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# A Cu<sub>3</sub>P–CoP hybrid nanowire array: a superior electrocatalyst for acidic hydrogen evolution reactions<sup>†</sup>

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It is highly attractive to construct cost-effective hybrid electrocatalysts with superior activity for the hydrogen evolution reaction (HER) in acids. In this communication, we report a novel structure consisting of a Cu<sub>3</sub>P–CoP hybrid nanowire array supported on carbon cloth (Cu<sub>3</sub>P–CoP/CC) as a superior HER electrocatalyst in acidic media. Owing to the synergistic effect between Cu<sub>3</sub>P and CoP, this Cu<sub>3</sub>P–CoP/CC catalyst exhibits superior catalytic HER performance, needing an overpotential of 59 mV to drive a current density of 10 mA cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 24 and 130 mV less than that for CoP/CC and Cu<sub>3</sub>P/CC, respectively. Moreover, this catalyst also shows high long-term electrochemical durability.

With the depletion of fossil fuels and increasing concern about environmental pollution, the development of energy storage and conversion devices is highly required.<sup>1–4</sup> Hydrogen has emerged as a sustainable and clean energy alternative to fossil fuels.<sup>5</sup> Electrochemical water splitting is considered as a promising technology for producing pure hydrogen.<sup>6</sup> High-efficiency catalysts for the hydrogen evolution reaction (HER) are a prerequisite to attain a high current density at a low overpotential.<sup>7,8</sup> Moreover, it is necessary to synthesize stable HER catalysts under strongly acidic conditions for proton exchange membrane (PEM)-based electrolysis units.<sup>9</sup> Although Pt is the best HER catalyst under acidic conditions, its scarcity and high cost limit its widespread use.<sup>8</sup> Therefore, it is highly desirable to develop efficient and inexpensive HER catalysts made of earth-abundant elements.

Transition metal-based catalysts have been widely investigated toward acidic HERs in recent years due to their high catalytic power.<sup>7,10–16</sup> Among these catalysts, transition metal phosphides are an important class of compounds with high electrical conductivity and chemical stability,<sup>17</sup> which are beneficial to promote the electrochemical performance of catalysts. CoP has received considerable attention as a non-noble-metal HER catalyst under acidic conditions due to its high catalytic activity and durability.<sup>18-22</sup> Cu<sub>3</sub>P, another HER catalyst in acids, however, has only received limited attention mainly due to its inferior catalytic activity over CoP.<sup>23,24</sup> For example, a CoP nanoarray requires a small overpotential of 67 mV to drive a current density of 10 mA cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>,<sup>19</sup> whereas a Cu<sub>3</sub>P nanoarray needs an overpotential of 143 mV to approach the same current density.<sup>23</sup> It is reported that atomic and electric coupling of the two metal phosphides can improve the HER activity owing to their component diversity and synergistic effect.<sup>25,26</sup> We thus believe that the HER activity of Cu<sub>3</sub>P can be effectively enhanced by forming a Cu<sub>3</sub>P–CoP hybrid, which, however, has not been reported yet.

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In this communication, we report a novel structure consisting of a Cu<sub>3</sub>P–CoP hybrid nanowire array supported on carbon cloth (Cu<sub>3</sub>P–CoP/CC) as an efficient catalyst for the HER in acidic media. This Cu<sub>3</sub>P–CoP/CC catalyst shows superior HER activity, requiring an overpotential of 59 mV to afford a catalytic current density of 10 mA cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 24 and 130 mV less than that for CoP/CC and Cu<sub>3</sub>P/CC, respectively. Moreover, this catalyst also demonstrates high long-term electrochemical durability.

Cu<sub>3</sub>P-CoP/CC was derived from its hydroxide precursor on CC via a phosphidation reaction (see ESI,† for preparation details). Fig. 1a shows the X-ray diffraction (XRD) pattern for the resulting Cu<sub>3</sub>P-CoP/CC. It shows peaks at 28.9°, 38.7°, 38.9°, 40.9°, 44.3°, 45.9°, and 53.4° indexed to the (012), (202), (210), (121), (300), (113), and (104) planes of the Cu<sub>3</sub>P phase (JCPDS No. 72-1330), respectively, and the diffraction peaks at 31.6°, 36°, 46°, 48.1°, 48.4°, and 56° can be assigned to the (011), (111), (112), (211), (202), and (020) planes of the CoP phase (JCPDS No. 29-0497), respectively. The other peaks correspond to CC. The scanning electron microscopy (SEM) images of the hydroxide precursor (Fig. 1b) indicate the full coverage of the bare CC with the nanowire array. Note that the phosphided product still retains the original morphology (Fig. 1c). The highresolution transmission electron microscopy (HRTEM) image (Fig. 1e) taken from a Cu<sub>3</sub>P-CoP nanowire (Fig. 1d) shows a well-resolved lattice fringe spacing with interplanar distances

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Fig. 1 (a) XRD pattern for  $Cu_3P-CoP/CC$ . SEM images of (b) the hydroxide precursor on CC and (c)  $Cu_3P-CoP/CC$ . (d) TEM image of the  $Cu_3P-CoP$  nanowires. (e) HRTEM image of a  $Cu_3P-CoP$  nanowire. (f) EDX elemental mapping images of Cu, Co, and P for  $Cu_3P-CoP/CC$ .

of 0.204 and 0.283 nm, corresponding to the (300) plane of  $Cu_3P$  and the (011) plane of CoP, respectively. Impressively, the overlap of the lattice fringes of  $Cu_3P$  and CoP indicates atomic coupling, leading to the formation of a synergistic effect between them.<sup>27</sup> The energy-dispersive X-ray (EDX) elemental mapping analysis confirms the uniform distribution of Cu, Co, and P elements within the nanoarray (Fig. 1f), which has a greatly positive influence on the synergistic effects between  $Cu_3P$  and CoP, which can further promote the catalytic performance of  $Cu_3P$ -CoP/CC.<sup>26</sup>

As shown in Fig. 2a, the X-ray photoelectron spectroscopy (XPS) survey spectrum of  $Cu_3P$ -CoP/CC suggests the existence of Cu, Co, and P elements. The Co  $2p_{1/2}$  region shows one peak at 797.9 eV and the Co  $2p_{3/2}$  region exhibits two peaks at 781.9 and 778.72 eV (Fig. 2b).<sup>28</sup> The Cu  $2p_{3/2}$  region exhibits one main peak at 932.96 eV (Fig. 2c). The P 2p region shows two peaks at 130.2 and 129.3 eV, reflecting the binding energies (BEs) of P  $2p_{1/2}$  and P  $2p_{3/2}$ , respectively, along with one peak at 133.9 eV (Fig. 2d). The peaks at 778.72 and 129.3 eV are close to the BEs for Co and P in CoP.<sup>29,30</sup> The peaks at 932.96 and 129.3 eV are close to the BEs for Cu and P in Cu<sub>3</sub>P,<sup>23</sup> and the peak at 133.9 eV for P can be assigned to oxidized P species arising from superficial oxidation of Cu<sub>3</sub>P-CoP as a result of air contact.<sup>31,32</sup> The Co 2p at BE of 778.72 eV is positively shifted from that of metallic Co (778.1–778.2 eV) and the Cu  $2p_{3/2}$  at a



Fig. 2 (a) XPS survey spectrum for Cu<sub>3</sub>P–CoP/CC. XPS spectra in the (b) Co 2p regions for Cu<sub>3</sub>P–CoP and CoP, (c) Cu  $2p_{3/2}$  regions for Cu<sub>3</sub>P–CoP and Cu<sub>3</sub>P, and (d) P 2p regions for Cu<sub>3</sub>P–CoP.

BE of 932.96 eV is positively shifted from that of metallic Cu (932.6 eV) while the P 2p at a BE of 129.3 eV is negatively shifted from that of elemental P (130.2 eV).<sup>32,33</sup> This suggests the transfer of electron density from Co and Cu to P.<sup>30,34,35</sup> Impressively, the Co  $2p_{1/2}$  and Co  $2p_{3/2}$  peaks of Cu<sub>3</sub>P–CoP show ~0.25 eV shifting to high binding energy compared with CoP and the Cu  $2p_{3/2}$  peak also shifts to high binding energy (932.96 eV) with regard to the Cu  $2p_{3/2}$  peak of Cu<sub>3</sub>P (932.7 eV). These results indicate the strong electron interactions between Cu<sub>3</sub>P and CoP in the Cu<sub>3</sub>P–CoP, suggesting the presence of synergistic effects between them, which is beneficial for the improvement of the catalytic performance for Cu<sub>3</sub>P–CoP/CC.<sup>26,27</sup>

The HER activity of  $Cu_3P$ -CoP/CC (loading: 2.05 mg cm<sup>-2</sup>) was measured in 0.5 M H<sub>2</sub>SO<sub>4</sub> using a typical three-electrode system with a scan rate of 5 mV s<sup>-1</sup>. Bare CC and Pt/C on CC were also tested under the same conditions for comparison. It is noteworthy that because the as-measured reaction currents cannot reflect the intrinsic behavior of the catalysts directly due to the effect of ohmic resistance, an iR compensation was applied to all the initial data.<sup>36</sup> Besides, overpotentials were recorded on a reversible hydrogen electrode (RHE) scale. Fig. 3a shows the linear sweep voltammetry (LSV) curves; Pt/C presents excellent HER activity and only demands an overpotential of 31 mV to drive a current density of 10 mA  $cm^{-2}$ , whereas bare CC shows poor catalytic activity for hydrogen evolution. Cu<sub>3</sub>P/CC and CoP/CC are also active for the HER, requiring overpotentials of 189 and 83 mV to drive a current density of 10 mA  $cm^{-2}$ . In contrast, Cu<sub>3</sub>P-CoP/CC shows enhanced HER catalytic activity and needs a much lower overpotential of only 59 mV to drive the same current density. The atomic and electric coupling of Cu<sub>3</sub>P and CoP is believed to be responsible for the enhanced HER activity of Cu<sub>3</sub>P-CoP due to the synergistic effect.<sup>25,26</sup> Considering the high activity of Cu3P-CoP/CC in acidic media, we also investigated its activity in alkaline media (1.0 M KOH). This catalyst also shows efficient activity, requiring an overpotential of



**Fig. 3** (a) LSV curves for bare CC, Cu<sub>3</sub>P/CC, CoP/CC, Cu<sub>3</sub>P–CoP/CC, and Pt/C on CC at a scan rate of 5 mV s<sup>-1</sup>. (b) Tafel plots of Cu<sub>3</sub>P/CC, CoP/CC, Cu<sub>3</sub>P–CoP/CC, and Pt/C on CC. (c) Multi-current process of Cu<sub>3</sub>P–CoP/CC without iR correction. (d) LSV curves of Cu<sub>3</sub>P–CoP/CC before and after 500 cyclic voltammetry cycles and time-dependent current density curve (blue) of Cu<sub>3</sub>P–CoP/CC.

208 mV to afford 20 mA cm<sup>-2</sup> (Fig. S1, ESI<sup> $\dagger$ </sup>). The Tafel plots of CoP/CC, Cu<sub>3</sub>P/CC, Cu<sub>3</sub>P-CoP/CC, and Pt/C are shown in Fig. 3b. These Tafel plots are fitted to the Tafel equation:  $\eta = b \log j + a$ , where *j* is the current density and *b* is the Tafel slope.  $Cu_3P$ -CoP/CC presents a Tafel slope of 58 mV dec<sup>-1</sup> which is much lower than that for  $Cu_3P/CC$  (96 mV dec<sup>-1</sup>) and CoP/CC (89 mV dec<sup>-1</sup>) but only 14 mV dec<sup>-1</sup> more than that for Pt/C. This implies much faster HER kinetics on Cu<sub>3</sub>P-CoP/CC than on Cu<sub>3</sub>P/CC and CoP/CC. Fig. 3c displays the multi-step chronopotentiometric curve for Cu<sub>3</sub>P-CoP/CC with the catalytic current density changing from 20 to 220 mA cm<sup>-2</sup> (20 mA cm<sup>-2</sup> per 500 s). At the starting current value, the potential immediately levels off at -0.15 V and remains unchanged for the remaining 500 s. Analogous results are observed for all current densities tested up to 220 mA cm<sup>-2</sup>, reflecting the excellent mass transport properties, outstanding conductivity and mechanical robustness of the Cu<sub>3</sub>P–CoP/CC electrode.<sup>37,38</sup> The LSV curve after 500 cyclic voltammetry cycles overlays almost exactly with the initial one (Fig. 3d), indicating superior stability of Cu<sub>3</sub>P-CoP/CC. Furthermore, when we operated the HER at a fixed overpotential of 95 mV, Cu<sub>3</sub>P-CoP/CC shows high long-term electrochemical durability with its activity being maintained for at least 15 h (Fig. 3d, blue curve). The SEM image of Cu<sub>3</sub>P-CoP/CC after 500 cyclic voltammetry cycles suggests the maintenance of its nanowire morphology (Fig. S2, ESI<sup>†</sup>), indicating the robust structure.

Fig. 4a–c display the cyclic voltammograms (CVs) collected in the region of 0.025 to 0.125 V. The double-layer capacitances  $(C_{\rm dl})$  for Cu<sub>3</sub>P/CC, CoP/CC, and Cu<sub>3</sub>P–CoP/CC are measured as 4.5, 8.2, and 18.2 mF cm<sup>-2</sup>, respectively (Fig. 4d), indicating that the Cu<sub>3</sub>P–CoP/CC has a much higher surface roughness and exposes more active sites for HER catalysis.<sup>39</sup> The synergistic effect between Cu<sub>3</sub>P and CoP can be further demonstrated by the turnover frequency (TOF),<sup>40</sup> the number of hydrogen molecules evolved per second per active site. To calculate the TOF values of



**Fig. 4** CVs of (a) CoP/CC, (b) Cu<sub>3</sub>P/CC, and (c) Cu<sub>3</sub>P-CoP/CC with various scan rates (10–170 mV s<sup>-1</sup>) in the region of 0.025 to 0.125 V. (d) The capacitive current densities at 0.075 V as a function of scan rate for CoP/CC, Cu<sub>3</sub>P/CC, and Cu<sub>3</sub>P-CoP/CC.

Cu<sub>3</sub>P/CC, CoP/CC, and Cu<sub>3</sub>P–CoP/CC, the number of active sites was evaluated from the electrochemical active surface area (ECSA, see ESI,<sup>†</sup> for calculation details).<sup>40,41</sup> As shown in Fig. S3 (ESI<sup>†</sup>), Cu<sub>3</sub>P–CoP/CC achieves a higher TOF value of 1.34 s<sup>-1</sup> than Cu<sub>3</sub>P/CC (0.11 s<sup>-1</sup>) and CoP/CC (1.03 s<sup>-1</sup>) at an overpotential of 200 mV, implying the intrinsic efficient HER activity of Cu<sub>3</sub>P–CoP/CC. Both the Tafel slope and TOF results indicate that Cu<sub>3</sub>P–CoP nanowires can realize the maximum intrinsic HER activity due to the synergistic effects.

Mass-normalized polarization curves for both the electrodes (Fig. S4, ESI<sup>†</sup>) show that  $Cu_3P$ -CoP/CC demands an overpotential of 76 mV for 10 mA mg<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 30 and 138 mV less than that for CoP/CC and Cu<sub>3</sub>P/CC, respectively. It suggests that the intrinsic HER catalytic activity of Cu<sub>3</sub>P-CoP/CC is also superior over CoP/CC and Cu<sub>3</sub>P/CC. In order to further illustrate the superior HER performance of Cu<sub>3</sub>P-CoP/CC, the catalytic kinetics was examined by electrical impedance spectroscopy (EIS). Compared with Cu<sub>3</sub>P/CC and CoP/CC, Cu<sub>3</sub>P-CoP/CC shows the smallest semicircle in the Nyquist plot, indicating the lowest charge-transfer resistance and superior charge transport kinetics (Fig. S5, ESI<sup>†</sup>).<sup>42</sup> According to the above results, we conclude that the synergistic effect is the critical factor for Cu<sub>3</sub>P-CoP/CC to achieve superior catalytic performance.

In summary, a Cu<sub>3</sub>P–CoP hybrid nanowire array has been developed on CC as a superior and durable HER electrocatalyst in acidic electrolytes, requiring an overpotential of 59 mV to drive a current density of 10 mA cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Its excellent electrocatalytic performance is mainly attributed to the synergistic effect between Cu<sub>3</sub>P and CoP with atomic and electric coupling. This work not only offers us an attractive earth-abundant catalyst material in water-splitting devices for large-scale production of hydrogen fuels, but also provides a new method for the rational design and development of Cu<sub>3</sub>P-based catalysts with enhanced HER activity.

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### Conflicts of interest

There are no conflicts to declare.

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