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Research Article

Hollow nanostructured rare-earth-containing high-entropy carbides: Facile electrochemical synthesis and effective electrocatalytic performance for hydrogen evolution

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Abstract: High-entropy carbides (HECs) have attracted growing attention as promising noble-metal catalyst alternatives for the hydrogen evolution reaction. Nevertheless, the reported HEC nanocrystals remain confined to dense solid structures with metallic components limited to groups IVB-VIB. The first synthesis of hollow nanostructured high-entropy carbides (HfNbTaTiZr)C, (HfNbTaTiZrRE)C

(RE=Gd, Ce, Y) and (HfNbTaTiZrCeY)C was achieved by a direct electroreduction process.

Electrolysis was conducted at 3.1 V using a graphite anode and a cathode prepared from mixed oxides/carbon additive powders in molten CaCl₂-NaCl at 800 °C. The effects of carbon sources on the microstructure of the product were systematically investigated. The results show that the microstructure of HECs can be easily tailored from solid to hollow particles by selecting different carbon sources. All as-synthesized HECs exhibit a single face-centered cubic phase and compositional homogeneity from the nanoscale to the microscale. It was found that the engineered hollow nanostructure, coupled with the incorporation of rare-earth elements, significantly enhanced electrocatalytic performance of HECs for hydrogen evolution in an alkaline electrolyte. Specifically, the HECs incorporated with dual rare-earth elements exhibited superior performance to those with a single element. Among them, (HfNbTaTiZrCeY)C demonstrates superior hydrogen evolution reaction performance with a low overpotential of 167 mV, a small Tafel slope of 58.8 mV·dec⁻¹, and a low charge transfer resistance of 2.7 Ω. This work not only establishes a facile method for synthesizing various hollow rare-earth-containing high-entropy carbide nanoparticles, but also provides a novel strategy for the design of high-performance non-noble metal-based catalysts.

Keywords: high-entropy carbides; hollow nanoparticles; hydrogen evolution reaction; rare earth; molten salt electrolysis

1 Introduction

The environmental pollution and energy crisis resulting from fossil fuel combustion have created an urgent need for clean and renewable energy sources [1–5]. The combination of zero carbon emissions, renewability, and high energy density makes hydrogen energy an ideal alternative to fossil fuels [6–8]. Electrocatalytic water splitting is widely recognized as a promising green route for generating hydrogen. Its efficiency is primarily governed by the electrocatalyst, which spurs extensive research in this field. Noble-metal-based electrocatalysts such as Pt, Ir, and Ru demonstrate exceptional performance for the hydrogen evolution reaction (HER). Nevertheless, their scarcity and high cost

limit their large-scale application [9,10]. Therefore, developing environmentally friendly, low-cost, and highly effective alternatives to noble-metal catalysts is imperative. Among various alternatives, transition metal carbides (TMCs) are considered to be one of the most promising candidates to replace Pt-based electrocatalysts due to their Pt-like d-band electronic structure, as well as their superior electrical conductivity and broader pH applicability compared to other transition metal compounds (e.g., oxides, sulfides, phosphides, and nitride) [11–15]. Nevertheless, primitive unary TMCs exhibit unsatisfactory intrinsic electrocatalytic activity, because they bind strongly to hydrogen intermediates (H^*), which severely limits their practical application [16,17]. Thus, continuous research efforts have been dedicated to tailoring TMCs through heteroatom doping, nanostructure construction, crystal facet engineering, hollow structure engineering and heterointerface engineering, aimed at enhancing their catalytic activity [13,18–23]. Despite considerable advances in transition metal carbide catalysts, their performance still falls short of that achieved by noble-metal-based catalysts.

Notably, the synergistic interaction among the multiple components in a single-phase solid solution can yield excellent catalytic performance that is significantly superior to their individual component counterparts due to the unique high-entropy effects, as confirmed in high-entropy alloys and oxides [24–27]. Unfortunately, the development of high-entropy carbide (HEC) catalysts remains at a nascent stage. This is primarily attributed to the difficulty of controllable fabrication of nano-sized HECs and the intrinsic chemical immiscibility of multi-metallic elements within the carbide lattice. Consequently, intense research efforts are underway to resolve these two challenges. Several synthetic routes have been developed for HEC nanocatalysts. Electrical-discharge-induced bulk-to-nanoparticle transformation recycles wire-cut machining waste to produce well-dispersed sub-10 nm HEC nanoparticles with dense surface defects [28]. Alternatively, ultra-fast joule heating achieves configurational-entropy controlled preparation of HEC nanoparticles with 4–9 transition metal constituents [29]. A recent nanoconfined impulse synthesis (NIS) route that employs CNT films as Joule-heating substrates has expanded the compositional space to 5–22 metallic elements, yielding

monodisperse ~20 nm HECs via a three-step ultrafast thermal process [30]. In another approach, the pyrolysis of metal-ion-impregnated ZIF-derived polyhedral carbon enables the synthesis of single-phase high-entropy carbides via configurational entropy and lattice distortion regulation [31]. Furthermore, solid-phase combustion synthesis realizes precise crystal facet engineering of HEC nanocrystals by generating transient liquid alloy intermediates during the reaction [32]. Nevertheless, all these reported materials are limited to dense solid structures.

As is well known, hollow nanostructures hold a distinct advantage for application as catalysts, as they possess intrinsic characteristics such as high surface-area-to-volume ratios and abundant inner voids. These structural attributes confer abundant active sites, low mass transport resistance and short charge transport pathways [33]. Hollow nanostructures are typically synthesized by template methods, which involve multi-step template preparation and often require specific, sometimes harsh, conditions for template removal [20,34]. Up to now, there have been few, if any, reports on the successful synthesis of hollow HECs.

In addition to building nano-hollow structures, the regulation of the electronic structure is also essential to further boost the catalyst's intrinsic activity. Recent studies confirm that rare-earth (RE) elements can effectively modulate the electronic structure of transition-metal-based alloys and oxides to enhance their catalytic activity [35–39]. However, rare-earth-containing high-entropy carbide catalysts have rarely been reported to date. This is attributed to the non-negligible atomic size mismatch between RE and transition metal elements, which greatly hinders the incorporation of RE atoms into HEC lattices. The fabrication of hollow nanostructures and the introduction of rare-earth elements in HEC systems both pose considerable challenges for conventional synthetic methods. Therefore, it is highly desired to develop a facile and direct method for fabricating rare-earth-containing HECs with hollow nanostructures to unlock their latent potential as catalysts. Molten-salt electrolysis stands out as a mild, low-temperature fabrication strategy for HECs, enabling the direct synthesis of nanomaterials from inexpensive precursors in a single electrolysis step. As pioneered by

Sure and Schwandt, single-phase (NbTaTiZrHf)C nanoparticles with sizes of 15–80 nm were successfully synthesized via electro-deoxidation of a metal oxide/graphite mixture in molten CaCl_2 at 900 °C [40]. Later, Yang et al. advanced this route by integrating anodic CO_2 capture with in-situ cathodic carburization, termed the MSCC-ET process. Using a $\text{LiCl-CaCl}_2\text{-KCl}$ ternary molten salt system at 980 °C, they successfully prepared (NbTaTiZrHf)C (20–100 nm) with CO_2 as the exclusive carbon source, and preliminarily verified its alkaline HER performance ($\eta_{10} = 350$ mV, Tafel slope = $61 \text{ mV} \cdot \text{dec}^{-1}$) [41]. However, these reports are confined to five-component, d-block HECs with solid particulate morphologies. Extending the molten-salt electrolysis to rare-earth-containing higher-order HECs (>5 metallic elements) remains unexplored, much less the deliberate construction of hollow nanostructures within these materials. Furthermore, beyond these compositional and structural challenges, the effects of rare-earth elements on the HER catalytic performance of transition-metal HECs have not been systematically studied.

In this study, a family of hollow rare-earth-containing high-entropy carbide (RE-HEC) nanoparticles has been successfully synthesized for the first time. These materials, exhibiting a single face-centered cubic structure, were obtained by a one-pot electroreduction process from oxides and carbon black in molten chlorides at 800 °C. This work systematically investigates the effects of carbon sources on the microstructure of the products. The phase composition, microstructure, elemental homogeneity, and hydrogen evolution performance of the as-synthesized HECs were explored in detail. As expected, the as-obtained hollow RE-HEC nanoparticles exhibit promising performance in terms of activity and stability when evaluated as electrocatalysts for HER.

2 Experimental

2.1 Sample preparation

Hafnium oxide (HfO_2 , 99.99%, microscale; Macklin), zirconium oxide (ZrO_2 , 99.99%, nanoscale; Macklin), titanium oxide (TiO_2 , 99%, nanoscale; J&K Scientific), tantalum pentoxide (Ta_2O_5 , 99.99%, microscale; Macklin), niobium oxide (Nb_2O_5 , 99.99%, microscale; Macklin), gadolinium oxide

(Gd₂O₃, 99.8%, nanoscale; Macklin), yttrium oxide (Y₂O₃, 99.00%, nanoscale; Macklin), cerium dioxide (CeO₂, 99.5%, nanoscale; Macklin), carbon black (CB, Tianjin Fengchuan), graphite (GP, 99.95%; Macklin) and calcium oxide (CaO, ≥95%; Sinopharm) powders were served as the starting materials. Powders of transition metal oxides, rare-earth oxides, and carbon black (or graphite) were weighed and mixed in a stoichiometric ratio, following the subsequent addition of 5.4 wt% calcium oxide. All transition metal and rare-earth elements in the precursor were mixed in equimolar proportions. The mixture was employed to synthesize the following target HECs: (HfNbTaTiZr)C (HEC-CB-0), (HfNbTaTiZrGd)C (HEC-CB-1), (HfNbTaTiZrGd)C (HEC-GP-1), (HfNbTaTiZrCe)C (HEC-CB-2), (HfNbTaTiZrY)C (HEC-CB-3) and (HfNbTaTiZrCeY)C (HEC-CB-4).

In detail, the mixed precursor powders were first ball-milled in anhydrous alcohol for 4 h. Subsequently, the dried mixture was uniaxially pressed at 8 MPa into a cylindrical precursor pellet (Ø10 × 1 mm), which was then sintered at 900 °C for 4 h under an argon atmosphere. The sintered precursor pellet was placed in a stainless-steel cup attached to a stainless-steel rod to form the cathode. A high-density graphite rod (Ø10 × 60 mm) served as the anode. A eutectic mixture of CaCl₂ and NaCl (AR; Tianjin Kemiou) was used as the electrolyte. It was first dried at 350 °C in air for 24 h and then heated from 300 °C to the target temperature of 800 °C at a controlled rate inside a sealed stainless-steel reactor under an Ar atmosphere. Then reaction chamber was continuously purged with ultra-high-purity argon to maintain a protective atmosphere.

A pre-electrolysis step was conducted at 2.9 V for 2 h to remove electrochemically active impurities from the melt. Subsequently, the electrochemical reduction of the sintered precursor pellet was carried out at a constant voltage of 3.1 V for 6 h. After electrolysis, the obtained sample was rinsed with tap water, sequentially immersed in distilled water (24 h) and ethanol (12 h), and finally dried for characterization. The schematic diagram of the synthesis process of high-entropy carbides is displayed in Fig. 1.

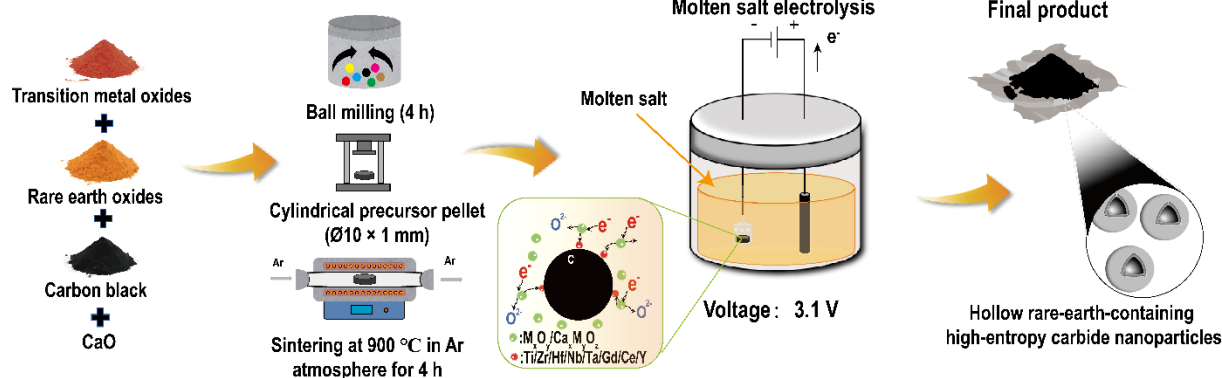


Fig. 1 Schematic diagram of the preparation of hollow rare-earth-containing high-entropy carbides

2.2 Characterization and analysis of samples

The phase composition of each sample was determined by X-ray diffraction (XRD, D/MAX-2500/PC, Japan) with Cu-K α radiation. The morphology and chemical composition of the samples were examined using a scanning electron microscope (SEM, ZEISS Gemini 300, Germany) coupled with energy-dispersive X-ray (EDX) spectroscopy. Further microstructural analysis was conducted by transmission electron microscope (TEM, FEI Tecnai G2 F20, America).

2.3 Electrochemical measurements

The HER performance of the obtained samples was measured by a three-electrode system. The as-prepared HEC powder (80 wt%) as the active material, polyvinylidene fluoride (PVDF, 10 wt%) as the binder, and carbon black (10 wt%) as the conductive agent were homogeneously mixed in N-methylpyrrolidone (NMP) to form a slurry. This slurry was drop-cast onto a nickel foam substrate (1×1 cm²), which was then dried at 50 °C for 12 h. The mass loading of the HEC powder on the electrode was 0.24 mg·cm⁻². Ag/AgCl was used as the reference electrode, and a platinum foil (1×1 cm²) served as the counter electrode. The electrolyte was 1.0 M KOH aqueous solution. The polarization curves were recorded by linear sweep voltammetry (LSV) from 0 to -0.35 V (vs. RHE) at a scan rate of 5 mV·s⁻¹, with 90% iR compensation applied. The solution resistance (Rs) required for iR correction was determined by electrochemical impedance spectroscopy (EIS), taken as the high-frequency

intercept of the Nyquist plot with the real axis. The corresponding Tafel slopes were then calculated based on the equation $\eta = a + b \log |j|$, where η is the overpotential and j is the current density. Electrochemical impedance spectroscopy (EIS) measurements were conducted over a frequency range of 0.1 Hz to 10^4 Hz. To investigate the double-layer capacitance, a series of cyclic voltammetry (CV) scans were conducted at scan rates from 2 to $100 \text{ mV} \cdot \text{s}^{-1}$ in a non-faradaic region. During the 140 h chronoamperometric test, the working electrode was vertically immersed in the electrolyte without external stirring. All electrochemical measurements were performed using a CHI 660F electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.). The measured potentials were referenced to the reversible hydrogen electrode (RHE) based on Equation (1).

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.0591 \times \text{pH} \quad (1)$$

3 Results and discussion

3.1 Effects of carbon sources on microstructure of high-entropy carbides

Fig. 2 presents the XRD patterns and microstructural characterization for nano-graphite (GP) and carbon black (CB). Graphite powder exhibits high crystallinity with a well-ordered layered structure, whereas carbon black powder is amorphous, exhibiting low crystallinity (Fig. 2a, c, e). It can be seen that carbon black powder is composed of nearly spherical particles with the average particle size less than 50 nm (Fig. 2b). On the other hand, graphite powder consists of irregular flake particles with particle sizes ranging from 0.5 to $2 \mu\text{m}$ (Fig. 2d). Obviously, carbon black possesses a higher specific surface area than graphite due to its fine particle size and amorphous structure, which facilitates greater interaction with surrounding materials.

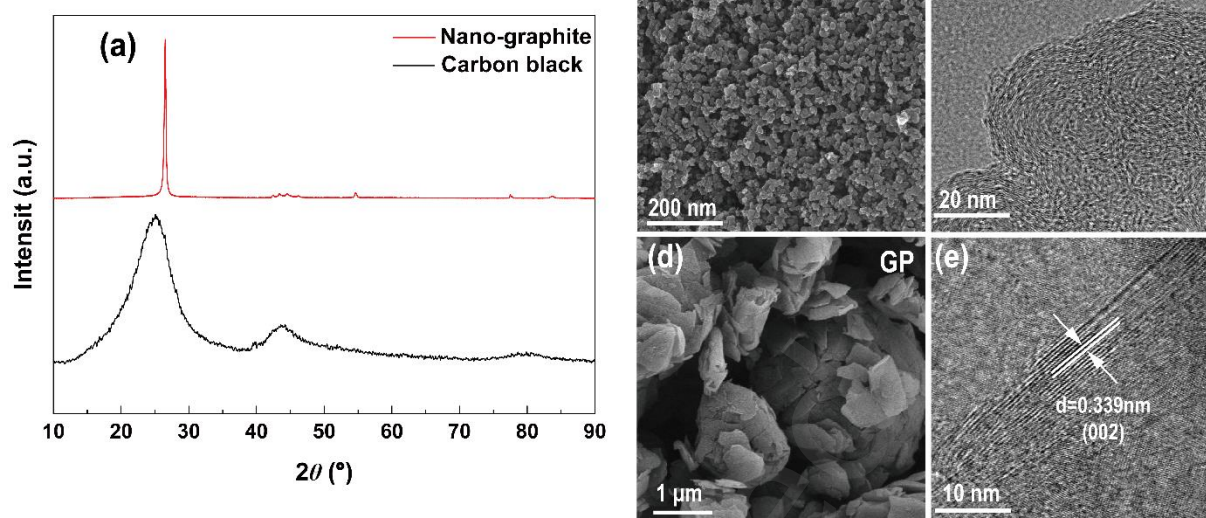
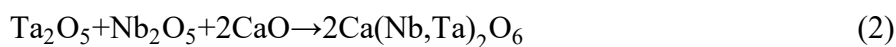


Fig. 2 XRD patterns (a), SEM images (b,d) and HRTEM images (c,e) of carbon black (CB) and graphite (GP).

The XRD patterns of the sintered oxides/carbon black (oxides/CB) and oxides/graphite (oxides/GP) precursor pellets are presented in Fig. 3a and b respectively. Distinct diffraction peaks corresponding to graphite are visible while carbon black was not detected due to its low crystallinity. Apart from the diffraction peaks attributed to the carbon additive, the remaining diffraction peaks are identical in both sintered oxides/CB and oxides/GP precursors. $\text{Ca}(\text{Nb,Ta})_2\text{O}_6$ and unreacted starting oxides (TiO_2 , Gd_2O_3 , ZrO_2 , HfO_2) are observed in both precursors. Obviously, Nb_2O_5 and Ta_2O_5 react with CaO to form calcium niobate-tantalate oxides during sintering, the corresponding chemical reaction is shown in Equation (2).



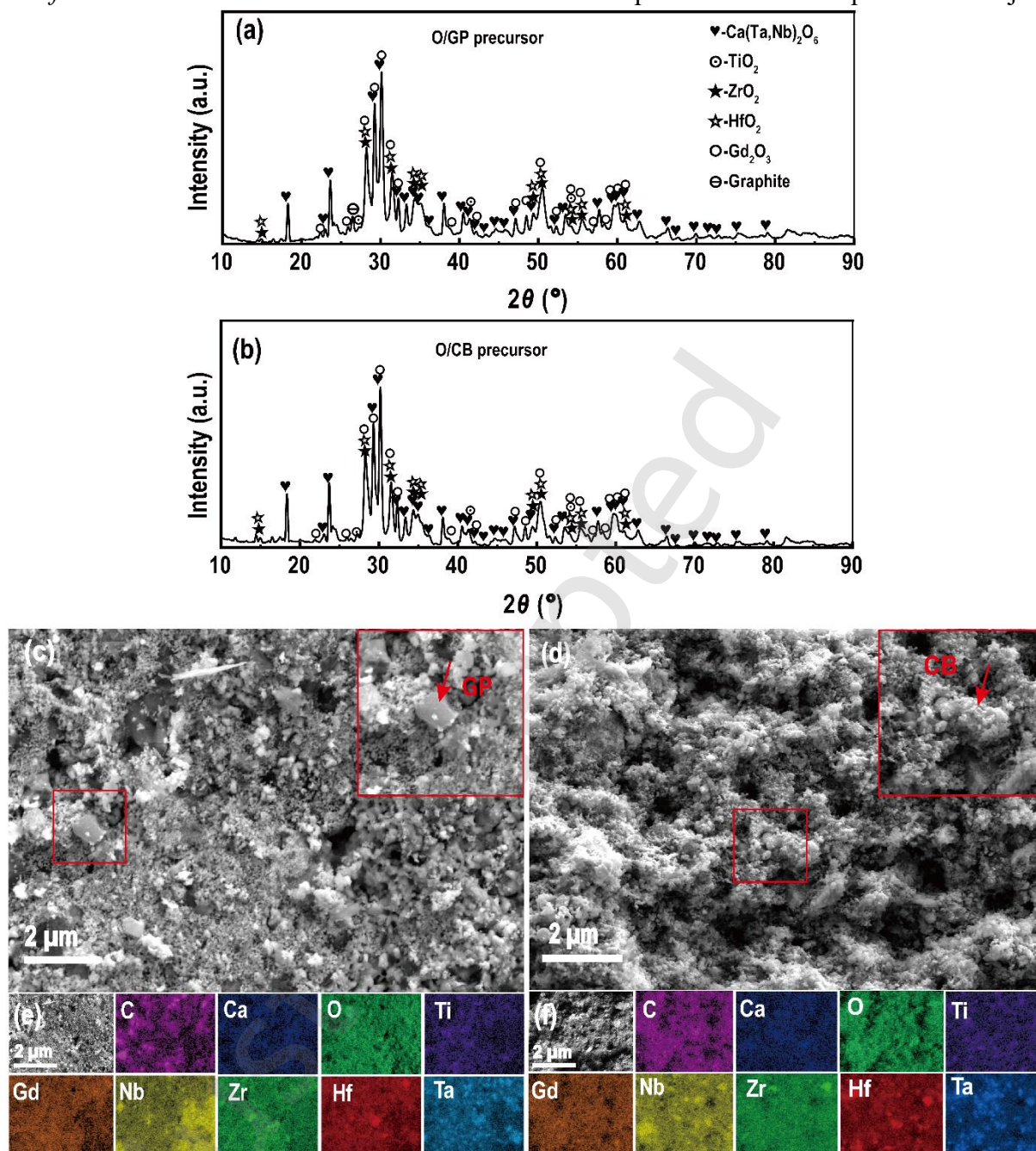


Fig. 3 XRD patterns, SEM images, and EDS elemental maps of (a, c, e) oxides/GP and (b, d, f) oxides/CB precursor pellets after sintering in Ar at 900 °C for 4 h.

In the process of synthesizing individual carbides via electroreduction in CaCl_2 -based molten salt, the in-situ formation of intermediate compounds (e.g., CaNb_2O_6 , CaHfO_3 , CaZrO_3 or CaTiO_3) inevitably occurs and is regarded as detrimental to the reduction process [42–45]. Here, Ex situ calcium-enriched oxides were formed during sintering by appropriately adding CaO to the precursor,

aiming to increase the speed and efficiency of the subsequent electroreduction process [46]. The morphology and elemental distribution of both types of sintered pellets are shown in Fig. 3c-f. Compared with graphite, carbon black particles exhibit tighter contact with adjacent particles and a more uniform distribution within the precursors owing to its smaller particle size and larger specific surface area.

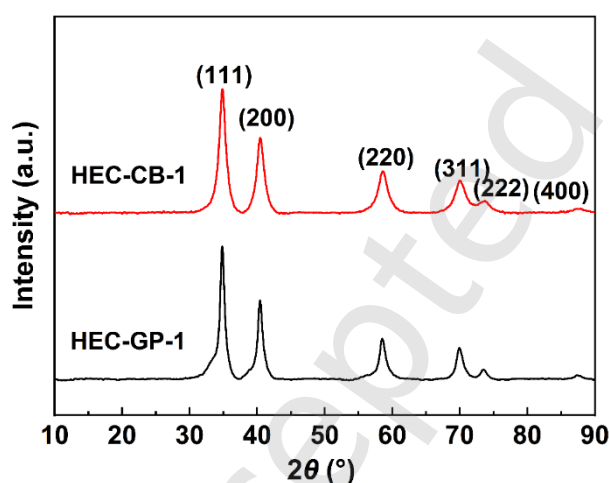


Fig. 4 XRD patterns of HEC-CB-1 and HEC-GP-1 powders synthesized from corresponding oxides/CB and oxides/GP precursors.

The XRD patterns of the products prepared via the electroreduction of the sintered oxides/CB and oxides/GP precursors are shown in Fig. 4. Two single-phase high-entropy carbides (HECs), denoted as HEC-GP-1 and HEC-CB-1, were successfully synthesized. The XRD patterns of both samples can be clearly indexed to a face-centered cubic (FCC) structure with the $Fm\bar{3}m$ space group. This structure is analogous to single carbides (i.e., TiC, ZrC, HfC, NbC and TaC). No other phases were observed. This suggests that a single-phase (HfNbTaTiZrGd)C solid solution was successfully synthesized using both graphite and carbon black as carbon sources. Notably, it is necessary to overcome atomic size mismatch for the successful incorporation of rare-earth atoms into transition-metal high-entropy carbides. The enhanced diffusion, facilitated by the combined effects of the molten salt medium and the applied electric field, is considered to be the major factor for the formation of the single-phase ceramic. The variations of phase composition

during the electrolysis process of the oxides/CB precursor were analyzed and shown in Fig. S1. These findings suggest that the main reaction pathway commences with extracting each metal via electro-deoxidation from its oxidized-state precursor, followed by the in-situ reaction of the freshly generated metals with surrounding carbon additives to form carbides, as shown in Equation (3) and (4). Ultimately, these carbides undergo entropy-driven spontaneous mixing at the atomic level to form a multicomponent single-phase solid solution. The byway, which involves the transient formation of calcium-containing intermediates (e.g., CaZrO_3 and CaHfO_3), merges with the main pathway. The lattice parameter derived from the XRD result of HEC-GP-1 was 0.4465 nm, while that of HEC-CB-1 was 0.4458 nm. The large broadening of the XRD peaks of HEC-CB-1 suggests that it consists of small crystalline domains.

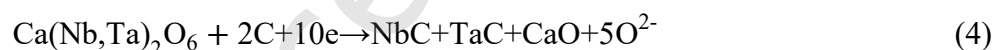


Fig. 5 displays SEM images and the corresponding EDS compositional maps of the as-synthesized HEC-GP-1 and HEC-CB-1. As shown in Fig. 5a and b, both products exhibit powder-like morphologies. The HEC-GP-1 powder is composed of irregular nanoparticles with a distribution of sizes. In contrast, the HEC-CB-1 powder consists of uniformly distributed near-spherical nanoparticles that agglomerate into clusters. The hollow microstructure is clearly revealed from the broken particles, both individual ones and clusters (insets of Fig. 5b). EDX area maps confirm that the two as-synthesized HECs show homogeneous elemental distribution at the micron scale (Fig. 5c, d). This further confirms the successful formation of $(\text{HfNbTaTiZrGd})\text{C}$ high-entropy carbides. It is noteworthy that the electrochemically synthesized particles were unable to undergo major coarsening. This is because the processing temperature (800 °C) was over 2000 °C below the presumed melting point of as-synthesized HECs and too low to induce any significant in situ sintering [40].

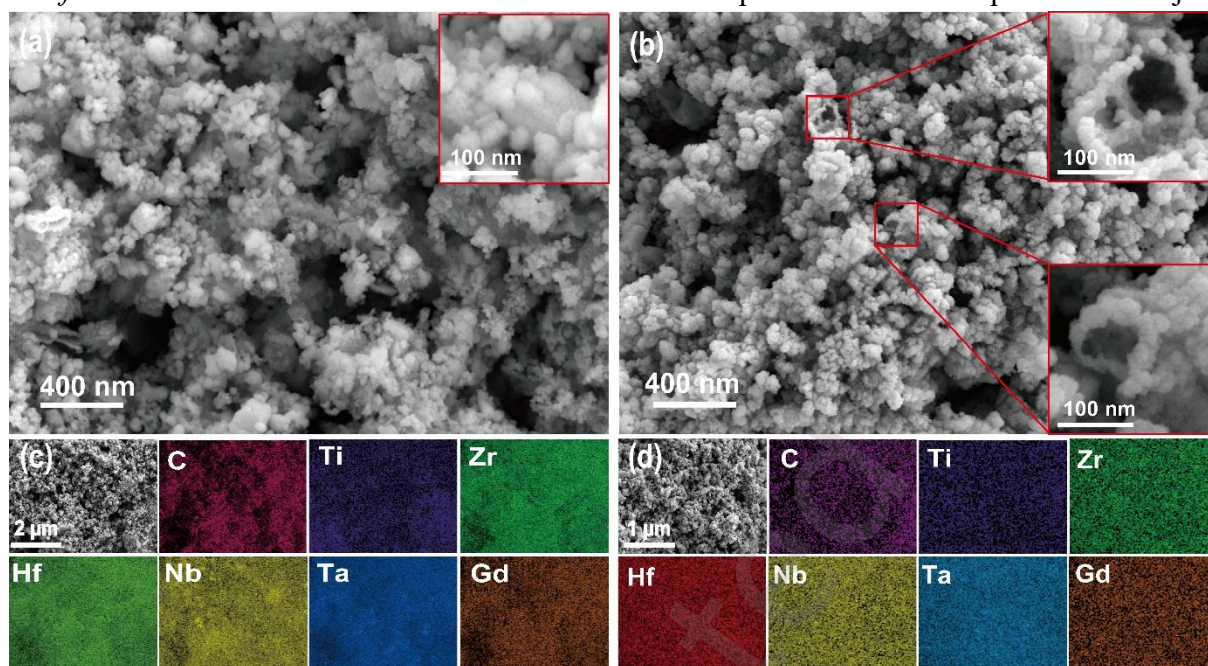


Fig. 5 SEM images and EDS elemental maps of as-synthesized high-entropy carbides. (a, c) HEC-GP-1; (b, d) HEC-CB-1.

The microstructure of HEC powders obtained using different carbon sources was further elucidated by transmission electron microscopy (TEM). The HEC-GP-1 powder consists of solid nanoparticles with the average particle size of 57 nm, which was determined by Gaussian fitting of the particle size distribution (Fig. 6a, c). The SAED pattern (Fig. 6b) is characterized by a series of concentric rings, which demonstrate the polycrystalline structure of HEC-GP-1. These rings correspond to the (111), (200), (220), (311), and (222) planes, confirming the FCC structure. The lattice parameter of 0.4466 nm, determined using the planes as reference, agrees with the value calculated from XRD analysis. High-resolution transmission electron microscopy (HRTEM) images (Fig. 6d) reveal a periodic lattice structure. The measured interplanar spacings correspond to the (200) and (111) planes of the FCC structure. The determined FCC crystal structure of HEC-GP-1 is in good agreement with the XRD result. The STEM-EDX maps (Fig. 6e) confirmed the compositional homogeneity at the nanoscale without observable segregation.

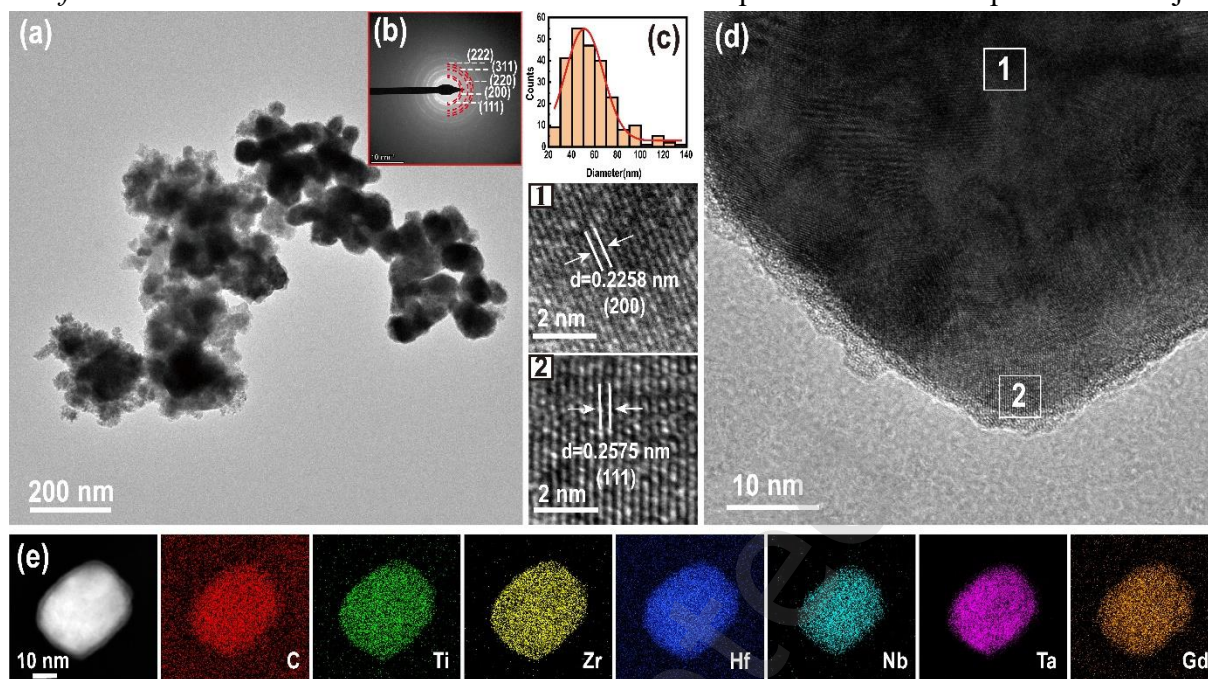


Fig. 6 Characterization of the product HEC-GP-1 using graphite as carbon source. (a) TEM image; (b) SAED pattern, (c) particle size distribution; (d) HRTEM images; the numbers on each HRTEM image correspond to the magnified regions marked in the main image; (e) Dark-field STEM image and corresponding EDS elemental maps.

On the other hand, the obtained HEC-CB-1 powder using carbon black as carbon source exhibits a hollow structure. This morphology is clearly evidenced by TEM images, which show a distinct contrast between the light interior and the dark margin (Fig. 7a, d). Moreover, the Hf, Nb, Ta, Ti, Zr, and Gd elements are mainly distributed in the shell of the particle (Fig. 7e), further confirming the hollow structure of HEC-CB-1. The hollow structure, as determined, is consistent with the SEM analyses. Based on the Gaussian fitting of the particle size distribution (Fig. 7c), the average particle size of the hollow particles was determined as 45 nm. The SAED pattern (Fig. 7b) reveals diffuse rings, indicating that the particles are composed of nanocrystalline domains. All the electron diffraction rings correspond to the crystallographic planes of the single FCC phase. A lattice parameter of 0.4461 nm was determined from the planes, which matches the value derived from the XRD analysis. Fig. 7d shows the HRTEM images acquired from different areas of the HEC-CB-1 single particle, in which some oriented nanocrystalline domains are displayed. These domains exhibit interplanar spacings that

correspond to the (111) and (200) planes of the FCC structure. In addition, some amorphized areas between the nanodomains were detected. The STEM-EDX maps (Fig. 7e) further confirmed the homogeneous distribution of all elements at the nanoscale.

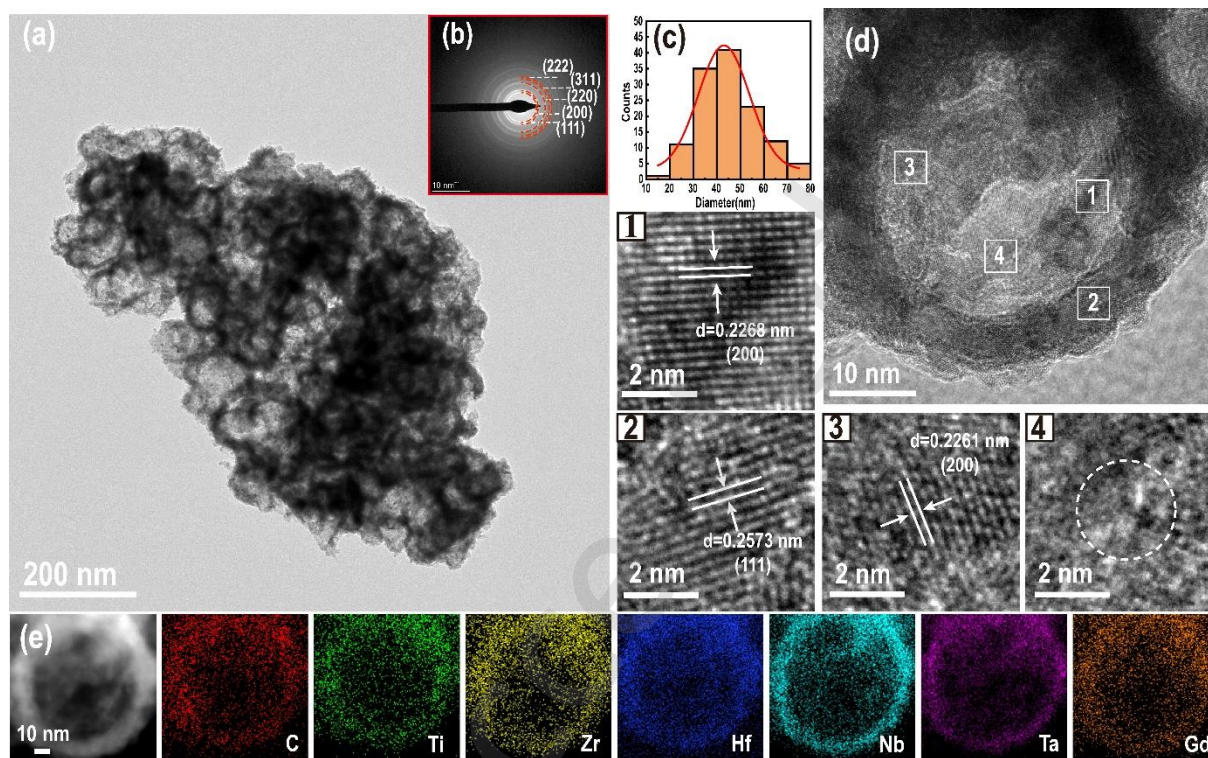


Fig. 7 Characterization of the product HEC-CB-1 using carbon black as carbon source. (a) TEM image; (b) SAED pattern; (c) particle size distribution; (d) HRTEM images; the numbers on each HRTEM image correspond to the magnified regions marked in the main image; (e) Dark-field STEM image and corresponding EDS elemental maps.

The above results indicate that $(\text{HfNbTaTiZrGd})\text{C}$, possessing a single FCC phase and homogeneous elemental distribution, was synthesized through a one-pot electrochemical process from both carbon sources. Notably, its morphology obtained with graphite was solid, whereas that from carbon black was hollow. The observed morphological divergence can be attributed to the crystallinity of the carbon source, which dictates whether the Kirkendall effect can occur. This aligns with the reported molten salt synthesis of hollow transition metal carbides [47]. In the electrochemical process, metal oxides are first electro-reduced to nascent metallic species. These active metal atoms then react in-situ with the carbon source to form carbides. When amorphous carbon black

is used, its disordered structure facilitates a uniform reaction with nascent metallic species at the interface. This allows for the formation of a continuous product shell enveloping the carbon core early in the process. Subsequently, carbon then diffuses outward through this shell faster than metals diffuse inward, thereby initiating the Kirkendall effect. The resultant net outward flux of carbon depletes the core, forming a hollow structure. In contrast, when crystalline graphite is used, its highly ordered and anisotropic structure hinders a uniform interfacial reaction. The diffusion of newly formed metal atoms along the ordered graphitic layers results in a discontinuous product shell. This hinders the establishment of a stable diffusion couple, thus preventing the Kirkendall effect and ultimately yielding a solid microstructure.

3.2 Comparative electrocatalytic HER performance of solid versus hollow high-entropy carbides

The electrocatalytic performance of the above two samples was characterized in 1 M KOH using a standard three-electrode system. As shown in Fig. 8a, the HEC-CB-1 catalyst exhibits higher HER activity than HEC-GP-1, as evidenced by its lower overpotential ($\eta_{10} = 234$ mV vs. 282 mV for HEC-GP-1) in the linear sweep voltammetry (LSV) curves. This enhanced activity is due to its engineered hollow structure. Furthermore, the Tafel slope of HEC-CB-1 ($81.2 \text{ mV} \cdot \text{dec}^{-1}$) is much smaller than that of HEC-GP-1 ($159.8 \text{ mV} \cdot \text{dec}^{-1}$), demonstrating markedly superior reaction kinetics (Fig. 8b) [48,49]. According to previous studies, hydrogen generation in alkaline media follows pathways which involve the Volmer discharge step, followed by either the Heyrovsky electrochemical desorption or Tafel recombination step, as shown in Equations (5), (6), and (7), respectively. Generally, the Tafel slope is a key kinetic parameter that identifies the rate-determining step (RDS) in the HER: a Volmer step ($120 \text{ mV} \cdot \text{dec}^{-1}$), a Heyrovsky step ($40 \text{ mV} \cdot \text{dec}^{-1}$), or a Tafel step ($30 \text{ mV} \cdot \text{dec}^{-1}$). Notably, the RDS for HER on HEC-GP-1 is the Volmer step, whereas it is the Heyrovsky step on HEC-CB-1. This shift clearly indicates that the kinetic barrier for the water dissociation (Volmer) step has been effectively overcome via fabricating the hollow structure.



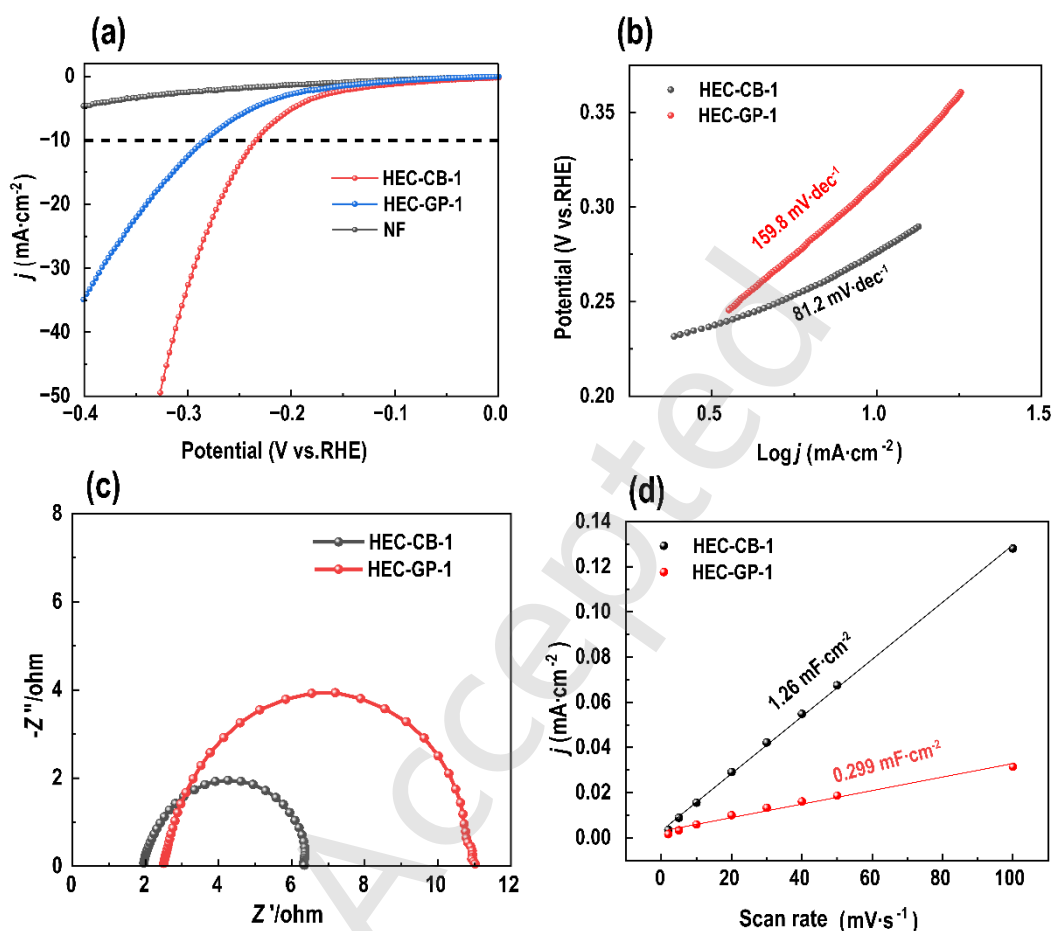


Fig. 8 Electrochemical parameters of obtained high-entropy carbide ceramics in 1.0 M KOH. (a) polarization curves; (b) Tafel plots; (c) Nyquist plots at -1.27 V (vs. RHE); (d) C_{dl} curves.

Moreover, electrocatalytic kinetics were also evaluated by electrochemical impedance spectroscopy (EIS), as shown in Fig. 8c. The semicircular features observed in both Nyquist plots are characteristic of the charge transfer resistance (R_{ct}), which reflects the kinetic barrier for charge transfer at the electrode surface. The R_{ct} is determined to be 4.4Ω for HEC-CB-1 and 8.4Ω for HEC-GP-1. The significantly lower R_{ct} of HEC-CB-1 can be attributed to its hollow structure, which facilitates charge and mass transfer, thereby reducing the overall R_{ct} [50]. The electrochemical active surface area (ECSA), which is typically evaluated via the double-layer capacitance (C_{dl}), is an important factor

affecting the catalytic activity of electrocatalysts [51,52]. Cyclic voltammetry (CV) scans in the non-faradaic region (Fig. S2) yielded the plot of current density versus scan rate (Fig. 8d), from which the C_{dl} values were calculated. The C_{dl} of HEC-CB-1 ($1.3 \text{ mF}\cdot\text{cm}^{-2}$) is substantially greater than that of HEC-GP-1 ($0.3 \text{ mF}\cdot\text{cm}^{-2}$), indicating a roughly 4.3-times larger ECSA. This greater ECSA suggests the exposure of more catalytic active sites, which is attributed to the hollow nanostructure of HEC-CB-1. Therefore, the designed hollow structure represents an effective strategy to significantly improve the catalytic activity, and thus the HER performance, of high-entropy carbide materials.

3.3 Comparative electrocatalytic HER performance of RE-Free, single-RE and dual-RE containing high-entropy carbides

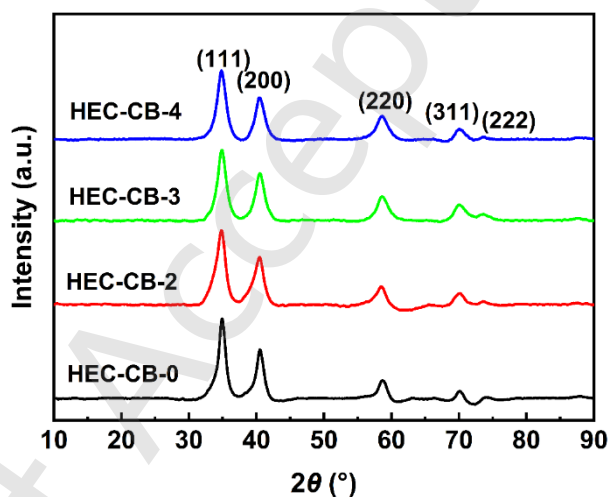


Fig. 9 XRD patterns of as-synthesized high-entropy carbides with different compositions from corresponding oxides/CB precursors.

To investigate the effect of incorporating rare-earth elements on the electrocatalytic HER performance of HECs, a series of hollow-structured HECs with compositions listed in Table 1 were synthesized using carbon black as the carbon source. For each sample from HEC-CB-0 to HEC-CB-4, the obtained electrolytic product consists of a single phase, which can be clearly assigned to the FCC structure (Fig. 3 and Fig. 9). The diffraction peaks exhibit a slight shift with the composition varies. The lattice parameters of the samples were calculated according to the XRD results and shown in Table 1. Generally, the incorporation of large-sized atoms

leads to lattice expansion in solid solutions [53]. Thus, according to this rule, the lattice parameters of HEC-CB-1, HEC-CB-2, and HEC-CB-3 increased by 0.0013 nm, 0.0017 nm, and 0.0013 nm, respectively, relative to rare-earth-free HEC-CB-0, due to the incorporation of large-sized Gd (0.180 nm), Ce (0.182 nm), and Y (0.180 nm). Notably, the simultaneous incorporation of Ce and Y in HEC-CB-4 gives rise to a significantly larger increase in the lattice parameter, reaching 0.005 nm.

Table 1 Calculated interplanar distances and lattice parameters for HECs from XRD analysis

Samples	Composition	Interplanar distance (nm)					Lattice parameter (nm)
		(111)	(200)	(220)	(311)	(222)	
HEC-CB-0	(HfNbTaTiZr)C	0.2565	0.2229	0.1572	0.1340	0.1282	0.4445
HEC-CB-1	(HfNbTaTiZrGd)C	0.2572	0.2227	0.1575	0.1345	0.1289	0.4458
HEC-CB-2	(HfNbTaTiZrCe)C	0.2578	0.2229	0.1579	0.1344	0.1287	0.4462
HEC-CB-3	(HfNbTaTiZrY)C	0.2571	0.2230	0.1577	0.1345	0.1287	0.4458
HEC-CB-4	(HfNbTaTiZrCeY)C	0.2595	0.2244	0.1584	0.1355	0.1298	0.4495

As shown in Fig.10, the synthesized HEC-CB-0, HEC-CB-2, HEC-CB-3 and HEC-CB-4 all possess hollow nanostructured morphology, which was also observed for HEC-CB-1. In addition, SAED patterns reveal their face-centered cubic crystal structure, which is further confirmed by the lattice fringes observed in high-resolution TEM images. According to the STEM-EDX elemental mapping results (Fig. S3-6), all elements were homogeneously distributed at the nanoscale.

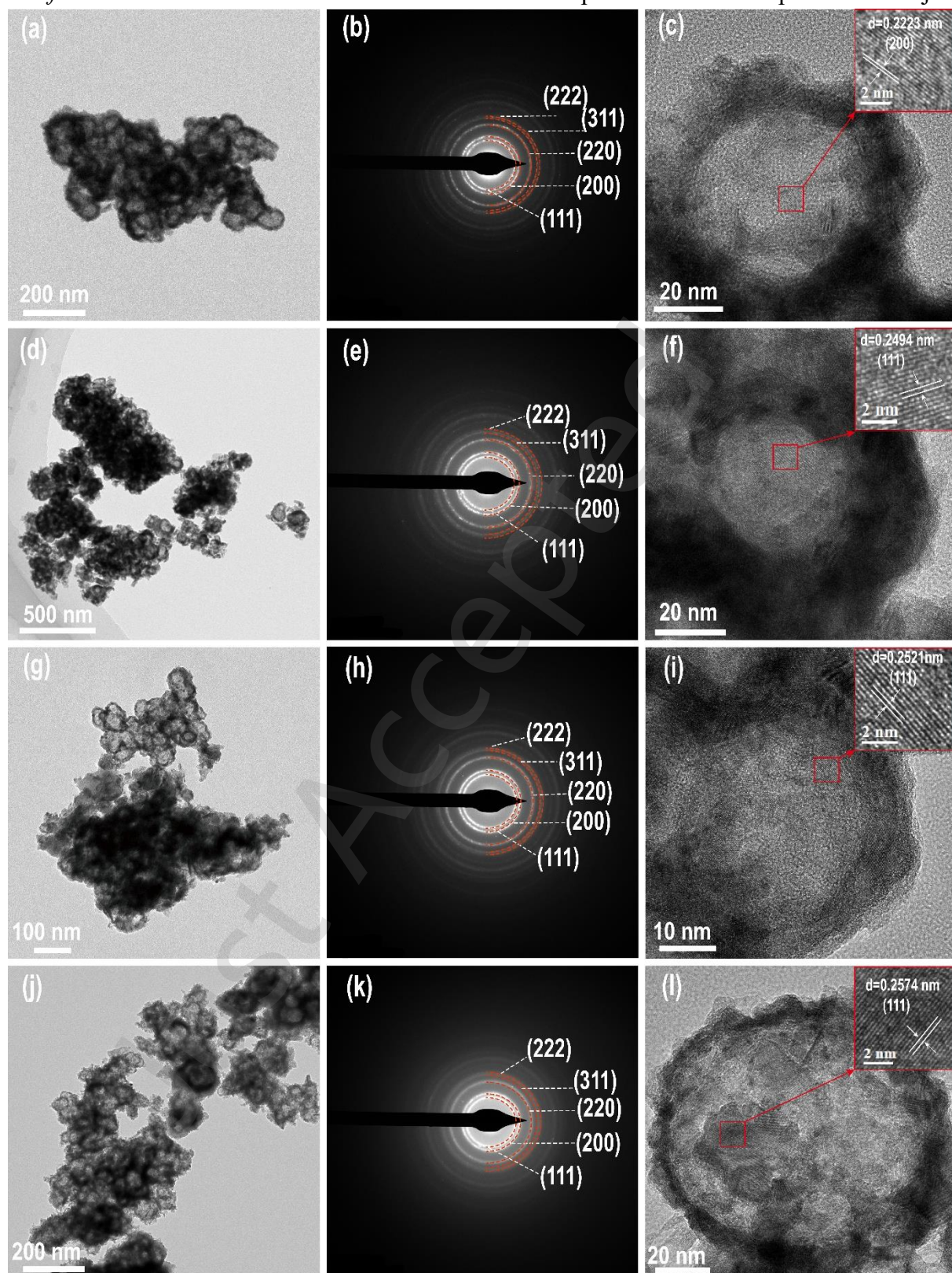


Fig. 10 TEM images, SAED patterns and HRTEM images of (a-c) HEC-CB-0, (d-f) HEC-CB-2, (g-i) HEC-CB-3 and (j-l) HEC-CB-4.

Fig. 11a displays the LSV curves of the samples. Their corresponding overpotentials at $10 \text{ mA} \cdot \text{cm}^{-2}$ (η_{10}) are summarized in Fig. 11b. It reveals that the activity trend follows the order: HEC-CB-3 (218 mV) > HEC-CB-2 (226 mV) > HEC-CB-1 (234 mV) > HEC-CB-0 (247 mV). Clearly, (HfNbTaTiZrRE)C (RE=Gd, Ce, Y) exhibits moderately enhanced catalytic activity over (HfNbTaTiZr)C. Such performance enhancement stems from the incorporation of RE elements into the solid-solution lattice of transition metal carbides. On one hand, this can be reasonably attributed to RE-induced electronic modulation via orbital coupling, which optimizes the d-band electronic structure of catalytically active sites, as well documented in previous studies [36,54,55]. On the other hand, owing to the larger atomic radii of rare-earth elements relative to transition-metal atoms, their lattice incorporation induces severe lattice distortion and further generates local lattice strain. As demonstrated in previous studies [28,38,56], such lattice strain can also modulate the electronic structure of active sites and thus shift the d-band center through a geometry-derived pathway. The synergistic interplay of lattice-strain and orbital-coupling effects optimizes the binding strength of H^* intermediates, thereby enhancing the intrinsic HER activity. Additionally, the occupancy of 4f orbitals of rare-earth metals can modulate the alkaline catalytic activity of (HfNbTaTiZrRE)C. The measured Tafel slopes (Fig. 11c) for the RE-free, Gd-, Ce-, and Y-containing HECs were 106.8, 81.2, 75.9, and $74.7 \text{ mV} \cdot \text{dec}^{-1}$, respectively. This result indicates that the hydrogen evolution reaction catalyzed by HEC-CB-0, HEC-CB-1, HEC-CB-2, and HEC-CB-3 follows the Volmer-Heyrovsky mechanism, with the Heyrovsky step as the RDS. (HfNbTaTiZrRE)C (RE=Gd, Ce, Y) exhibits a relatively low Tafel slope, suggesting that only a minimal rise in overpotential is required to drive a remarkable rise in current density. This phenomenon demonstrates the superior reaction kinetics imparted to HECs by the incorporation of a single RE component.

Moreover, The Nyquist plots and corresponding equivalent circuit are presented in Fig. 11d. The R_{ct} for HEC-CB-3, HEC-CB-2, HEC-CB-1 and HEC-CB-0 was determined as 3.8, 4.4, 5.0, and 11.4Ω , respectively. The much lower R_{ct} of (HfNbTaTiZrRE)C (RE=Gd, Ce, Y) suggests that adding RE

elements to HECs considerably enhances charge transfer kinetics. The double-layer capacitance (C_{dl}) can be calculated by closed CV curves to estimate the ECSAs of the as-prepared electrocatalysts (Fig. S7 and Fig. 11e). The C_{dl} was calculated to be 2.1, 1.5, 1.3 and 1.1 $\text{mF}\cdot\text{cm}^{-2}$ for HEC-CB-3, HEC-CB-2, HEC-CB-1 and HEC-CB-0, respectively. This implies that incorporating RE elements into HECs increases ECSA, thereby exposing more active sites. Briefly, in the alkaline electrolyte, $(\text{HfNbTaTiZrRE})\text{C}$ ($\text{RE}=\text{Gd}, \text{Ce}, \text{Y}$) exhibits a marked improvement in HER performance over $(\text{HfNbTaTiZr})\text{C}$, among which $(\text{HfNbTaTiZrY})\text{C}$ shows the highest performance.

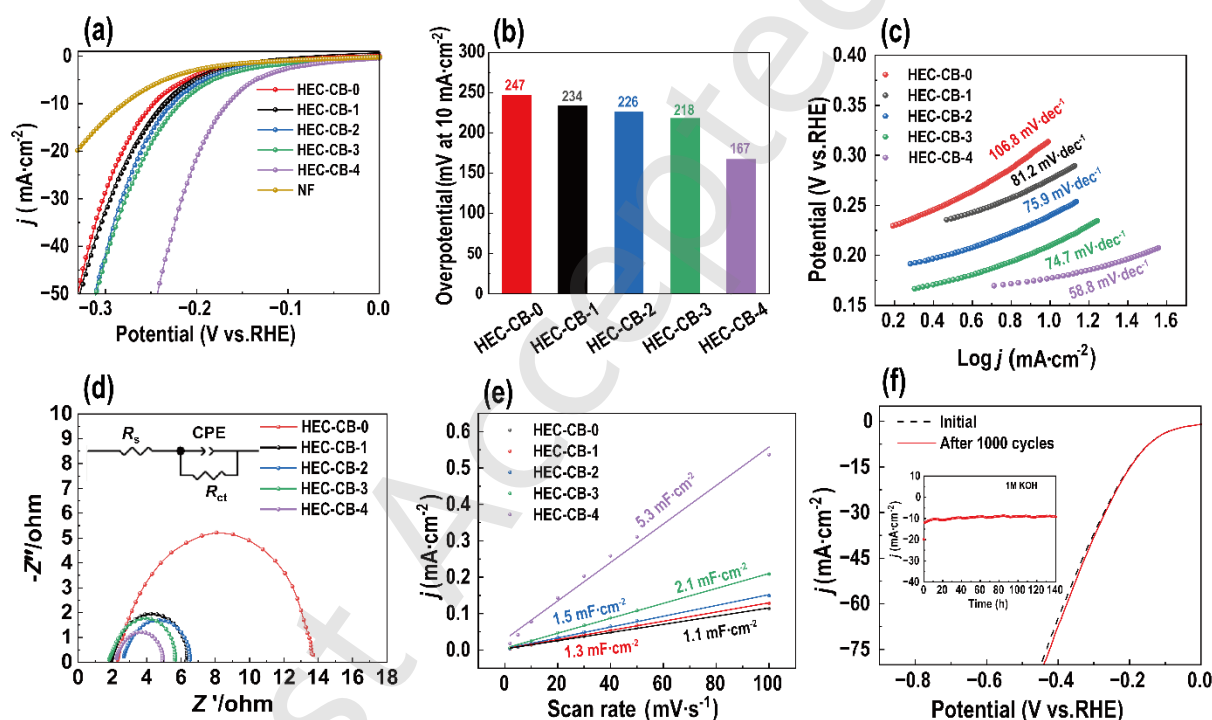


Fig. 11 Electrochemical parameters of as-synthesized hollow-structured high-entropy carbide ceramics in 1.0 M KOH. (a) polarization curves; (b) overpotentials at 10 mA cm^{-2} ; (c) Tafel plots; (d) Nyquist plots at -1.27 V (vs. RHE); (e) C_{dl} curves; (f) stability test of HEC-CB-4 after 1000 CV cycles, with the inset showing the chronoamperometric (I-T) curve of HEC-CB-4.

With the aim of further improving the performance, we tentatively introduced dual rare-earth elements and synthesized $(\text{HfNbTaTiZrCeY})\text{C}$, denoted as HEC-CB-4. Electrochemical characterization confirms its optimal HER performance, with the lowest overpotential ($\eta_{10} = 167 \text{ mV}$), smallest Tafel slope ($58.8 \text{ mV}\cdot\text{dec}^{-1}$), minimal charge transfer resistance (2.7Ω), and largest double-

layer capacitance ($6.3 \text{ mF} \cdot \text{cm}^{-2}$) among all samples (Fig. 11). These findings collectively demonstrate that the dual RE incorporation into transition-metal-based HECs can not only construct more electroactive sites but also accelerate electrocatalytic kinetics, thereby yielding enhanced HER performance that far surpasses the single-RE counterparts $(\text{HfNbTaTiZrRE})\text{C}$ ($\text{RE}=\text{Ce}, \text{Y}$). This superior activity arises from the synergistic effects of two distinct RE species, Ce and Y [57]. The lattice parameter of $(\text{HfNbTaTiZrCeY})\text{C}$ (0.4495 nm) is markedly larger than those of $(\text{HfNbTaTiZrCe})\text{C}$ (0.4462 nm) and $(\text{HfNbTaTiZrY})\text{C}$ (0.4458 nm). Simultaneous introduction of two large-radius rare-earth atoms would induce larger lattice distortions, thereby generating increased local strain and more carbon vacancies [53,58,59], which likely tune the d-band center of active sites toward the optimal position for H^* adsorption [60]. Furthermore, the distinct electronic configurations and electronegativities of Ce and Y enable bimetallic synergistic modulation of the electronic structure around active sites, further refining the intermediate binding strength for enhanced HER performance [57,61]. Electrocatalyst stability is crucial for practical applications. Stability tests were performed on HEC-CB-4. As shown in Fig. 11f, the η_{10} value remains stable at 167 mV after 1000 CV cycles, with the LSV curve showing negligible shift. The stable chronoamperometry (I-t) curve (inset, Fig. 11f) further confirms the outstanding electrochemical stability of HEC-CB-4 under alkaline conditions. Additionally, TEM images confirm that the hollow structure of HEC-CB-4 is retained after the 140-hour stability test (Fig. S8a). The corresponding HRTEM image still shows the lattice fringes of the (111) planes, and the SAED pattern continues to exhibit diffraction rings assignable to the FFC structure (Fig. S8b, c). Moreover, dark-field STEM image with EDX area maps reveals that all elements retain a uniform distribution after the stability test (Fig. S9).

As expected, HEC-CB-4 exhibits excellent HER activity and long-term stability compared with most reported high-entropy catalysts and its constituent unary carbide-based catalysts, highlighting its potential as an efficient and durable electrocatalyst for alkaline HER (Table S1). Building on this foundation, future research will explore the rational compositional design of hollow high-entropy

carbide catalysts by systematically screening and integrating candidate transition metals from groups IVB–VIB and rare-earth elements, which is expected to substantially enhance catalytic activity.

4 Conclusions

In this work, hollow high-entropy carbides (HECs), namely (HfNbTaTiZr)C, (HfNbTaTiZrRE)C (RE=Gd, Ce, Y) and (HfNbTaTiZrCeY)C, were successfully synthesized for the first time by a direct electroreduction process using a mixture of metal oxides and carbon black in molten CaCl₂-NaCl at 800 °C. The as-synthesized HEC powders consist of nanoparticles and exhibit a single face-centered cubic (FCC) structure with homogeneous chemical composition at both the nanoscale and the microscale. Importantly, the type of carbon source has a significant regulatory effect on the morphology of the product. The formation of hollow structures is promoted by amorphous carbon black. In contrast, the high crystallinity of graphite inhibits the development of internal voids, resulting in solid particles. It was found that the electrocatalytic performance of HECs for HER is noticeably enhanced by the tailored hollow nanostructure compared to their solid counterparts. Furthermore, a further enhancement is achieved by introducing rare-earth elements into hollow HECs. Specifically, while a single rare-earth component already improves hydrogen evolution performance relative to rare-earth-free HECs, the incorporation of dual rare-earth components yields a more substantial improvement. Notably, (HfNbTaTiZrCeY)C as the electrocatalyst shows the best activity in 1.0 M KOH with the overpotential (η_{10}) of 167 mV, Tafel slope of 58.8 mV·dec⁻¹ and charge transfer resistance of 2.7 Ω . Moreover, it exhibits excellent electrochemical and structural stability over 140 h. This work provides a facile strategy for the direct synthesis of nano-sized hollow rare-earth-containing HECs with diverse compositions, thereby opening new avenues for the design of advanced HEC-based materials for applications in catalysis, energy conversion and storage, and beyond.

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Author contributions

Hongxia Liu: Writing-original draft, Supervision, Investigation, Funding acquisition, Conceptualization. **Jinqiao Zhang:** Investigation, Data curation, Visualization, Software, Methodology. **Shiyu Qin:** Visualization, Investigation, Methodology, Formal analysis. **Wen Ma:** Writing -review & editing, Methodology, Conceptualization, Supervision, Funding acquisition. **Yu Bai:** review & editing, Methodology, Conceptualization.

Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

Electronic Supplementary Material (ESM)

Supplementary material (XRD patterns of the products of sintered oxides/CB precursors electrolyzed at 800 °C under 3.1 V for different times. The closed CV curves of HEC-CB-0, HEC-CB-1, HEC-GP-1, HEC-CB-2, HEC-CB-3 and HEC-CB-4. Dark-field STEM image with EDX area maps of as-synthesized HEC-CB-0, HEC-CB-2, HEC-CB-3, HEC-CB-4. TEM image, SAED pattern, HRTEM images and Dark-field STEM image with EDX area maps of HEC-CB-4 after the 140-hour stability test. HER performances and stability of HEC-CB-4 in this work and other analogous catalysts in 1 M KOH.) is available in the online version of this article.

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