Electrocatalytic Isoxazoline-Nanocarbon Metal Complexes

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Supporting Information Placeholder

ABSTRACT: We report the synthesis of new carbon nanomaterial-based metal chelates that enable the effective electronic coupling to electrocatalytic transition metals. In particular, multi-walled carbon nanotubes (MWCNTs) and few layered graphene (FLGs) were covalently functionalized by the microwave-assisted cycloaddition with nitrile oxides to form metal-binding isoxazoline functional groups with high densities. The covalent attachment was evidenced by Raman Spectroscopy and the chemical identity of the surface functional groups were confirmed by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The functional carbon nanomaterials effectively chelate precious metals Ir(III), Pt(II) and Ru(III), as well as earth-abundant metals such as Ni(II), to afford materials with metal contents as high as 3.0 at%. The molecularly dispersed nature of the catalysts is confirmed by X-ray absorption spectroscopy (XAS) and energy-dispersive X-ray spectroscopy (STEM-EDS) elemental mapping. The interplay between the chelate structure on graphene surface and its metal binding ability has also been investigated by a combination of experimental and computational studies. The defined ligands on the graphene surfaces enable the formation of structurally precise heterogeneous molecular catalysts. The direct attachment of the isoxazoline functional on the graphene surfaces provides strong electronic coupling between the chelated metal species and the conductive carbon nanomaterial support. We demonstrate that the metal-chelated carbon nanomaterials are effective heterogeneous catalysts in the oxygen evolution reaction with low overpotentials and tunable catalytic activity.

INTRODUCTION

Carbon nanomaterials, such as single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs) and graphene, are an attractive class of materials with unique physical, mechanical and electronic properties[1–8] that hold great potential in energy,[9–12] catalysis,[13–16] sensing[17–23] and biomedical[24–28] applications. Pristine carbon nanomaterials lack the functionalities required for specific applications or processing, and as a result, extensive research efforts have targeted their functionalization.[29–34] These methods include non-covalent physisorbed attachments of small molecules and polymers to the surface by hydrophobic/π–π interactions and the covalent addition reactions with the edges, ends, or sidewalls.

We have endeavored to create robust methods for the attachment of transition metal binding ligands to create functional carbon nanomaterials for chemical sensing[35–38] and catalysis.[39–44] Our specific objectives are to create metal-functionalized nanomaterials that could maintain or enhance the expected activity of the metal species. [45–46] To this end, covalent attachment of multidentate metal chelates have been targeted to create nanostructures with predictable structures and properties. Metal chelation can provide access to heterogeneous molecular catalysts that possess both good electrochemical electron transfer properties and precise structural control at the molecular level.

In the present investigation we have focused on the attachment of metal chelates based on isoxazoline to graphene surfaces. As shown in Figure 1, the 2-pyridyl isoxazole ring provides for a strong metal-carbon nanomaterial connection. The preconstructed chelating ligand provides for predictability of the metal complex structure and the overlap of the ligand's p-orbitals to the π-electronic states of the graphene surface allows for effective electronic coupling between a bound metal complex and the carbon naomaterial.[47] Moreover the distributed chelating ligands tend to stabilize low nuclearity transition metal compositions and thereby reduce the formation of aggregates and nanoparticles.[48–49] The isoxazoline moiety can be effectively added to the graphene surfaces by 1,3-dipolar cycloadditions of nitrile oxides. Various kinds of carbon nanomaterials have been shown to undergo cycloaddition with nitrile oxides experimentally[50-52] and have also been studied computationally.[53] In this report, we apply this strategy to MWCNTs and few-layered graphene (FLG) to create a broad spectrum of transition metal functionalized carbon nanomaterials that serve as efficient heterogeneous molecular catalysts for oxygen evolution reaction (OER), which is considered as the bottleneck of water splitting process for clean energy conversion.[54–59] Furthermore, our complexation strategy is highly general and can be applied in many other important catalytic processes.

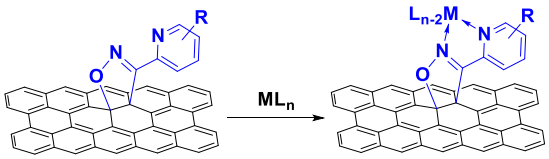
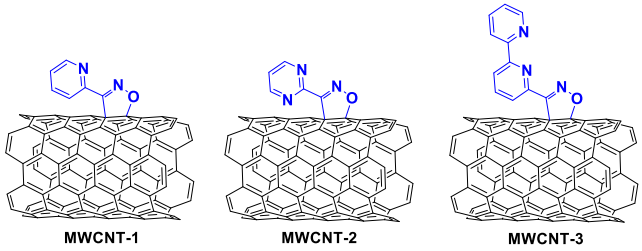


Figure 1. Schematic depiction of metal chelation by isoxazoline functional groups on carbon nanomaterial surface.

RESULTS AND DISCUSSION

We began our investigations by functionalizing MWCNTs with 2-pyridyl, 2-pyrimidyl and 2,2'-bipyridyl isoxazole rings. We have previously reported similar structures based on C_{60} that formed well defined Re(I), Pt(II) and Ir(III) complexes.[47] The reactive nitrile oxide intermediates that we previously utilized can undergo a number of side reactions in addition to the functionalization of the nanomaterials. In the present one-pot procedure, we first generate nitrile oxide dimers by base treatment of *N*-hydroxyl imidoyl chlorides. Thermal cracking of these dimers local to the MWCNT surface is achieved by microwave irradiation of a dispersion in *o*-dichlorobenzene (*o*DCB). The high microwave absorptivity of MWCNTs provides for localized heating and has been shown to be a versatile method to effectively functionalize carbon nanomaterials.[60–66] In the present case this local heating generates the nitrile-oxide groups proximate to the graphene surfaces. In our procedure, microwave irradiation serves two purposes: a) it provides sufficient thermal energy for the *in situ* generation of the nitrile oxide reactive species *via* a retro-cycloaddition of the preformed dimers[67–68] and b) locally activates the carbon nanomaterials surfaces and reactive intermediates. As shown in Scheme 1, this method can produce functionalized MWCNTs (**MWCNT-1**, **MWCNT-2** and **MWCNT-3**) containing bidentate or tridentate ligands for metal chelation.



Scheme 1. Structures of isoxazoline-functionalized multi-walled carbon nanotubes (MWCNTs). MWCNTs are simplified as SWCNTs in illustration for clarity.

The successful covalent modification on MWCNTs is revealed by Raman spectroscopy. Figure 2 shows the Raman spectra of pristine MWCNTs (**p-MWCNT**), **MWCNT-1**, **MWCNT-2** and **MWCNT-3** under 633nm laser excitation. Apart from the prominent G-band (~1600 cm^{-1}) and D-band (~1350cm^{-1}), significant band broadening and higher spectral intensity in the valley between the G and D bands are observed. The latter is in part the result of the increase in satellite bands attributed to limit-sized sp^2 domains resulting from the covalent functionalization. Control experiments in the absence of nitrile oxide showed no change in Raman signals (Figure S1). Following an established procedure,[69] detailed Raman peak deconvolution has been performed (Figure S2) and the Raman chemical functionalization degree (CFD) for the functionalized MWCNTs are shown in Table 1, reflecting the extent of covalent modification. Moreover, the G-band peaks of the functionalized MWCNTs are shifted to the lower wavenumber when comparing to that of **p-MWCNT** (Figure S3), indicating the electronic effects of the surface functional groups on the MWCNTs.[70–71]

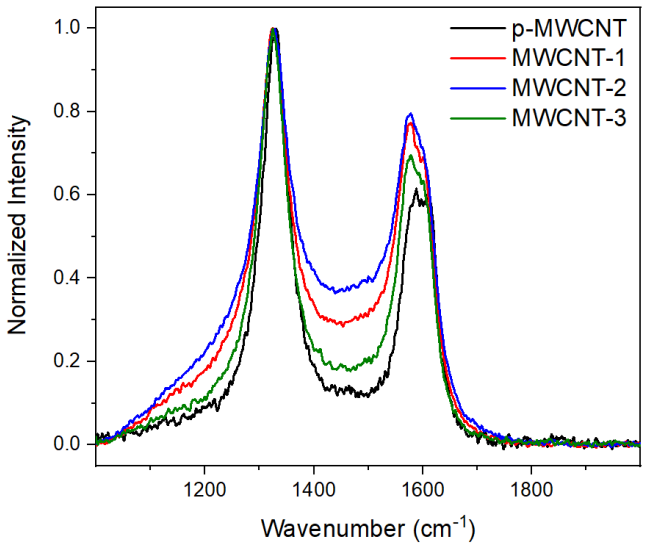


Figure 2. Raman spectra of **p-MWCNT** (black), **MWCNT-1** (red), **MWCNT-2** (blue) and **MWCNT-3** (green) collected with 633nm laser excitation.

The chemical identity of the surface functional groups was analyzed by X-ray photoelectron spectroscopy (XPS). The XPS survey scans of the functionalized MWCNTs (Figure S4–7) showed significant increase in nitrogen and oxygen content as summarized in Table 1. Specifically, **MWCNT-1**, **MWCNT-2** and **MWCNT-3** are found to contain nitrogen at 7.5, 13.7 and 4.9 atomic percent and oxygen at 5.6, 6.2 and 4.7 atomic percent, respectively. To preclude the possibility of simple physisorption of functional groups, control experiments were performed where no heating was applied to generate the reactive nitrile oxide intermediate, and only minimal incorporation of nitrogen content was observed (Figure S8). High resolution XPS spectra in N 1s region are shown in Figure 3 and reveals the local environment of the nitrogen species present. Characteristic pyridinic N 1s peaks at around 398.6 eV[72] are found in all functionalized MWCNTs, and the isoxazole N 1s peaks are at around 400.4 eV.[53] Both signals are in agreement with the N 1s peaks observed in the small molecule analog **C$_{60}$-1** reported previously (Figure S9).[47] The ratios of the two characteristic peaks agree with their anticipated atomic stoichiometry. Derived from the ratio between pyridinic N 1s and C 1s peaks, the degrees of functionalization were found to be 4.6, 5.6 and 1.6 functional groups per 100 CNT carbon atoms for **MWCNT-1**, **MWCNT-2** and **MWCNT-3**, respectively. These ratios are in agreement with the Raman CFD values (Figure S10).

Table 1. Characterization of functionalized MWCNTs.

Sample	Raman CFD[1]	XPS composition (at%)			Weight loss at 800 °C (%)
		C 1s	N 1s	O 1s	
p-MWCNT	0.40	98.8	0.0	1.2	2
MWCNT-1	1.14	86.9	7.5	5.6	14
MWCNT-2	1.15	80.3	13.7	6.2	31
MWCNT-3	0.58	90.4	4.9	4.7	12

In order to gain molecular-level structural information of the surface functional groups, the modified MWCNTs were analyzed by time-of-flight secondary ion mass spectrometry (ToF-SIMS), a highly sensitive surface analytical technique that has high mass resolution for the acquisition of molecular information from the surface of a material.[73] The MWCNT surfaces are bombarded with Bi_3^+ and the secondary ions are evaluated by mass spectrometry in the context of fragments originating from the surface functional groups. As shown in Figure 4, significantly more signals, which attributes to unsaturated hydrocarbon fragments, are observed in the functionalized MWCNTs as compared to the pristine unfunctionalized material. In particular, unambiguous peaks at 78, 79 and 155 m/z are indicative of the pyridyl, pyrimidyl and bipyridyl fragments, respectively. These specific fragments attributed to the different isoxazole groups that had been covalently fused to the MWCNTs. Prominent C_nN^- peaks, which originate from the nitrogen-containing functional groups,[74] are observed in the functionalized MWCNTs in negative mode (Figure S12).

The collective evidence from Raman, XPS and ToF-SIMS analysis supports that MWCNTs have been successfully ovalently functionalized by cycloaddition of nitrile oxides to give the structures shown in Scheme 1.

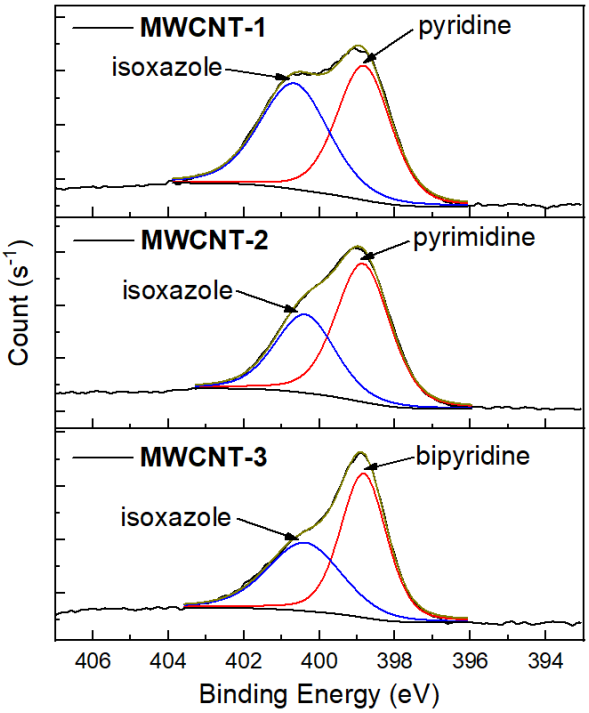


Figure 3. XPS N 1s spectra of **MWCNT-1** (top), **MWCNT-2** (middle) and **MWCNT-3** (bottom).

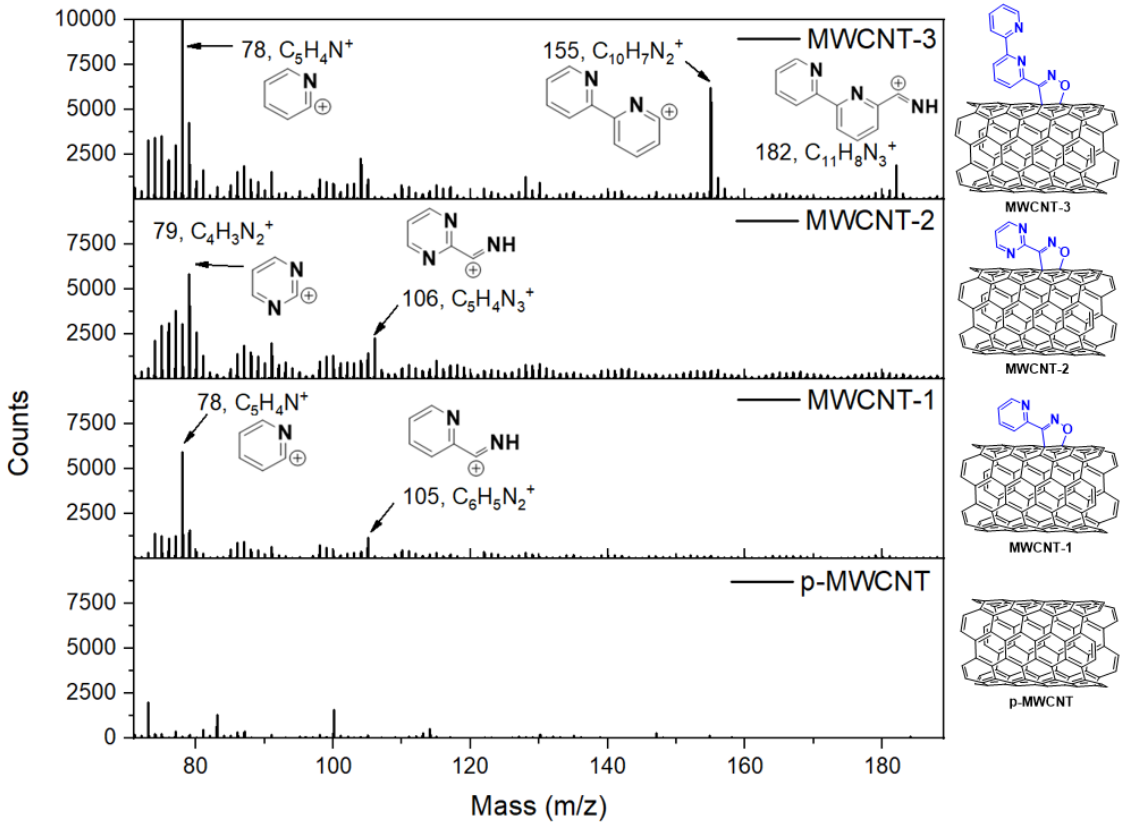
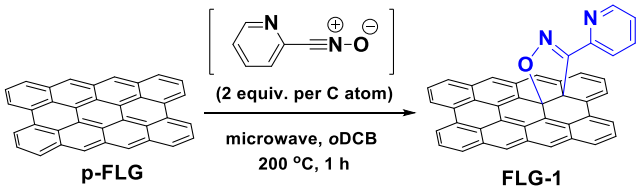


Figure 4. ToF-SIMS spectra of **p-MWCNT**, **MWCNT-1**, **MWCNT-2** and **MWCNT-3** in positive mode. MWCNTs are simplified as SWCNTs in illustration for clarity.



Scheme 2. Synthesis of isoxazoline functionalized few-layered graphene.

We have been interested to see if our methods could be generalized to functionalize other carbon nanomaterials including few-layer graphene. As shown in Scheme 2, few-layered graphene (**p-FLG**) nanoplatelets was subject to the microwave conditions and *in situ* generation of 2-pyridyl nitrile oxide to yield the isoxazoline functionalized product **FLG-1**. Successful covalent modification of the graphene layers was confirmed by the significant increase in D/G band ratio in the Raman spectra (Figure S13). The average number of layers of the material was found to have increased slightly as indicated by the diminished 2D/G band ratio,[75] wherein the aggregation may be promoted by microwave heating. A remarkably high degree of functionalization of 7.7 functional groups per 100 graphene carbon atoms in **FLG-1** was determined by XPS (Figure S14). Notably, this material is among the most densely functionalized graphene reported to date (Table S3). This result is particularly exciting because it is challenging to covalently functionalize graphene layers as a result of the lack of basal plane curvature.[76–77] A high resolution XPS spectrum of the N 1s region confirmed the identity of the 2-pyridyl isoxazole functional group by the characteristic pyridinic and isoxazole N 1s peaks with the expected stoichiometry (Figure S15). The high functionalization efficiency is likely facilitated by the high dispersibility of **p-FLG** in *o*DCB as a result of its smaller domain size. As shown in Figure 5, at a concentration of 0.1 mg/mL, **FLG-1** is easily dispersed in water with mild bath sonication. This solution is stable for weeks whereas pristine **p-FLG** has insignificant dispersibility in water. The stark increase in hydrophilicity of **FLG-1** represents a clear macroscopic manifestation of its highly functionalized nature.

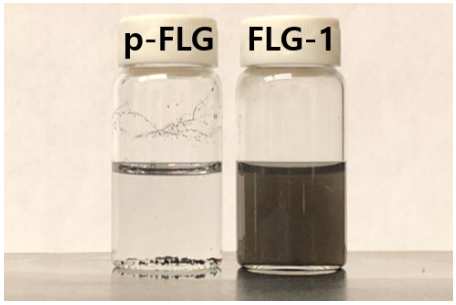
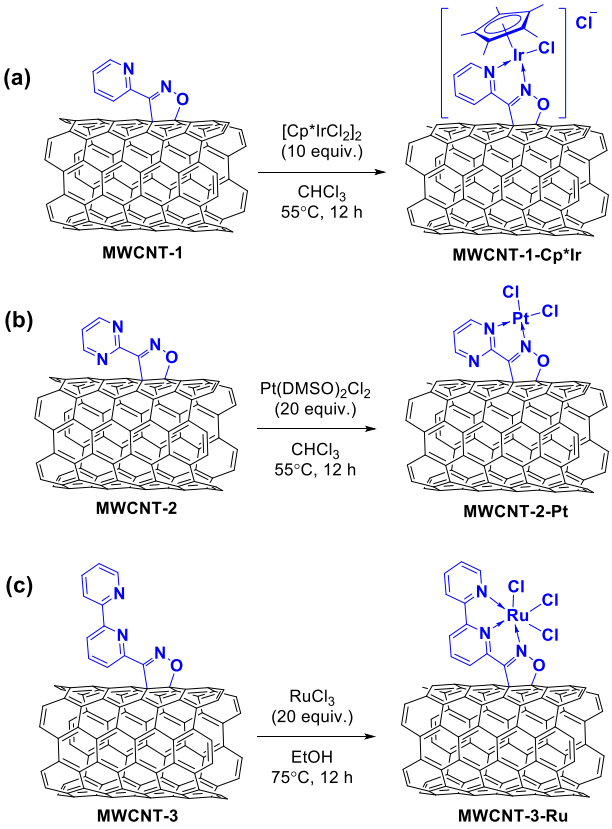


Figure 5. Photographs of dispersions of **p-FLG** (left) and **FLG-1** (right) in water (0.1 mg/mL).



Scheme 3. Metal chelation reactions of isoxazoline functionalized MWCNTs. The equivalent of metal precursors are relative to the amount of functional groups determined by XPS. MWCNTs are simplified as SWCNTs in illustration for clarity.

We have explored the metal binding properties of isoxazoline functionalized MWCNTs and FLG (Scheme 3) with $[Cp^*IrCl_2]_2$ (Cp^* = η^5-C_5Me_5), *cis*-$Pt(DMSO)_2Cl_2$ (DMSO = dimethyl sulfoxide) and $RuCl_3$ hydrate. The selected metal species are well-known to complex pyridinic nitrogens. The isoxazoline functionalized MWCNTs were dispersed in chloroform or ethanol by bath sonication, mixed with the metal complex precursors, and then heated for 12 hours before collection by filtration. After extensive washing with ethanol, *N*,*N*-dimethylformamide and acetone to remove the unbound metal species, the resulting materials was evaluated with XPS (Figure S17−19). As summarized in Table 2, all of the added metallic elements were observed by XPS. In particular, **MWCNT-1-Cp*Ir** displayed a 2.5 at% or 26 wt% Ir(III), **MWCNT-2-Pt** was found to contain 3.0 at% or 30 wt% Pt(II), and **MWCNT-3-Ru** was found to contain 0.9 at% or 7 wt% Ru(III). The immobilized metal species were also found to have mostly identical binding energies by XPS with their homogenous precursors, suggesting unperturbed oxidation state of the metal species (Figure S20−22). This observation is in stark contrast with the previous reports of spontaneous reduction of Ru(III) and Pt(II) compounds by pristine CNTs,[78–79] thereby showcasing the stabilizing effect resulted from the surface chelating groups. **FLG-1** has also shown good metal-binding ability by incorporating 3.0 at% or 29 wt% of Ir(III) (Figure S23). Moreover, beyond the scope of precious metals, earth-

abundant Ni(II) can also be effectively chelated to **MWCNT-1** (Scheme S1, Figure S24–25). All evidence suggests that our platform has general utility for the formation of metal-carbon nanomaterial complexes.

Table 2. Elemental composition of metal-chelated MWCNTs.

Sample	XPS composition (at%)				
	C 1s	N 1s	O 1s	Cl 2p	Metal
MWCNT-1-Cp*Ir	76.3	6.8	6.9	7.5	2.5 (Ir 4f)
MWCNT-2-Pt	68.2	14.4	9.4	5.0	3.0 (Pt 4f)
MWCNT-3-Ru	87.5	4.2	5.2	2.2	0.9 (Ru 3p)
FLG-1-Cp*Ir	72.6	9.2	6.7	8.5	3.0 (Ir 4f)
MWCNT-1-Ni	83.4	6.4	5.4	2.8	2.0 (Ni 2p)

To test the hypothesis that metal binding occurred *via* metal chelation rather than simple physisorption, we evaluated the high resolution XPS spectra of the N 1s regions of the metal-MWCNT composite materials (Figure 6). Comparing to the spectra of the starting materials in Figure 3, we find that the characteristic pyridinic peaks at 398.6 eV have decreased significantly whereas new peaks have emerged at around 400.3 and 401.5 eV. These peaks correspond to the chelated pyridinic N 1s peaks and chelated isoxazole N 1s peaks respectively, which as expected have slightly higher binding energy than their non-chelated counterparts.[80–81] We further measured the XPS N 1s spectrum of $[(ppy)_2IrCl]_2$ (ppy = 2-phenylpyridine) as an external reference to confirm the binding energy of the chelated pyridinic nitrogen (Figure S26).

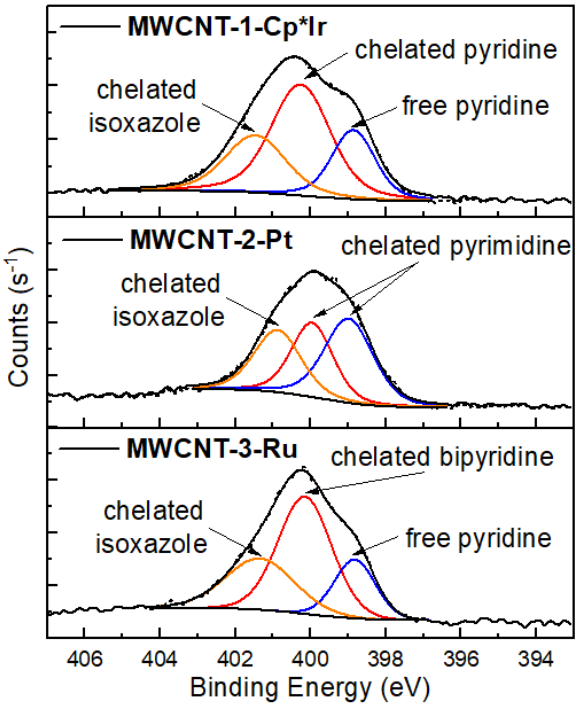


Figure 6. XPS N 1s spectra of **MWCNT-1-Cp*Ir** (top), **MWCNT-2-Pt** (middle) and **MWCNT-3-Ru** (bottom).

It was important to further demonstrate that the metal species chelated on the carbon nanomaterials are molecularly dispersed as opposed to separating into nanoparticles/clusters. In this context **MWCNT-1-Cp*Ir**, as a representative composition, was imaged using a scanning transmission electron microscope (STEM) and the map of the respective elements are revealed by energy dispersive spectroscopy (EDS). As shown in Figure 7, nitrogen and iridium species are found to be uniformly dispersed on MWCNT and their locations seem to correlate with each other. **MWCNT-1-Cp*Ir** has also been analyzed by STEM-EDS at multiple locations and lower magnification to ensure the dispersive nature of the iridium species is consistent throughout the material (Figure S28). X-ray absorption spectroscopy (XAS) studies were also performed to support our claim that the chelated metal species are molecularly dispersed on the modified carbon nanomaterials. In the extended X-ray absorption fine structure (EXAFS) analysis (Figure 8), **MWCNT-1-Cp*Ir** is shown to have a local coordination structure distinctive from those of the reference Ir foil and IrO_2, indicating the absence of Ir-Ir bond and IrO_2 clusters in the material. A broad scattering peak is observed for **MWCNT-1-Cp*Ir** that covers a range of distance from 2.0 Å to 2.5 Å and can be attributed to the existence of Ir–C, Ir–N and Ir–Cl bonds, comparable with those of reference compounds $[Cp^*IrCl_2]_2$ and $Cp^*(bpy)IrCl_2$ (bpy = 2,2′-bipyridine). Moreover, consistent with the XPS results, the X-ray absorption near-edge structure (XANES) at the Ir L_3-edge (Figure 8) shows that the white line peak position of **MWCNT-1-Cp*Ir** is very similar to that of $[Cp^*IrCl_2]_2$, suggesting the unperturbed oxidation state of Ir(III) after the metal chelation process. Similarly, the molecular dispersed nature of other metal-functionalized carbon nanomaterials such as **MWCNT-1-Ni** is also evidenced by XAS results (Figure S29).

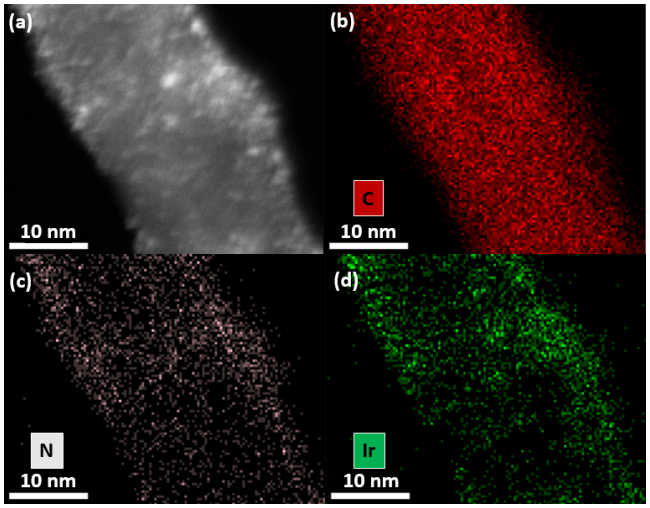


Figure 7. (a) HAADF-STEM image of **MWCNT-1-Cp*Ir**. (b-d) STEM-EDS elemental mapping of **MWCNT-1-Cp*Ir**.

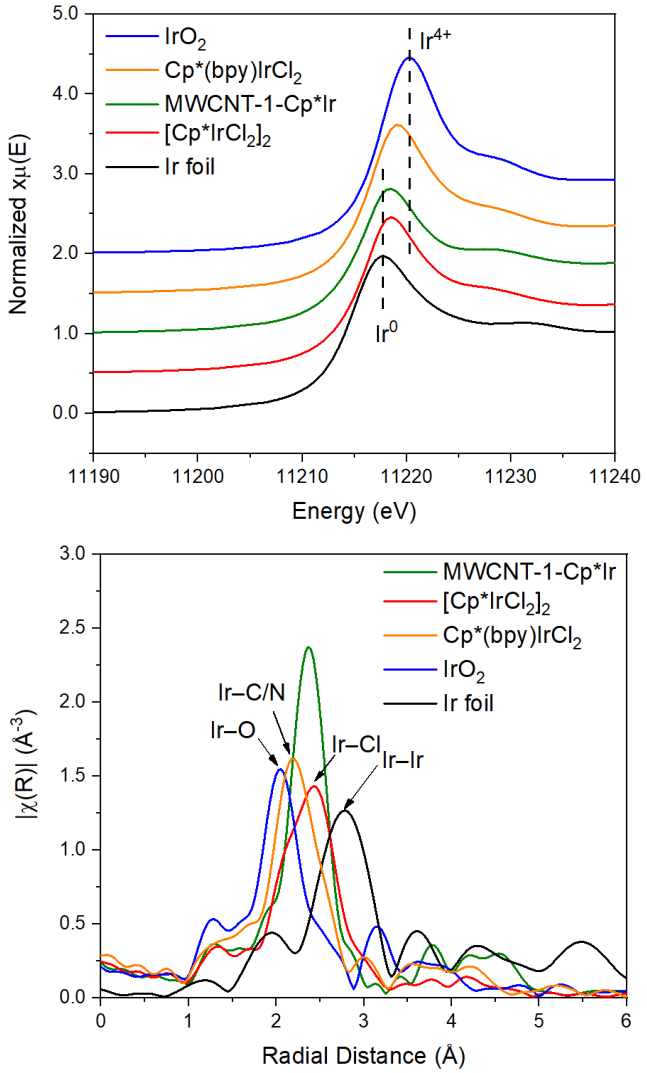


Figure 8. XANES data (top) and Fourier-transformed EXAFS spectra (bottom) at the Ir L_3-edge of **MWCNT-1-Cp*Ir**, $[Cp^*IrCl_2]_2$, $Cp^*(bpy)IrCl_2$, IrO_2 and Ir foil.

To further understand the metal chelating ability of the isoxazoline-nanocarbon materials, we employed computational tools to investigate the thermodynamics of the metal chelation events on graphene surface. In a representative system, **MWCNT-1-Ni** has been modeled as **G-1-Ni** on a finite-size polybenzenoid (36 fused benzene rings) hydrocarbons and the energetics of the ligand substitution process has been studied. Unrestricted DFT method was used as radical character has been reported in polyacenes and graphene fragments.[82–85,53] Energy calculations suggest that the ground state Ni(II)-containing species are likely to be high spin (Table S4). The formation of **G-1-Ni** is found to be exothermic with a ΔG of -3.3 kcal/mol (Figure S43). Slight curvature has been observed in the optimized graphene structures due to the edge effect. To give a more realistic representation of the graphene plane, an additional limit has been imposed on the structures where the optimization was performed with the outermost carbon atoms frozen. The optimized structure of **G-1-Ni_frozen** is shown in Figure 9a, where a dihedral angle of 21.4 degree is observed between the pyridine and the isoxazole rings. The ΔG of chelation in this case (ΔG_frozen) was found to be slightly higher (-2.0 kcal/mol) yet still thermodynamically favorable. For reference, metal chelation of the small molecule analog **Py-Iso** has also been evaluated (Figure S44). A simple distortion-interaction analysis shows a reasonable distortion energy of 9.3 kcal/mol (**G-1_frozen→G-1_distort_frozen**) for the pyridine ring to rotate and move into the position for metal chelation. As shown in Figure 9a and S47, the H on the 3-position of the pyridine ring is in close contact with the graphene plane. Therefore, we are interested to probe the substituent steric effect on metal chelation. To this end, an additional methyl group has been introduced to the 3-position of the pyridine ring (**MWCNT-4**, Figure S30) to increase the steric bulk. Attempt to synthesize **MWCNT-4-Ni** (Scheme S2) was unsuccessful with only trace Ni(II) incorporation (Figure S31, Table S1). This experimental observation is in good agreement with computational results where the formation of **G-4-Ni_frozen** was found to be unfavorable (Figure S45). The optimized structure of **G-4-Ni_frozen** (Figure 9b) shows a highly distorted chelate structure with a large dihedral angle of 44.1 degree between the pyridine and the isoxazole rings. The ΔΔG of chelation between the H-substituted and methyl-substituted isoxazoline graphene was found to be 8.3 kcal/mol, suggesting a six order of magnitude difference in equilibrium constants. These results highlight the structure-activity relationship between the steric bulk of the pyridyl-isoxazoline moieties on graphene and their ability to chelate metal species.

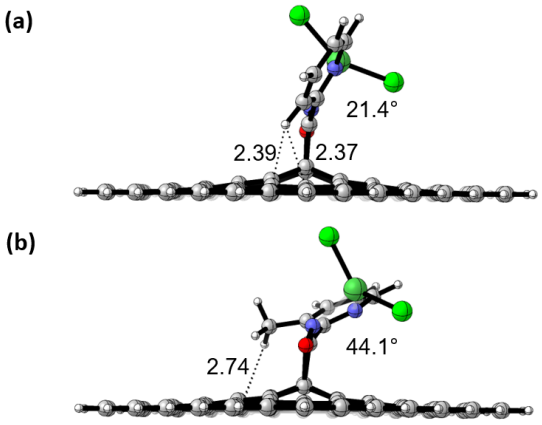


Figure 9. Optimized structures of (a) **G-1-Ni_frozen** and (b) **G-4-Ni_frozen** fragments. All distances are shown in Å.

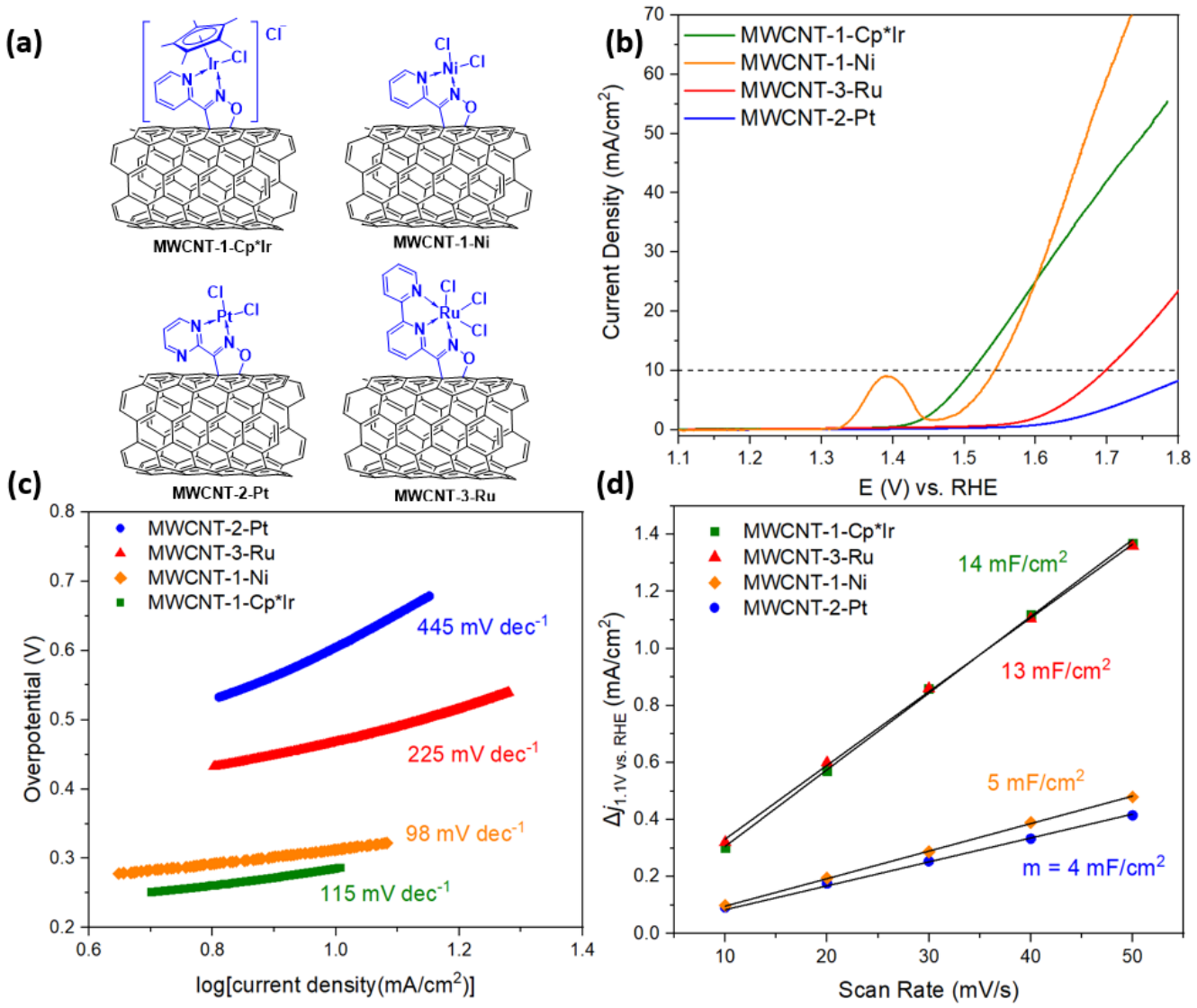


Figure 10. (a) Structures of metal-functionalized MWCNTs. MWCNTs are simplified as SWCNTs in illustration for clarity. (b) LSV curves of **MWCNT-1-Cp*Ir** (green), **MWCNT-1-Ni** (orange), **MWCNT-2-Pt** (blue) and **MWCNT-3-Ru** (red) for OER in 1 M KOH. (c) Tafel plots of different catalysts for OER in 1 M KOH. (d) Estimation of double-layer capacitance C_{dl} by fitting the current-density variation at 1.1 V vs RHE against the scan rate.

These dense functionalization of transition metal on carbon nanomaterials represents a new platform for heterogeneous catalysis. The structure of the isoxazoline ligands with a π-electronic system proximate to the graphene facilitates electronic coupling. This with the conducting properties carbon nanomaterials, and molecularly dispersed nature of the metal species, was expected to provide highly active electrocatalysts or precatalysts. As a proof of concept, the catalytic performance in the oxygen evolution reaction (OER) has been evaluated by linear sweep voltammetry (LSV) and Tafel slope analysis. The electrochemically active surface area (ECSA) is also characterized by estimating the double-layer capacitance (C_{dl}). The functionalized MWCNTs were dispersed in ethanol, mixed with 5 wt% Nafion solution and subsequently dropcasted on carbon paper electrode to fabricate the working electrode for the OER process in 1 M KOH electrolyte. As shown by its LSV curve in Figure 10b, **MWCNT-1-Cp*Ir** exhibits excellent OER activity with an overpotential of 280 mV at 10 mA/cm^2, which places it among the best performing CNT-based OER catalysts reported.[86–95] The molecular analogs of **MWCNT-1-Cp*Ir** have been extensively studied as water oxidation catalysts.[96–101] For reference the commercial carbon paper electrode, **p-MWCNT**, and **MWCNT-1** were found to possess poor OER activity with overpotentials greater than 600 mV (Figure S32). Notably, **MWCNT-1-Cp*Ir** outperformed the mixture of pristine MWCNTs and commercial IrO_2 with the same metal loading (**IrO_2/p-MWCNT**, 25 wt% Ir) in terms of overpotentials, current density and kinetics in OER catalysis (Figure S32−33). This feature confirms that covalent functionalization of metal chelators on MWCNTs to integrate transition metal complexes produces more efficient catalysts. In contrast, even though the Ir(III) content is higher in **FLG-1-Cp*Ir**, its OER activity was found to be less than ideal (Figure S32), possibly due to poor contact between the

material and the electrode, and/or the lower conductance of the highly functionalized FLG.

The OER performance of several other transition metal-MWCNT complexes were evaluated (Figure 10). **MWCNT-3-Ru** showed moderate OER activity with an overpotential of 460 mV, whereas **MWCNT-2-Pt** was found to be OER inactive. The inferior OER performance of the high metal content **MWCNT-2-Pt** is unexpected and may be attributed to a ligand effect and/or the lower conductance as a result of the high degree of functionalization. **MWCNT-3-Ru** has significantly lower metal content than **MWCNT-1-Cp*Ir** as a result of the lower degree of functionalization in **MWCNT-3**. However, **MWCNT-1-Ni**, which contains earth-abundant Ni(II), was found to not only possess excellent OER activity similar to **MWCNT-1-Cp*Ir** with an overpotential of 310 mV, but also faster OER kinetics as illustrated by Tafel analysis (Figure 10c). Moreover, the current density of **MWCNT-1-Ni** reaches 69 mA/cm^2 at an overpotential of 500 mV, which is more than two times higher than that of the **IrO_2/p-MWCNT** mixture (25 wt% Ir) at the same overpotential (33 mA/cm^2). This is particularly exciting as nickel represents a low-cost substitute for precious metal oxides that are widely used as OER catalysts industrially.[102−103] The long-term stability of **MWCNT-1-Ni** was also evaluated by chronopotentiometry (CP) at a current density of 10 mA/cm^2, and no significant loss of OER activity was observed after 16 hours of operation (Figure S35). XPS analysis of **MWCNT-1-Ni** after CP shows a near complete loss of chlorine content and slight changes in Ni 2p peaks (Figure S36−37), suggesting the speciation of nickel chlorides to nickel hydroxides/oxyhydroxides during the OER process. To further characterize the catalytically active metal species, EXAFS analysis of **MWCNT-1-Ni** after OER shows a Ni local coordination environment that closely resembles to that of $Ni(OH)_2$ (Figure S38). Notably, a prominent oxidation peak is observed at around 1.4 V for **MWCNT-1-Ni**, which corresponds to the Ni^{II}/Ni^{III} oxidation event.[104−106] XANES results at Ni K-edge (Figure S38) also reveal that the white line position of **MWCNT-1-Ni** shifted to a higher energy after OER, suggesting an increase in oxidation state for the Ni center, further supporting the formation of nickel oxyhydroxides during OER. Moreover, comparing the total charge transfer in this oxidation event to the amount of Ni(II) dropcasted on the carbon paper electrode, we found that about 88% of the deposited Ni(II) is accounted for in this oxidation (Figure S39), thereby underscoring the efficient electrochemical coupling between the metal center and MWCNTs.

Our complexation strategy provides molecular level structural control of the heterogeneous catalyst and as such the catalytic activity can be modulated by the surrounding ligand structures. To probe this aspect, we have synthesized a series of Ir(III)-MWCNT complexes bearing different ligands, as shown in Figure 12a. **MWCNT-1-ppyIr** is synthesized *via* ligand substitution from $[(ppy)_2IrCl]_2$ precursor and **MWCNT-2-Cp*Ir** is derived from **MWCNT-2** and $[Cp^*IrCl_2]_2$ (Scheme S3). Their chemical compositions are characterized by XPS which reveals the comparable levels of Ir(III) content with **MWCNT-1-Cp*Ir** (Figure S40−41, Table S2). Tof-SIMS was particularly useful in unambiguously assigning and distinguishing the ligand structures present on these Ir(III)-MWCNT complexes. As shown in Figure 11, $[ppy_2Ir]^+$ and $[Cp^*IrCl]^+$ ions were the dominate ions and thereby support the proposed structures of **MWCNT-1-ppyIr** and **MWCNT-1-Cp*Ir**, respectively.

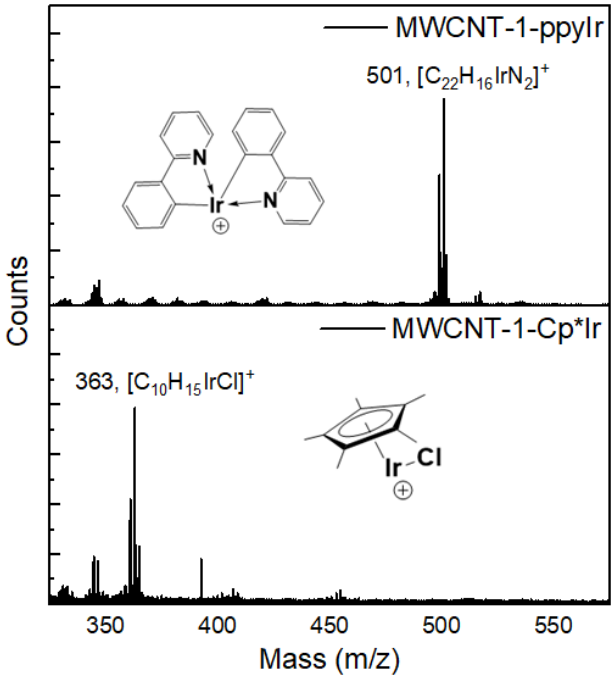


Figure 11. ToF-SIMS spectra of **MWCNT-1-ppyIr** (top) and **MWCNT-1-Cp*Ir** (bottom) in positive mode, showing fragments from their respective molecular precursors.

The OER performance of **MWCNT-1-ppyIr** and **MWCNT-2-Cp*Ir** are compared with that of **MWCNT-1-Cp*Ir** in Figure 12. Interestingly, both variants of **MWCNT-1-Cp*Ir** were found to be less active in OER. The overpotentials of **MWCNT-1-ppyIr** and **MWCNT-2-Cp*Ir** are determined to be 480 mV and 690 mV, respectively. The OER kinetics and ESCA are also found to follow the same trend: **MWCNT-1-Cp*Ir** > **MWCNT-1-ppyIr** > **MWCNT-2-Cp*Ir**, despites having similar Ir(III) contents. The difference in their OER activity seems to correlate with the catalytic activity of their molecular analogs for water oxidation. For the cyclometalated **MWCNT-1-ppyIr**, its molecular analog was reported to be inactive in water oxidation due to the lack of an accessible coordination site.[107] On the other hand, the Cp*-Ir(III) water oxidation catalysts bearing weaker donor pyrimidyl ligands display lower catalytic activity than their pyridyl counterparts.[97,101] To evaluate whether this reasoning in the context of molecular catalysts applies analogously to heterogeneous surface-bound catalysts, we have also performed computational studies to probe the ligand effect (pyridyl vs. pyrimidyl) on OER activity. In our studies, **MWCNT-1-Cp*Ir** and **MWCNT-2-Cp*Ir** were represented by simplified models each supported by a 6 x 6

slab of graphene: **G-1-Ir** and **G-2-Ir**, respectively. The free energy profile of the OER reaction was calculated following the well-established four-electron water nucleophilic attack (WNA) mechanism.[97,99,101,108–112] The most stable structures of key intermediates and their computed energies are summarized in Figure 13a. At an external potential that renders the overall process thermoneutral (+1.19 V relative to the computational hydrogen electrode (CHE)), the potential determining steps (pds) have been identified in the OER pathways for **G-1-Ir** and **G-2-Ir** (Figure 13b). For the electron-deficient **G-2-Ir**, both formation of the oxo and subsequent attack by water were found to be significantly less favorable than for the pyridine-based **G-1-Ir**. The difference in theoretical overpotentials was found to be 443 mV, which is consistent with the 410 mV difference observed experimentally. Moreover, the change in pds could significantly impact the OER kinetics, as demonstrated by the drastically different Tafel slopes observed between **MWCNT-1-Cp*Ir** and **MWCNT-2-Cp*Ir** (Figure 12c)**.** Although other factors could plausibly contribute to the difference in catalytic efficiency, these results suggest that the ligand electronic effect could be a considerable influence. More importantly, the present results demonstrate that we can tune the catalytic activities of heterogeneous molecular catalysts to a significant extent through rational ligand design. As a result, our strategy of metal complexation on carbon nanomaterials holds great potential in creating new avenues for catalyst discovery for many other significant processes.

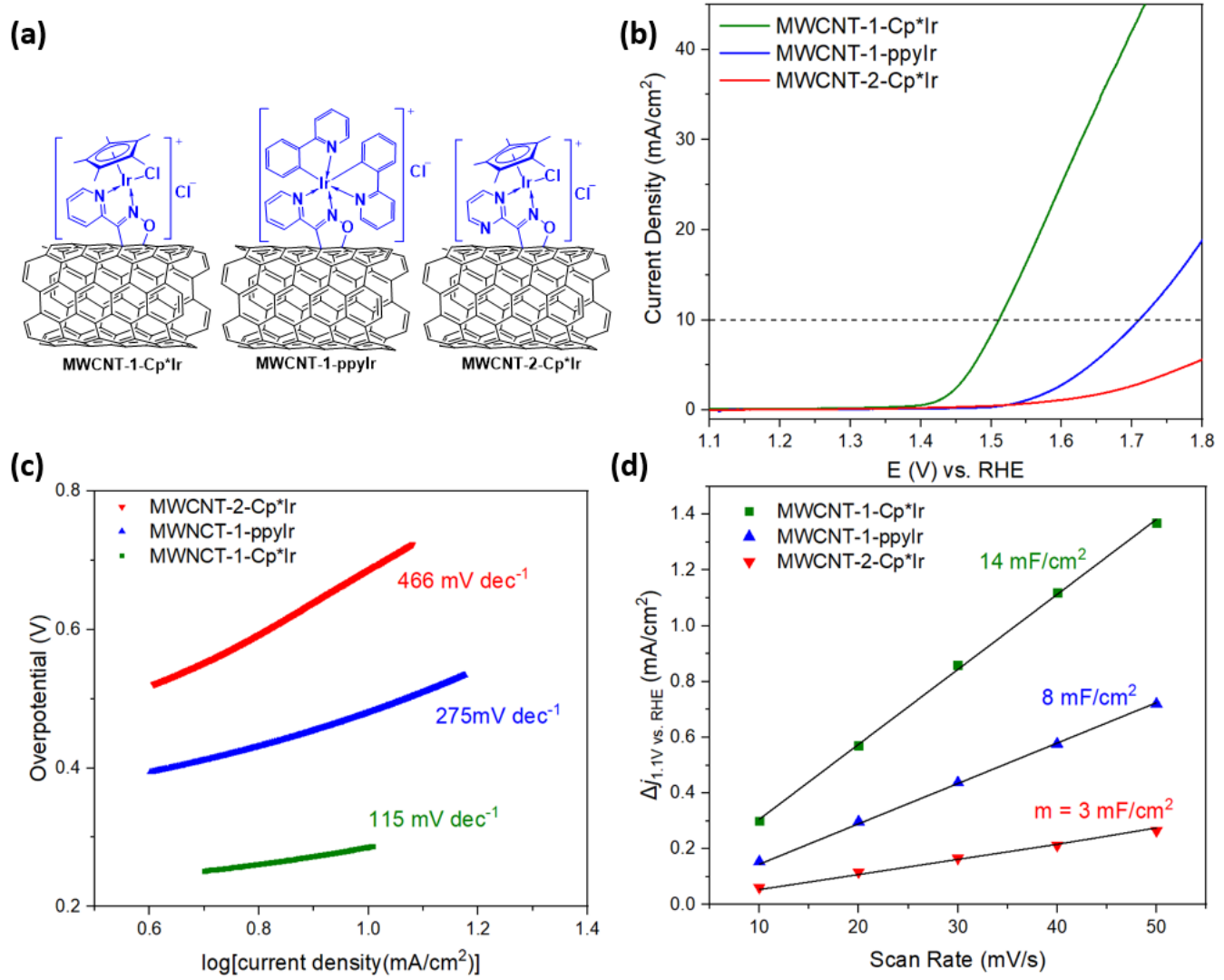


Figure 12. (a) Structures of metal-functionalized MWCNTs. MWCNTs are simplified as SWCNTs in illustration for clarity. (b) LSV curves of **MWCNT-1-Cp*Ir** (green), **MWCNT-1-ppyIr** (blue) and **MWCNT-2-Cp*Ir** (blue) for OER in 1 M KOH. (c) Tafel plots of different catalysts for OER in 1 M KOH. (d) Estimation of double-layer capacitance C_{dl} by fitting the current-density variation at 1.1 V vs RHE against the scan rate

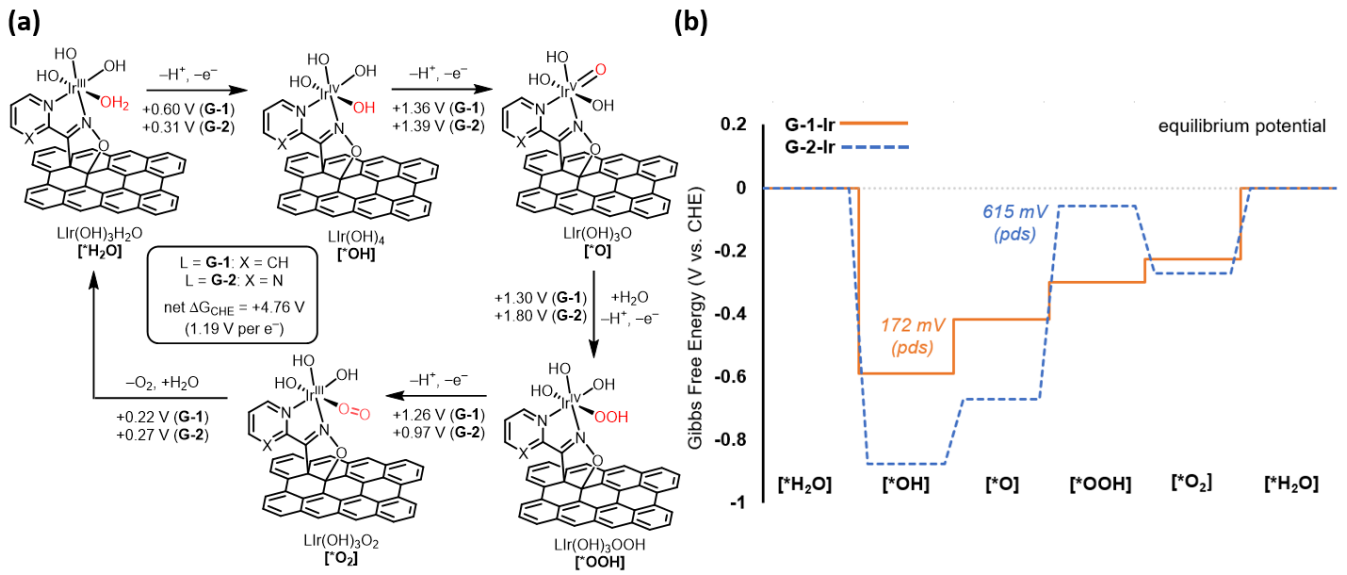


Figure 13. (a) Proposed OER pathway and computed energies for **G-1-Ir** and **G-2-Ir** modeled on (6 x 6) graphene fragment. The graphene model in illustration is truncated for clarity. (b) OER Energy profile diagrams at the equilibrium potential (+1.19 V vs. CHE) for **G-1-Ir** (orange, solid) and **G-2-Ir** (blue, dotted). The potential-determining steps (pds) of OER are indicated.

CONCLUSION

We have synthesized a new class of metal chelating carbon nanomaterials and demonstrated their utility in transition metal-based electrocatalysis. Isoxazoline surface functionalization is efficient and was found to create covalent ligands that give consistent results indicative of the expected molecular structures. The electroactivity is also consistent with the structures that were designed to produce effective electronic coupling between the chelated metal complexes and the carbon nanomaterial support. We probed the electrocatalytic activity of these modified materials with applications in oxygen evolution reaction. The results described herein suggest that this approach to create functionalized nanomaterials has great promise for new designer heterogeneous catalytic systems.

ASSOCIATED CONTENT

Instrumentation and materials; experimental details; additional characterization data; additional electrochemical test results; optimized Cartesian coordinates and energies; NMR spectra of new compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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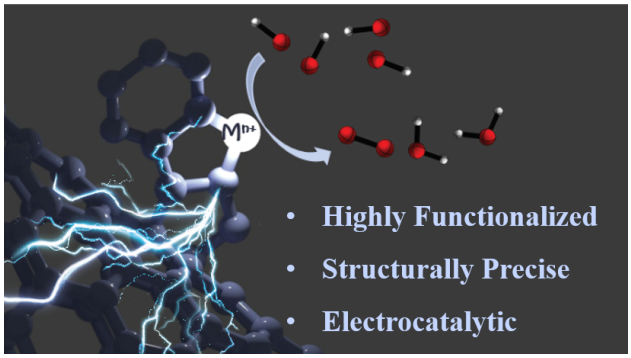
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