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Alleviating the competitive adsorption of hydrogen and hydroxyl intermediates on Ru by d–p orbital hybridization for hydrogen electrooxidation†

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Strengthening the hydroxyl binding energy (OHBE) on Ru surfaces for efficient hydrogen oxidation reaction (HOR) in alkaline electrolytes at the expense of narrowing the effective potential window (EPW) increases the risk of passivation under transient conditions for the alkaline exchange membrane fuel cell technique. Herein, an effective Ru/NiSe₂ catalyst was reported which exhibits a gradually enhanced intrinsic activity and slightly enlarged EPW with the increased degree of coupling between Ru and NiSe₂. This promotion could be attributed to the optimized electron distribution and d-band structures of Ru surfaces weakening the hydrogen binding energy and especially the OHBE through the strong d–p orbital hybridization between Ru and NiSe₂. Unlike the conventional way of strengthened OHBE enhancing the oxidative desorption of hydrogen intermediates (H_{ad}) via the bi-functional mechanism, the weakened OHBE on this Ru/NiSe₂ model catalyst alleviates the competitive adsorption between H_{ad} and the hydroxyl intermediates (OH_{ad}), thereby accelerating the HOR kinetics at low overpotentials and hindering the full poisoning of the catalytic surfaces by strongly adsorbed OH_{ad} spectators at high overpotentials. The work reveals a missed but important approach for Ru-based catalyst development for the fuel cell technique.

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Introduction

Alkaline exchange membrane fuel cells (AEMFCs) are regarded as next-generation technology for hydrogen-to-electric energy conversion.^{1–3} One of the most important advantages is that the electrocatalysts for the cathodic oxygen reduction reaction could get rid of the dependence on platinum group metals (PGMs) compared to the proton exchange membrane-based counterpart operated under harsh acidic conditions.^{4–6} Nevertheless, the anodic hydrogen oxidation reaction (HOR) in high pH electrolytes suffers from more complex catalytic mechanisms and thus sluggish kinetics.^{7,8} Especially for benchmarked commercial Pt/C, two orders of magnitude lowered catalytic activity results in the incremental usage of PGMs, inevitably raising the system cost.⁹ Therefore, developing highly effective and low-cost alkaline HOR catalysts is critically desirable for the further commercialization of AEMFCs.

Ru is a promising alternative catalyst in alkaline HOR because of its moderate activity but significantly lower price.^{10–12} Compared to Pt, elementary Ru possesses slightly stronger

hydrogen binding energy (HBE) and greatly enhanced oxophilicity (hydroxyl binding energy, OHBE), which are two crucial thermodynamic descriptors related to hydrogen electrocatalysis.^{10,13} Meanwhile, the relationship between the alkaline HOR catalytic behaviors and the OHBE of the Ru surfaces is still under debate.^{14–19} Conventionally, Ru due to its exceedingly strong oxophilicity is susceptible to being occupied by oxygenated species like the adsorbed hydroxyl (OH_{ad}) in a high coverage.^{11,14,20} In this case, the OH_{ad} species would act as the spectators and inhibit the dissociative adsorption of H₂. Hence, Ru-based catalysts usually exhibit a narrowed effective potential window (EPW) for the HOR, falling short of the needed 0.3 V vs. a reversible hydrogen electrode (RHE) to greatly reduce the risk of passivation under transient conditions for practical AEMFC devices.^{21,22} Another opinion is that the OHBE of Ru is still insufficient especially when near the hydrogen equilibrium potential (~0 V vs. RHE).^{18,19,23} Appropriate enhancement of the OHBE could also promote the desorption of H_{ad} through the bi-functional pathways, that is, the enriched oxygenated species at the electrode/electrolyte interfaces could participate in the reaction directly to accelerate the formation of H₂O. For example, strengthening the OHBE of the Ru surface via either material design (like alloying and doping)^{17–19} or electrolyte engineering (like the alkali metal cation effect)^{14,24} can indeed improve the HOR activity. These two contradictory viewpoints make it difficult to provide a general strategy to optimize Ru-based catalysts. Moreover, the enhanced OHBE would also

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result in the ultimately narrowed EPW due to the fully adsorbed OH_{ad} poisoning the active sites for H_2 dissociative adsorption, which seems closely related to the OHBE but has been less discussed.²⁴ It could be argued that the OHBE enhancement approaches are at the expense of the EPW to accelerate the alkaline HOR kinetics at low overpotentials. Hence, revealing the exact functions of OH_{ad} species on Ru surfaces towards alkaline HOR is of great importance to understanding the reaction mechanism and guiding the design of high-performance catalysts without narrowing the EPW.

In this work, a support-optimization strategy is conducted to investigate the alkaline HOR catalytic behaviors of Ru-based catalysts as well as the roles of OH_{ad} species. NiSe_2 , a typical transition metal selenide with good electrical conductivity,²⁵ chemical stability, and relatively weak oxophilicity,^{26,27} has been adopted to gradually replace the commercial carbon black supports to anchor Ru nanocrystals, denoted as $\text{Ru}/\text{NiSe}_2/\text{C}-X$ (where $X = 10, 20, 30$, or 80 , representing the mass percent of NiSe_2 in the catalysts). Among them, $\text{Ru}/\text{NiSe}_2/\text{C}-20$ exhibits a 2–3 times enhanced mass activity compared to Ru/C . It is found that the strong interactions between Ru and NiSe_2 lead to significant electron transfer from NiSe_2 to Ru, which is in contrast to what is observed for carbon-supported Ru catalysts. Both experiments and density functional theory (DFT) calculations confirm the weakened HBE and especially OHBE, resulting in improved HOR activity near the hydrogen equilibrium potential and a broadened EPW. Two catalytic modes have been proposed to describe the roles of weakly/strongly adsorbed OH_{ad} on Ru-based catalysts, elucidating the OHBE-related EPW and the reason that either weakening or strengthening the OHBE can accelerate the alkaline HOR kinetics.

Results and discussion

To obtain the well-defined structures of the support surfaces, NiSe_2 octahedrons were synthesized *via* a solvothermal method with the exposure of (111) facets.²⁸ The cubic phase and morphology could be confirmed by the X-ray diffraction (XRD) pattern (PDF#65-1843) and scanning electron microscope (SEM) image shown in Fig. S1†. Then, a series of $\text{Ru}/\text{NiSe}_2/\text{C}-X$ catalysts were constructed through microwave reduction²⁹ in the presence of RuCl_3 as the precursor and NiSe_2 octahedrons or carbon blacks as the supports (see the Experimental section in the ESI† for details). Fig. 1a shows the XRD patterns of the $\text{Ru}/\text{NiSe}_2/\text{C}-X$ catalysts. Among them, $\text{Ru}/\text{NiSe}_2/\text{C}-80$ is simply denoted as Ru/NiSe_2 due to no extra addition of carbon supports. Apart from Ru/C which was prepared without adding any selenide during the synthesis, all the samples exhibit distinct diffraction peaks of cubic NiSe_2 . However, there is no obvious pattern of Ru species possibly due to the small size and weak crystallinity, consistent with that of Ru/C . X-ray photoelectron spectroscopy (XPS) was further performed to explore the surface components and chemical states, which confirmed the existence of Ru, Ni, Se, C, and O species (Fig. S2†). To avoid the interferences from the signal of C 1s, Fig. 1b exhibits the high-resolution XPS spectra of Ru 3p for the five samples.^{30,31} The two groups of characteristic peaks located at around 462

and 485 eV could be attributed to Ru 3p_{3/2} and 3p_{1/2} for metallic Ru⁰, respectively.³¹ Interestingly, these peaks gradually shift to negative binding energy with the increased amount of NiSe_2 , from 462.2 eV of Ru 3p_{3/2} for Ru/C to 461.1 eV for Ru/NiSe_2 . This suggests the formation of electron-rich Ru surfaces owing to the interactions between the metals and the supports that cause partial electron transfer from NiSe_2 to Ru.

Transmission electron microscopy (TEM) was conducted to further confirm the structures of $\text{Ru}/\text{NiSe}_2/\text{C}-20$. Fig. 1c and S3† show that small Ru nanoparticles with an average size of 2.7 nm are well dispersed on the surfaces of NiSe_2 octahedrons. Similar structures could also be observed according to Fig. S4† for Ru/NiSe_2 , suggesting the anchoring effect of NiSe_2 to obtain the ultra-fine Ru nanoparticles. The selected area electron diffraction (SAED) pattern of $\text{Ru}/\text{NiSe}_2/\text{C}-20$ shows the polycrystalline diffraction character where the ring corresponds to the (002) plane of Ru, and the two spots marked by yellow circles correspond to the (200) and (311) planes of NiSe_2 (inset of Fig. 1c). For comparison, the TEM image of Ru/C is exhibited in Fig. S5,† showing the Ru nanoparticles with an average size of 3.2 nm dispersed on carbon supports. The high-resolution TEM (HRTEM) image of $\text{Ru}/\text{NiSe}_2/\text{C}-20$ shown in Fig. 1d presents the distinctly exposed interplanar spacing of 0.26 nm inside the polyhedron, corresponding to the (210) facet of NiSe_2 . Small Ru nanocrystals exist at the surface of NiSe_2 as marked by dotted yellow lines, showing the interplanar spacings of 0.21 and 0.23 nm, corresponding to the (002) and (100) facets of hexagonal close-packed (*hcp*) Ru. The high-angle annular dark field scanning TEM (HAADF-STEM) image as shown in Fig. 1e clearly displays the atomic stacking of “ABABAB...”, indicating the formation of the thermodynamically stable *hcp* structure, which could be further confirmed by the corresponding fast Fourier transform (FFT) pattern along the [100] zone axis (Fig. 1f).³² The energy dispersive X-ray spectroscopy (EDS) elemental mapping images depict the quasi-core@shell structure, demonstrating the supported Ru nanocrystals on the surfaces of NiSe_2 octahedrons (Fig. 1g). The atomic ratios of Ru/Ni for the four samples of $\text{Ru}/\text{NiSe}_2/\text{C}-X$ ($X = 10, 20$, and 30) and Ru/NiSe_2 were determined by EDS to be 2.73, 1.89, 1.30, and 0.47, respectively (Table S1†).

To evaluate the alkaline HOR performance of the as-prepared catalysts, rotating disk electrode (RDE) measurements in a standard three-electrode system were carried out in 0.1 M KOH solution. The exact mass ratios of Ru were quantified by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), in which the loadings of Ru on the electrodes for all these samples are presented in Table S2.† Fig. 2a presents the negatively scanned HOR polarization curves at the rotating speed of 1600 rpm in an H_2 -saturated solution. Meanwhile, the current density would almost disappear in the same potential range in an N_2 -saturated electrolyte (Fig. S6†), verifying the faradaic process of hydrogen oxidation. The apparent current density gradually rises with the addition of NiSe_2 supports, leading to $\text{Ru}/\text{NiSe}_2/\text{C}-20$ exhibiting the highest apparent activity and an enlarged EPW compared to Ru/C . Further increasing the content of NiSe_2 would degrade the catalytic performance. Fig. S7† shows the cyclic voltammetric (CV) curves



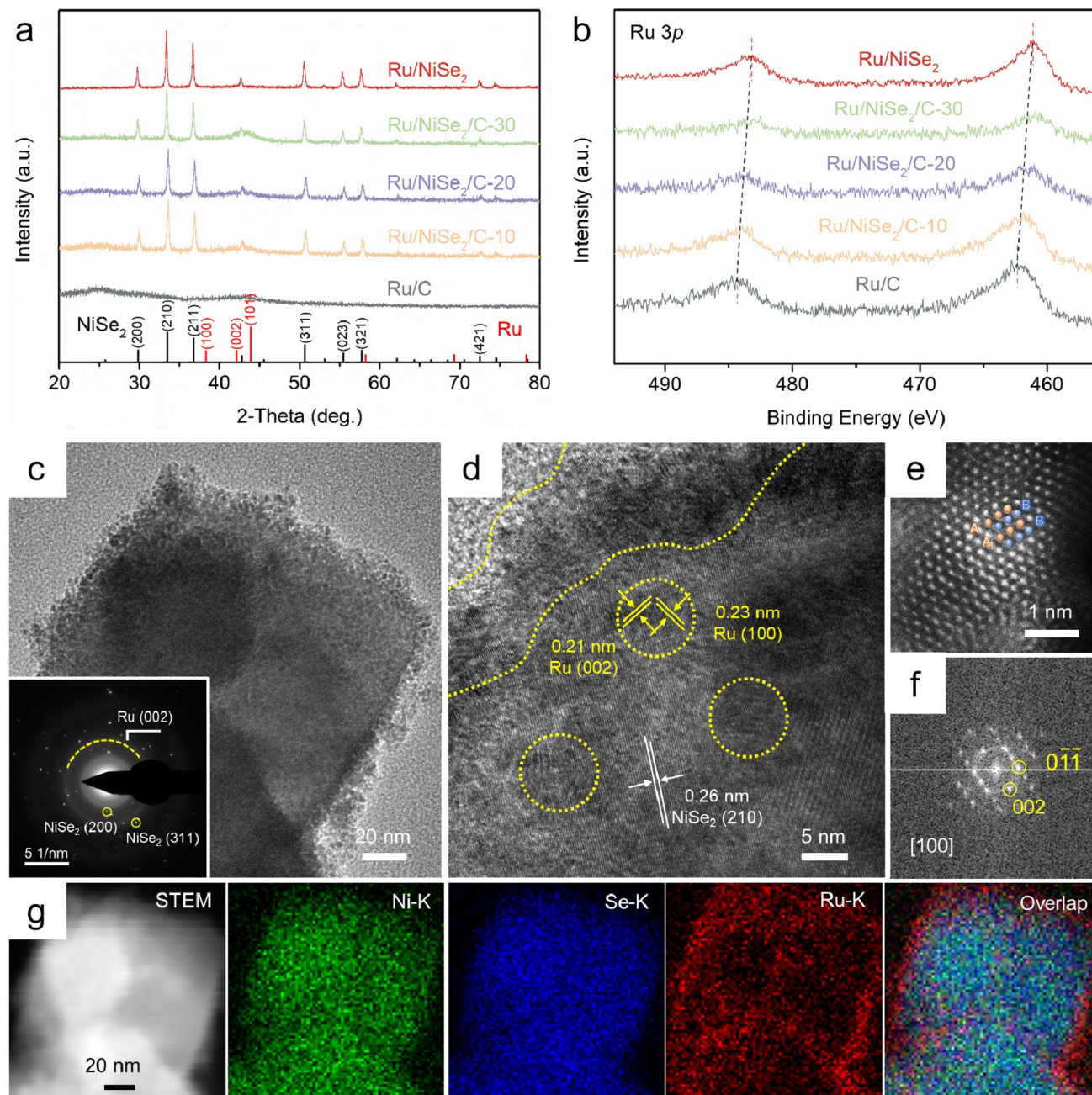


Fig. 1 (a) XRD patterns and (b) high-resolution XPS spectra of Ru 3p for Ru/C, Ru/NiSe₂/C-10, Ru/NiSe₂/C-20, Ru/NiSe₂/C-30, and Ru/NiSe₂. (c) TEM (inset: SAED pattern) and (d) HRTEM images of Ru/NiSe₂/C-20, where Ru nanocrystals are marked by dotted yellow lines and circles. (e) HAADF-STEM image. (f) Corresponding FFT pattern of a single Ru nanocrystal. (g) EDS mapping images of Ru/NiSe₂/C-20.

of Ru/NiSe₂/C-20 and NiSe₂/C, in which no characteristic redox peaks of Ni or Se species could be seen during the HOR. This means that NiSe₂ would not contribute to the CV of Ru/NiSe₂/C-20. Typically, the kinetic current density (j^k) for Ru/NiSe₂/C-20 was analyzed to circumvent the effect of mass (H₂)-transport by performing the electrochemical tests at different rotating rates from 2500 to 625 rpm (Fig. S8†). The corresponding Koutecky–Levich plot shows a slope of 14.6 cm² mA⁻¹ rpm^{-1/2}, similar to the theoretical value of 14.8 cm² mA⁻¹ rpm^{-1/2},³³ indicating a two-electron process of the HOR. Therefore, the j^k

value after being normalized by the mass of Ru ($j^{k,m}$) for Ru/NiSe₂/C-20 could be extracted according to the Koutecky–Levich equation,³⁴ which reaches 2.51 mA μg_{Ru}⁻¹ at the overpotential of 50 mV and is higher than that of Ru/C (0.97 mA μg_{Ru}⁻¹), Ru/NiSe₂/C-10 (1.90 mA μg_{Ru}⁻¹), Ru/NiSe₂/C-30 (1.80 mA μg_{Ru}⁻¹), Ru/NiSe₂ (0.32 mA μg_{Ru}⁻¹), and most of the reported Ru-based catalysts (Fig. 2b, and Tables S2 and S3†).

Exchange current density (j^0) is an important parameter to evaluate the performance of the HOR, which could be extracted from the Tafel plot (Fig. 2c) according to the Butler–Volmer

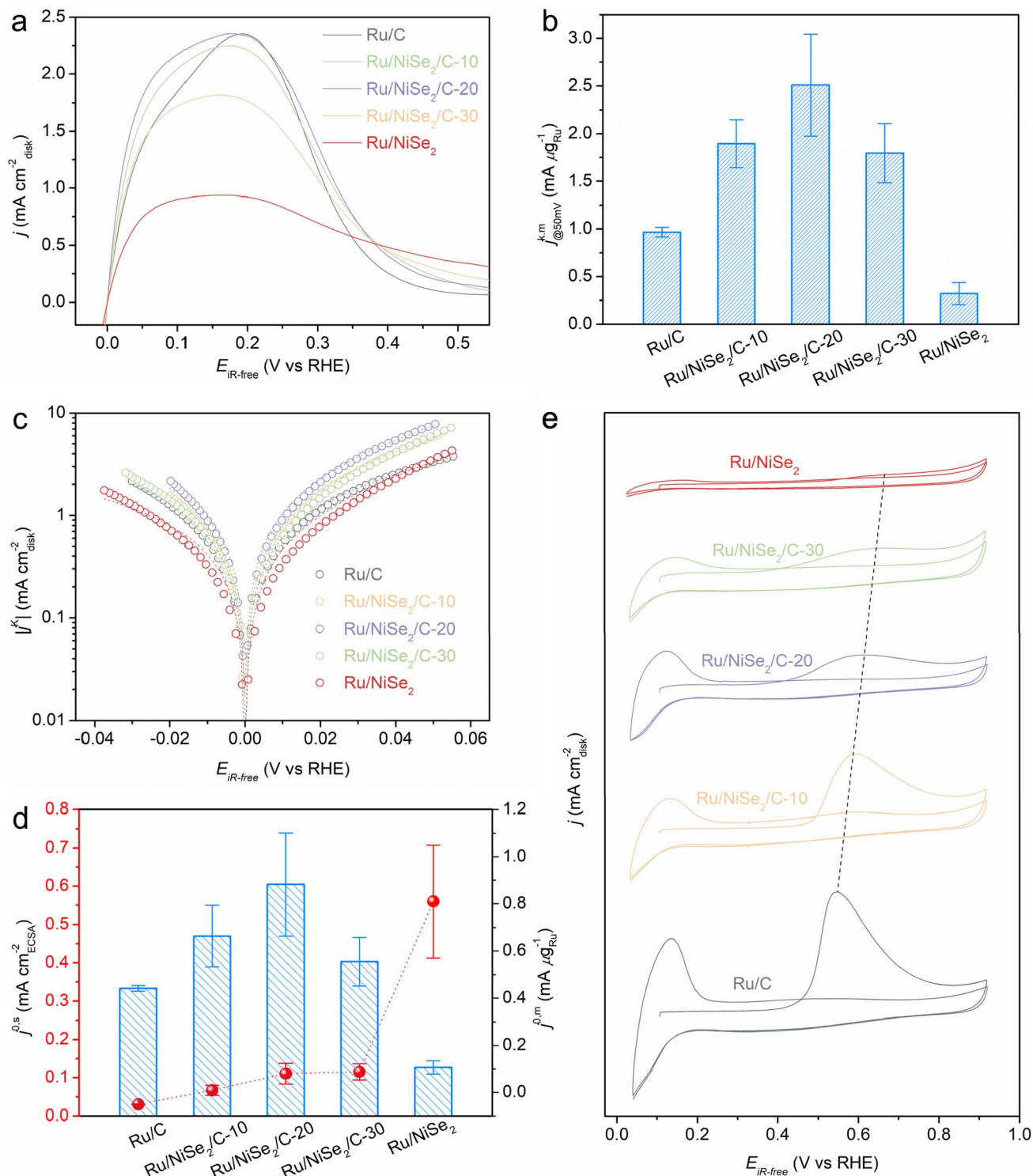


Fig. 2 (a) HOR polarization curves and (b) corresponding $j^{\text{k,m}}$ values at 0.05 V vs. RHE of Ru/C, Ru/NiSe₂/C-10, Ru/NiSe₂/C-20, Ru/NiSe₂/C-30, and Ru/NiSe₂. (c) Tafel plots with Butler–Volmer fitting lines and (d) extracted exchange current densities normalized by the ECSA and the mass of Ru, respectively. (e) CO-stripping curves of the five samples.

equation.^{35,36} A similar trend is obtained for the j^{0} values normalized by the mass of Ru ($j^{\text{0,m}}$) for the above catalysts, in which Ru/NiSe₂/C-20 possesses the highest $j^{\text{0,m}}$ of 0.88 mA μg_{Ru}⁻¹ and surpasses most of the reported Ru-based catalysts

(Fig. 2d, Tables S2 and S3†). To reveal the reason for the formation of this volcanic relationship between the mass activities and the contents of NiSe₂ supports, electrochemically active surface areas (ECSAs) were further measured *via* the CO-

Based on the above analysis of physical characterizations and electrochemical tests, it is speculated that the intrinsic activity of Ru-based catalysts towards alkaline HOR could be facilitated by NiSe₂ supports. For the sake of corroborating this viewpoint, DFT calculations and further experiments were executed. Ru clusters with 13 atoms supported on NiSe₂(111) or graphene(001) slabs were constructed as the models for

Therefore, a conclusion could be drawn based on the reported literature and this work that either the rational strengthened or weakened OHBE could accelerate the alkaline

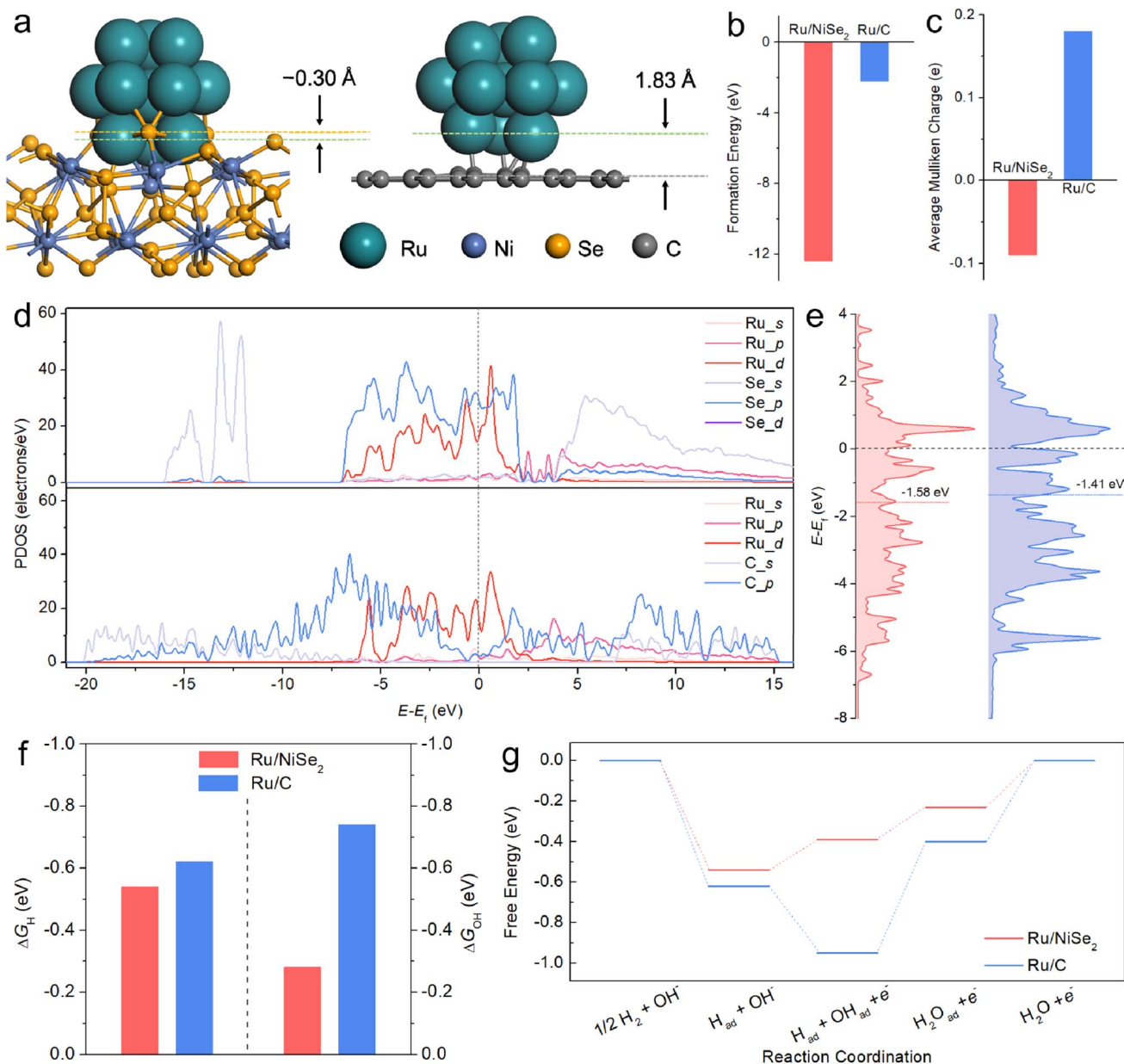


Fig. 3 (a) Models of the *hcp*-Ru₁₃ clusters on NiSe₂(111) and graphitized C(001) representing Ru/NiSe₂ and Ru/C, respectively. (b) Formation energy of the metal-support coupling process and (c) average Mulliken charge of Ru/NiSe₂ and Ru/C. (d) PDOS and (e) corresponding d-band structures of Ru/NiSe₂ and Ru/C. (f) Calculated ΔG_H and ΔG_{OH} of the most stable Ru sites on Ru/NiSe₂ and Ru/C, and (g) corresponding reaction pathways for alkaline HOR.

HOR catalytic kinetics for Ru-based catalysts and oppositely change their EPWs. The reasons why contradictory approaches lead to the same activity trend should be thoroughly explored. Fig. 4a presents the HOR polarizations normalized to their corresponding maximum current density, which better reflects the changes in the relative current density *versus* the increased content of NiSe₂ supports. It is clearly observed that the increased NiSe₂ content causes the gradually raised current density at potentials lower than ~ 0.15 V vs. RHE as well as the gradually enlarged potential at the current density dropping to half of its maximum value (denoted as $E_{dec}@1/2j_{max}$) as summarized in Fig. 4b. Considering the structural sensitivity

of the catalytic surfaces for alkaline HOR, the active sites with different coordination environments, such as the terrace or the edge sites and the supports surrounded or removed sites, usually possess different binding energies to the crucial intermediates and thus different performances on an actual catalyst.^{32,44} Hence, we divide the HOR region into three parts, the weak H_{ad} adsorption area (H^w) at low overpotentials, the strong H_{ad} adsorption area (H^s) at high overpotentials, and the OH_{ad} adsorption area (poisoned surface) at the potential more positive than ~ 0.3 V vs. RHE. On one hand, while Ru/C shows the lowest ratio of H^w, increasing the content of NiSe₂ supports can effectively improve the H^w proportion, finally leading to

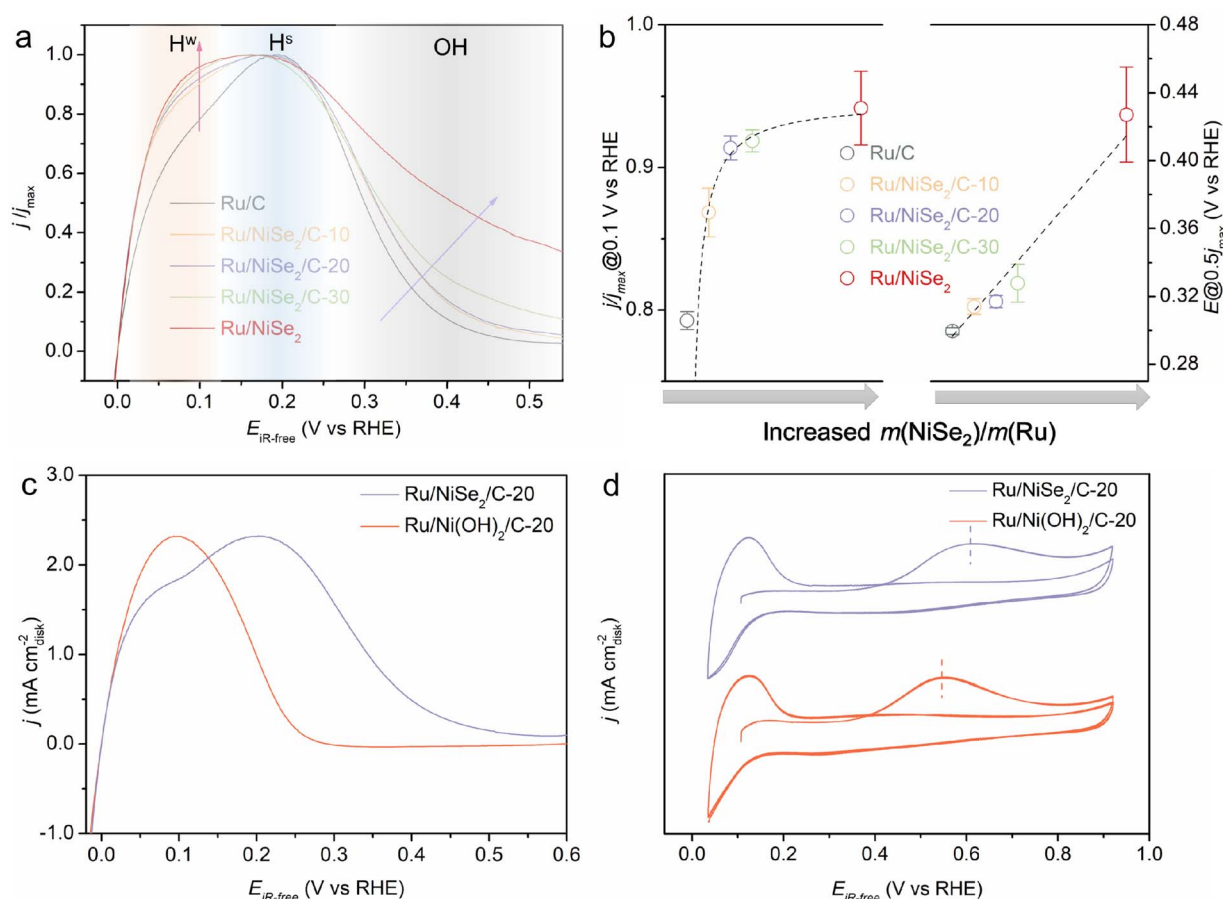
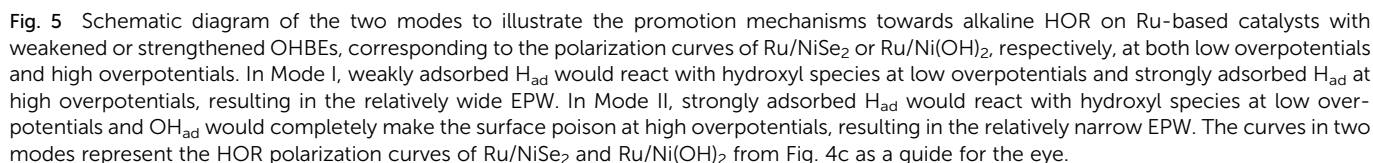


Fig. 4 (a) Normalized HOR polarizations and (b) the relationships of the relative current densities at 0.1 V vs. RHE or the potential at the declined current densities dropping to half of their maximum values ($E_{\text{dec}}@1/2j_{\text{max}}$) with the increased content of NiSe_2 . (c) HOR polarizations and (d) CO-stripping curves of $\text{Ru/NiSe}_2/\text{C}-20$ and the *in situ* formed $\text{Ru/Ni(OH)}_2/\text{C}-20$ after electrooxidation treatment.

the monotonically enhanced intrinsic activity at low overpotentials. This could be attributed to the weakened adsorption of OH_{ad} species originating from the strong interactions between Ru and NiSe_2 alleviating the competitive adsorption of H_{ad} and OH_{ad} . Thereby more active sites for the dissociative adsorption of H_2 could be provided. On the other hand, the weakened OHBE would result in more difficult oxidative desorption (Volmer step) of the over-strongly adsorbed H_{ad} through the bi-functional mechanism.^{13,45,46} Thus, it would happen at higher overpotentials, positively shifting the H^{s} area as well as the $E_{\text{dec}}@1/2j_{\text{max}}$ that is defined as a parameter to evaluate the completely poisoned Ru surfaces by OH_{ad} spectators. In contrast, the performance enhancement from the strengthened OHBE based on previous research might derive from another mode. We speculate that the stronger OHBE would boost the oxidative desorption of the strongly adsorbed H_{ad} and hence accelerate the alkaline HOR kinetics. However, the competitive adsorption between H_{ad} and OH_{ad} would be more significant, leading to the negatively shifted $E_{\text{dec}}@1/2j_{\text{max}}$. That means the promotion strategy of strengthening the OHBE of Ru-based catalysts is at the expense of the narrowed EPW.

For the further verification of this viewpoint, $\text{Ru/NiSe}_2/\text{C}-20$ was electrochemically treated by 100 cycles of cyclic voltammetry in the potential range between 0.0 and 1.2 V vs. RHE, denoted as $\text{Ru/Ni(OH)}_2/\text{C}-20$. After that, NiSe_2 supports would be irreversibly oxidized into Ni(OH)_2 due to the high potential condition,^{47,48} which could be further confirmed by Raman spectroscopy where a new Raman peak appeared after electrochemical high-potential reconstruction at 1075 cm^{-1} assigned to the second-order acoustic mode of $\beta\text{-Ni(OH)}_2$ (Fig. S17†).⁴⁹ It is known that the *in situ* formed Ni(OH)_2 would enhance the OHBE of the supported Ru.⁵⁰ As shown in Fig. 4c, $\text{Ru/Ni(OH)}_2/\text{C}-20$ exhibits obviously improved HOR activity at low overpotentials, similar to the reported Ru-based catalysts.^{14,24,32} However, the HOR current density begins to decline at about 0.1 V with the negatively shifted $E_{\text{dec}}@1/2j_{\text{max}}$. Fig. 4d depicts the negatively shifted CO-stripping peak of the *in situ* formed $\text{Ru/Ni(OH)}_2/\text{C}-20$ at 0.54 V vs. RHE compared to that of $\text{Ru/NiSe}_2/\text{C}-20$ (0.60 V vs. RHE) and even Ru/C (0.55 V vs. RHE). The OHBE of the Ru site on Ru/Ni(OH)_2 has also been calculated, which theoretically proves the enhanced oxophilicity of the Ru surface originated from the *in situ* phase transformation from NiSe_2 to Ni(OH)_2 (Fig. S18†). These results are in line with the





activity and the EPW monotonically increase with the increased content of NiSe₂. The coupling of Ru with NiSe₂ can significantly regulate the electron structures and weaken the OHBE, which alleviates the competitive adsorption of H_{ad} and OH_{ad} and provides more active sites for the formation of weakly adsorbed H_{ad} with high activity. Different from the previous results, we propose two possible promotion modes to qualitatively illustrate that the opposite regulations of the OHBE on the surface of Ru yield a similar consequence of the accelerated alkaline HOR kinetics at low overpotentials but a different trend about the EPW. This is finally attributed to the discrepant roles of OH_{ad} species with different OHBEs and at different overpotentials. This work provides another approach to design novel Ru-based catalysts with high activity towards alkaline HOR by rationally weakening the OHBE, without the expense of the narrowed EPW.

Data are available upon request from the authors.

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

The authors declare no competing financial interests.

In conclusion, we reported a d-p coupling strategy to improve the alkaline HOR performance of Ru catalysts by using NiSe₂ octahedrons as supports. Specifically, Ru/NiSe₂/C-20 exhibits the mass-normalized j^k (at the overpotential of 50 mV) and j^0 values of 2.51 and 0.88 mA $\mu\text{g}_{\text{Ru}}^{-1}$, respectively, which is 2.6 and 2.0 times compared to that of Ru/C. Moreover, the intrinsic

- 45 I. T. McCrum and M. T. M. Koper, *Nat. Energy*, 2020, **5**, 891–899.
- 46 Y.-H. Wang, X.-T. Wang, H. Ze, X.-G. Zhang, P. M. Radjenovic, Y.-J. Zhang, J.-C. Dong, Z.-Q. Tian and J.-F. Li, *Angew. Chem., Int. Ed.*, 2021, **60**, 5708–5711.
- 47 L. Wang, X. Wang, S. Xi, Y. Du and J. Xue, *Small*, 2019, **15**, 1902222.
- 48 Y. Shi, W. Du, W. Zhou, C. Wang, S. Lu, S. Lu and B. Zhang, *Angew. Chem., Int. Ed.*, 2020, **59**, 22470–22474.
- 49 M. Aghazadeh and H. Rad, *J. Mater. Sci.: Mater. Electron.*, 2022, **33**, 1–17.
- 50 T. Jiang, K. Li, S. Park, K. Zheng, Y. Meng, Y. Yuan, Z. Liu, Z. Zhu, X. Zheng, S. Liu and W. Chen, *Nano Lett.*, 2022, **22**, 1741–1749.

