

1 **High-performance Bifunctional hollow structures Cobalt-based**
2 **Phosphides Catalysts for Water Splitting**

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21 **Abstract**

22 Cobalt phosphides electrocatalysts have great potential for water splitting, but
23 the unclear active sites hinder the further development of cobalt phosphides. Wherein,
24 cobalt phosphides hollow structure (CoP-HS, CoP₂-HS and CoP₃-HS) catalysts based
25 on same sacrificial template were prepared. Surprisingly, these cobalt phosphides
26 exhibited similar OER but quite different HER performances. The identical OER
27 performance of these CoP_x-HS in alkaline solution were attributed to the similar
28 surface reconstruction to CoOOH. CoP-HS exhibited the best catalytic activity for
29 HER among these CoP_x-HS, originating from the adjusted electronic density of
30 phosphorus to affect absorption-desorption process on H. Moreover, CoP-HS
31 displayed good performance (cell voltage of 1.47 V at a current density of 10 mA
32 cm⁻²) and high stability in 1 M KOH. This work could provide the guidance for the
33 future investigations on transition metal phosphides for water splitting from material
34 design to mechanism understanding.

35

36 **1. Introduction**

37 Hydrogen will almost certainly play a role in future renewable energy plans.^{1,2}
38 Generation of hydrogen by sustainable electrochemical processes from water is an
39 appealing strategy.^{3,4} Electrochemical water splitting involves two reactions: the
40 cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction
41 (OER). Presently, platinum (Pt) and noble metal oxides, including ruthenium dioxide
42 (RuO₂) and iridium dioxide (IrO₂), are the state-of-the-art electrocatalysts to drive
43 HER and OER, respectively.⁵ Nevertheless, the scarcity and associated high costs of
44 these noble metals severely restrict their large scale application.⁶ Hence, the lower
45 product cost, tolerance of catalysts working conditions for both reactions, the
46 development of bifunctional catalysts, free from Pt-group metals, has gained
47 increasing attention.^{7,8,9}

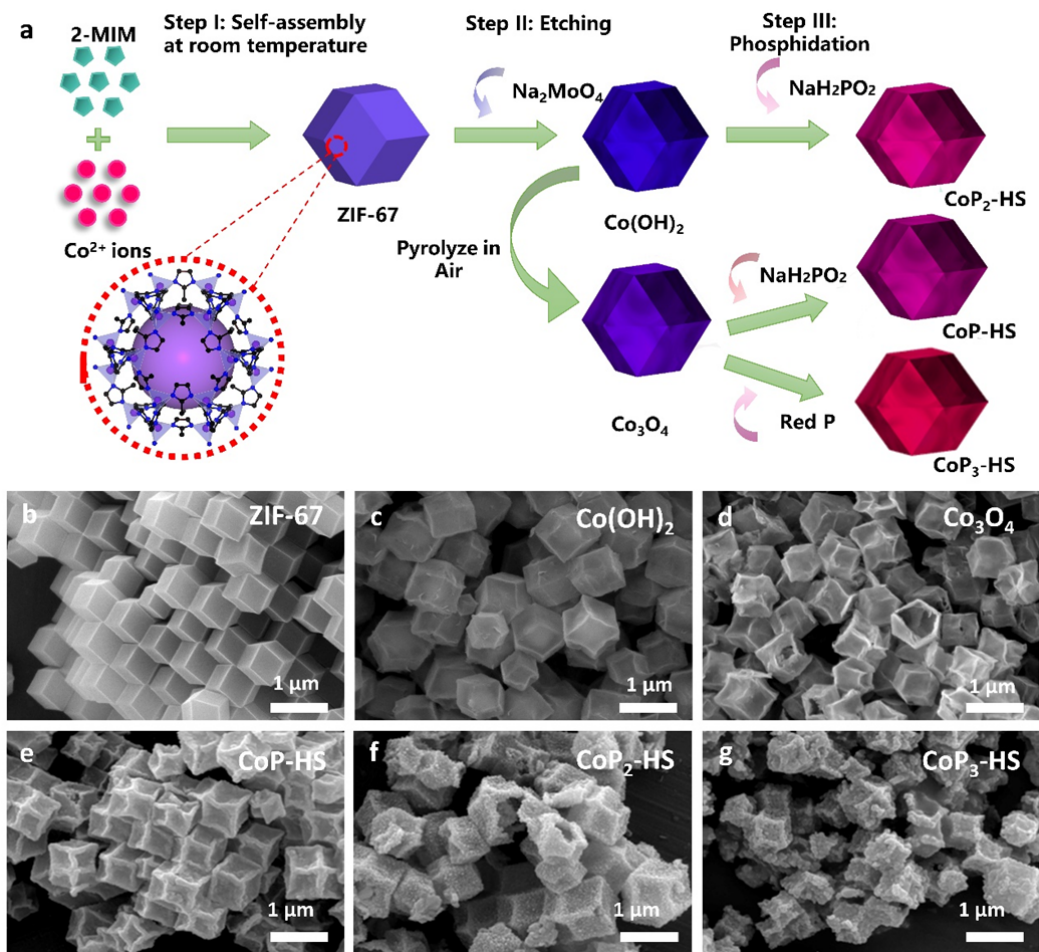
48 Different transition metal-based catalysts have been explored as bifunctional
49 catalysts for electrochemical water splitting, such as oxides, hydroxides, borides,
50 selenides, nitrides and so on.^{10,11,12,13} Among these nonprecious metal electrocatalysts,
51 transition metal phosphides (TMPs) are considered as the promising alternatives
52 catalyst for both HER and OER. In particular, cobalt phosphides have attracted the
53 most attention due to their high catalytic activity and durability in alkaline solution.¹⁴
54 For instance, Yoo and co-workers reported that porous CoP nanoparticles exhibit good
55 HER and OER activities owing to the increase of the accessible catalytic active
56 sites.¹⁵ However, the poor conductivity, unclear active sites and low reaction kinetics
57 hinder the practical use of cobalt phosphides.

58 To further improve electrochemical performance of TMPs, two approaches have
59 been proposed: (1) Rational design of nanostructures to increase the number of
60 exposed active sites and promote ion transport, such as nanoneedle, nanosheet,
61 core-shell and hollow nanostructure.^{16,17,18,19} Among those, hollow nanostructured
62 catalysts materials have attracted a lot of research interests, because the high
63 surface-to-volume ratio, low density and small transmission lengths of mass and
64 charge.²⁰ For example, compared with Ni–Co–P nanosheets, the Ni–Co–P hollow
65 nanobricks are demonstrated as the more efficient bifunctional electrocatalysts for
66 overall water splitting with a potential of 1.62 V to reach the current density of 10 mA
67 cm^{-2} .²¹ (2) Understanding of active sites in cobalt phosphides. The mechanism of
68 water splitting on cobalt phosphides is still under debate due to the complicate phase
69 and structure change and unclear active sites. Some studies announced that the cobalt
70 phosphides are stable during OER cycling.^{22,23,24} Others believe that cobalt
71 phosphides transform to oxide/oxyhydroxide during OER.²⁵ Besides, cobalt
72 phosphides have various stoichiometries, such as Co_2P , CoP , CoP_2 and CoP_3 .

73 In this work, based on the same ZIF-67 sacrificial template, a series of cobalt
74 phosphides with a similar, hollow morphology were synthesized. The resulting
75 catalyst exhibits similar nanocages with a porous structure. Interestingly, the different
76 cobalt phosphides showed similar OER performance but different HER performance.
77 In-depth structural characterizations and electrochemical studies show that the
78 different cobalt phosphides convert during OER to the active catalyst. After cycling in
79 alkaline solution, the active surface for all catalysts becomes oxyhydroxide which had

80 a similar activity with an overpotential of 270~280 mV at a current density of 10 mA
81 cm^{-2} for OER. On the contrary, all the cobalt phosphides with hollow structures
82 remained stability during HER test. Among these catalysts, CoP-HS nanocages
83 showed the best catalytic activity for HER with an overpotential of -116 mV which
84 could be the catalytically active sites for HER at a current density of -10 mA cm^{-2} in 1
85 M KOH. Density functional theory (DFT) computation revealed that the P-sites in
86 $\text{CoP}_x\text{-HS}$ are the primary catalytically active site for HER, and the calculated ΔG_{H^*}
87 based on P-sites of CoP-HS agrees well with the corresponding normalized HER
88 performances. When CoP-HS//CoP-HS were used for water splitting, a current
89 density of 10 mA cm^{-2} is achieved at a remarkably low cell voltage of 1.47 V, which is
90 due to the hollow structure of the catalysts and the high activity of the P-sites in CoP.

91 **2. Results and discussion**

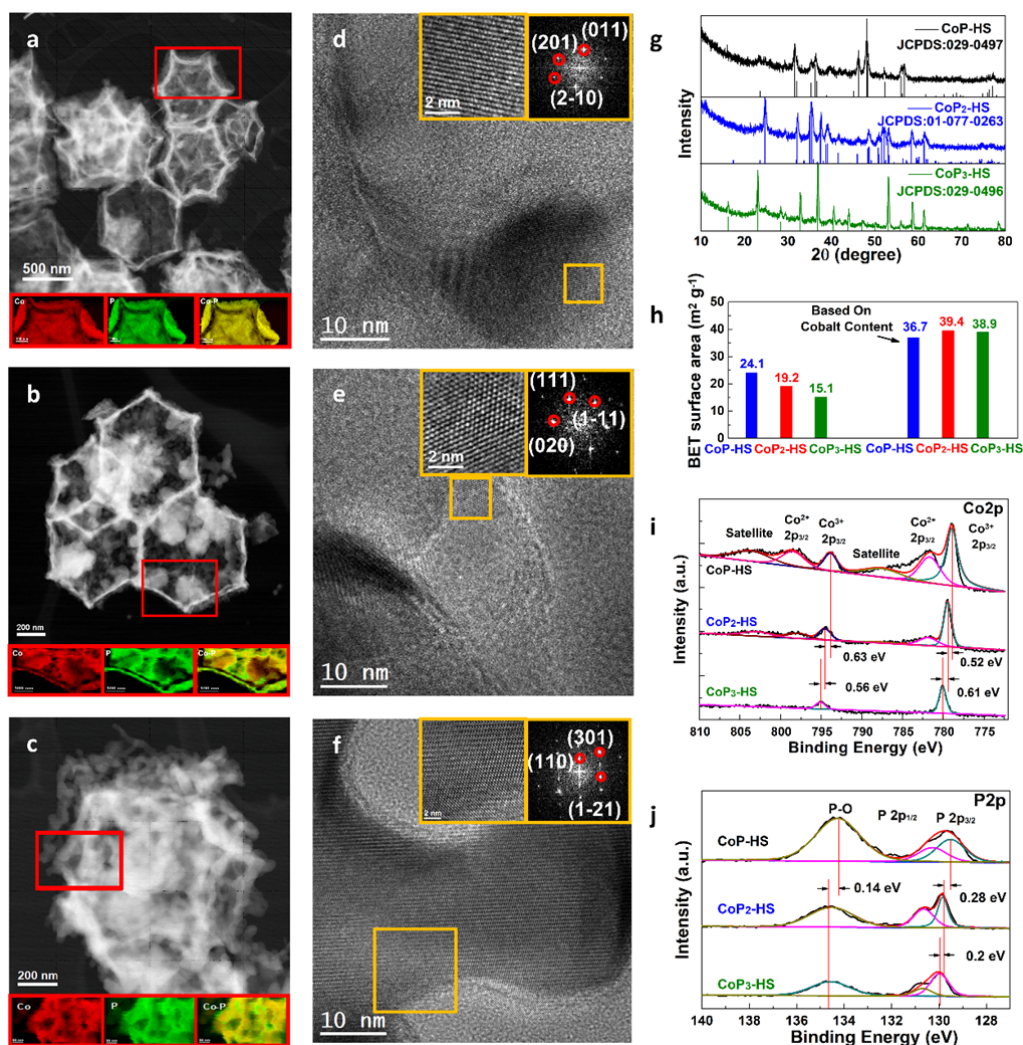


92
 93 **Figure 1.** (a) Schematic illustration of the synthesis process of hollow cobalt phosphides
 94 nanocages. SEM images of pure ZIF-67 (b), $\text{Co}(\text{OH})_2$ (c), Co_3O_4 (d), CoP-HS (e), $\text{CoP}_2\text{-HS}$ (f)
 95 and $\text{CoP}_3\text{-HS}$ (g).

96 The synthesis process of the three different cobalt phosphides nanocages are
 97 shown in **Figure 1a**. In order to ensure the same morphology for all CoP_x catalysts
 98 were synthesized based on the same ZIF-67 sacrificial template. The rhombic
 99 dodecahedral ZIF-67 particles are shown in **Figure S1a**. Next, the ZIF-67 particles
 100 were converted into hollow $\text{Co}(\text{OH})_2$ structures by the reaction of with an aqueous

101 Na_2MoO_4 solution based on the Kirkendall effect.^{26,27} Co_3O_4 nanocages were
102 fabricated by annealing the hollow $\text{Co}(\text{OH})_2$ particles at 500 °C in air. Subsequently,
103 the hollow $\text{Co}(\text{OH})_2$ and Co_3O_4 particles were annealed together with NaH_2PO_2 in N_2
104 atmosphere together at 700 °C, resulting in the formation of hollow CoP_2 particles
105 (named $\text{CoP}_2\text{-HS}$) and hollow CoP particles (named CoP-HS), respectively. Hollow
106 CoP_3 particles (named $\text{CoP}_3\text{-HS}$) was prepared by annealing Co_3O_4 particles with red
107 phosphorus in N_2 at 700 °C. As shown in **Figure 1b**, the prepared rhombic
108 dodecahedron shape ZIF-67 particles exhibited a uniform particle size of
109 approximately 800 nm and perfectly flat facets. The X-ray diffraction (XRD) pattern
110 of ZIF-67 matched well with the simulated pattern (**Figure S1a**), which demonstrates
111 the purity of the starting phase. It clearly shows that during these transformations, the
112 initial morphology and particle size of ZIF-67 is preserved (**Figure 1c&1d**). Because
113 the structure was transformed from solid to hollow, the surface of the $\text{Co}(\text{OH})_2$ and
114 Co_3O_4 nanocages becomes wrinkled and protuberance-like. The formation of hollow
115 structure of $\text{Co}(\text{OH})_2$ and Co_3O_4 can be identified from several broken samples. XRD
116 pattern presented in **Figure S1b** shows the presence of both $\alpha\text{-Co}(\text{OH})_2$ and
117 $\beta\text{-Co}(\text{OH})_2$ in the prepared $\text{Co}(\text{OH})_2$. As shown in **Figure S1c**, the diffraction pattern
118 of the Co_3O_4 is in good agreement with the standard pattern of Co_3O_4 (JCPDS 1-1152)
119 powder. The uniform distribution of Co and P in the synthesized Co_3O_4 was proven by
120 the energy-dispersive X-ray (EDX) (**Figure S2**). After phosphidation, the three cobalt
121 phosphides have the original polyhedron shape of the ZIF-67 precursor. The diameters
122 of these particles are in the range of 600 to 800 nm. As shown in **Figure S3**, the

123 overlap of P and Co elements in SEM-EDS mapping confirms the homogeneous
 124 formation of all three cobalt phosphides (CoP-HS, CoP₂-HS, and CoP₃-HS).



125
 126 **Figure 2.** TEM images of CoP-HS (a), CoP₂-HS (b) and CoP₃-HS (c). EELS chemical
 127 composition maps of CoP-HS (a), CoP₂-HS (b) and CoP₃-HS (c) obtained from area inside the red
 128 square on the HAADF STEM micrograph. Individual Co L_{2,3}-edges at 779 eV (red), P
 129 L_{2,3}-edges at 132 eV (green) and composite of Co-P. HRTEM images and corresponding indexed
 130 power spectra (FFT) of CoP-HS showing a CoP orthorhombic crystal with Pnma phase along its
 131 [12-2] axis (d), CoP₂-HS showing a CoP₂ monoclinic crystal with P2₁/C phase along its [10-1]
 132 axis (e) and CoP₃-HS showing a CoP₃ cubic crystal with Im3 phase along its [-113] axis (f). (h)
 133 BET surface area of CoP-HS, CoP₂-HS and CoP₃-HS based on cobalt content. (g) XRD patterns of

134 CoP-HS, CoP₂-HS, and CoP₃-HS. XPS spectra of Co 2p (i) and P 2p (j) for CoP-HS, CoP₂-HS and
135 CoP₃-HS.

136 The well-defined nanocage-shaped structure and particle sizes (range from 600
137 nm to 800 nm) of the three cobalt phosphides are also confirmed by transmission
138 electron microscopy (TEM) images (**Figure 2**). The EELS chemical composition
139 maps of the three cobalt phosphides were obtained from the region inside the red
140 square in the HAADF STEM micrograph, shown in **Figure 2a-c**, for CoP-HS,
141 CoP₂-HS, and CoP₃-HS, respectively. As can be seen in these maps, Co and P are
142 uniformly distributed in the selected nanostructure. But the P signal is stronger in
143 CoP₂-HS and CoP₃-HS. A HRTEM micrograph was taken from the nanoparticle
144 inside the orange square (**Figure 2d**). Details of this region and its corresponding
145 power spectrum reveals that this nanoparticle has a crystal phase that is in agreement
146 with the CoP-HS orthorhombic phase (space group = Pnma) with $a=5.0760 \text{ \AA}$,
147 $b=3.2770 \text{ \AA}$ and $c=5.5990 \text{ \AA}$. From the crystalline domain in **Figure 2d**, the CoP-HS
148 lattice fringe distances are 0.286 nm, 0.237 nm, and 0.199 nm, at 78.95° and 122.43°
149 which correspond to the orthorhombic CoP phase, visualized along its [12-2] zone
150 axis. For the CoP₂-HS sample, a HRTEM micrograph was taken from the nanoparticle
151 inside the orange square (**Figure 2e**). Details of this region and its corresponding
152 power spectrum, reveals that this nanoparticle has a crystal phase that is in agreement
153 with the CoP₂-HS monoclinic phase (space group = P21/C) with $a=5.5510 \text{ \AA}$,
154 $b=5.5490 \text{ \AA}$ and $c=5.6140 \text{ \AA}$. From the crystalline domain in **Figure 2e**, the CoP₂-HS
155 lattice fringe distances are 0.277 nm, 0.272 nm, and 0.281 nm, at 60.83° and 121.60°

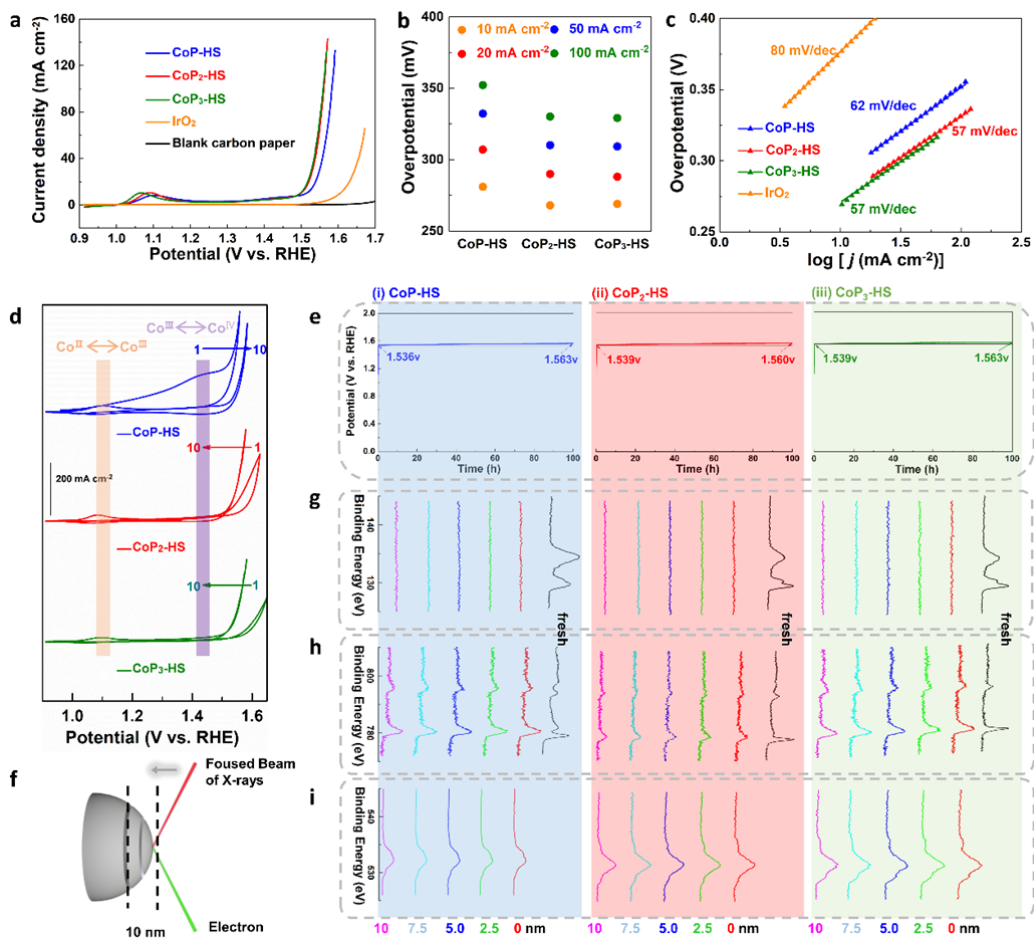
156 which correspond to the monoclinic CoP₂-HS phase, visualized along its [10-1] zone
157 axis. As illustrated in **Figure 2f**, the CoP₃-HS cubic phase (space group = Im3) with
158 a=b=c=7.7112 Å can be proven from the corresponding power spectrum from a
159 HRTEM micrograph taken from the nanoparticle inside the orange square. The
160 CoP₃-HS lattice fringe distances (**Figure 2f**) are 0.553 nm, 0.243 nm, 0.313 nm and
161 0.313 nm, at 46.97°, 72.21° and 106.50° which could be interpreted as the cubic
162 CoP₃-HS phase, visualized along its [-113] zone axis.

163 The crystalline structures and successful phosphidation process of these samples
164 are also confirmed by the XRD (**Figures 2g**). The experimental XRD patterns match
165 well with corresponding standard three cobalt phosphide crystal structures (ICDD
166 PDF: 029-0497 for CoP-HS, ICDD PDF: 01-077-0263 for CoP₂-HS and ICDD PDF:
167 029-0496 for CoP₃-HS) without unidentified peaks. These results indicate that the
168 Co(OH)₂ and Co₃O₄ were completely converted into the intended cobalt phosphides.
169 The Brunauer-Emmett-Teller (BET) specific surface area and pore size distributions
170 of the as-synthesized three cobalt phosphides were determined by N₂ sorption
171 experiments. The N₂ adsorption-desorption isotherms and Barrett-Joyner-Halenda
172 (BJH) pore-size distribution of CoP-HS, CoP₂-HS and CoP₃-HS nanocages are shown
173 in **Figure S4**. All of the cobalt phosphides show a type-IV isotherm loop, which
174 indicates the mesoporous characteristics of the materials. For the three cobalt
175 phosphides, the major pore size distributions are displayed at a region of 1.5 to 3.0 nm.
176 Moreover, BET surface areas of CoP-HS, CoP₂-HS and CoP₃-HS are 24.1, 19.2 and
177 15.1 m² g⁻¹ (**Figure 2h**), respectively. With increasing phosphorus content, the

178 specific surface area decreased. Interestingly, after normalizing the specific surface
179 areas to the mass of cobalt, the normalized specific surface areas of all three cobalt
180 phosphides are similar (**Figure 2h**). This phenomenon can be explained by the same
181 self-sacrificing template was used. All these results prove that the successful synthesis
182 of three different cobalt phosphides (CoP-HS, CoP₂-HS and CoP₃-HS) with similar
183 structure and morphology by the presented top-down strategy.

184 X-ray photoelectron spectroscopy (XPS) is used for the analysis of chemical
185 state and the overall electronic structure of these catalysts. As shown in **Figure S5**, the
186 XPS survey spectrums of three cobalt phosphides reveal the existence of Co and P.
187 The Co 2p spectra of the CoP-HS (**Figure 2i**) is deconvoluted into six peaks, which
188 binding energies located at 778.9, 793.8, 787.6 eV that can be assigned to Co 2p_{3/2},
189 and binding energies located at 781.7, 798.5, 803.8 eV that can be assigned to Co 2p_{1/2}.
190 Among them, the peaks centered at 787.6 and 803.8 eV are the satellite peaks of 2p_{2/3}
191 and 2p_{1/2}, respectively. The binding energy at 778.9 and 793.8 eV can be attributed to
192 Co³⁺, and those located at 781.7 and 798.5 eV belong to Co²⁺. Compared with CoP,
193 the Co 2p peaks in CoP₂-HS and CoP₃-HS shifted to a higher binding energy. The
194 main reason of this shift is due to the higher P content in CoP₂-HS and CoP₃-HS. A
195 higher concentration of electronegative phosphorus shifts the peaks of Co³⁺ to higher
196 binding energies. In addition, compared to the Co²⁺ peaks in the three cobalt
197 phosphides, there is a gradual decrease in the peak intensities from CoP-HS to
198 CoP₃-HS. In the P 2p spectrum of CoP-HS (**Figure 2j**), the peaks located at 129.5,
199 130.3 and 134.2 eV are indexed to P 2p_{3/2}, P 2p_{1/2} in cobalt phosphide and surface

200 oxidation of P, respectively.²⁸ Compared with CoP₃-HS, the peaks of CoP-HS and
 201 CoP₂-HS in P 2p_{3/2}, P 2p_{1/2} region shifted to lower binding energy. The negative shift
 202 of P 2p binding energy, induced by changing cobalt-phosphorus composition, shows
 203 the enhanced electron occupation, which can give rise to the improvement of the
 204 electron-donating ability of the catalyst.²⁹



205
 206 **Figure 3.** (a) The LSV curves of CoP-HS, CoP₂-HS, CoP₃-HS, IrO₂ and carbon paper measured in
 207 1.0 M KOH solution toward OER at a scan rate 10 mV/s after activation by 50 CV cycles between
 208 0.0 V and 0.85 V (vs. Hg/HgO) at a scan rate 50 mV/s. (b) The data of CoP-HS, CoP₂-HS and
 209 CoP₃-HS at different current density. (c) The corresponding Tafel plots for the samples. (d) The
 210 CV curves obtained at the 1st and 10th cycles at a scan rate of 10 mV/s in a 1.0 M KOH solution.
 211 (e) The potential of CoP-HS, CoP₂-HS and CoP₃-HS versus time at a current density of 20 mA

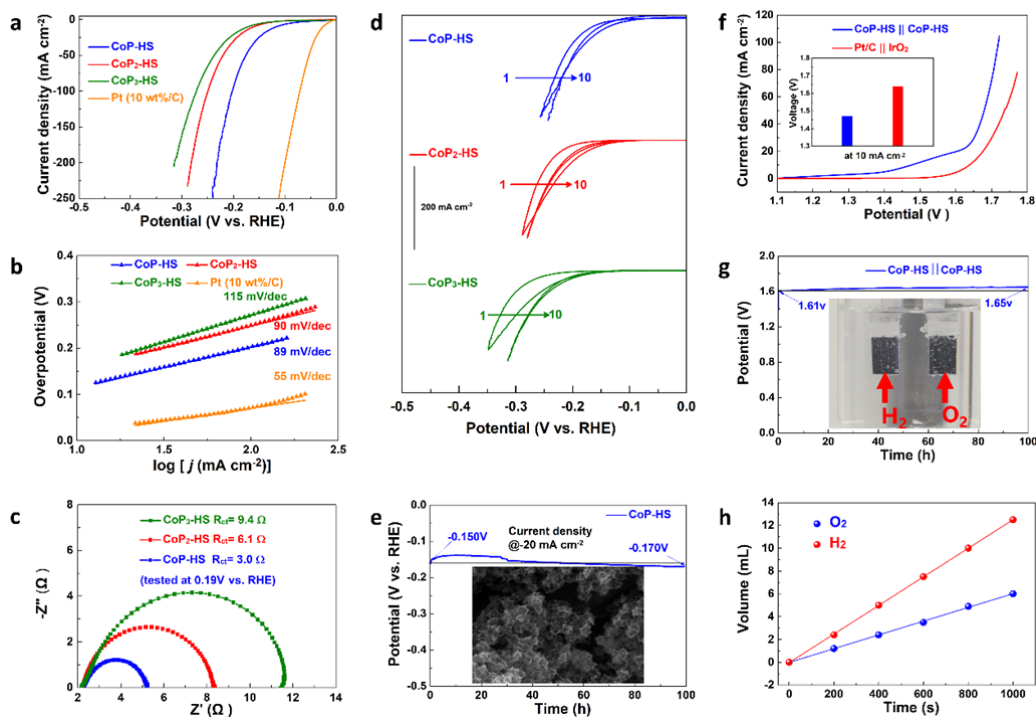
212 cm^{-2} in 1.0 MKOH. (All the tests were taken on carbon paper). (f) The schematic of surface
213 composition investigation via XPS in different depths after ion beam etching. (g) High-resolution
214 P 2p XPS spectra of the fresh CoP-HS, fresh CoP₂-HS, fresh CoP₃-HS and post-OER samples. (h)
215 High-resolution Co 2p XPS spectra of fresh CoP-HS, fresh CoP₂-HS, fresh CoP₃-HS and
216 post-OER sample. (i) High-resolution O 1s XPS spectra of the post-OER CoP-HS, post-OER
217 CoP₂-HS and post-OER CoP₃-HS samples.

218 Cobalt based phosphides are considered as promising bifunctional catalysts for
219 both HER and OER. Firstly, the electrocatalytic OER performance of three cobalt
220 phosphides were examined in 1.0 M KOH using a three-electrode system and
221 different electrodes were prepared by coating carbon paper with approximately 1 mg
222 cm^{-2} of catalyst. The active site of cobalt based phosphides for OER is still on debate.
223 Even though, cobalt based phosphides have been reported as catalysts for OER,^{23,24,30}
224 the structure and phase changes occurring during OER tests cannot be ignored. To
225 investigate the phase changes of three cobalt phosphides, the CV curves of three
226 cobalt phosphides at the 1st, 3rd, 5th, and 10th cycle were measured. As illustrated in
227 **Figure 3d&S6**, at the 1st cycle, the OER performance of CoP-HS seems better than
228 CoP₂-HS and CoP₃-HS, which could be explained by unstable of CoP_x-HS system.
229 Furthermore, as the number of cycles increases, the OER performance of CoP₂-HS
230 and CoP₃-HS improves, while the OER performance of CoP-HS decreases. At the
231 10th cycle the CV curves of CoP-HS, CoP₂-HS and CoP₃-HS almost overlap.
232 Therefore, all catalysts were first activated by 50 CV cycles at a scan rate 50 mV/s
233 between 0.0 V and 0.85 V (vs. Hg/HgO). LSV with *iR*-correction are used for
234 evaluated the OER performances of these catalysts (**Figure 3a**). For the purpose of

235 comparison, The OER performances of commercial IrO₂ and bare carbon paper were
236 also investigated. As shown in **Figure 3a**, the CoP-HS requires an overpotential of
237 281 mV at a current density of 10 mA cm⁻². Similar performance of the CoP₂-HS and
238 CoP₃-HS catalysts can be achieved, which overpotentials of resp. 268 mV and 269
239 mV at a current density of 10 mA cm⁻². All these catalysts show better performance
240 than commercial IrO₂ (375 mV). Meanwhile, the bare carbon paper hardly shows any
241 electrocatalytic activity for OER even at high overpotential (**Figure 3a**). The
242 corresponding Tafel slopes are derived from plotting overpotential against log (j)
243 (**Figure 3c**). CoP₂-HS and CoP₃-HS exhibit a similar Tafel slope of 57~62 mV dec⁻¹.
244 The Tafel slope results suggest that CoP-HS, CoP₂-HS and CoP₃-HS have similar
245 charge transfer kinetics during OER. The electrochemical durability of the catalyst is
246 a key parameter for practical application. The electrocatalytic stability of different
247 cobalt phosphides electrodes were investigated by chronopotentiometry at a constant
248 current density of 20 mA cm⁻² (**Figure 3e**). The chronopotentiometry curves show that,
249 after 100 h, the catalytic activity of CoP-HS, CoP₂-HS and CoP₃-HS dropped by
250 6.5 %, 6.0% and 7.7%, respectively. This result suggests a good electrochemical
251 stability of all three cobalt phosphides for the OER in alkaline solution. At the cycling
252 tests, the three cobalt phosphides prepared in this paper show almost identical results
253 (1.563 V for CoP-HS, 1.560 V for CoP₂-HS and 1.563 V for CoP₃-HS, vs. RHE),
254 which indicates that the P composition does not influence the OER performance of
255 cobalt based phosphides in an alkaline medium. This could be caused by the
256 oxidization of the similar structure of CoP-HS, CoP₂-HS and CoP₃-HS surface during

257 the OER test. After the OER electrochemical durability test, SEM and EDS
258 measurements were conducted to characterize the morphologies and surface
259 compositions of the three cobalt phosphides. The SEM images show that the
260 morphology and structure of three cobalt phosphides are reasonably retained after
261 OER durability test (**Figure S7a-c**). But the surface composition of three cobalt
262 phosphides changes showing a loss of phosphorous after long-term OER durability
263 test in an alkaline medium (**Figure S7d**). This result is consistent with previous
264 papers. Metal-based materials, such as metal chalcogenides, metal pnictides and metal
265 carbides, are partly or completely transformed to oxides or (oxy) hydroxides under
266 sufficiently extended periods during alkaline OER testing^{22,31,32}. To further investigate
267 the post-OER electrodes, the XPS was used to analyze the electrodes. Combining a
268 sequence of ion gun etch cycles, more quantified vertical information and information
269 evolution with thicknesses was obtained by depth-profiling X-ray photoelectron
270 spectroscopy (**Figure 3f**). As shown in **Figure 3g**, the characteristic signals for
271 phosphorous almost completely disappears from the surface. As for cobalt, only two
272 broad peaks corresponding to oxidized cobalt species were observed on the surface
273 for all three cobalt phosphides after OER (**Figure 3h**), which is consistent with a
274 previous report on CoOOH.³³ To further validate the formation of CoOOH, the O/Co
275 peak area ratio of was calculated based on the XPS detection at the surface and the
276 result is about 2:1 (**Figure 3h&i**). Argon ion sputtering was applied to remove the
277 oxidized surface (2.5 nm/per step) of the three cobalt phosphides after OER and
278 measured again to observe the XPS signals of P 2p (**Figure 3g**), Co 2p (**Figure 3h**),

279 and O 1s (**Figure 3i**). However, XPS results remain unchanged, which indicate the
 280 complete transformation of the near surface region of all three cobalt phosphides (the
 281 active region) during OER durability test. This explains the similar OER
 282 performance after durability test. According to these results, the near surface region of
 283 all three cobalt phosphides transform via self-reconstruction into CoOOH. Therefore,
 284 P composition will not affect the OER performance in an alkaline medium. After the
 285 conversion into CoOOH, these catalysts have comparable or better OER activity than
 286 reported metal-based phosphides electrocatalysts as shown in **Table S1**.



287

288 **Figure 4.** (a) The LSV curves of CoP-HS, CoP₂-HS, CoP₃-HS and Pt/C measured in 1.0 M KOH
 289 toward HER at scan rate 10 mV/s. (b) The corresponding Tafel plots for the samples in 1.0 M
 290 KOH. (c) Nyquist plots of CoP-HS, CoP₂-HS and CoP₃-HS in 1.0 M KOH. (All the tests were
 291 taken on carbon paper). (d) The CV curves of CoP-HS, CoP₂-HS and CoP₃-HS measured in 1.0 M
 292 KOH solution for 1st and 10th cycles at a scan rate 10 mV/s. (e) The chronopotentiometry curve

293 of CoP-HS at the current density of -20 mA cm^{-2} for 100 h in 1 M KOH. The inset in (e) is the
294 SEM image of CoP-HS after 100 h HER stability measurement in 1 M KOH. (f) Overall water
295 splitting performance based on the CoP||CoP and Pt/C||IrO₂ electrodes in 1 M KOH. The inset in (f)
296 is the potential of CoP||CoP and Pt/C||IrO₂ at a current density of -10 mA cm^{-2} . (g) Long-term
297 durability test of CoP in the two-electrode electrolyzes at 20 mA cm^{-2} for overall water splitting.
298 The inset in (g) is optical image during the overall water splitting. (h) Amount of H₂ and O₂ as a
299 function of time.

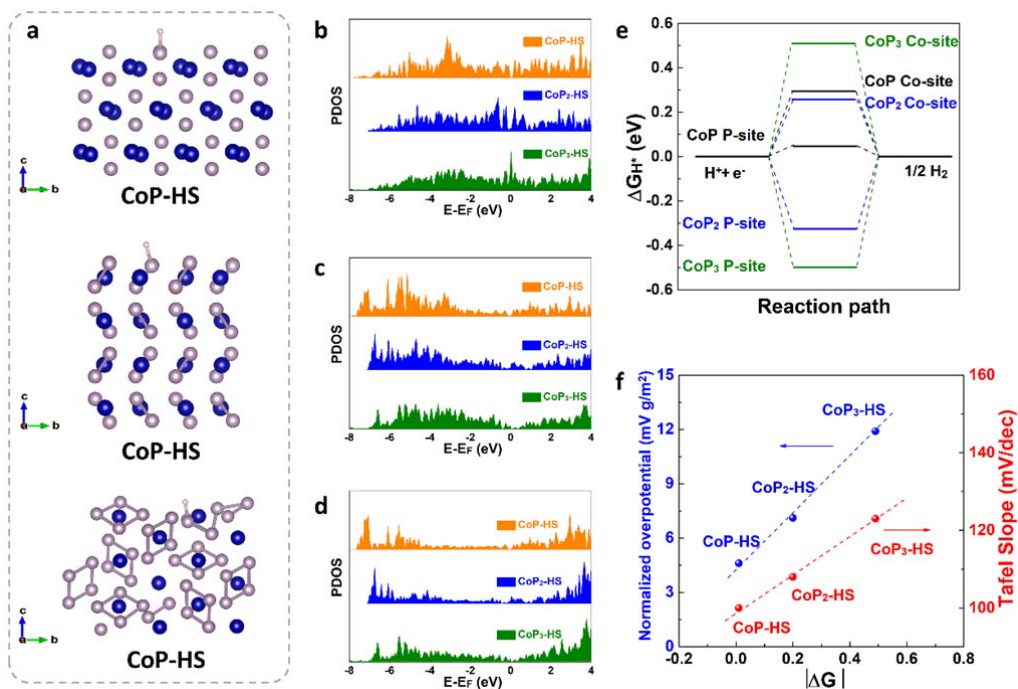
300 On the contrary, the catalytic process of cobalt based phosphides for HER is
301 different from OER. Based on previous studies, the P sites in cobalt phosphides could
302 be the active site for HER. To investigate the HER activity of three cobalt phosphides,
303 LSV curves after CV scans in 1.0 M KOH were recorded at a scan rate of 10 mV/s,
304 and all the curves were IR corrected (**Figure 4a**). As expected, the HER activity of
305 bare carbon paper is negligible (**Figure S8a**), and the Pt/C exhibits the best activity
306 with an overpotential of 25 mV at the current density of -10 mA cm^{-2} . 116 mV is
307 required for the CoP-HS to achieve the current density of -10 mA cm^{-2} , which is much
308 lower than that of CoP₂-HS (159 mV) and CoP₃-HS (170 mV). The Tafel plots
309 derived from the LSV polarization curves are displayed to estimate the reaction
310 kinetics. As expected, the Tafel slope of commercial Pt/C is 34 mV dec^{-1} (**Figure 4b**),
311 which is consistent with the reported value.³⁴ The Tafel slope of CoP-HS, CoP₂-HS
312 and CoP₃-HS is 89, 90, and 115 mV dec^{-1} , respectively. According to literature, the
313 HER occurs through three different individual steps, which are named Volmer,
314 Heyrovsky, and Tafel reaction.³⁵ The Tafel values of three cobalt phosphides indicate
315 that a Volmer-Heyrovsky reaction, which happens on the surface of catalysts, is the

316 rate-determining step. Moreover, electrochemical impedance spectroscopy was used
317 to investigate the electron transfer kinetics during the HER process. As shown in
318 **Figure 4c**, the Nyquist plots of different catalysts are measured at -0.19 V. The inset
319 in **Figure 4c** displays the equivalent circuit model. The intersection of the plots on the
320 real axis represents the solution resistance (R_s) and the diameter of the semi-circle
321 represents the charge transfer resistance (R_{ct}) across the electrode-solution interface,
322 respectively.³⁶ CoP-HS possesses the smallest R_{ct} value.³⁷ The phase and
323 electrochemical stability of the three cobalt phosphides during HER are investigated
324 in the same way as in the OER experiments. Firstly, the CV curves of three cobalt
325 phosphides at the 1st, 3rd, 5th, and 10th cycles were conducted. As illustrated in
326 **Figure 4d&S9**, after 3 CV cycles, the CV curves of the three cobalt phosphides
327 display only minor changes, which indicates that three cobalt phosphides reach a
328 stable electrochemical state in a short period of time. Overall, CoP-HS is always
329 displaying the best HER performance in three cobalt phosphides. It could be
330 explained by XPS that the bonding energy of P 2p negatively shifted with the decrease
331 of P concentration in cobalt phosphides (CoP-HS <CoP₂-HS <CoP₃-HS), indicating
332 the enhanced electron occupation to improve the electron-donating ability.²⁹
333 Chronopotentiometry was conducted to evaluate the stability of these catalysts. After
334 100 hours durability test, CoP retained good catalytic activity with a 17% decrease in
335 potential (**Figure 4e**). After 100 hours of OER, SEM, XPS, and SEM-EDX were used
336 to investigate the morphology, structure and composition of CoP-HS (**Figure**
337 **4e&S10**). As shown in the SEM images, the CoP-HS preserves its morphological

338 integrity (inset of **Figure 4e**). Based on the XPS results (**Figure S10a**), phosphorous
339 can be clearly detected after HER test, which is different to the situation for OER
340 (**Figure 3g**). Moreover, the chemical composition analyzed by SEM-EDS chemical
341 mapping shows that the atomic ratio of Co/P is close to 1.3 (**Figure S10b**), which
342 indicates the stability of CoP-HS during HER test in alkaline medium. All these
343 results prove that CoP-HS shown high stability for HER. Compared with recent
344 reports, the HER performance of CoP-HS is comparable or better than most cobalt
345 based HER electrocatalysts in alkaline solution (**Table S2**). In view of the stability of
346 the three cobalt phosphides in acid solution, the HER activity of CoP-HS, CoP₂-HS
347 and CoP₃-HS were also explored in 0.5 M H₂SO₄ (**Figure S11**). Similar results to the
348 HER in alkaline solution are achieved in that CoP-HS was still the best catalysts
349 (**Figure S12**) and comparable to other CoP catalysts reported in literature (**Table S3**).
350 The electrochemical stability of these three cobalt phosphides during HER in acid
351 solution were investigated via CV test at various cycles (**Figure S13**), and 100 hours
352 stability test at the current density of -20 mA cm⁻² in 0.5 M H₂SO₄ (**Figure S14a**).
353 Finally, the high stability on phase structure of CoP-HS in acid solution was proven
354 via SEM, XPS, and SEM-EDS of the CoP-HS after 100 hours HER stability
355 measurement (**Figure S14b-d**).

356 According to the above results, the CoP-HS electrocatalyst was used as both
357 anode and cathode for water splitting in a two-electrode configuration in 1.0 M KOH
358 at 25°C. As shown in **Figure 4f**, a current density of 10 mA cm⁻² is achieved at a
359 remarkably low cell voltage of 1.47 V, which is better than that of the benchmark

360 Pt/C||IrO₂ system with the same mass loading. Compared with literature, the water
361 splitting performance of CoP-HS is comparable or better than most of the cobaltbased
362 water splitting electrocatalysts in alkaline solution (**Table S4**). The long-term
363 operational stability of the CoP-HS||CoP-HS system was evaluated by
364 chronopotentiometry test at a current density of 20 mA cm⁻². After 100 h, almost no
365 degradation can be observed, indicating the stability of the CoP-HS||CoP-HS for
366 alkaline water electrolysis (**Figure 4g**). The H₂ and O₂ generated from the alkaline
367 electrolyzer were quantitatively collected by the water drainage method and displayed
368 in **Figure S15**. The volume–time curve in **Figure 4h** reveals a volume ratio of 2.07:1
369 for the collected H₂ to O₂, which approaches the theoretical 2:1 ratio for water
370 electrolysis. Based on the measured volume ratio, the Faradaic efficiency is estimated
371 to be ≈100% by considering the airtightness of the device. All these results
372 demonstrate that the prepared CoP-HS bifunctional catalyst is a promising candidate
373 catalyst for alkaline water electrolysis.



374

375 **Figure 5.** (a) Optimized configurations of CoP-HS, CoP₂-HS and CoP₃-HS for the DFT
 376 calculation. (b) Projected density of states (PDOS) plots of P 3p orbitals. (c) PDOS plots of P 3p
 377 orbitals in CoP-HS, CoP₂-HS and CoP₃-HS when H was adsorbed. (d) PDOS plots of H 1s orbitals
 378 in CoP-HS, CoP₂-HS and CoP₃-HS when H was adsorbed. (e) HER free energy changes of
 379 CoP-HS, CoP₂-HS and CoP₃-HS at P-sites and Co-sites. (f) The correlation between the HER free
 380 energy changes based on P-sites of CoP_x-HS and the normalized overpotential as well as Tafel
 381 slope.

382 In order to gain insights into the electrocatalytic HER activity of the CoP-HS,
 383 CoP₂-HS and CoP₃-HS, DFT calculations were performed. According to the XRD and
 384 TEM results, the selected configurations of CoP-HS, CoP₂-HS and CoP₃-HS are
 385 shown in **Figure 5a** based on stable facets. As P was determined as the active center
 386 in all three cobalt phosphides system, the difference of electronic structure on P of the
 387 parent CoP_x-HS were investigated via DFT (**Figure 5b**). As shown in the **Figure 5b**,
 388 it could be observed that the energy shift upwards with P composition increasing in

389 CoP_x-HS system, which indicates that CoP₃-HS has the strongest covalent interaction
390 between Co and P. The difference in electronic structure of CoP-HS, CoP₂-HS, and
391 CoP₃-HS can affect the electron transfer process during electrocatalytic reactions.
392 Moreover, the interaction effects on surface adsorbents of three cobalt phosphides
393 display the trend of CoP-HS <CoP₂-HS <CoP₃-HS, which means that CoP₃-HS has
394 the strongest H adsorption. After H adsorption, a significant rearrangement of
395 electrons in CoP_x-HS could be observed in P 3p (**Figure 5c**) compared with their
396 corresponding parent CoP_x-HS (**Figure 5b**). Similarly, CoP-HS is the best catalyst in
397 the CoP_x-HS for desorption process with the most negative position on electronic
398 distribution. The calculation results of PDOS of H 1s on three cobalt phosphides agree
399 well with the PDOS of P 3p (**Figure 5d**). When H is adsorbed on the surface, the P 3p
400 orbital shifts downwards in all three cobalt phosphides, but especially in CoP-HS,
401 leading to more filled antibonding states of the H 1s orbital and hence resulting in a
402 weakened H-P bond, which is beneficial for the desorption of H₂. To understand the
403 effect of changes from the electronic structure in three cobalt phosphides on HER, the
404 free energy of hydrogen chemisorption on the surface of the selected CoP-HS,
405 CoP₂-HS and CoP₃-HS configurations were calculated by DFT. Details of the possible
406 configurations of CoP_x-HS are given in **Figure S16-18**, with the corresponding
407 calculated ΔG_{H^*} values in **Figure S19**. As shown in **Figure 5e**, the final ΔG_{H^*} values
408 of CoP_x-HS from optimized configurations on Co- and P-sites are 0.24 eV and 0.01
409 eV for CoP-HS, 0.23 eV and -0.32 eV for CoP₂-HS and 0.44 eV and -0.50 eV for
410 CoP₃-HS, respectively. Generally speaking, a smaller ΔG_{H^*} will translate into a better

411 HER activity.³⁸ To understand the intrinsic correlation between P-sites/Co-sites in
412 CoP_x-HS and HER activity, the normalized LSV curves of CoP_x-HS in 1.0 M KOH
413 toward HER were calculated (**Figure S20**). As shown in **Figure 5f**, the calculated
414 ΔG_{H^*} based on P-sites of CoP_x-HS follows a quite similar trend with the normalized
415 overpotential and Tafel slope, indicating the important role of P-sites on the surface of
416 CoP_x for the HER process. Meanwhile, no significant correlation exists between
417 Co-sites and the HER performance (normalized overpotential and Tafel slope) for the
418 CoP_x-HS system (**Figure S21**). Therefore, it is likely that the surface
419 absorption/desorption capacity on P-sites of CoP_x-HS is the intrinsic rate-determining
420 factor for the HER process.

421 **3. Conclusions**

422 ZIF-67 MOF was used to synthesize porous CoP-HS, CoP₂-HS and CoP₃-HS
423 nanocages. As confirmed by experimental results, the cobalt phosphides work as
424 pre-catalyst for OER rather than as the active materials. After cycling in alkaline
425 solution, the near surface region of all three Co-phosphides transformed to
426 oxyhydroxide, resulting in identical OER performance after cycling. On the contrary,
427 the different cobalt phosphides exhibited a high stability and clear different catalytic
428 activities for the HER. CoP-HS nanocages showed the best catalytic activity for HER
429 with an overpotential of -116 mV at a current density of -10 mA cm⁻² in 1 M KOH.
430 Based on density functional theory (DFT) calculations, the calculated ΔG_{H^*} on P-sites
431 were lower than those on Co-sites in CoP_x-HS system. Moreover, the calculated ΔG_{H^*}

432 based on P-sites of CoP-HS follows a quite similar trend with the normalized
433 overpotential and Tafel slope, indicating the important role of P-sites for the HER
434 process. Moreover, no significant correlation between Co-sites and the HER
435 performance (overpotential and Tafel) for all the CoP_x-HS was found. This indicates
436 that the P-sites are probably the catalytically active sites for HER. When
437 CoP-HS//CoP-HS were used as bifunctional catalysts for water splitting in a cell
438 device, a current density of 10 mA cm⁻² is achieved at a remarkably low cell voltage
439 of 1.47 V, which is one of the best bifunctional catalysts among the once reported in
440 literature. This excellent electrochemical performance of CoP-HS for overall water
441 splitting is derived from the hollow structure and high activity of P-sites in CoP-HS.
442 These results shed new light on the design and development of other transition metal
443 phosphides materials for water splitting.

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462 **Author Contributions**

463 W. Z and N. H conceived and designed the research, coordinated the work, made the
464 visualization of the experiment results, performed the mechanism analysis. J. A and X.
465 H conducted TEM and performed the corresponding data analysis. W. Z, X. Z and M.
466 X conducted the BET and XPS, and W. Z performed the data analysis. C. Z conducted
467 the first principles calculation, W. Z and N. H performed the data analysis. W. G, S. X
468 and Z. Z conducted the SEM and XRD, W. Z and N. H performed the data analysis. P.
469 S and K. W assisted in the electrochemistry test. W. Z wrote the manuscript, and C. Z,
470 X. Z, J. L and J. F assisted in revising the manuscript. All co-authors contributed to
471 this work.

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