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# Surface enrichment of iridium on IrCo alloys for boosting hydrogen production<sup>†</sup>

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We report a facile synthesis of an Ir surface-enriched IrCo alloy catalyst and its excellent activity which outperforms commercial Pt/C for the hydrogen evolution reaction (HER) in acidic media showing fast kinetics. The as-synthesized catalyst exhibits low overpotentials of merely 9 mV and 29.3 mV to afford current densities of 10 and 100 mA cm<sup>-2</sup>, respectively, a turnover frequency of 1.25 s<sup>-1</sup>, a low Tafel slope of 23.7 mV dec<sup>-1</sup>, and stability for 100 h at a high current density of 100 mA cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. Experiments and density functional theory (DFT) calculations indicate that the enrichment of Ir atoms on the outer surface of IrCo alloys is responsible for the effectively optimized free energy of hydrogen adsorption, which boosts the kinetics and HER performance. Our finding provides an insight into the metal surface enrichment on alloy nanoparticles (NPs).

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# Introduction

Developing reliable renewable energy sources is one of the critical challenges to meet the growing global energy demand and diminish the reliance on dwindling fossil fuels.1-9 Among various carbon-free energy sources, hydrogen produced from the cathodic HER of water electrolysis is considered to be the cleanest fuel with high gravimetric energy density and a promising fuel to fulfill both stationary and transportation needs.<sup>10,11</sup> In this regard, much effort has been devoted to developing efficient catalysts.<sup>12-20</sup> Given that the HER kinetics is sluggish in alkaline solution, the catalysts in acidic media are desirable.<sup>21</sup> Most of the non-noble metal-based catalysts<sup>22-26</sup> and noble metal catalysts27-31 work well in alkaline water electrolysis; however, a limited range of materials (such as platinum group metals-based catalysts) can survive under corrosive acidic conditions.32-35 To date, Pt and Pt-based catalysts are well known for their best performance toward the HER in acidic media due to their optimal binding energy with hydrogen. However, Ir-based catalysts recently received considerable attention as a viable alternative to Pt with good HER

performance.<sup>36</sup> Specifically, Ir NPs were grown on 3D graphite, and Ir–W alloy nanodendrites were reported, which displayed high activity for the HER under acidic conditions comparable with state-of-the-art Pt/C.<sup>37,38</sup> However, these catalysts still require high voltage for driving large current density. As a result, the design and synthesis of electrocatalysts that can operate efficiently at high-current density in a harsh acidic environment remain great challenges.

In this direction, alloying noble metals with earth-abundant transition metals is a potential alternative strategy not only to intensively reduce the amount of expensive precious metals but also to offer new heterogeneous catalysts with improved HER activity and stability compared to their parent metals. For an alloy system, surface segregation is a common phenomenon that has a considerable impact on chemical reactions.39-42 It leads to modifying the surface atomic arrangement and electronic structure, which facilitates the catalysis process. Farsi et al. employed DFT to calculate the segregation energies  $(E_{seg-1-bulk})$  of bimetallic alloys composed of all transition metals and noble metals (Pt, Ir, Pd, and Rh).39 It is shown that some alloys possess positive segregation in which earth-abundant metals prefer to locate inside the core while their counterparts tend to segregate towards the surface, which is paramount in the interaction between the active site and electrolyte, leading to the variation of adsorption-desorption energy of intermediates in the HER process. Therefore, a well-conditioned surface that preferentially attracts the hydronium ions and forms a hydrogen molecule is required for the enhancement of HER kinetics.

Inspired by the above considerations, we herein demonstrate a facile mechano-pyrolysis approach of IrCo bimetallic alloys on N-doped graphene ( $G_N$ ) with excellent catalytic HER performance and durability, surpassing the state-of the-art Pt/



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C catalyst. Specifically, the synthesized catalyst loaded on carbon fiber paper requires an overpotential of 9 mV *versus* the reversible hydrogen electrode (RHE) to achieve a current density of 10 mA cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte and a low overpotential of 29.3 mV (the lowest ever) for a current density of 100 mA cm<sup>-2</sup>. It also shows a turnover frequency of  $1.25 \text{ s}^{-1}$ , a small Tafel slope of 23.7 mV dec<sup>-1</sup>, and good stability for 100 h in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte at 100 mA cm<sup>-2</sup>. Both experiments and DFT calculations were employed to reveal that the enrichment of Ir atoms on the outer surface of IrCo alloys provides the effectively optimized free energy of hydrogen adsorption, boosts kinetics and drastically improves the HER performance. This catalytic performance is better than that of all other materials reported for the HER in an acidic environment.

# **Experimental section**

### Synthesis of catalysts

A mixture of 0.5 g melamine, 0.25 g glucose, 0.05 g  $IrCl_3 \cdot xH_2O$ , 0.5 g  $Co(acetate)_2$  and 2.72 g zirconium dioxide balls of 3 mm in diameter was placed in a mixer machine (AR-100) and agitated at 400 rpm for 3 min. The fine light-pink powder was transferred into a tube furnace and then annealed at 750 °C for 4 h under N<sub>2</sub> gas with a heating rate of 3 °C min<sup>-1</sup>. After naturally cooling down to room temperature, the black product was leached in 100 mL of 2 M H<sub>2</sub>SO<sub>4</sub> at 80 °C for 8 h. The resulting powder was washed thoroughly with hot H<sub>2</sub>O by vacuum filtration and subsequently dried in an oven at 60 °C. The collected powder was denoted as IC1-G<sub>N</sub>.

To optimize the reaction temperature, IC1- $G_{N}$ \_650 and IC1- $G_{N}$ \_850 were synthesized by the same procedure as that used for IC1- $G_{N}$  but at different temperatures of 650 and 850 °C, respectively.

The same procedure was also adopted to prepare IC2- $G_N$  and IC3- $G_N$  with different Co(acetate)<sub>2</sub> contents: 0.3 g and 0.7 g, respectively.

For comparison with the IC1- $G_N$  catalyst, the IC catalyst was synthesized by another procedure. First, 100 mg carbon was well dispersed in 60 mL H<sub>2</sub>O by sonication for 30 min. Then, 50 mg IrCl<sub>3</sub>·H<sub>2</sub>O and 132 mg CoCl<sub>2</sub>·H<sub>2</sub>O were added into the above solution and stirred for 12 h at room temperature. 2 mL NH<sub>3</sub>·H<sub>2</sub>O solution was added into the mixture and stirred another 12 h, followed by water evaporation on a hot plate. The collected black powder was transferred into a tube furnace and calcined at 500 °C for 4 h under N<sub>2</sub> gas with a heating rate of 3 °C min<sup>-1</sup>. Subsequently, the product was collected by washing with hot H<sub>2</sub>O several times to remove residual ions, and dried in an oven.

### Hydrophilic pretreatment of carbon fiber paper (CFP)

The cut-out CFP (area: 0.25 cm<sup>2</sup>) was cleaned by sonication in a mixture of ethanol and nitric acid for 12 h and washed thoroughly with  $H_2O$  and ethanol. CFP was then dried in an oven at 60 °C for further use.

### Materials characterization

The morphology and structure of all samples were characterized by high resolution transmission electron microscopy (HR-TEM, JEM-2100F with an acceleration voltage of 200 kV) and high resolution X-ray diffraction (HR-XRD, Rigaku X-ray diffractometer/D/ MAX2500V/PV with Cu K $\alpha$  radiation, 35 kV, and 200 mA) in the  $2\theta$  range of 20–90°. X-ray photoelectron spectroscopy (XPS) data were obtained by using K-alpha (Thermos fisher, UK). The loading amounts and elemental compositions of the catalysts were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). Extended X-ray absorption fine structure (EXAFS) data of the prepared catalysts were collected in transmission mode using ionization detectors (Oxford) at the Pohang Accelerator Laboratory (PAL).

### **Electrochemical characterization**

All of the electrochemical measurements were performed in a three-electrode system at room temperature on BIO Logic using the as-prepared CFP and graphite rod as the working electrode and the counter and reference electrodes, respectively. The catalyst ink was prepared by dispersing 5 mg powder in a solution containing 380  $\mu$ L IPA, 600  $\mu$ L H<sub>2</sub>O and 20  $\mu$ L Nafion, followed by ultrasonication for 2 h to form a homogeneous catalytic ink. Then, 60 µL of the catalyst ink was pipetted on the CFP (area:  $0.25 \text{ cm}^2$ ) and dried at room temperature. Other catalysts were also cast on CFP with the same procedure and loading. For comparison, commercial Pt/C (20 wt%) and Ir/C powder (20 wt%) catalyst inks were also prepared with the same method. Cyclic voltammetry (CV) was performed at a scan rate of 50 mV s<sup>-1</sup> for 20 cycles in a range from 0.06 to -0.14 V (vs. RHE) prior to linear sweep voltammetry (LSV) measurements to make the electrode surface fully wet. To evaluate the HER activity, LSV was carried out at a scan rate of 2 mV cm<sup>-2</sup> in  $H_2$  saturated 0.5 M  $H_2SO_4$  solution with 95% *iR*-compensation. Double-layer capacitance  $(C_{dl})$  was determined using CV cycles in a non-faradaic potential region (0.1260-0.186 V vs. RHE) with a sweep rate of 5–25 mV s<sup>-1</sup>. The average current at a constant potential of 0.155 V vs. RHE was plotted vs. the scan rate and the  $C_{\rm dl}$  value was obtained as the slope determined from its linear plot. The electrochemical active surface area (ECSA) of all catalysts was estimated from the  $C_{dl}$  by diving the  $C_{dl}$  value by the specific capacitance (ECSA =  $C_{\rm dl}/C_{\rm s}$ , where a  $C_{\rm s}$  value of 0.035 mF cm<sup>-2</sup> was employed according to the reported literature). Then, the current densities of the samples were normalized by the ECSA values according to the equation:

$$j_{\text{ECSA}} = \frac{j}{\text{ECSA}}$$

Electrochemical impedance spectroscopy (EIS) was performed at a potential of -21.7 mV vs. RHE over a frequency range from 10 kHz to 10 mHz. The catalyst stability test was conducted by chronoamperometry measurements at a constant applied potential of -87.7 V vs. RHE (without *iR* compensation) at room temperature.



**Fig. 1** (a) Schematic illustration of the fabrication procedure of  $IC1-G_N$ . (b and c) TEM images and NP size distribution of the prepared catalyst. (d) HRTEM image. (e) HAADF-STEM image of an IrCo NP, and intensity profiles along the (f) blue line and (g) green line, respectively. Scale bars: (b) 50 nm. (c) 10 nm. (d) 1 nm.

# **Results and discussion**

Fig. 1a displays a schematic diagram of the catalyst synthesis. Briefly, glucose, melamine,  $IrCl_3 \cdot xH_2O$ , and  $Co(acetate)_2 \cdot 4H_2O$ were thoroughly mixed together using a mixer to form a homogeneous mixture, followed by a calcination treatment in a N<sub>2</sub> flow. Under the thermal conditions, the carbonization of glucose induced polymerization of melamine to form G<sub>N</sub> sheets which replace graphene oxide precursors, and then encapsulated the alloy NPs. The collected powder was then leached with acid and washed with water in order to discard the unreacted species (see the ESI<sup>†</sup> for more details). The final product is denoted as the IC1-G<sub>N</sub> catalyst. High-resolution transmission electron microscopy (HR-TEM) was employed to investigate the morphologies and structures of the synthesized IC1-G<sub>N</sub> catalyst. As illustrated in Fig. 1b and c, the NPs with a diameter in the range of 3-10 nm are evenly distributed over entire G<sub>N</sub>. The bright-field HR-TEM image of IC1-G<sub>N</sub> shows a clear lattice fringe spacing of 0.213 nm corresponding to the (111) plane of IrCo alloys (Fig. 1d). Scanning transmission electron microscopy (STEM) is employed to obtain more detailed atomic information. Due to the highly sensitive Z-contrast of atoms in highangle annular dark field STEM (HAADF-STEM), the intensity of Ir atoms is higher than that of Co atoms. As shown in Fig. 2e,

the differences in contrast are visible in which the weak and strong brightness dots of the image correspond to the lightest element (Co) and the heaviest element (Ir), respectively. The intensity profiles (Fig. 2f and g) were obtained along the M1 and  $M_2$  lines of the NPs (Fig. 2e). The intensity columns are diverse in both profiles, in which the lower columns are associated with Co atoms, whereas the higher ones are associated with Ir atoms. This result indicates that some columns are Ir rich compared to others. The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and corresponding elemental mapping images are shown in Fig. S2.† The fast Fourier transformation (FFT) pattern shows the existence of the (111) lattice plane, which is consistent with the (111) plane of the cubic structure of IrCo alloys observed in the XRD analysis (Fig. S3a and b<sup>+</sup>). The EDS line scanning profiles reveal the distribution of both Ir and Co elements across the whole nanoparticles, as strongly verified using the EDS spectrum, which demonstrates the formation of IrCo alloys (Fig. S3c-e<sup>†</sup>).

Inductively coupled plasma optical emission spectroscopy (ICP-OES) shows that the content of Ir in IC1- $G_N$  is ~5.0 wt% (Table S1<sup>†</sup>).

Fig. 2a shows the high-resolution X-ray diffraction (HR XRD) patterns of IC1- $G_N$ , Co- $G_N$ , and Ir- $G_N$ . The diffraction peaks for the bare Co (Co- $G_N$ ) and IC1- $G_N$  located at 44.23°, 51.53°, and

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**Fig. 2** Structural characterization. (a) X-ray diffraction pattern of  $IC1-G_N$ ,  $Co-G_N$ , and  $Ir-G_N$ . (b and c) XANES spectra (b) and Fourier-transformed EXAFS spectra (c) for the Ir L<sub>III</sub>-edge of  $IC1-G_N$ , commercial Ir/C, and IrCl<sub>3</sub> precursors.

75.87° are assigned to the (111), (200), and (220) planes of the cubic ( $Fm\bar{3}m$ ) Co (JCPDS no. 01-089-4307), respectively. The crystal plane peaks of Co in IC1-G<sub>N</sub> are slightly shifted compared to those in bare Co, indicating that the Ir atoms alloyed with Co atoms likely locate on the outermost surface rather than stay in the Co bulk.<sup>43</sup> Additionally, the phase of bimetallic IrCo alloys with a broad diffraction peak located at 42.40° for IC1-G<sub>N</sub> can be indexed to the (111) plane of the cubic ( $Fm\bar{3}m$ ) IrCo (JCPDS no. 03-065-9327).

Ex situ X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses were carried out to probe the local atomic and electronic structures of IC1-G<sub>N</sub>. The Ir L<sub>III</sub>-edge XANES spectra of IC1-G<sub>N</sub> are illustrated in Fig. 2b, together with those of the commercial Ir/C and IrCl<sub>3</sub> precursors for comparison. The white line shape of IC1-G<sub>N</sub> is analogous to that of commercial IrC (Ir<sup>0</sup>) with a slightly lower amplitude, which is different from that of  $IrCl_3$  precursors ( $Ir^{3+}$ ). This is ascribed to the oxidation state of Ir (which is very close to zero) or the predominant metallic phase in IC1-G<sub>N</sub>.<sup>44,45</sup> This is beneficial for enhancing the catalyst stability due to high metal corrosion resistance. The slight decline in the white line intensity of the as-synthesized catalyst at the Ir  $L_{III}$  edge is caused by heteroatomic interactions in NPs.40 This observation shows that Ir in IC1-G<sub>N</sub> possesses less empty d orbital states compared to that in Ir/C and thus more electron density may transfer from Co to Ir, which positively affects the Ir intrinsic activity during electrocatalysis.46 As shown in the XANES spectra of the Co K-edge in Fig. S4,† the white line shape of Co of IC1-G<sub>N</sub> is different from that of Co foil, in which the intensity peak of the as-prepared sample is higher than that of Co foil, showing the variation of the Co 3d-band electron density. Fig. 2c shows the corresponding Fourier-transformed (FT)  $k^3$ -weighted extended XAFS (EXAFS) spectra of the catalyst. The scattering peak at ~2.59 Å reveals the Ir-Ir bond in commercial Ir/C, while the peak that appears at 1.99 Å could be ascribed to the Ir-Cl bond in IrCl<sub>3</sub> precursors.<sup>47</sup> The conspicuous peak at 2.44 Å is attributed to the Ir-Co bond due to shorter Ir-Co bonds than the Ir-Ir bond. The differences in intensity and position of this peak from those of commercial Ir/C and IrCl<sub>3</sub> precursors further verify the formation of IrCo alloys in IC1-G<sub>N</sub>.

The HER performance of the synthesized catalysts was evaluated in a three-electrode system in H2-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. Fig. 3a shows the linear sweep voltammetry (LSV) curves of IC1-G<sub>N</sub>, IC2-G<sub>N</sub>, IC3-G<sub>N</sub>, IC, and commercial Ir/C and Pt/C as the benchmarks. In Fig. 3b, IC1-G<sub>N</sub> shows remarkably enhanced catalytic activity with small overpotentials (19.4 and 29.3 mV, respectively) to deliver current densities of 50 and 100 mA  $\rm cm^{-2}$ , which are better than those of IC (23.1 and 33.7 mV), and commercial Ir/C (22.2 and 35.1 mV) and Pt/C (24.1 and 43.6 mV). To the best of our knowledge, the IC1-G<sub>N</sub> catalyst shows the lowest overpotential at 100 mA cm<sup>-2</sup> among the recently reported values (Fig. 3c).48-55 To determine the influence of annealing temperature on HER performances, we investigated IC1-G<sub>N</sub> at different temperatures of 650, 750, and 850 °C, while 750 °C is found to be the optimum pyrolysis temperature (Fig. S5<sup>†</sup>). At an overpotential of 29.3 mV (vs. RHE), IC1- $G_N$  exhibited a mass activity of 1.662 A mg<sub>Ir</sub><sup>-1</sup> which is 5.1 and 6.2 times greater than those obtained for commercial Ir/C and Pt/C, respectively (Table S2<sup>†</sup>). Additionally, we observed a Tafel slope of 23.7 mV  $dec^{-1}$  (Fig. 3d), which is smaller than those of IC (25.4 mV dec<sup>-1</sup>), and commercial Ir/C (27 mV dec<sup>-1</sup>) and Pt/C (28 mV dec<sup>-1</sup>), indicating its superior HER reaction kinetics. Thus, the HER mechanism has the Volmer-Tafel reaction as the rate determining step, in which the chemisorbed hydrogen atoms are recombined to generate hydrogen molecules. The double-layer capacitance  $(C_{dl})$  was determined and electrochemical impedance spectroscopy (EIS) of the catalysts was performed to elucidate the intrinsic HER catalytic activity.<sup>56,57</sup> The capacitance C<sub>dl</sub> was estimated using the cyclic voltammetry method in a potential window free of the faradaic current region at different scan rates (5 to 25 mV s<sup>-1</sup>). As displayed in Fig. 3e and S6,<sup>†</sup> the C<sub>dl</sub> of IC1-G<sub>N</sub> was determined to be  $67.7 \text{ mF cm}^{-2}$ , larger than those of IC2-G<sub>N</sub> (58.9 mF cm<sup>-2</sup>), IC3- $G_N$  (64.4 mF cm<sup>-2</sup>), IC (51.2 mF cm<sup>-2</sup>), Ir/C (63.1 mF cm<sup>-2</sup>) and Pt/C (62.7 mF cm<sup>-2</sup>), indicating that IC1-G<sub>N</sub> has the most abundant active sites on the surface among the investigated catalysts. The ECSA of IC1-G<sub>N</sub>, IC2-G<sub>N</sub>, IC3-G<sub>N</sub>, IC, and commercial Ir/C and Pt/C was calculated to be 1934, 1681, 1840, 1461, 1803 and 1792 cm<sup>2</sup>, respectively. A consistent trend in HER activity is also observed in Fig. 3f where LSV curves are normalized against the ECSA determined from  $C_{dl}$ 



**Fig. 3** Electrochemical performance of IC1- $G_N$ , IC2- $G_N$ , IC3- $G_N$ , IC, and commercial Ir/C and Pt/C in H<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> medium. (a) LSV curves (with 95% *iR* compensation). (b) Comparison of HER overpotentials required to achieve the current density of 10, 50 and 100 mA cm<sup>-2</sup> in H<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. (c) Comparison of HER overpotentials at 50 and 100 mA cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution to that reported in the literature (corresponding to the reference numbers<sup>48-55</sup> from left to right). (d) Tafel plots. (e) Double-layer charging current *vs.* the scan rate of IC1- $G_N$ . (f) Comparison of the HER current density (normalized with the ECSA) at  $\eta = 23.9$  mV *vs.* RHE. (g) EIS Nyquist plots. The inset shows the equivalent electrical circuit diagram. (h) Chronoamperometry (CA) test results of IC1- $G_N$  in 0.5 M H<sub>2</sub>SO<sub>4</sub> medium with an applied overpotential of 87.7 mV *vs.* RHE for 100 h (without *iR* compensation). (i) LSV curves before and after the stability test.

measurements. These results confirm the superior intrinsic catalytic activity of IC1-G<sub>N</sub>. In addition, EIS was employed to study the electrochemical behavior in which the semicircle in the Nyquist plot corresponds to the charge transfer resistance ( $R_{ct}$ ) (Fig. 3g).<sup>58</sup> The inset of Fig. 3g shows the equivalent circuit, which includes three components such as solution resistance ( $R_{sol}$ ),  $R_{ct}$ , and constant phase element (CPE), for the analysis of the impedance spectra. The IC1-G<sub>N</sub> catalyst exhibits  $R_{ct}$  of 5.7  $\Omega$ , which is lower than those of IC (6.2  $\Omega$ ) and other catalysts. This proves a fast faradaic reaction process, which increases the electron-transfer of materials and facile HER kinetics. The turnover frequency (TOF), another important parameter of merit for examining the intrinsic activity,<sup>59</sup> was estimated, where the number of surface Ir atoms was employed as the number of active sites. At the same overpotential of 29.3 mV, the

TOF value of IC1- $G_N$  is  $1.25 \text{ s}^{-1}$ , which is 2.17, 1.04, 1.26, 5.16, 6.09 times greater than those of IC2- $G_N$ , IC3- $G_N$ , IC, and commercial Ir/C and Pt/C, respectively (Table S3<sup>†</sup>). This result is in agreement with its outstanding performance toward the HER. The stability, which was investigated using chronoamperometry, is another imperative index to evaluate the electrocatalytic efficiency.<sup>60</sup> For practical applications, the performance of the catalysts must be maintained under high-current-density conditions over long-term operation. Fig. 3h shows the durability test of the IC1- $G_N$  catalyst at a constant current density of 100 mA cm<sup>-2</sup> for a total of 100 h, and there is a negligible loss of HER performance at that current density. Fig. 3i shows the excellent stability of the as-synthesized catalyst under harsh acidic conditions. Interestingly, although the activity of IC1- $G_N$  after the stability test at low overpotentials

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exhibits a slight increase compared with that before testing, it can be improved at high overpotential, due to some inactive species on the surface of the catalyst which was leached out into the electrolyte during testing. In order to detect this metal dissolution amount, with a post-chronoamperometry test, the electrolyte was collected and analyzed by ICP-OES. The concentrations of dissolved Ir and Co per mg of IC1-G<sub>N</sub> were determined to be 49 and 83  $\mu$ g L<sup>-1</sup>, respectively (Table S4<sup>†</sup>). Furthermore, TEM, HAADF-STEM, the corresponding elemental mapping, and XRD analysis results (Fig. S7 and S8<sup>†</sup>) of IC1-G<sub>N</sub> after 100 h durability test show a negligible change in the morphology and structure. The long-term durability of IC1-G<sub>N</sub> resulted from several factors: (i) the high surface area of the catalyst offers large catalytically active sites, (ii) the high electrical conductivity of metals promotes fast electron transfer at electrode-electrolyte interfaces during the HER, and (iii) a few N-doped graphitic layers protect NPs from degradation.

DFT calculations were carried out to reveal the electrocatalytic activity of the  $IC1-G_N$  catalyst toward the HER. In general, two reaction steps of Volmer–Heyrovsky and Volmer– Tafel types are known to be involved in the HER:

(i) Volmer reaction:

$$* + H^+ + e^- \rightarrow H^*$$

(ii) Heyrovsky reaction:

$$H^+ + e^- + H^* \rightarrow H_2 + T$$

or

Tafel reaction:

$$H^* + H^* \rightarrow H_2 + 2^*$$

In the first step of the HER, H-adsorption takes place through the Volmer reaction with the reaction rate proportional to H adsorption strength, while the second step involves the desorption of H<sub>2</sub> either through the Heyrovsky or Tafel mechanism with the reaction rate inversely proportional to the H adsorption strength. In order to maximize the reaction rate, the Sabatier principle61 suggests that these two reaction steps of H adsorption and H<sub>2</sub> desorption should be established at thermoneutral bonding, *i.e.* at  $\Delta G_{\rm H} = 0$ . According to the Brønsted-Evans-Polanyi (BEP) principle<sup>61</sup> a linear relationship exists between the kinetic barrier and the free-binding energy of a reaction. We calculated the reaction free energy using the computational hydrogen electrode model at 0 V versus RHE, that is, the equilibrium potential of the HER. The detailed computational methods are given in the ESI.† The calculated Gibbs free energy ( $\Delta G_{H^*}$ ) at a particular active site is often a good indicator for predicting the HER activity. A smaller absolute  $\Delta G_{H^*}$  value generally implies a better catalytic activity.<sup>62</sup> We assessed the  $\Delta G_{H^*}$  values of the energetically favorable Ir-111, Co-111, IrCo-111, and Pt-111 surfaces for adsorption of hydrogen at all the possible adsorption sites on these surfaces. We observed that the hydrogen adsorption at Ir

or Co defect sites and h-sites-a/b usually has a strong binding energy as compared to that of the metal top site that favours the Volmer-Tafel mechanism. We tuned the H-adsorption strength by alloying with Co. The results show that IC1-G<sub>N</sub>-(IrCo-111) has an excellent HER activity on the Ir top site which favours the Volmer and Heyrovsky reaction pathway with the  $\Delta G_{H^*}$  value of IrCo-111 (-0.07 eV at the top site of Ir) closer to zero than those of Ir-111, Co-111, and other theoretical models. The resulting structures of all the considered model surfaces and their corresponding  $\Delta G_{H^*}$  values are presented in Fig. 4, S9 and S10.<sup>†</sup> The excellent electrocatalytic performance is attributed to the synergistic effect of binary Ir-Co, which is interacting through the electron transfer of d-orbital electrons. Our finding demonstrates that alloying Ir with Co enables to optimize the binding energy of H compared to their parent metals and to significantly improve the intrinsic electrocatalytic activity. Our DFT energetics supports that the Ir-enrichment at the IrCo IC1-G<sub>N</sub> surface leads to the enhancement of HER activity with a remarkably reduced absolute  $\Delta G_{H^*}$  value.

To gain deeper insights into the alloying effect on the enhancement of HER activity and selectivity, we calculated the projected density of states (PDOS) of Ir-111, Co-111, and IrCo-111 and compared the electronic structure of these models (Fig. S11<sup>†</sup>). The d-band centers of Ir-111, IrCo-111, and Co-111 are found to be -2.29, -1.19, and -1.82 eV, respectively. A slight shift in the d-band center towards the Fermi level and a broadening of the d-band state indicate that the electrons are relatively more localized near the Fermi level as compared to their parent metals' bulk electronic structures. The electron charge density map and the interlayer charge transfer behavior between the adsorbed H\* and Ir-Co atomic layers are shown in Fig. 4b and S12.<sup>†</sup> The charge density difference is defined as  $\Delta \rho$  $= \rho_{H^*-surface} - \rho_{surface} - \rho_{H}$ , where  $\rho_{H^*-surface}$ ,  $\rho_{surface}$ , and  $\rho_{H}$ represent the charge densities of the hydrogen adsorbed at the surface, the surface, and the adsorbed hydrogen, respectively. The planar-averaged charge density along the z direction and 3D charge density map are presented in Fig. 4b, where the dotted



Fig. 4 (a) Calculated HER-free energy on the surface of IrCo with Ir atoms on top of IC1- $G_N$  and commercial Ir/C and Pt/C at a hollow (h) site, and Co hollow site of Co- $G_N$ . (b) Difference in plane-averaged charge densities along the *z*-direction and 3D isosurface of the local charge density changed from the pure atomic states (with an isovalue of 0.00075 e Bohr<sup>-3</sup>), where the blue and red colors represent the charge depletion and charge accumulation. The horizontal dashed lines indicate the positions of the adsorbed hydrogen and IrCo atomic layers which are labeled as H and I<sub>1</sub> to I<sub>5</sub>, respectively. Yellow and blue balls denote Ir and Co, respectively.

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lines denote the position of the adsorbed H\* and Ir-Co atomic layers, labeled as H and l1 through l5, respectively. The loss and gain in the electron density is represented by blue and red colors, respectively. It is demonstrated that the electrons are transferred from cobalt to iridium; however, the charge redistribution is mainly found in the interfacial region between the adsorbed H\* and the top two layers of the IrCo-111 surface. However, the intra-atomic charge transfer is more important than the interatomic charge transfer between H\*, Ir and Co atoms. An enhanced catalytic activity is attributed to the faster rate of charge transfer between the adsorbed H\* atom and the adjacent Ir and Co atoms which is due to the difference in their electronegativity. Herein, we also demonstrate that the coordination of Ir-Co atoms playing an important role towards the HER activity and selectivity is ascribed more likely to the electronic properties and charge transfer rate. The effect of the coordinating atoms and the HER activity at various defect sites are presented in Fig. S9.† The stronger hydrogen adsorption energy reveals a faster rate of charge transfer (Fig. S9<sup>†</sup>). The Bader charge<sup>63</sup> analysis shows that 0.34 e<sup>-</sup> is transferred from Co to Ir. However, the adsorbed hydrogen also gains a weak charge transfer of 0.09 e<sup>-</sup> from Ir, resulting in a net gain (0.33 e<sup>-</sup>) of the Ir charge. The DFT results are consistent with the XAFS analysis and experimental findings. The fast charge transfer occurs at the interface between the IrCo-111 surface and adsorbed hydrogen. The interfacial layers  $(l_1 \text{ and } l_2)$  indicate rapid HER kinetics.

## Conclusions

In summary, we successfully developed a highly energy-efficient and durable HER catalyst under acidic conditions. The outstanding HER activity of the IC1-G<sub>N</sub> catalyst was achieved with the lowest overpotential ever of 29.3 mV vs. RHE at a current density of 100 mA  $\text{cm}^{-2}$ , long-term operation of 100 h in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte at a high current density of 100 mA cm<sup>-2</sup>, a turnover frequency of 1.25 s<sup>-1</sup>, and a low Tafel slope of 23.7 mV dec $^{-1}$ . The combination of experimental analysis and theoretical calculations revealed that the interaction between Co and Ir atoms enables the tunable electronic state of Ir atoms on top of IrCo NPs, leading to the effectively optimized hydrogen adsorption free energy, promoting rapid kinetics, and thereby accelerating the electrocatalytic activity toward hydrogen evolution. This work sheds light on the behavior of metal surface enrichment on alloy NPs in the hydrogen evolution reaction.

# Conflicts of interest

There are no conflicts to declare.

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### Notes and references

- 1 N. T. Suen, S. F. Hung, Q. Quan, N. Zhang, Y. J. Xu and H. M. Chen, Chem. Soc. Rev., 2017, 46, 337.
- 2 Z. W. She, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov and T. F. Jaramillo, Science, 2017, 355, eaad4998.
- 3 J. N. Tiwari, A. N. Singh, S. Sultan and K. S. Kim, Adv. Energy Mater., 2020, 10, 2000280.
- 4 X. Tian, P. Zhao and W. Sheng, Adv. Mater., 2019, 31, 1808066.
- 5 J. Zhu, L. Hu, P. Zhao, L. Y. S. Lee and K. Y. Wong, Chem. Rev., 2020, 120, 851.
- 6 J. N. Tiwari, N. K. Dang, S. Sultan, P. Thangavel, H. Y. Jeong and K. S. Kim, Nat. Sustain., 2020, 3, 556.
- 7 T. N. Tran, M. Y. Song, T. H. Kang, J. Samdani, H. Y. Park, H. Kim, S. H. Jhung and J. S. Yu, ChemElectroChem, 2018, 5, 1944.
- 8 N. K. Dang, J. N. Tiwari, S. Sultan, A. Meena and K. S. Kim, Chem. Eng. J., 2021, 404, 126513.
- 9 M. Ha, D. Y. Kim, M. Umer, V. Gladkikh, C. W. Myung and K. S. Kim, Energy Environ. Sci., 2021, 14, 3455.
- 10 G. Zhao, K. Rui, S. X. Dou and W. Sun, Adv. Funct. Mater., 2018, 28, 1803291.
- 11 I. Staffell, D. Scamman, A. V. Abad, P. Balcombe, P. E. Dodds, P. Ekins, N. Shah and K. R. Ward, Energy Environ. Sci., 2019, 12, 463.
- 12 X. Yu, J. Zhao, L. R. Zheng, Y. Tong, M. Zhang, G. Xu, C. Li, J. Ma and G. Shi, ACS Energy Lett., 2018, 3, 237.
- 13 J. Kim, H. Kim, W. J. Lee, B. Ruqia, H. Baik, H. S. Oh, S. M. Paek, H. K. Lim, C. H. Choi and S. I. Choi, J. Am. Chem. Soc., 2019, 141, 18256.
- 14 X. Wang, C. Xu, M. Jaroniec, Y. Zheng and S. Z. Qiao, Nat. Commun., 2019, 10, 4876.
- 15 Y. Ito, T. Ohto, D. Hojo, M. Wakisaka, Y. Nagata, L. Chen, K. Hu, M. Izumi, J. I. Fujita and T. Adschiri, ACS Catal., 2018, 8, 3579.
- 16 L. Najafi, S. Bellani, R. O. Nuñez, M. Prato, B. M. Garcia, R. Brescia and F. Bonaccorso, ACS Nano, 2019, 13, 3162.
- 17 C. Wu, M. Zhang, F. Chen, H. Kang, S. Xu and S. Xu, Dalton Trans., 2020, 49, 13339.
- 18 X. Zheng, H. Nie, Y. Zhan, X. Zhou, H. Duan and Z. Yang, J. Mater. Chem. A, 2020, 8, 8273.
- 19 S. Oh, H. Kim, Y. Kwon, M. Kim, E. Cho and H. Kwon, J. Mater. Chem. A, 2016, 4, 18272.
- 20 S. Sultan, M. H. Diorizky, M. Ha, J. N. Tiwari, H. Choi, N. K. Dang, P. Thangavel, J. H. Lee, H. Y. Jeong, H. S. Shin, Y. K. Kwon and K. S. Kim, J. Mater. Chem. A, 2021, 9, 10326.
- 21 Y. Zheng, Y. Jiao, A. Vasileff and S. Z. Qiao, Angew. Chem., Int. Ed., 2018, 57, 7568.
- 22 N. Yao, P. Li, Z. Zhou, Y. Zhao, G. Cheng, S. Chen and W. Luo, Adv. Energy Mater., 2019, 9, 1902449.

- 23 Y. Wu, X. Tao, Y. Qing, H. Xu, F. Yang, S. Luo, C. Tian, M. Liu and X. Lu, *Adv. Mater.*, 2019, **31**, 1900178.
- 24 W. Zhang, Y. Tang, L. Yu and X. Y. Yu, *Appl. Catal., B*, 2020, **260**, 118154.
- 25 Q. Ma, C. Hu, K. Liu, S. F. Hung, D. Ou, H. M. Chen, G. Fu and N. Zheng, *Nano Energy*, 2017, **41**, 148.
- 26 N. Mahmood, Y. Yao, J. W. Zhang, L. Pan, X. Zhang and J. J. Zou, *Adv. Sci.*, 2018, 5, 1700464.
- 27 D. H. Kweon, M. S. Okyay, S. J. Kim, J. P. Jeon, H. J. Noh, N. Park, J. Mahmood and J. B. Baek, *Nat. Commun.*, 2020, 11, 1278.
- 28 Z. Zhuang, Y. Wang, C. Q. Xu, S. Liu, C. Chen, Q. Peng,
  Z. Zhuang, H. Xiao, Y. Pan, S. Lu, R. Yu, W. C. Cheong,
  X. Cao, K. Wu, K. Sun, Y. Wang, D. Wang, J. Li and Y. Li, *Nat. Commun.*, 2019, **10**, 4875.
- 29 J. N. Tiwari, A. M. Harzandi, M. Ha, S. Sultan, C. W. Myung, H. J. Park, D. Y. Kim, P. Thangavel, A. N. Singh, P. Sharma, S. S. Chandrasekaran, F. Salehnia, J.-W. Jang, H. S. Shin, Z. Lee and K. S. Kim, *Adv. Energy Mater.*, 2019, **9**, 1900931.
- 30 H. Jin, S. Sultan, M. Ha, J. Tiwari, M. G. Kim and K. S. Kim, *Adv. Funct. Mater.*, 2020, **30**, 2000531.
- 31 V. Ramalingam, P. Varadhan, H. C. Fu, H. Kim, D. Zhang, S. Chen, L. Song, D. Ma, Y. Wang, H. N. Alshareef and J. H. He, *Adv. Mater.*, 2019, 31, 1903841.
- 32 C. Hu, E. Song, M. Wang, W. Chen, F. Huang, Z. Feng, J. Liu and J. Wang, *Adv. Sci.*, 2020, 2001881.
- 33 Z. J. Wang, M. X. Li, J. H. Yu, X. B. Ge, Y. H. Liu and W. H. Wang, *Adv. Mater.*, 2020, **32**, 1906384.
- 34 D. Liu, X. Li, S. Chen, H. Yan, C. Wang, C. Wu, Y. A. Haleem, S. Duan, J. Lu, B. Ge, P. M. Ajayan, Y. Luo, J. Jiang and L. Song, *Nat. Energy*, 2019, 4, 512.
- 35 H. Cheng, N. Yang, G. Liu, Y. Ge, J. Huang, Q. Yun, Y. Du, C. J. Sun, B. Chen, J. Liu and H. Zhang, *Adv. Mater.*, 2020, 32, 1902964.
- 36 C. Li and J. B. Baek, ACS Omega, 2020, 5, 31.
- 37 J. Zhang, G. Wang, Z. Liao, P. Zhang, F. Wang, X. Zhuang,E. Zschech and X. Feng, *Nano Energy*, 2017, 40, 27.
- 38 F. Lv, J. Feng, K. Wang, Z. Dou, W. Zhang, J. Zhou, C. Yang, M. Luo, Y. Yang, Y. Li, P. Gao and S. Guo, *ACS Cent. Sci.*, 2018, 4, 1244.
- 39 L. Farsi and N. A. Deakins, *Phys. Chem. Chem. Phys.*, 2019, 21, 23626.
- 40 J. Tang, L. Deng, H. Deng, S. Xiao, X. Zhang and W. Hu, J. *Phys. Chem. C*, 2014, **118**, 27850.
- 41 A. Boucly, E. Fabbri, L. Artiglia, X. Cheng, D. Pergolesi, M. Ammann and T. J. Schmidt, *Chem. Mater.*, 2020, 32, 5256.
- 42 M. Li, M. Luo, Z. Xia, Y. Yang, Y. Huang, D. Wu, Y. Sun, C. Li, Y. Chao, W. Yang, W. Yang, Y. Yu and S. Guo, *J. Mater. Chem. A*, 2019, 7, 20151.
- 43 Q. Wang, X. Huang, Z. L. Zhao, M. Wang, B. Xiang, J. Li, Z. Feng, H. Xu and M. Gu, *J. Am. Chem. Soc.*, 2020, **142**, 7425.

- 44 D. D. Babu, Y. Huang, G. Anandhababu, X. Wang, R. Si, M. Wu, Q. Li, Y. Wang and J. Yao, *J. Mater. Chem. A*, 2019, 7, 8376.
- 45 J. Mao, W. Chen, W. Sun, Z. Chen, J. Pei, D. He, C. Lv, D. Wang and Y. Li, *Angew. Chem., Int. Ed.*, 2017, 56, 11971.
- 46 X. Han, X. Wu, Y. Deng, J. Liu, J. Lu, C. Zhong and W. Hu, *Adv. Energy Mater.*, 2018, **8**, 1800935.
- 47 Q. Wang, C. Q. Xu, W. Liu, S. F. Hung, H. B. Yang, J. Gao,
  W. Cai, H. M. Chen, J. Li and B. Liu, *Nat. Commun.*, 2020, 11, 4246.
- 48 H. Zhang, W. Zhou, X. F. Lu, T. Chen and X. W. Lou, Adv. Energy Mater., 2020, 10, 2000882.
- 49 Z. Luo, H. Zhang, Y. Yang, X. Wang, Y. Li, Z. Jin, Z. Jiang, C. Liu, W. Xing and J. Ge, *Nat. Commun.*, 2020, **11**, 1116.
- 50 X. K. Wan, H. B. Wu, B. Y. Guan, D. Luan and X. W. Lou, *Adv. Mater.*, 2020, **32**, 1901349.
- 51 J. Cai, Y. Song, Y. Zang, S. Niu, Y. Wu, Y. Xie, X. Zheng, Y. Liu, Y. Lin, X. Liu, G. Wang and Y. Qian, *Sci. Adv.*, 2020, 6, eaaw8113.
- 52 J. Mahmood, M. A. R. Anjum, S. H. Shin, I. Ahmad, H. J. Noh, S. J. Kim, H. Y. Jeong, J. S. Lee and J. B. Baek, *Adv. Mater.*, 2018, **30**, 1805606.
- 53 T. Zheng, C. Shang, Z. He, X. Wang, C. Cao, H. Li, R. Si, B. Pan, S. Zhou and J. Zeng, *Angew. Chem.*, 2019, **131**, 14906.
- 54 L. Li, B. Wang, G. Zhang, G. Yang, T. Yang, S. Yang and S. Yang, *Adv. Energy Mater.*, 2020, **10**, 2001600.
- 55 A. M. Harzandi, S. Shadman, M. Ha, C. W. Myung, D. Y. Kim,
  H. J. Park, S. Sultan, W. S. Noh, W. Lee, P. Thangavel,
  W. J. Bin, S. Lee, J. N. Tiwari, J. H. Park, Z. Lee, J. S. Lee
  and K. S. Kim, *Appl. Catal.*, *B*, 2020, 270, 118896.
- 56 S. Anantharaj, S. R. Ede, K. Karthick, S. S. Sankar, K. Sangeetha, P. E. Karthik and S. Kundu, *Energy Environ. Sci.*, 2018, **11**, 744.
- 57 Q. Sun, Y. Dong, Z. Wang, S. Yin and C. Zhao, *Small*, 2018, 14, 1704137.
- 58 P. Thangavel, M. Ha, S. Kumaraguru, A. Meena, A. N. Singh, A. M. Harzandi and K. S. Kim, *Energy Environ. Sci.*, 2020, 13, 3447.
- 59 J. N. Tiwari, S. Sultan, C. W. Myung, T. Yoon, N. Li, M. Ha, A. M. Harzandi, H. J. Park, D. Y. Kim, S. S. Chandrasekaran, W. G. Lee, V. Vij, H. Kang, T. J. Shin, H. S. Shin, G. Lee, Z. Lee and K. S. Kim, *Nat. Energy*, 2018, 3, 773.
- 60 J. Hou, Y. Wu, B. Zhang, S. Cao, Z. Li and L. Sun, Adv. Funct. Mater., 2019, 29, 1808367.
- 61 K. S. Exner, Curr. Opin. Electrochem., 2021, 26, 100673.
- 62 B. Yang, J. Xu, D. Bin, J. Wang, J. Zhao, Y. Liu, B. Li, X. Fang, Y. Liu, L. Qiao, L. Liu and B. Liu, *Appl. Catal.*, *B*, 2021, 283, 119583.
- 63 R. F. W. Bader, Acc. Chem. Res., 1985, 18, 9.