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Modulating electronic structure of CoP electrocatalysts towards enhanced hydrogen evolution by Ce chemical doping in both acidic and basic media

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ABSTRACT

Doping foreign metal ions into catalysts is considered as an effective approach to optimize the catalytic sites and improve their performance. Here, we develop and demonstrate the concept of rare-earth elemental doping by Ce into host catalysts of CoP in modulating their electronic structures and decreasing their adsorption free energy of hydrogen for the enhanced hydrogen evolution reaction (HER) performance via a complementary theoretical and experimental approach. In contrast to undoped catalysts, the Ce-doping can facilitate lower overpotential, Tafel slope and charge transfer resistance as well as larger electrochemically active surface area and turnover frequency to deliver superb catalytic activity and stability. In particular, the catalyst with optimized doping amount exhibits ultra-low overpotentials of 54 and 92 mV at $10 \, \mathrm{mA \, cm^{-2}}$ in acidic and basic media, respectively, among many recently-reported CoP-based catalysts. Doping Ce into CoP not only illustrates benefits in improving the catalytic property for HER, but also opens up a novel view of doping rare earth elements into electrocatalysts for regulating their physiochemical and electrochemical properties.

1. Introduction

Hydrogen generation from electrochemical water splitting driven by renewable energy sources have long been considered as an effective and environmental-friendly method to produce clean fuels for the sustainable society [1–3]. In this regard, earth-abundant transitional metal alloys, and their nitrides, sulfides, phosphides and selenides are widely investigated as cathode catalysts for hydrogen evolution reaction (HER) [4–10]. Various strategies of optimizing their morphologies, compositions, crystal phases, exposed facets and others are as well explored to enhance the catalytic activity [11–17]. Doping different elements, including metals or non-metals into the catalysts, is a useful approach to modify the physicochemical and electronic properties to further improve their catalytic performance. In specific, apparent reduction in the energy barrier of hydrogen adsorption for hybrid catalysts of FeS_2 nanosheets-carbon nanotubes was experimentally

achieved by the cobalt doping, along with the detailed theoretical model developed to explain their enhanced HER activity in acid [12].

At the same time, due to unique properties of 4 f electrons, rare earth (RE) elements are not only extensively studied for optical, electrical and high-temperature catalysis related applications [18], but also attract more and more attentions in electrochemical utilizations. Recent advances in the successful alloying of RE elements (e.g. Ce, Pr, Gd) with other metals as well as the combination of cerium oxide with other transition metal compounds have demonstrated significant improvement in their electrocatalytic properties for HER, oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) [19–25]. Ni/CeO_2 nano-interfaces coupled with carbon nanotubes (CNTs) can practically promote the HER processes by expediting the dissociation of water molecules and subsequently lowering the hydrogen binding energy, as illustrated by density functional theory (DFT) calculations [21]. Also, substantially improved ORR activity of the NiO_x

films can be achieved by combining the Ce doping and gold support in alkaline media, where the superior activity is owing to the synergy of electronic, geometric and support effects [24]. Moreover, RE elements can as well be employed to control the crystal strain in regulating the activity, stability and reactivity of Pt-based alloy catalysts for ORR [25]. All these have evidently indicated that introducing RE elements into the host lattice can effectively modulate the electronic and geometric structures in order to improve the catalytic activity of electrocatalysts for efficient electrochemical energy conversion, which opens up a novel route to enhance the electrode materials.

Recently, there are numerous literatures devoted to evaluate the electronic effects of doping 3d transitional metals (*e.g.* Fe, Mn and Ni) into electrocatalysts [12,26,27]. However, it is lacking of a thorough understanding on the role of doped RE elements with 4 f orbitals in host catalysts for electrocatalysis. Herein, cobalt phosphide (CoP) is selected as a model cathode material to systematically investigate the effect of Ce doping for HER by complementary theoretical and experimental approaches. In particular, DFT calculations exhibit the positive benefits of Ce-doping for the decreased hydrogen adsorption energy and modified Bader charge of Co, which facilitate the HER processes. Experimental findings of remarkable improvements in the catalytic property of Ce-doped CoP catalysts for HER in both acidic and basic electrolytes are also obtained, being consistent with the theoretical analysis.

2. Results and discussion

Initially, we assess the electronic structures of CoP surface and analyze the origin of differences in HER processes upon the introduction of foreign Ce ions by DFT calculations. As the adsorption free energy of hydrogen (ΔG_{H*}) has been shown to be a good descriptor of materials for catalyzing hydrogen generation [28–31], ΔG_{H*} was used in this work to evaluate the catalytic activity of catalysts for HER. In general, a good HER catalyst should have a $\Delta G_{H*} \approx 0$ eV to benefit the subsequent H_2 generation. All computational details are also presented in Supporting information and Fig. S1, S2, Table S1, S2 and S3. Usually, the HER process can be summarized into a three-state diagram with an initial H^+ state, an intermediate adsorbed H^* state and a final H_2 state in acidic electrolytes [27]. For the orthorhombic structure of CoP, several typical facets of (211), (002), (101) and (100) were chosen to study the changes in the surface adsorption energy of hydrogen.

Fig. 1 displays the calculated free energy diagram for hydrogen

evolution on different surfaces of both CoP and Ce-doped CoP. On clean CoP(211) and CoP(002) surfaces, hydrogen preferentially adsorbs at the Co-Co bridge site with a relatively strong exothermic adsorption free energy of −0.46 eV (211) and −0.49 eV (002), respectively. With the introduction of Ce, the initial Co-Co bridge site is broken and the new Ce-Co bridge site is formed, leading to the hydrogen atom transferring from bridge site to the Co-top site (Fig. 1**a'** and **c'**). The values of ΔG_{H*} on Ce-doped CoP(211) and CoP(002) are then reduced to 0.09 eV and −0.16 eV, accordingly. Similar phenomena of the reduction in ΔG_{H*} by Ce doping have also occurred on CoP(101) and CoP(100) surfaces, in which the value of ΔG_{H*} decreases from −0.33 eV to −0.11 eV for CoP(101) and from −0.96 eV to −0.54 eV for CoP(100), respectively (Table S2). From the analysis above, a preliminary conclusion can be drawn that the doping of Ce ions into CoP catalysts could decrease the absolute value of ΔG_{H*}, making the hydrogen adsorbed neither too strong nor too weak on the surface and enhancing the subsequent H_2-production. In order to confirm this argument, we selected the (211) facet to calculate the kinetic energy barrier profiles of HER on both Ce-doped CoP and undoped CoP (Fig. S2), which shows that the weakened adsorption of H by Ce-doping does benefit the kinetics of H_2 generation. As shown in Fig. S2, two hydrogen atoms are adsorbed weakly on the surface of the Ce-doped CoP(211) with the adsorption energy approaching to zero, and the subsequent H_2 generation only needs to surpass a low kinetic barrier of 0.17 eV. In contrast, the adsorption of two hydrogen atoms is relatively stable with an adsorption energy of 0.43 eV on the surface of the undoped CoP (211), and the subsequent H_2 generation has to overcome a barrier of 0.49 eV, much higher than that on the Ce-doped CoP (211) surface. The Bader charge analysis (Table S3) has further shown that the doping of Ce changes the electronic state of Co from positively to negatively charged due to the electron transfer from Ce to Co. Especially, for Ce-doped CoP(211) and CoP(002) surfaces (Fig. S3), Co atoms neighboured to foreign Ce atoms suffer an apparent charge decrease of about 0.2 e, leading to the partial reduction of Co. While smaller changes in Bader charge for farther Co atoms are also observed, decrease in Bader charge of Co atoms with Ce doping would result in the hydrogen preferentially adsorbed at the Co-top site and hence a smaller adsorption free energy. Thus, we could expect that the doping of Ce into CoP can alter their electronic states and potentially enhance the hydrogen adsorption ability, and better electronic state might benefit the electrochemical HER process.

To shed light validating the above theoretical analysis, CoP nanowires with/without Ce doping supported on Ti plates are then
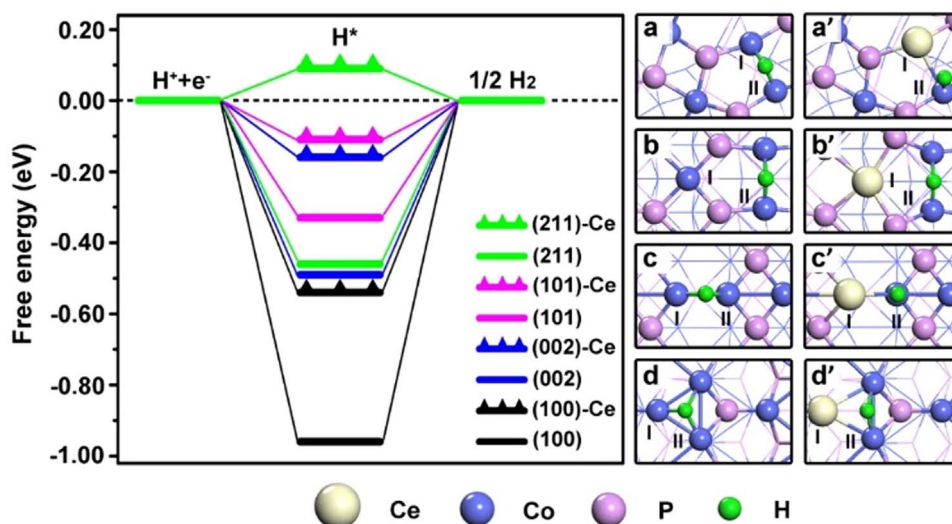

Fig. 1. Calculated free energy diagram for HER on CoP and Ce-doped CoP. (a)-(d) are the optimized adsorption structures of H* on the (211), (101), (002) and (100) surfaces of CoP, correspondingly. (a')-(d') are the optimized adsorption structures of H* atom on the (211), (101), (002) and (100) surfaces of Ce-doped CoP, respectively.
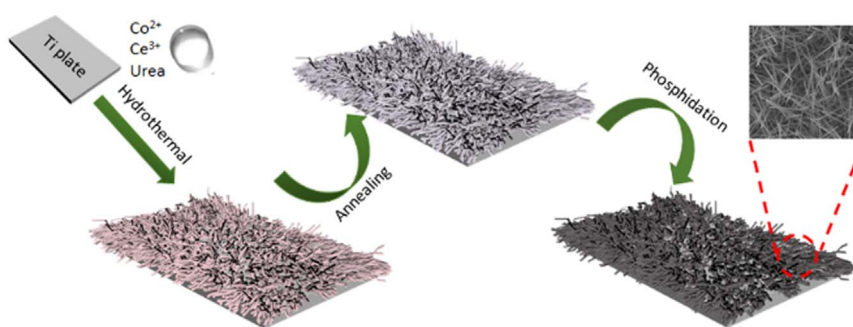
Fig. 2. Synthetic process of CoP and Ce-doped CoP nanowires supported on Ti plates.

prepared to evaluate their HER activity with a consistent and fair comparison. The overall synthetic process of CoP and Ce-doped CoP nanowires on Ti plates involves three steps (Fig. 2): (1) hydrothermal synthesis of Co-based precursors, (2) formation of metal oxides by low temperature annealing, and (3) low-temperature chemical-vapor-based phosphidation, while the detailed process is described in the Supporting information.

Fig. S4 and Fig. 3 show the structural characterizations of initial Co_3O_4 and Ce-doped Co_3O_4 samples as well as corresponding phosphidated samples, respectively, where the theoretical Ce-doping level is controlled at $x = 0.1$ (x is the theoretical molar ratio of Ce^{3+} to (Ce^{3+} + Co^{2+})). The actual Ce-doping concentration was 2.9%, determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Table S4). Typical scanning electron microscopy (SEM) images of the Co_3O_4 and Ce-doped Co_3O_4 precursors show the wire-like morphologies with the length of tens of micrometers (Fig. S4). X-ray diffraction (XRD) patterns (Fig. S4) reveal the cubic phase structures (PDF # 43–1003) for both samples, without any other phases related to CeO_2 being

observed. After phosphidation, the nanowire morphologies of CoP and Ce-doped CoP are well-preserved, maintaining the length of tens of micrometers and diameter of hundreds of nanometers (Fig. 3**a** and **b**). Similarly, both samples of CoP and Ce-doped CoP supported on Ti plates are found to be well-matched to the orthorhombic phase of CoP (PDF # 29–0497) [32], also without any peak indexing to CeO_2 species. XRD results indicate no apparent specie of CeO_2 is formed but Ce-doped CoP nanowires are obtained during the synthetic process. As a sensitive technique in studying the surface chemical species, Raman spectroscopy is employed to further examine as-prepared catalysts. Evidently, there is no characteristic Raman peak of CeO_2 located at ~460 or 600 cm^{-1} for the Ce-doped CoP nanowires (Fig. S5) [33] and clear lattice fringes with interplanar spacings of 0.279 and 0.189 nm are observed under high-resolution transmission electron microscopy (HR-TEM, Fig. 3**d**), corresponding to the (002) and (211) planes of CoP respectively, in which all these suggest the reliable Ce doping in CoP without formation of CeO_2 species. To further assess the Ce doping distribution, dark-field TEM (DF-TEM) and energy-dispersive X-ray
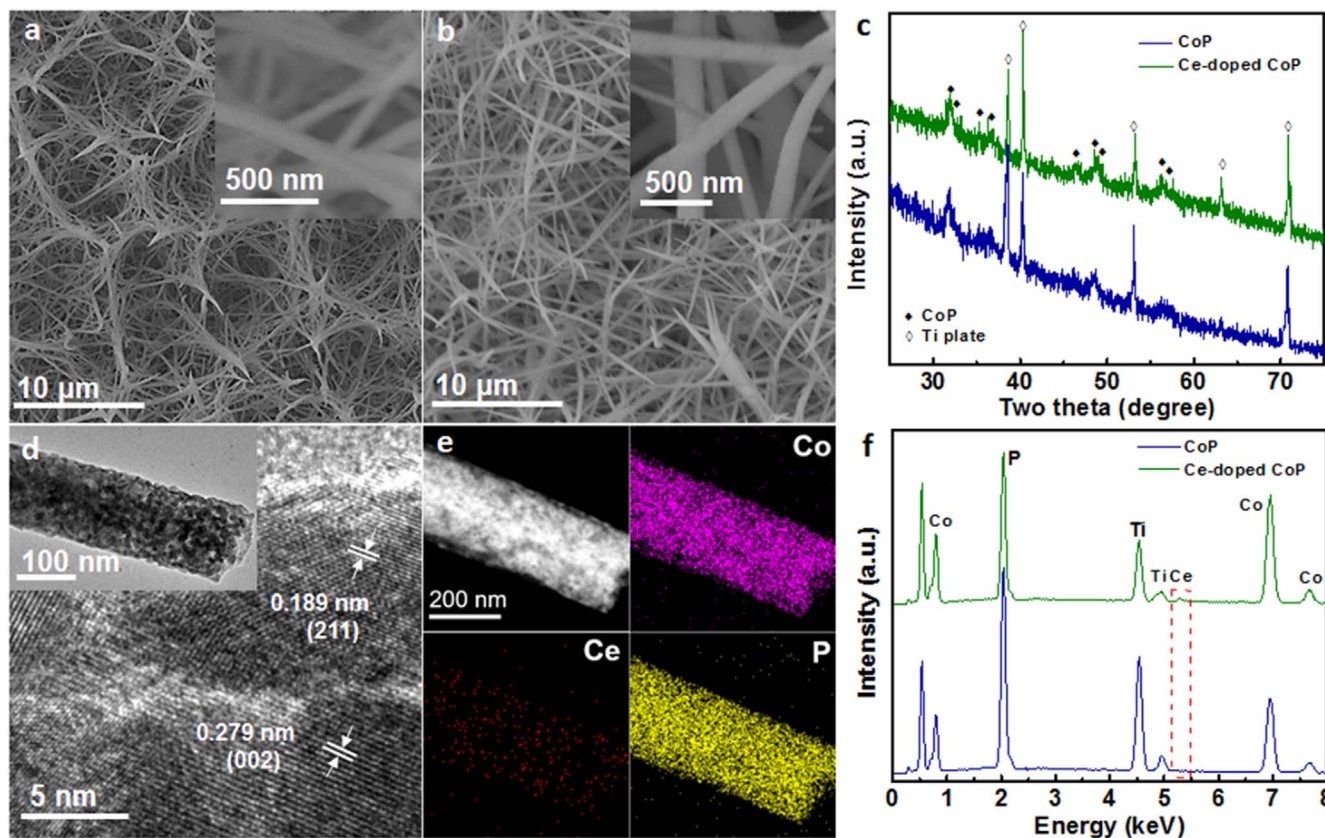

Fig. 3. Typical SEM images of (a) CoP and (b) Ce-doped CoP nanowires. (c) XRD patterns of CoP and Ce-doped CoP nanowires on Ti plates. (d) TEM and HR-TEM images of Ce-doped CoP nanowires. (e) DF-TEM image of Ce-doped CoP, and element mapping images of Co, Ce and P, respectively. (f) EDS results.

spectroscopy (EDS) are utilized, demonstrating the existence of Ce element as well as its uniform distribution along with Co and P constituents. Thus, we could confirm the successful Ce doping and its uniform distribution in CoP with the preservation of its original morphology and phase structure.

Surface chemical states of Co and P, together with the doped Ce were then studied by X-ray photoelectron spectroscopy (XPS). Comparison of XPS data at the binding energy range of ~880–925 eV reveals the existence of Ce for Ce-doped CoP and the absence of Ce element for undoped one (Fig. S6a and S6b), further illustrating the successful doping of Ce into CoP. For Co $2p_{3/2}$ spectra of both undoped and Ce-doped samples (Fig. S6c), peaks at the binding energy of 778.7 eV can be ascribed to the partial positive-charged cobalt species ($Co^{\delta+}$) while those of 781.7 eV are corresponded to oxidized Co species [32,34,35]. For P 2p spectra (Fig. S6d), peaks at 129.5 and 130.2 eV can be correlated to partial negative-charged phosphorus species and peaks at 134.4 eV are assigned to oxidized phosphorus species [32]. The oxidized Co and P species are generally believed to come from the surface oxidation of CoP after exposure to the ambient [32,34]. Furthermore, based on the peak fitting analysis of Co $2p_{3/2}$ spectra, the ratio of $Co^{\delta+}$ for Ce-doped CoP (43%) is larger than that for CoP (33%), consistent with above theoretical computation results of the reduction of Co species by electron transfer from Ce to Co. Since $Co^{\delta+}$ species are well-known to play an indispensable role in the hydrogen-hydrogen bond formation, the difference in this $Co^{\delta+}$ content is expected to affect their HER activity [8].

Along with many recent reports on the efficient and stable HER catalyzed by CoP and its derivatives in various media [36–40], we focus on the effect of Ce doping in CoP on HER catalytic properties. Thus, series of Ce-doped CoP catalysts with various doping contents were synthesized with various molar ratio $x = [Ce^{3+}]/([Ce^{3+}] + [Co^{2+}])$ and x = 0.05, 0.1, 0.2 and 0.3. For all catalysts, structural characterizations showed similar morphology and phase to those of the Ce-doped CoP (x=0.1, Fig. S7). Actual doping amounts of Ce are presented in Table S4. Electrochemical performance of catalysts was performed using a three-electrode electrochemical cell in 0.5 M H_2SO_4 firstly. The measured polarization curves of the undoped and doped CoP nanowire electrodes suggest that they are highly active HER electrocatalysts (Fig. S8). Among them, the Ce-doped CoP catalysts with actual 2.9% Ce delivered the optimized catalytic HER performance with the highest activities and smallest Tafel slopes. Thus, it (denoted as Ce-doped CoP) was selected to study the difference as compared with undoped CoP catalyst in details.

Fig. 4a and Fig. 4d show catalytic HER activity of CoP, Ce-doped CoP and commercial Pt/C catalysts on the reversible hydrogen electrode (RHE) in both acid (0.5 M H_2SO_4) and alkaline (1 M KOH) electrolytes. The commercial Pt/C catalyst performs the best with the smallest overpotential and Tafel slope to drive a large current density. To reach the current densities of 10 and 100 mA cm^{-2} in acid, overpotentials required for the Ce-doped CoP electrocatalyst are 54 and 120 mV, correspondingly (Fig. 4a), which are much smaller than the ones (74 and 163 mV, respectively) of undoped CoP. The extracted Tafel slope of 54.0 mV/dec of Ce-doped CoP is also smaller than that of CoP (59.3 mV/dec), further demonstrating the better catalytic properties of Ce-doped CoP catalyst (Fig. 4b) in acid. For the case of hydrogen generation in alkaline solution, in order to drive the current densities of 10 and 100 mA cm^{-2}, external overpotentials for Ce-doped CoP are only 92 and 161 mV, respectively; while those for undoped CoP are 139 and 222 mV, correspondingly (Fig. 4d). The smaller Tafel slope of Ce-doped CoP (63.5 mV/dec) is also witnessed as compared with that of undoped CoP (70.3 mV/dec) indicating the better catalytic activity of Ce-doped CoP in alkaline (Fig. 4e). The activities of Ce-doped CoP based on mass density in acid and alkaline are also better than those of CoP (Fig. S8). More importantly, the excellent performance of Ce-doped CoP nanowires supported on Ti plates is readily observed with the ultra-low overpotential of 54 and 92 mV in both acidic and basic solutions, accordingly, for the current density of 10 mA cm^{-2} for HER, which are much better than many recently-reported cobalt phosphide electrocatalysts and their derivatives as summarized in Table S5 and S6.
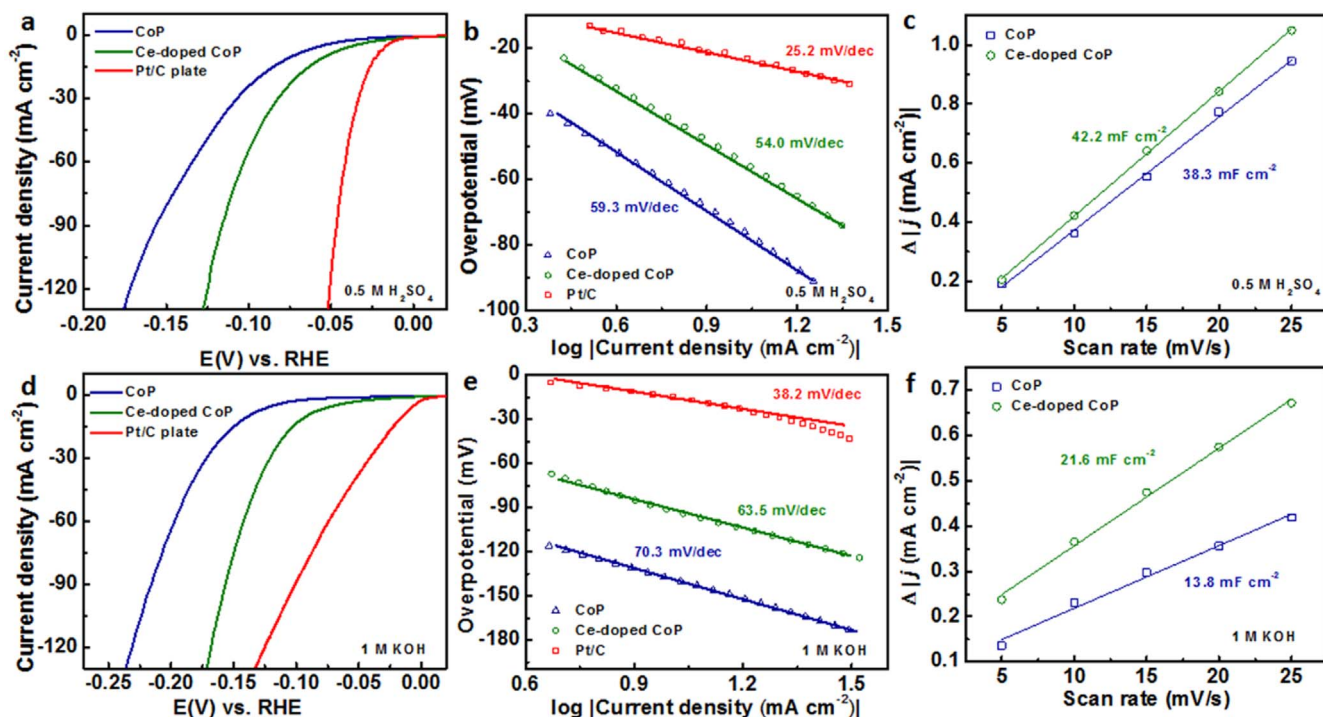

Fig. 4. HER performance of CoP and Ce-doped CoP nanowire catalysts in 0.5 M H_2SO_4 and 1 M KOH electrolytes. Polarization curves (with iR corrections) of CoP, Ce-doped CoP and Pt/C catalysts with a scan rate of 5 mV/s in (a) 0.5 M H_2SO_4 and (d) 1 M KOH solutions. Tafel slopes for CoP and Ce-doped CoP in (b) 0.5 M H_2SO_4 and (e) 1 M KOH derived from (a) and (d), respectively. Capacitive current densities as a function of scan rates for CoP and Ce-doped CoP catalysts in (c) 0.5 M H_2SO_4 and (f) 1 M KOH to calculate the double layer capacitances (C_{dl}), correspondingly.
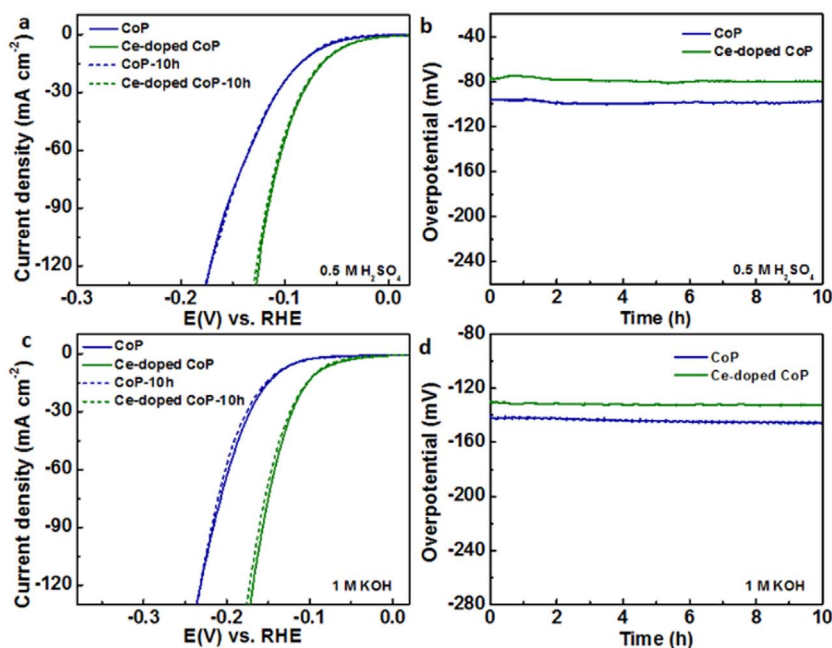
Fig. 5. Durability tests of CoP and Ce-doped CoP in both acidic and basic electrolytes. Polarization curves (with iR corrections) for CoP and Ce-doped CoP before and after 10 h' stability tests in (a) 0.5 M H_2SO_4 and (c) 1 M KOH solutions, respectively. Stability tests of CoP and Ce-doped CoP using the chronopotentiometric measurements (without iR corrections) with the fixed current density of 10 mA cm^{-2} in (b) 0.5 M H_2SO_4 and (d) 1 M KOH solutions.

In addition, with the purpose to evaluate the difference in intrinsic catalytic property induced by the Ce doping, various electrochemical characterizations, including turnover frequency (TOF), electrochemically active surface area (ECSA) and electrochemical impedance spectroscopy (EIS), were performed (details in Supporting information). As indicated from Fig. S10a and S10b, the Ce-doped CoP catalysts illustrate significantly larger TOF values than those of the undoped CoP (Fig. S10a) in acid. TOF value at each active site of Ce-doped CoP is determined to be 0.36 s^{-1} at an overpotential of 100 mV, which is 2.6 times larger than that (0.14 s^{-1}) of undoped CoP, suggesting the higher catalytic HER activity for Ce-doped CoP. ECSA can reveal the actual active surface areas of catalysts for electrocatalysis, which is proportional to the double layer capacitance (C_{dl}) of catalysts [41]. As shown in Fig. S11, Fig. 4**d** and **f**, the C_{dl} of Ce-doped CoP (42.2 and 21.6 mF cm^{-2} in acid and alkaline, respectively) is larger than that of undoped CoP (38.3 and 13.8 mF cm^{-2} in acid and alkaline, correspondingly), implying that doping Ce into CoP results in an increase in its electrochemically surface areas with more exposed active sites in both acidic and basic electrolytes to promote hydrogen evolution [41,42]. For EIS results in Fig. S12, semicircles at both high and low frequencies are indexed to the charge-transfer resistances (R_{ct}) and hydrogen adsorption kinetics, respectively [15,43]. Nyquist plots indicate clearly the much smaller R_{ct} of Ce-doped CoP as compared with those of CoP catalyst in both acid and alkaline (Fig. S12), suggesting the better charge-transfer property for Ce-doped CoP to accelerate the turnover of proton and adsorbed water molecules [43]. Moreover, semicircles at low frequencies describes the HER kinetic barriers of adsorbed H_{ads} intermediate. The smaller semicircle of Ce-doped CoP as compared with CoP in alkaline solution (Fig. S12b) reveals the smaller resistance of H_{ads} to facilitate water dissociation and hydrogen formation caused by Ce doping [15]. All these have explicitly designated the advantages of Ce doping in improving the ESCA, turnover of absorbed hydrogen species and electrical conductivity for the enhanced catalytic activity and stability of Ce-doped CoP electrocatalysts for HER, which is in a perfect agreement with the theoretical studies above.

Catalytic stability is important for practical applications of electrocatalysis. Durability tests using the chronopotentiometry method were performed in the acidic and basic electrolyte for 10 h (Fig. 5). Impressively, when the current density was fixed at 10 mA cm^{-2} for

HER, a small fluctuation in overpotential (~80 mV, without iR corrections) as well as polarization curves before and after 10 h' test were witnessed for the excellent stability of the Ce-doped CoP catalysts in acid (Fig. 5**a** and **b**). Similarly, the undoped CoP catalysts showed a good stability under the overpotential of ~ 100 mV with some fluctuations (Fig. 5**a**). Despite the small fluctuations in overpotentials in alkaline solution, Ce-doped CoP requires a relatively smaller overpotential of ~131 mV (without iR corrections) to drive the current density of 10 mA cm^{-2} while it is ~144 mV (without iR corrections) for undoped CoP for the long-term and stable hydrogen generation (Fig. 5**d**). Polarization curves (Fig. 5**c**) before and after test in alkaline electrolytes also demonstrated the good durability of both electrocatalysts while Ce-doped CoP preserved its superb catalytic activity as contrasted with undoped CoP.

3. Conclusions

In summary, a concept of rare-earth elemental doping by Ce into the host electrocatalysts of CoP in modulating their electronic structures and decreasing their adsorption free energy of hydrogen for the enhanced HER performance is proposed and confirmed by theoretical computations, followed by the experimental validation. Using this general strategy, we demonstrate that the Ce-doped CoP catalysts exhibit superb catalytic activity and durability for HER in the both acidic and basic electrolyte as compared with undoped CoP catalysts. The remarkable enhancement can be attributed to the higher content of active catalytic Co species as well as the faster turnover of absorbed hydrogen species for the more efficient hydrogen formation, which are consistent with the theoretical analyses. Given the highly improved catalytic activity and stability towards HER, one can anticipate that the rare-earth elemental doping into catalysts would open up a new avenue for next-generation sustainable electrochemical water splitting.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2017.06.002.

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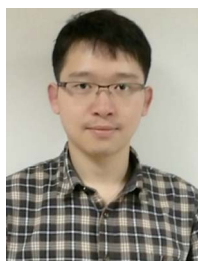
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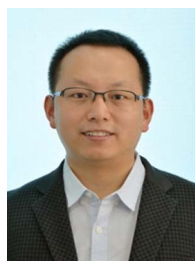
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