more effective for activating the inert carbon surface, thus providing additional opportunities for tailoring the metal particle-support interaction and their associated catalytic characteristics. Indeed, metal single atoms have been incorporated into carbon frameworks (i.e.,...
single-atom catalysts) to catalyze a serial of electrochemical processes. For example, a variety of metal atoms or their clusters (e.g., Fe, Co, Ni, Cu, Pt, Ru, and Pd) have been coordinated on carbon surface for electrocatalysis of water splitting, nitrogen fixation, and CO₂ reduction etc. [7] Besides directly serving as the active sites, these metal centers on the carbon surface, as mentioned above, might have the capability for interacting with secondary metal nanoparticles when they are loaded together on a carbon substrate, which is rarely investigated to the best of our knowledge.

Taking Ru nanoparticles on a carbon substrate as a prototype system, our density functional theory (DFT) calculations suggest that enhanced charge transfer occurs at the interface between the substrate and Ru nanoparticles, when proper single metal atoms (e.g., Fe, Co, and Ni) are doped in the carbon support. This can effectively reshape the electronic structure of the Ru nanoparticles and enables the optimization of electrocatalytic activity. [8] To experimentally validate this prediction, Ru nanoparticles, an ideal alternative for the high-cost Pt, were loaded on an O-doped graphene substrate decorated with non-noble-metal single atoms (Fe, Co, or Ni) to serve as model electrocatalysts. Hydrogen evolution reaction (HER), which is hindered by the excessively strong binding of H atoms on pristine Ru surface, [9] was chosen as a prototype reaction. This hybrid catalyst comprised of both Ru nanoparticles and dispersed metal atoms exhibits an ultralow Tafel slope of 22.8 mVdec⁻¹ and an extremely low overpotential of 13 mV at a current density of 10 mAcm⁻², which is the highest performance reported by far to the best of our knowledge. This clearly confirms that Ru nanoparticles are the active centers and the atomic Co species enhanced HER activity, which is well consistent with the DFT calculation results. Thus, this work offers a universal strategy for precisely tailoring the electronic structure, activity, and stability of metal nanoparticles via a non-destructive and flexible route for various electrocatalytic reactions.

**Results and Discussion**

First, this strategy was conceptually investigated by DFT calculations. As shown in Figure 1a, a highly stable Ru₅₅ cluster with cuboctahedral geometry and a diameter of about 1.2 nm was adopted and supported on an O-doped graphitic nanosheet with highly dispersed transition metal single atoms (denoted as M₆@OG, with M = Fe, Co, and Ni). The shape and size effects on the activity of metal nanoparticles have been extensively explored [10] and thus will not be considered here. The electronic density of states (DOS) in Figure 1d reveals that the decoration of single metal atoms introduces prominent states near the Fermi level, which activate the inert carbon surface and remarkably enhance its interaction with Ru₅₅. Specifically, the binding strength of Ru₅₅ on Fe/Co/Ni₆@OG substrates becomes over 3.5 eV stronger than that of Ru₅₅ on OG without metal-atom decoration, as demonstrated in Figure 1c.

This enhanced nanocluster-substrate interaction is attributed to the charge transfer from the dispersed metal atoms (Fe, Co, and Ni) to OG (Figure 1a). Bader charge analysis suggests that these transferred electrons (0.87–0.93e) are carried by the C atoms nearby the O atoms (electron-rich C sites in Figure 1a), which would occupy the Cπz orbitals and break the π conjugation of the graphitic sheet. As a result, the carbon substrate is more reactive to interact with Ru₅₅, gaining more electrons from Ru₅₅ in comparison with Ru₅₅/OG (Table 1), and inducing significant charge redistribution on the nanocluster. As illustrated in Figure 1b, for Ru₅₅/M₆@OG, the Ru atoms close to the interfacial region show a more positive charge density of 0.20–0.22e compared to 0.13e for Ru₅₅/OG), indicative of a weakened binding strength with H⁺ species and possibly higher activity for

| Model     | Ebind [eV] | ε_d [eV] | CT (e) | CT₁ (e) | ΔG₂Θ H⁺ [eV] |
|-----------|------------|----------|--------|---------|---------------|
| Ru₅₅     | –          | –        | 0.03   | –       | –0.27         |
| Ru₅₅/G   | 6.98       | –        | 1.41   | 0.19    | –0.23         |
| Ru₅₅/OG  | 9.88       | –        | 1.58   | 0.13    | –0.11         |
| Ru₅₅/Fe/OG | 14.44     | –        | 1.65   | 0.20    | 0.02          |
| Ru₅₅/Co/OG | 13.78     | –        | 1.63   | 0.21    | 0.05          |
| Ru₅₅/Ni/OG | 13.41     | –        | 1.61   | 0.22    | 0.04          |
| Co₁/Ru₅₅/OG | 6.62      | –        | 1.36   | –0.15   | –0.41         |

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**Table 1:** Key parameters of Ru nanoclusters supported on various graphene-based substrates.

[52x109]
HER. Therefore, our DFT calculations suggest that single metal atoms and Ru nanoparticles can be synergized via their electronic coupling with O-doped graphene substrate, which allows delicate modulation of the activity of Ru nanoparticles.

To verify this hypothesis, Ru/M@OG analog materials were fabricated by a simple salt-template method (Supporting Information, Scheme S1). Specifically, NaCl was used as the template, and glucose and metal chlorides were employed as carbon and metal source, respectively. These chemicals were firstly dissolved in deionized water, in which process the metal ions spontaneously coordinate with the -OH group of glucose. Afterward, the mixture was freeze-dried. Ultrathin precursor layers, containing metal ions that were immobilized by glucose molecules, wrapped around the NaCl crystals at this stage. Subsequently, the materials were annealed at 700 °C in an inert atmosphere. During this process, glucose was carbonized into graphene nanosheets. Part of Co ions and Ru ions were still coordinated with O or C to form single atoms, while the rest was reduced and aggregated into metal nanoparticles. Finally, Ru/M@OG samples were obtained after removing of NaCl template by washing in water. For comparison, Ru/OG was synthesized via the same procedure as Ru/M@OG except for the absence of non-noble metal salt in the feeding mixture.

The structure of Ru/Co@OG was characterized by transmission electron microscopy (TEM). As shown in Figure 2 and S1, metal nanoparticles are uniformly dispersed on the surface of carbon nanosheets, and the mean diameter of metal clusters is around 1.5 nm (Figure 2a). The distance between crystal planes of metal particles is 0.23 nm, which can be assigned to the (100) facet of Ru (Figure 2b). Under the dark-field and high-resolution TEM (HRTEM) observation, a large number of bright dots, which represent single atoms, can be clearly seen around the metal nanoparticles (Figure 2c). Linear scanning result (Figure 2d) shows that most of the particles contain only Ru element and small amount particles contain Ru and Co element. EDS-based elemental mapping images (Figure 2e) present Ru element mainly distributed on the particles, while cobalt element appears more randomly and distributed on the whole sample. According to the above results, Ru/Co@OG contains metallic Ru particles, a small amount of Co-doped Ru particles, and single atoms. Furthermore, the contents of cobalt in the prepared samples were tuned by increasing the cobalt precursor amount in the feeding system to 1.7 times of Ru/Co@OG, and the corresponding sample was named Ru/Co$_{1.7}$@OG. The size of Ru particles on Ru/Co$_{1.7}$@OG is similar to that of Ru/Co@OG (Figure S2). For Ru/Ni@OG and Ru/Fe@OG, almost the same structures with Ru/Co@OG were observed, as shown in Figure S3.

HAADF-STEM images (Figure S4) show that Ru particles and atoms coexist on Ru/OG. The metal contents of synthesized catalysts were characterized by an inductively coupled plasma-optical emission spectrometer (ICP-OES) and shown in Table S1. All the samples are with similar Ru content of 6.9 wt.%, to 9.0 wt.%. The Co content in Ru/Co@OG and Ru/Co$_{1.7}$@OG is 0.9 wt.% and 1.6 wt.%, respectively. The ratio of Co content in Ru/Co@OG and Ru/Co$_{1.7}$@OG is the same as in the precursors.

X-ray photoelectron spectroscopy (XPS) was performed to analyze the chemical state of the metal species on Ru/Co@OG. The XPS sweep scan confirmed the presence of C, O, Co, and Ru elements on Ru/Co@OG (Figure S5). For the Ru/Co@OG sample, the high-resolution spectrum of Ru 3p3/2 (Figure 3a) can be deconvoluted into two species at 462.4 and 465.0 eV, which can be attributed to the metallic Ru and oxidized Ru$^{+}$ species, respectively. Meanwhile, the peaks at 484.5 and 487.0 eV can be assigned to the same species as well. In contrast, for the Ru/OG material, the peak positions of the corresponding Ru 3p3/2 species are located at 462.1 and 464.2 eV. Compared with the Ru/OG sample, the binding energy of the metallic Ru species on Ru/Co@OG was positively shifted by approximately 0.3 eV, indicating an electron-deficient feature on the Ru nanoparticles for Ru/Co@OG than Ru/OG. On the other hand, in the high-resolution O1s spectra of the Ru/Co@OG sample, only one...
The former can be assigned to the Ru and Tafel slope, and high h in the Th and 2.4 60 2021 h value of 24 mV, which is higher than j. Furthermore, the Th wavelet transforms (WT) of 2021 www.angewandte.org h that can be contributed to Ru particles, which further assessed in a 1.0 MK OH electrolyte in comparison with Ru/Co@OG. As shown in the linear scanning voltammetry (LSV) curves (Figure 4a), Ru/Co@OG and commercial Pt/C catalysts. A ss hown in the linear plotting of Ru-based catalysts and commercial Pt/C. d) Comparison of ηh and Tafel slope of Ru/Co@OG with representatively HER electrocatalysts.[15,13,15] The electronic structure of Co species was also charac- terized. According to the XANES of Co K-edge (Figure S6a), the adsorption edge of Ru/Co@OG is between those of Co foil and CoO, verifying the valence state of Co is between 0 to +2. Two distinct peaks appear at 1.5 Å and 2.4 Å in the EXAFS spectrum for Co K-edge of Ru/Co@OG sample (Figure S6b). The former is due to the Co-O sites of atomic Co coordinated with O on graphene, and the latter is attributed to the interaction of Co with Ru in Co-doped Ru particles, respectively. The structures of Co-O sites and Co-doped Ru particles were fitted (Table S2 and Figure S6c), which was well matched with the measured EXAFS of Ru/ Co@OG. For Co-O sites, Co was coordinated with 4 oxygen atoms. The above verifies the existence of atomic Co on Ru/ Co@OG.

Based on the above characterization results on microstructure and electronic structure of Ru/Co@OG, it is clear that both atomic Co coordinated by four O atoms and Ru nanoparticles were dispersed on catalyst substrate. Atomic Co on substrate enhances the charge transfer from Ru nanoparticle to substrates, which is fully consistent with our theoretical prediction. The enhanced EMSI provides a wide possibility for tailoring the catalytic activity of Ru particles.

The electrocatalytic activity of Ru/Co@OG for HER was assessed in a 1.0 M KOH electrolyte in comparison with Ru/ O-G and commercial Pt/C catalysts. As shown in the linear scanning voltammetry (LSV) curves (Figure 4a), Ru/Co@OG possessed the highest current density among the materials in the whole potential range. Remarkably, Ru/Co@OG also presented an ultralow overpotential of merely 13 mV at the current density of 10 mA cm\(^{-2}\) (\(\eta_h\)), which is much lower than that of Ru/OG (48 mV) and Pt/C (31 mV). In the meantime, Co@OG without the Ru nanoparticle loading only exhibited a negligible HER activity (Figure S8). This clearly demonstrates that the Ru species on Ru/Co@OG is actually the active sites for HER, while Co species just enhance the HER activity of Ru species.

To further confirm this, the HER activity of Ru/Co\(_{1.7}\)@OG was measured. The corresponding LSV curve for Ru/ Co\(_{1.7}\)@OG shows a \(\eta_h\) value of 24 mV, which is higher than that of Ru/Co@OG (Figure 4b). Thus, HER activity of Ru/ Co\(_{1.7}\)@OG is lower than Ru/Co@OG, which may be attributed to the low atomic Co content due to the aggregation induced by over high addition of Co in the synthesis system. Thus, it is clearly shown that atomic Co plays a decisive role in the HER enhancement of Ru/Co@OG.

Subsequently, the HER kinetics of the hybrid catalysts were analyzed (Figure 4c). As shown, Ru/Co@OG gives the lowest Tafel slope of 22.8 mV dec\(^{-1}\). In contrast, the Tafel slope for Ru/Co\(_{1.7}\)@OG, Ru/OG, and commercial Pt/C are 27.0, 32.4, and 31.4 mV dec\(^{-1}\), respectively, indicating the HER over the catalyst follows the Volmer-Tafel mechanism and the Tafel step is rate-limiting.[15a,16] Furthermore, the exchange current density (\(j_0\)) was also calculated based on Tafel plots. The \(j_0\) value of Ru/Co@OG is 2.93 mA cm\(^{-2}\), which is about two times higher than that of Pt/C (1.56 mA cm\(^{-2}\)). To the best of our knowledge, the Ru/Co@OG catalyst demonstrates the lowest \(\eta_h\) and Tafel slope values among the representative HER electrocatalysts in alkaline electrolytes (Figure 4d). In short, the low \(\eta_h\) and Tafel slope, and high \(j_0\) clearly illustrate the superior catalytic activity of Ru/Co@OG for HER.
Electrochemical impedance spectroscopy (EIS) measurement was conducted to measure the conductivity of those electrocatalysts. The fitted EIS data (Figure S9) shows a semicircular shape, and the diameters of semicircular reflect the charge transfer resistance of electrocatalysts. It clearly confirms that Ru/Co@OG presented the lowest charge transfer resistance and fastest charge transfer than the other electrocatalysts, leading to the most efficient HER performance.

Assuming all the Ru sites are active, the turnover frequencies (TOF) values of Ru/Co@OG is 6.2 s⁻¹ at the overpotential of 100 mV, which outperforms most of the reported electrocatalysts by far (Figure S10). Considering the cost of catalysts, the price activity of HER for Ru/Co@OG and Pt/C was calculated and shown in Figure S11. At the overpotential of 100 mV, the price activity for Ru/Co@OG is 15 times greater than that of the commercial Pt/C. The durability of Ru/Co@OG was evaluated in 1 M KOH. After 10000 cycles during the potential window of −0.07 V to −0.38 V, the HER activity exhibits an increase in η100 of only 3 mV, indicating the excellent stability of Ru/Co@OG for HER (Figure S12).

The superior HER activity of Ru/Co@OG than Ru/OG suggests that the atomically dispersed Co species on the O-doped graphene substrate played a key role for the enhancement of HER activity. For comparison, the HER activity of Ru/Ni@OG and Ru/Fe@OG were also measured under the same condition as that for Ru/Co@OG. Ru/Ni@OG shows a similar HER activity to that of Ru/Co@OG, and Ru/Fe@OG exhibits a little inferior activity with η100 of 28 mV (Figure S13). However, all of Ru/Co@OG, Ru/Ni@OG, and Ru/Fe@OG show much higher HER activity than that of Ru/OG. This further confirms that the introduction of atomic Co, Ni, and Fe species on O-doped graphene substrate can significantly enhance the HER activity.

To differentiate the actual contribution of Ru species in the nanoparticle form and those in single-atoms form on the Ru/Co@OG for HER electrocatalysis, poisoning experiments were carried out using ethylenediaminetetraacetic acid disodium (EDTA) and potassium thiocyanate (KSCN) as the complexing reagents. EDTA is dominantly coordinated with Ru single atoms, but KSCN can be coordinated with both Ru nanoparticles and single atoms. Thus, EDTA will suppress the activity of Ru single atoms, while KSCN can deactivate all the Ru species. As shown in Figure S14, upon the addition of EDTA in the electrolyte, the HER current density on Ru/Co@OG only slightly decreased compared with that in the pristine electrolyte without EDTA. In sharp contrast, the introduction of 10 mM KSCN in electrolyte would significantly decrease the HER current density on Ru/Co@OG by poisoning Ru particles and increase the η100 up to 166 mV. The significant activity gap for the electrocatalysis performance of Ru/Co@OG poisoned by EDTA and KSCN thus clearly suggests it is the Ru nanoparticles that are the main active sites for HER, rather than the Ru single atoms on the Co@OG. Furthermore, the effect of the Ru nanoparticles number on Ru/Co@OG for HER activity was explored. The result shows that the HER activity was significantly decreased, as the decrease of the number of Ru nanoparticles (Figure S14b). Thus, the decisive role of Ru nanoparticles for HER was further proved.

To better understand the enhanced HER performance of Ru/Co@OG, we calculated the free adsorption energy for H* species (ΔGads) and kinetic barrier for water dissociation (Ea), which are the key parameters to characterize HER activity in alkaline media, for the Ru5@ nanocluster supported on various substrates. As displayed in Figure 5a, Ru5@Co@OG shows the optimal adsorption strength towards H species with ΔGads of −0.05−0.05 eV, in which the active sites are the center of the triangle forming by interfacial Ru atoms (Figure S15). Besides, water dissociation on Ru5@Co@OG is found to be exothermic with an enthalpy change of −0.57 eV and involves a small kinetic barrier Ea = 0.66 eV (Figure S16), close to that of Ru5 (0.47 eV), and both can occur readily at ambient condition. However, the freestanding Ru5@ cluster has much stronger binding strength for H* species (ΔGads = −0.27 eV), leading to a sluggish Volmer-Tafel mechanism for HER in the alkaline media. In comparison, Ru5@Co@OG has over-strong binding with H species with ΔGads = −0.15−0.11 eV (Figure S15), due to the less electron transfer from the Ru5@ nanocluster to the substrate as mentioned at the beginning (Table 1). Furthermore, to exclude the possibility of Co doping into the Ru nanoparticles, we also considered a model of alloyed nanocluster Co0.5Ru4.5 supported on O-doped graphene. Co0.5Ru4.5@OG provides too strong binding with H* species, having ΔGads = −0.41−0.12 eV that is unfavorable for the formation of H2 from the adsorbed H* species (Figure S20). Besides, single Co or Ru atoms anchored on O-doped graphene has the too weak or too strong binding capability with H* species, yielding ΔGads = 0.60 and −0.38 eV, respectively, which further confirms the synergistic interaction between Co single atoms and Ru nanoparticles on the O-doped graphene substrate for efficient HER electrocatalysis (see Figure S21−S23 for details). The activities of Ru5@ nanocluster and single metal atoms on the graphene-based substrates show a clear linear relation with the d band center of transition metal atoms, as evident in Figure 5b and Figure S24. In particular, the support of Co@OG lowers the d band center of Ru5@ nanocluster to −2.55 eV compared to −2.28 and −2.52 eV for freestanding Ru5@ and Ru5@Co@OG, respectively, again manifesting the effective tuning of the
electronic structure of Ru nanoparticles by the single-metal-atom-dispersed graphene substrate. According to the d band theory,[20] a lower d band center corresponds to more occupancy of antibonding state between Ru@CoO@OG and H* adsorbate, which results in weaker but more optimal H* binding strength for hydrogen evolution. Therefore, both the computed electronic structures and catalytic properties of Ru nanoparticles on O-doped graphene substrates demonstrate that the decoration of single metal atoms on the substrate can significantly enhance the EMSI between the supported metal nanoparticles and the substrate, affording the precise design of high-efficiency metal nanoparticles for a certain reaction.

**Conclusion**

We demonstrated that atomically dispersed metal species on the carbon substrate can remotely communicate with the supported metal nanoparticles, inducing synergistic electronic coupling with the nanomaterials and enabling the control of their electrocatalytic activity. Proposed by DFT calculations, it is suggested that modification of O-doped graphene substrate with single metal atoms can effectively enhance the EMSI with the Ru nanoparticles supported on it and redistribute the electron of Ru nanoparticles, resulting in optimized adsorption free energy of H* species on Ru particles and enhanced HER activity. Confirmed by experimental results, the fabricated hybrid of Ru nanoparticles dispersed on metal-doped graphene (Ru/M@OG) indeed exhibited enhanced HER activity than that of Ru@OG. In alkaline electrolyte, Ru/CoO@OG showcased exceptional performance with an overpotential of 13 mV at the current density of 10 mAcm⁻² and ultralow Tafel slopes of 22.8 mVdec⁻¹, outperforming the commercial Pt/C electrocatalyst. Furthermore, the metal atoms on the O-doped graphene strengthen the binding of Ru nanoparticle on the substrate to prevent their ripening and enhance stability. This work successfully demonstrated the most active Pt-free catalyst for HER, and provided new insights into the modulation mechanism of EMSI between atomic metal doped carbon and the supported metal nanoparticles to rationally design electrocatalysts.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** electrocatalysis · electronic structures · hydrogen evolution · metal nanoparticles · metal–carbon interactions

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