Molecular Functionalization of NiO Nanocatalyst for Enhanced Water Oxidation by Electronic Structure Engineering

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Tuning the local environment of nanomaterial-based catalysts has emerged as an effective approach to optimize their oxygen evolution reaction (OER) performance, yet the controlled electronic modulation around surface active sites remains a great challenge. Herein, directed electronic modulation of NiO nanoparticles was achieved by simple surface molecular modification with small organic molecules. By adjusting the electronic properties of modifying molecules, the local electronic structure was rationally tailored and a close electronic structure-activity relationship was discovered: the increasing electronic density around surface Ni sites, accelerating the reaction kinetics and improving OER activity, and vice versa. Detailed investigation by operando Raman spectroelectrochemistry revealed that the electron-withdrawing modification facilitates the charge-transfer kinetics, stimulates the catalyst reconstruction, and promotes abundant high-valent γ-NIOH reactive species generation. The NiO–C₆F₆ catalyst, with the optimized electronic environment, exhibited superior performance towards water oxidation. This work provides a well-designed and effective approach for heterogeneous catalyst fabrication under the molecular level.

Introduction

The oxygen evolution reaction (OER) plays a pivotal role as the “anodic half-reaction” in sustainable energy conversion strategies, such as electrochemical water splitting, CO₂ reduction, and nitrogen reduction.[1] Limited by the multi-proton coupled electron transfer process, the OER suffers from sluggish kinetics and is the bottleneck for most renewable energy systems. To lower the OER overpotential, first-row transition-metal oxides have been investigated as cost-effective heterogeneous catalysts over the past years. Plenty of studies suggested that the local structure around surface active sites is essential to heterogeneous catalysis.[2,3] Adjustment of the local environment is thus considered an effective approach to improve the OER activity.

To date, two approaches have been developed for local electronic modulation on OER catalysts, including heteroatom doping and defect engineering. Several efficient OER catalysts have been fabricated by these methods, such as NiFe, CoFe, NiFeCr, NiV catalysts.[3] However, since these methodologies are mainly based on bulk materials modification, it remains challenging to rationally tailor the local electronic structure at catalyst surface, which can directly impact the OER catalysis at the electrocatalyst/electrolyte interface. Moreover, the structural complexity of multi-metal OER catalysts renders it difficult to gain deeper mechanistic understanding, for example, the identification of the real active center, the investigation of electronic structure-activity relationships.[4] In addition, recent reports revealed that a self-reconstruction of catalyst commonly occurs at catalyst surfaces during the OER process, deriving the oxy(hydroxide) layer as the true OER active phase.[5] It is thus
highly favorable to rationally adjust the surface electronic structure of the catalyst, and thereby directly influence the catalyst reconstruction, tuning the OER activity. Hence, exploration of simple and effective strategies for directed electronic modulation at catalyst surface are greatly desired.

In this work, we turn to molecular functionalization approach to rationally modulate the surface electronic structure of NiO nanocatalyst, and thereby directly tailor the catalyst self-reconstruction process, improving the OER activity. Through the covalent grafting reaction between organic diazonium salts and metal oxides, ultrasmall (1–3 nm) NiO nanoparticles are functionalized with a series of aryl groups bearing different substituents (Figure 1). By adjusting the electronic properties of the substituents, the electronic structure around surface Ni sites has been explicitly modulated and the OER activity has been systematically regulated, that is, the introduction of electron-withdrawing groups decreases the electron density around Ni and improves the OER activity, and vice versa. Detailed investigations indicated that the strong electron-withdrawing molecular modification affects the charge transfer kinetics and facilitates the catalyst surface reconstruction, generating abundant γ-NiOOH active phase. The NiO–C$_6$F$_5$ catalyst, possessing the strongest electron-withdrawing functionalization, exhibits superior performance towards OER.

Results and Discussion

Ultrasmall NiO nanoparticles were synthesized as a model heterogeneous OER catalyst, as the small particle size is expected to enlarge the catalyst surface area, promote coordinatively unsaturated site exposure, and facilitate the surface molecular modification via covalent bonds. The HRTEM image of the obtained NiO sample shows non-aggregated ultrasmall nanoparticles with particle size of 1–3 nm (Figures 2a and S3), and the XRD pattern presents typical nickel oxide diffraction peaks at 37.2, 43.2, and 62.8° (Figure S1). Based
on the XRD peak width, the averaged particle size was calculated to be 2.4 nm, illustrating the formation of ultrasmall NiO nanocrystals.[15] A series of aryl-groups with different substitution were introduced to the NiO nanoparticle surface through the grafting reaction between diazonium salts and nickel oxide (Figure 1a).[18] The substitution groups were adjusted to be 4-MeO-, 4-CO₂H, 3,5-Cl₂-, 4-NO₂-, and 2,3,4,5,6-F₅-, giving molecularly modified samples of NiO–CH₂OₓMe, NiO–CH₂CO₂Me, NiO–CH₂Cl₂, NiO–CH₂NO₂, and NiO–CF₃ (Figure 1b). Dictated by the varied Hamnett parameters of substitutions, the electronic property of modifying aryl-groups can be systematically regulated: the highest Hamnett parameter (0.98) of 2,3,4,5,6-F₅- demonstrates the strongest electron-withdrawing ability of –CF₃ group in this series, while the lowest Hamnett parameter (~0.27) of 4-MeO– expresses the highest electron-donating property of the local CH₂OₓMe group (Figure S5).[9] The different electronic features of the molecular modification is expected to distinctively influence the local electronic environment at NiO nanoparticles surface.

XRD, TEM, and high-resolution (HR)TEM were firstly performed to characterize the crystalline structure of modified NiO samples. The XRD pattern of all modified NiO samples show typical NiO diffraction patterns, without apparent peak change compared with the parent NiO nanoparticles (Figure S6). The TEM images display ultrasmall nanoparticles with particle sizes of 1–4 nm, and the HRTEM images show distinct lattice fringes with an interplanar spacing of 0.21 nm (Figures S7–S11). No obvious particle aggregation or surface amorphousness was observed after molecular modification. The TEM energy-dispersive X-ray spectroscopy (EDS) spectra of NiO–CF₃ and NiO–CH₂Cl₂ samples exhibit distinct F and Cl fluorescence signals, illustrating the successful molecular modification.

Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) was employed to study the molecular modification at NiO nanoparticle surface (Figure 2b). All the modified NiO samples show additional characteristic peaks of the organic modification compared to bare NiO nanoparticles: the NiO–CF₃ spectrum shows C≡C stretch at 1005 cm⁻¹,[18] the NiO–CH₂NO₂ spectrum shows NO₂ stretching and scissoring absorption modes at 1517, 1343, and 854 cm⁻¹,[8b,10c] the NiO–CH₂CO₂H spectrum exhibits C=O stretching at 1698 cm⁻¹,[18] and the NiO–CH₂OMe spectrum presents OMe stretches at 1460, 1440 cm⁻¹, Ar–O stretches at 1294, 1250 cm⁻¹, Ar–O–CH₂ stretch at 1027 cm⁻¹, and O–CH₃ rocking mode at 1178 cm⁻¹.[8b,10c] Aryl-group-related characteristic vibrations are also present at 1550–1600 cm⁻¹ and 1450–1500 cm⁻¹ for all modified NiO samples, yet distinctly affected by the different electronic properties of substituents.[8b,10c] The NiO–CH₂OMe sample presents a strong absorption band at 1499 cm⁻¹, which is absent for other samples, consistent with the principle that this aryl-group IR band is only IR active when the aryl-group has an electron-donating substituent.[8b,10c] In 1550–1600 cm⁻¹ region, the NiO–CH₂Cl₂ and NiO–CF₃ samples show much lower peak intensity at 1601 cm⁻¹ compared to the peak at 1564 cm⁻¹, in sharp contrast to NiO–CH₂NO₂ (comparable peak intensity at 1594 and 1574 cm⁻¹) and NiO–CH₂OMe.

The substitution groups were adjusted to be 4-MeO-, 4-CO₂H, 3,5-Cl₂-, 4-NO₂-, and 2,3,4,5,6-F₅-, giving molecularly modified samples of NiO–CH₂OₓMe, NiO–CH₂CO₂Me, NiO–CH₂Cl₂, NiO–CH₂NO₂, and NiO–CF₃ (Figure 1b). Dictated by the varied Hamnett parameters of substitutions, the electronic property of modifying aryl-groups can be systematically regulated: the highest Hamnett parameter (0.98) of 2,3,4,5,6-F₅- demonstrates the strongest electron-withdrawing ability of –CF₃ group in this series, while the lowest Hamnett parameter (~0.27) of 4-MeO– expresses the highest electron-donating property of the local CH₂OₓMe group (Figure S5).[9] The different electronic features of the molecular modification is expected to distinctively influence the local electronic environment at NiO nanoparticles surface.

The present 1550–1600 cm⁻¹ band is assigned to C–H rock band of the organic modification.[19] By the varied Hamnett parameters of substitutions, the functionalization amount of –CF₃, –CH₂NO₂, –CH₂CO₂H, and –CH₂OMe was estimated to be 2.11, 2.55, 3.31, and 2.37 nm⁻², indicating their comparable coverage at the NiO surface.[12] The molecular modification can be further confirmed by the X-ray photoelectron spectroscopy (XPS) spectra of NiO–CF₃, NiO–CH₂NO₂, and NiO–CH₂Cl₂, which present distinct F, N, and Cl signals, respectively (Figure 2c–e). Together with EDS and DRIFTS, these results demonstrate the successful molecular modification of the NiO by aryl-groups with comparable coverage.

Then, to investigate the electronic modulation by molecular modification, XPS was performed on all the modified samples. As shown in Figure 3, the bare NiO sample shows Ni peaks at 856.1, 853.9 eV, and O peaks at 529.1, 531.2 eV, which can be attributed to the Ni²⁺ –O and Ni²⁺ –OH species,[13] indicating the generation of Ni(OH)₂ at NiO surface when exposed to air.[6a] Interestingly, the nickel oxide-related Ni and O peaks were markedly shifted upon functionalization of the NiO particles. The NiO–CH₂OMe sample shows Ni peaks at 856.0 and 853.8 eV and an O peak at 531.1 eV, which are 0.1 eV lower in energy compared with bare NiO, indicating the higher electron

Figure 3. High-resolution core XPS spectra of a) Ni 2p and b) O 1s of bare NiO and all modified NiO samples. c) Normalized Ni K-edge XANES spectra of NiO, NiO–CF₃, reference Ni foil, and reference NiO samples. d) Fourier transformations of k-weighted EXAFS spectra of bare NiO and NiO–CF₃ samples.
density on the surface Ni species. In contrast, the NiO–C₆H₄CO₂H, NiO–C₆H₅Cl, and NiO–C₆H₅NO₂ samples show Ni peaks at 856.4 eV and O peaks at 531.6 eV, which show 0.3 and 0.4 eV shifts towards higher energy compared with the bare NiO, illustrating their decreased electron density around surface Ni species. The strongest electron-withdrawing pentafluorophenyl-modified NiO sample shows a Ni peak at 856.7 eV and O peak at 531.7 eV, which are 0.6 and 0.5 eV positively shifted compared with bare NiO, presenting the highest value among all modified NiO samples. To sum up, the Ni and O binding energies increase with an order of NiO–C₆H₄OMe < NiO < NiO–C₆H₄CO₂H ≈ NiO–C₆H₅Cl < NiO–C₆H₅NO₂ < NiO–C₆F₅, demonstrating the successive electronic structure modulation by the varied electron-withdrawing abilities of –C₆H₄OMe < –C₆H₄CO₂H = –C₆H₅Cl = –C₆H₅NO₂ < –C₆F₅. All the molecular modified NiO samples show an additional peak in the O spectra in the range of 532.8–533.2 eV, which can be assigned to the O–C bond, indicating the formation of O–C bond linkage between NiO and the organic molecules.

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy were performed on the strongest electron-withdrawing modified NiO–C₆F₅ samples to investigate its local structure. In the XANES region, a characteristic pre-edge peak is presented at 857.6 eV and an O peak at 531.7 eV, which are 0.6 and 0.5 eV positively shifted compared with bare NiO, presenting the highest value among all modified NiO samples. To sum up, the Ni and O binding energies increase with an order of NiO–C₆H₄OMe < NiO < NiO–C₆H₄CO₂H = NiO–C₆H₅Cl < NiO–C₆H₅NO₂ < NiO–C₆F₅, demonstrating the successive electronic structure modulation by the varied electron-withdrawing abilities of –C₆H₄OMe < –C₆H₄CO₂H = –C₆H₅Cl = –C₆H₅NO₂ < –C₆F₅. All the molecular modified NiO samples show an additional peak in the O spectra in the range of 532.8–533.2 eV, which can be assigned to the O–C bond, indicating the formation of O–C bond linkage between NiO and the organic molecules.

Figure 4. a) Polarization curves of bare NiO and modified NiO samples on glassy carbon electrode in 1 M KOH. b) Overpotentials at 1 mA cm⁻² current density and c) calculated TOFs at 450 overpotential of bare NiO and all modified NiO samples. d) Polarization curves of bare NiO and NiO–C₆F₅ on carbon fiber paper electrode in 1 M KOH. e) Chronopotentiometric curve of NiO–C₆F₅ on carbon fiber paper electrode at 320 mV overpotential. f) Quantification and comparison of the experimental and theoretical O₂ evolution amount by electrolysis of NiO–C₆F₅ for OER under 250 mV overpotential.
OER activity, which is systematically affected by the molecular modification. The NiO–C₃H₅OMe sample requires 340 mV overpotential for 1 mA cm⁻² current density and achieves 5.62 mA cm⁻² current density under 450 mV overpotential, which presents a repressed catalytic activity compared to the bare NiO. In sharp contrast, the NiO–C₂H₄Cl₂, NiO–C₂H₄NO₂, and NiO–CF₃ samples show lower overpotential requirements of 293, 287, and 257 mV for 1 mA cm⁻² current density, and higher catalytic current densities of 13.17, 18.98, and 23.17 mA cm⁻² under 450 mV overpotential, demonstrating their sequentially improved OER activity. The NiO–C₆H₄CO₂H exhibits 310 mV overpotential for 1 mA cm⁻² and 8.93 mA cm⁻² current density under 450 mV overpotential, which is approximate to the bare NiO nanoparticles and can be related to the electron-neutral property of –C₆H₄CO₂⁻ under alkaline conditions.

Turnover frequencies (TOFs) were calculated by assuming that all the Ni ions are active sites (Figure 4c and Table 1). The TOF values of NiO–C₆H₄CO₂H, NiO–C₂H₄Cl₂, NiO–C₂H₄NO₂, and NiO–CF₃ are calculated to be 0.013, 0.020, 0.028, and 0.035 s⁻¹, which are sequentially increased compared with 0.010 s⁻¹ for bare NiO and indicate their monotonically improved intrinsic activity. Conversely, NiO–C₃H₅OMe shows a decreased TOF value of 0.008 s⁻¹, showing a suppressed intrinsic activity compared to bare NiO. Tafel slopes were calculated by plotting the OER performances versus the current density and achieves 133 mV dec⁻¹ of bare NiO, illustrating the accelerated OER kinetics. In contrast, the NiO–C₆H₄OMe sample shows a Tafel slope of 156 mV dec⁻¹, much higher than the native NiO nanoparticles and signifies the retardation of OER kinetics with electron-donating group. Altogether, the overpotential, current density, TOF, and Tafel slope performances follow a similar OER activity trend with NiO–C₃H₅OMe < bare NiO < NiO–C₂H₄CO₂H < NiO–C₂H₄Cl₂ < NiO–C₂H₄NO₂ < NiO–CF₃. By plotting the OER performances versus the Hammett sigma constants, a reasonable correlation can be presented between catalytic activity and the electronic properties of the modifying molecules: increasing electron-withdrawing strength readily decreases the electron density around surface Ni sites, accelerating catalytic kinetics and improving OER performance (Figures 4b, c and S18).

The OER performance of the best catalyst, NiO–CF₃, was further evaluated on carbon fiber paper (CFP) as a 3D electrode substrate. The CFP/NiO–CF₃ electrode shows an overpotential of 260 mV for 10 mA cm⁻² current density (Figure 4d). High current densities of 50 and 100 mA cm⁻² can be achieved for CFP/NiO–CF₃ by increasing the overpotential to 350 and 380 mV, confirming its prominent activity. In chronoamperometry measurements under 320 mV overpotential (Figure 4e), no obvious deterioration in current density was observed during 10 h electrolysis, which indicates the excellent stability of the catalyst. This high stability is further confirmed by the TEM image of the NiO–CF₃ catalyst after long-term electrolysis, which indicated that nanoparticle size remained between 1–4 nm, displaying no apparent aggregation (Figure S19). Typical F, Ni, and O signals can be observed on the EDS spectrum, verifying the durability of the modified NiO–CF₃ catalyst. By comparison of experimental and theoretical O₂ evolution during electrolysis under 250 mV overpotential, the OER faradaic efficiency was estimated to be 93.6 % for the CFP/NiO–CF₃ electrode, indicating that the vast majority of consumed charges was contributed to catalytic water oxidation (Figure 4f).

The above OER performance results illustrate that, through our simple covalent functionalization approach, the water oxidation activity is rationally tailored by the directed electronic modulation and an efficient NiO–CF₃ water oxidation catalyst is achieved with the adjusted molecular modification. Then, we performed a series of experiments to gain insightful understanding on the influence of –CF₃ modification on the activity. Electrochemical surface area (ECSA) is one of the key factors that may impacted by the surface molecular modification. The ECSA values of bare NiO and NiO–CF₃ were estimated from their double-layer capacitance (Cdl) (Figures S20 and S21). The linear slope of NiO–CF₃ was calculated to be 0.16 mF cm⁻², close to 0.19 mF cm⁻² for bare NiO. This negligible difference in ECSA indicates that the molecular modification does not impact the active surface area of the catalyst.

The wettability of bare NiO and molecular modified NiO samples were evaluated by water contact angle measurement (Figure S22). The NiO–CF₃ sample presents contact angle of 103.9°, which is higher than 77.7° of bare NiO. The decreased hydrophilicity of NiO–CF₃ can be attributed to the hydrophobicity of grafted molecules. No clear correlation was observed between the hydrophilicity and OER performance, which indicate that the change of wettability cannot account for the significantly influenced activity.

Charge transfer also plays an essential role in water oxidation reaction at catalyst surface. To investigate the influence of molecular modification on charge-transfer kinetics, electrochemical impedance spectroscopy (EIS) was conducted on NiO and NiO–CF₃ (Figure S5a). The NiO–CF₃ sample shows a charge transfer resistance (Rct) of 56.3 Ω, which is much lower compared with 152.4 Ω of bare NiO. The diminished resistance demonstrates that the –CF₃ molecular modification greatly facilitates the charge-transfer kinetics. A catalyst self-reconstruction of Ni²⁺ –NiOOH is reported to commonly occur at Ni-based water oxidation catalyst, generating γ-NiOOH as the surface active phase. To study the

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**Table 1. Summary of Hammett sigma constants and calculated TOF values under 450 mV overpotential of bare NiO and all molecule modified NiO samples on GCE.**

| Sample          | Hammett parameter | TOF (s⁻¹) |
|-----------------|-------------------|-----------|
| NiO–C₃H₅OMe     | −0.27             | 0.008     |
| NiO             | 0                 | 0.010     |
| NiO–C₂H₄CO₂H    | 0                 | 0.013     |
| NiO–C₂H₄Cl₂     | 0.74              | 0.020     |
| NiO–C₂H₄NO₂     | 0.78              | 0.028     |
| NiO–CF₃         | 0.98              | 0.035     |

[a] The –C₆H₄CO₂H group is deprotonated under alkaline conditions (–C₆H₄CO⁻), behaving as electron-neutral property.
The catalytic mechanism of Ni-based OER catalysts remains a long-term scientific discussion topic, the formation of NiOOH species is accepted to play a pivotal role as the key intermediate in water oxidation. The nucleophilic addition of water molecules on the catalysts would be the first key step in the catalytic cycle. The electron-withdrawing modification can promote the local electron-de-localalization at NiO surface, decreasing the electron density around the active Ni species and modulating the catalyst local structure. On one hand, the more electrophilic Ni site can favor the nucleophilic addition of water as well as the deprotonation in the Ni$_2$$^+$—NiOOH reconstruction, achieving improved OER activity. On the other hand, with specific proton affinity, the −C$_6$F$_5$ group is proposed to promote proton shuttling at the catalyst surface, which can accelerate the deprotonation process, stimulate the generation of key intermediate, and improve the catalytic performance. Benefiting from the synergistic promotion effect, the NiO−C$_6$F$_5$ catalyst exhibits outstanding performance towards water oxidation. Further OER activity improvements and deeper mechanistic understanding can be achieved by directed molecular functionalization with optimized electronic properties.

Conclusions

We achieve directed electronic modulation of NiO through surface molecular modification, and thereby directly tailor the oxygen evolution reaction (OER) activity. By adjusting the electronic properties of the modifying molecules, the electronic environment around active sites is rationally modulated and the OER activity is systematically regulated: the electron-withdrawing modification decreases the electron density at the surface Ni species and improves the OER activity, and vice versa. The strong electron-withdrawing −C$_6$F$_5$ molecular modification can effectively facilitate the charge-transfer kinetics, promoting the reconstruction of Ni$_2$$^+$−NiOOH, and thus greatly enhancing the OER performance. This work opens a new avenue for heterogeneous OER catalyst design at the molecular level, demonstrating the significant impact of local electronic structure on the OER active species generation and catalytic activity.
Experimental Section

Materials

Nickel(II) acetylacetone [Ni(C₅H₇O₂)₂], anhydrous tert-butanol [(C₅H₇OH), potassium hydroxide (KOH), 4-nitrobenzenediazoxium tetrafluoroborate (C₆H₆N₂O₂BF₄), 3,5-dichlorophenyldiazonium tetrafluoroborate (C₆H₅Cl₂N₂BF₄), 4-methoxybenzenediazoxium tetrafluoroborate (C₆H₅OCH₃N₂BF₄), 2,3,4,5,6-pentafluorobenzonitrile (C₆F₅CN), nitrosyl tetrafluoroborate (NOBF₄), anhydrous acetone (CH₃COCH₃), anhydrous dichloromethane (CH₂Cl₂), and acetonitrile (CH₃CN) were purchased from Sigma-Aldrich. 4-carboxybenzenediazoxium tetrafluoroborate (C₆H₅COCH₃N₂BF₄) was purchased from Chemtronica AB (Sweden). The water used for electrolyte solutions was deionized using a Millipore Milli-Q UF Plus system (15–18 MΩ cm resistivity).

Synthesis of pentafluorophenyldiazonium tetrafluoroborate (C₆F₅N₂BF₄)

The pentafluorophenyldiazonium tetrafluoroborate was synthesized according to an available literature procedure.235 5 mmol pentafluorobenzonitrile was firstly dissolved in 1 mL acetone, and then added dropwise over the course of 30 min to a mixture of pulverized nitrosyl tetrafluoroborate (5 mmol, 915 mg) in dry acetone (1 mL) at −30 °C for 30 min. After stirring at −30 °C for 1 h, 7.5 mL dry dichloromethane was added to the mixture. The desired pentafluorophenyldiazonium tetrafluoroborate could be obtained by filtration and drying in vacuum.19F NMR spectroscopy confirmed formation of the desired product:19F NMR (377 MHz, CDCl₃): δ = −119.54 (tt, J = 21.4, 16.6 Hz), −123.43 (m), −151.31 (broad singlet, BF₄⁻), −152.47 ppm (m).

Synthesis of ultrasmall NiO nanoparticles

The ultrasmall NiO nanoparticles were synthesized following a reported solvothermal method.34 0.4 g Ni(acac)₂ was firstly mixed with 35 mL tert-butanol under vigorous stirring at 50 °C to form a suspension. The suspension was transferred into an autoclave reactor and hermetically sealed. The reaction was performed by heating at 205 °C for 20 h. After the reaction, the ultrasmall nanoparticles were obtained by washing with ethanol for 3 times and drying at 80 °C.

Functionalization of NiO nanoparticles with organic molecule

The NiO nanoparticles were functionalized by suspending approximately 100 mg of NiO nanoparticles in Milli-Q water with 0.1 M NaOH under N₂ atmosphere, and then adding dropwise approximately 5 mL of a 10 mg mL⁻¹ solution of the corresponding diazonium tetrafluoroborate salt: pentafluoro-phenyldiazonium tetrafluoroborate, 4-nitrobenzenediazoxium tetrafluoroborate, 3,5-dichlorophenyldiazonium tetrafluoroborate, 4-carboxybenzenediazoxium tetrafluoroborate, or 4-methoxybenzenediazoxium tetrafluoroborate. The mixed solutions were stirred overnight, after which the products were collected by centrifugation and washing with water. The resulting functionalized NiO samples were obtained by drying under vacuum.

Physical characterization

Powder XRD was performed on Bruker D5000 X-ray diffraction diffractometer with CuKα radiation (λ = 1.5406 Å), SEM images and EDS spectra were recorded with JEOL JSM 7401 equipped with an EDS system. TEM images and HRTEM images were taken on a JEOL JEM2100F transition electron microscope. DRIFTS spectra were measured on a Thermo Scientific Nicolet iSS FT-IR spectrometer. UV/Vis spectra were carried on PerkinElmer Lambda 750 UV/Vis spectrophotometer. XPS spectra were acquired by a Thermo VG ESCALAB250 surface analysis system with monochromatized AlKα, small-spot source and 500 μm concentric hemispherical energy analyzer. All the spectra energy was calibrated by setting the adventitious carbon peak to 284.6 eV.

Determination of the molecule loading amount

The degree of molecular modification was determined by the UV/Vis absorption method. A standard curve was obtained by plotting the UV/Vis absorption of stock solutions of the respective diazonium slats at different concentrations. The remaining concentration of diazonium salt of the solution after NiO functionalization was determined based on their UV/Vis absorption intensity. The molecule loading amount was calculated by the difference between the initial molecular amount and the molecular concentration after NiO functionalization.

Electrode preparation

4 mg of the respective samples were dispersed in a mixed solution of 32 μL 5% Nafion (ethanol solution), 200 μL ethanol, and 768 μL H₂O and sonicated for over 1 h to make a finely dispersed suspension. For GCEs, 10 μL of the obtained suspension was drop-casted on pre-polished GCE and the resulting electrodes were dried at 50 °C for 30 min. For the CFP electrode, 100 μL of the catalyst suspension was drop-casted on pre-cleaned GF electrode and the resulting electrodes were dried at 50 °C for 30 min.

Electrochemical characterization

All electrochemical experiments were performed on a CH Instrument 660E potentiostat. The electrochemical cell was built by a three-electrode system with the as-prepared samples electrode as the working electrode, a standard Ag/AgCl electrode as the reference electrode and a platinum foil (4 cm²) as the counter electrode. All the applied potentials were converted to reversible hydrogen electrode (RHE) using the equation E (vs. RHE) = E (vs. Ag/AgCl) + 0.059pH + 0.197 V. The overpotential was calculated with equation η = E (vs. RHE) − 1.23 V. For evaluation of the OER activity, linear sweep voltammetry (LSV) was performed from low initial potential to high final potential with a scan rate of 5 mVs⁻¹. 95% IR compensation was applied with the current interrupt method by the software supplied with the potentiostat. The Tafel slopes were calculated by plotting the overpotential η against log (j) from the LSV curves. Chronoamperometry measurement was performed to assess the durability of the catalyst. CV was operated under scan rate of 100 mVs⁻¹ to investigate the catalyst redox behavior. The catalytic TOF values are determined according to TOF = j/A/F, where j is the catalytic current density, A is the surface area of the electrode, F is the Faraday constant, and m is the number of moles of the active sites. In this work, we assume that all the Ni ions are active sites for water oxidation. By catalyst loading amount calculation, the m is calculated to be 5.36 × 10⁻⁷ mole. The faradaic efficiency was measured in a N₂-purged sealed cell. The quantity of O₂ gas evolution was determined every 15 min by GC (Shimadzu GC-204C) every 15 min. The faradaic efficiency was calculated by the equation: faradaic efficiency = 4F × nO₂/Q, where F is the Faraday constant, nO₂ is the measured O₂ amount, and Q is the consuming charge amount. ECSA was measured by the non-faradaic C⁰ method. CV was performed at the potential window of 0–0.1 V vs.
Ag/AgCl, with different scan rates of 30, 50, 70, and 90 mV s⁻¹. By plotting \( J \propto (\Delta J - \bar{J}) \) at 0.05 V vs. Ag/AgCl against the scan rate, the linear slope, which is twice \( C_w \), is used to represent ECSA. EIS was carried out in the catalytic OER region with the frequency ranged from 0.1–10⁴ Hz under an applied potential of 1.58 V.

**XAS data analysis**

The XAS spectra were measured at P-64 beamline, PETRA III, DESY, Hamburg. The samples and reference Ni foil were measured simultaneously in transmission mode. The data processing (pre-edge, post-edge background removal and normalization) and structural modelling (Fourier transformation and data fitting) were performed using EXAFS PAK.⁴¹ The k²-weighted EXAFS oscillations were analyzed by nonlinear least-squares fit of the data to the EXAFS equation. The various model parameters: average coordination number (CN), mean interatomic distances (R), Debye-Waller factor coefficients (σ²), and threshold energy (Eo) were refined. The theoretical phases and amplitudes used in the refinements were calculated using the FEFF7.

In order to directly compare all of the NiO modified samples, a two-shell model based on bulk NiO rock salt structure was used to fit the EXAFS data. The Fourier transform fitting of the EXAFS spectra was performed until approximately 3 Å which contains the main single scattering contributions. Hence, a single Ni–O scattering path was used to describe the 6 nearest neighboring oxygen atoms (\( R_{\text{Ni}} = 2.08 \) Å) in the first coordination shell. For fitting the second shell, a single Ni–Ni scattering path (\( R_{\text{Ni}} = 2.954 \) Å) was used for both the samples. In addition, a third Ni–C scattering path (\( R_{\text{Ni}} = 2.72 \) Å) was necessary to obtain a better fit in NiO–C₁₂_F₄ (best fit in Figure S16). The \( S_{\text{e}} \) was refined separately for each sample, while the number of single scattering paths for Ni–O, Ni–Ni and Ni–C as well as their lengths, and Debye-Waller factors were allowed to refine together. In the present study, the single scattering contributions up to approximately 3 Å have been used for structural modelling and have been found sufficient to describe the local structure as reported in literature.⁴¹

**Operando Raman spectra**

Operando Raman spectra of bare NiO and NiO–C₁₂_F₄ samples were collected by a confocal Raman microscope (RM 1000, Renishaw) under OER in an ambient air condition. The reference electrode and counter electrode were Ag/AgCl (3 mm) and Pt wire, respectively. The excitation source was emitted by a frequency doubled Nd:YAG laser with the wavelength of 532 nm. The power of laser through the surface of the electrode from the side to avoid the bubble scattering. Each operando Raman spectra was recorded with an acquisition time of 10 s with 5–10 sweeps under current-time (i–t) measurement at a constant potential using a confocal Raman microscope coupled with a 90°-degree angled Olympus 10 x objective. The electrochemical cell was made of quartz and stood in front of the objective. All spectra were calibrated against the value of 520.7 cm⁻¹ of a silicon wafer. The resolution of each spectra is 1 cm⁻¹.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** catalyst self-reconstruction · electrocatalysis · molecular modification · nanomaterials · water oxidation

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