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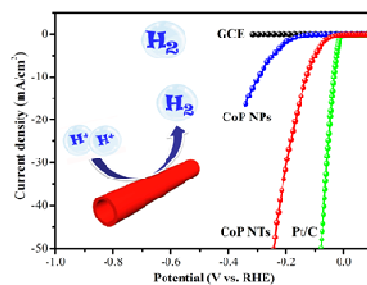


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CoP nanotubes were fabricated by phosphidation of Co salt inside an anodic aluminum oxide template as an efficient hydrogen-evolving electrocatalysts.

## Template-Assisted Synthesis of CoP Nanotubes to Efficiently Catalyze Hydrogen-Evolving Reaction

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**For the first time we demonstrate a template-assisting synthesis to make CoP nanotubes (CoP NTs) through low-temperature phosphidation of Co salt inside a porous anodic aluminium oxide template followed by dilute HF etching. Such CoP NTs exhibit excellent hydrogen-evolution catalytic activity and durability in an acidic medium, which is superior to their nanoparticles counterparts with a Faradaic yield of nearly 100%. The fundamental insight for the catalytic enhancement mechanism is also explored.**

The depletion of fossil fuels and increased environmental concerns has raised an urgent demand to search clean and sustainable alternative energy sources.<sup>1</sup> Hydrogen is a promising and green chemical fuel for future energy applications.<sup>2</sup> Electrolysis of water is a simple way to produce hydrogen with high purity, but an efficient hydrogen evolution reaction (HER) electrocatalyst is usually required to achieve high current density at low overpotential. Platinum as the best HER catalyst suffers from terrestrial scarcity and high cost.<sup>3</sup> The proton exchange membrane (PEM) technology use highly acidic conditions, thus acid-stable HER catalysts are required in PEM-based electrolysis units.<sup>4</sup> Although there are some available HER catalysts, such as nickel or nickel-based alloy<sup>5</sup> working in alkaline solution, but their long-term stability in strong acid condition needs significant improvement. Thus considerable research effort has been paid to develop acid-

stable non-noble metal HER catalysts, among which the metal Mo-based compounds such as MoS<sub>2</sub>, MoS<sub>x</sub>, MoSoy/RGO, MoS<sub>2</sub>/MoO<sub>3</sub>, MoSe<sub>2</sub>, MoSe<sub>2</sub>/RGO, MoB, Mo<sub>2</sub>C, Mo<sub>2</sub>C/XC, NiMoN<sub>x</sub> and Co<sub>0.6</sub>Mo<sub>1.4</sub>N<sub>2</sub><sup>6</sup> etc., have received particular attention and great progress has been achieved in the past years.

An ideal HER electrocatalyst should feature prominent five attributes including nanoscale dimension to maximize the number of exposed active sites, high aspect ratio to improve catalytic activity per geometric area, porous structure to enhance fast mass transport of reactants and products,<sup>6c</sup> good electrical conductivity to facilitate electronic transfer<sup>7</sup> and unique physico-chemical nature to have high intrinsic catalytic<sup>8</sup> activity towards HER. Transition metal phosphide (TMPs) are formed from the alloying of metals and phosphorus with good electrical conductivity.<sup>9</sup> They have been widely used as catalysts for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN).<sup>9,10</sup> Both HDS and HER rely on the reversible binding of the catalyst and hydrogen, with hydrogen dissociation to yield H<sub>2</sub>S in HDS while with protons bound to the catalyst to promote hydrogen evolution in HER.<sup>11</sup> Therefore TMPs could serve as active catalysts towards HER. Indeed, previous work has shown that Ni<sub>2</sub>P nanoparticles and FeP nanosheets catalyze electrochemical generation of hydrogen from water.<sup>12</sup> CoP hollow nanoparticles have also been developed as an effective HER catalyst,<sup>13</sup> but the catalyst preparation suffers from the involvement of several kinds of organic solvents and multiple tedious steps.

Herein, we report an organic solvent-free method to synthesis of CoP nanotubes (CoP NTs). It was prepared via low-temperature phosphidation of Co salt inside a porous anodic aluminum oxide (AAO) template. It has been reported<sup>14</sup> that cobalt phosphide is stable in acids except a mixture of nitric and hydrofluoric acid. Thus CoP NTs can be obtained by etching the template with dilute HF solution. The as-prepared CoP NTs are used as a HER electrocatalyst in an acidic electrolyte with excellent activity and durability superior to CoP nanoparticles (CoP NPs). The Faradaic yield (FY) for hydrogen production is close to 100%.

The X-ray diffraction (XRD) patterns of CoP NTs and CoP NPs (see Experimental Section for preparation details) are shown in Fig. 1a. Both samples present characteristic diffraction peaks of CoP

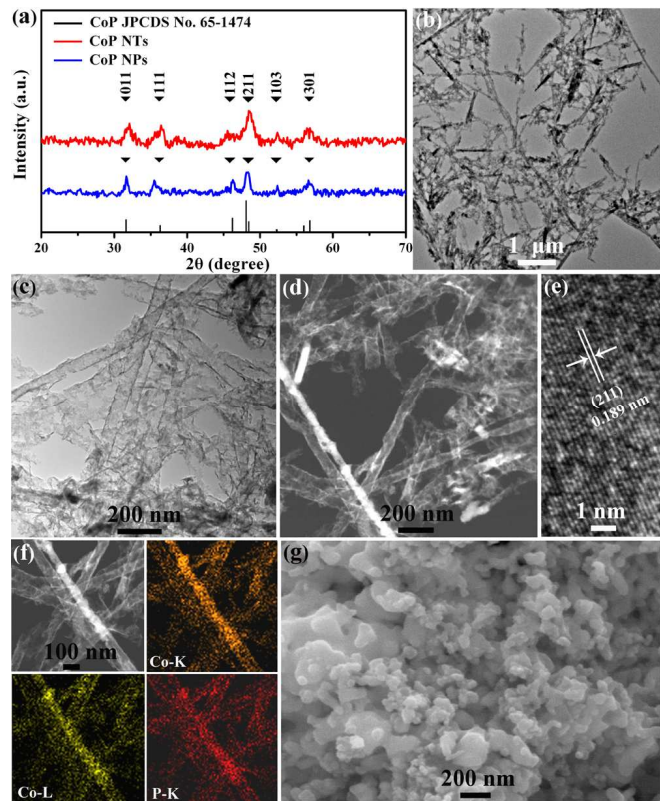
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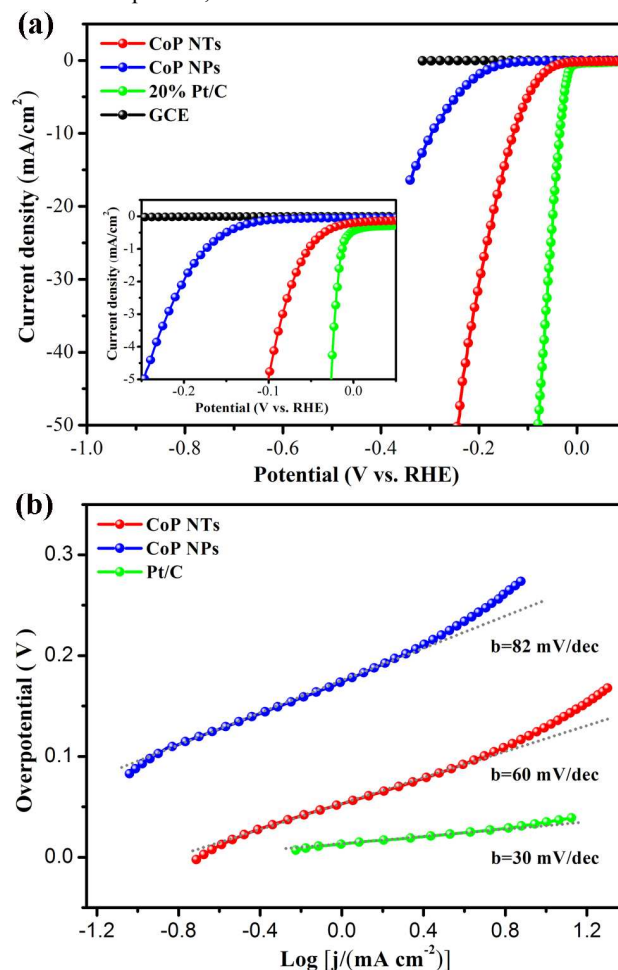
(JCPDS No. 65-1474). Fig. 1b shows the low magnification transmission electron microscopy (TEM) image of CoP NTs, indicating the formation of large amount of one-dimensional (1 D) nanostructures. The high magnification TEM image (Fig. 1c) clearly reveals its tubular nature. The formation of nanotubes is further verified by the scanning TEM (STEM) observation as shown in Fig. 1d. The high resolution TEM (HRTEM) image taken from a single nanotube (Fig. 1e) reveals clear lattice fringes with an interplane distance of 0.189 nm corresponding to (211) plane of CoP.<sup>15</sup> The energy dispersive X-ray (EDX) elemental mapping images of Co and P for CoP NTs show that both Co and P elements are uniformly distributed in the whole nanotubes as shown in Fig. 1f. All these observations strongly confirm the successful synthesis of CoP NTs. It is noteworthy that same preparation without the use of AAO template, however, only produces CoP NPs (Fig. 1g).



**Fig. 1** (a) XRD patterns of CoP NTs and CoP NPs. (b) Low and (c) high magnification TEM images of CoP NTs. (d) STEM image of CoP NTs. (e) HRTEM image of CoP NTs. (f) EDX elemental mapping images of Co and P for CoP NTs. (g) Typical SEM image of CoP NPs.

We examined the HER catalytic performance of the CoP NTs in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte using a typical three-electrode setup. For comparison, bare GCE, CoP NPs and commercially available Pt/C (20 wt %) with the same loading were also studied. A saturated calomel electrode (SCE) reference electrode was used but was calibrated by a reversible hydrogen electrode (RHE) using a Pt foil immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> saturated with high purity hydrogen before each electrochemical measurement, and all potentials in this work are reported versus RHE. Compensation of Ohmic losses was performed for all electrochemical measurements. Fig. 2a shows the polarization curves of CoP NTs, CoP NPs, Pt/C and bare GCE. The Pt/C catalyst exhibits expected HER activity with a near zero overpotential while the bare GCE does not affect the activity towards HER. It is clearly observed that CoP NTs have a much more rapid rise of cathodic currents than CoP NPs when the potential turns more

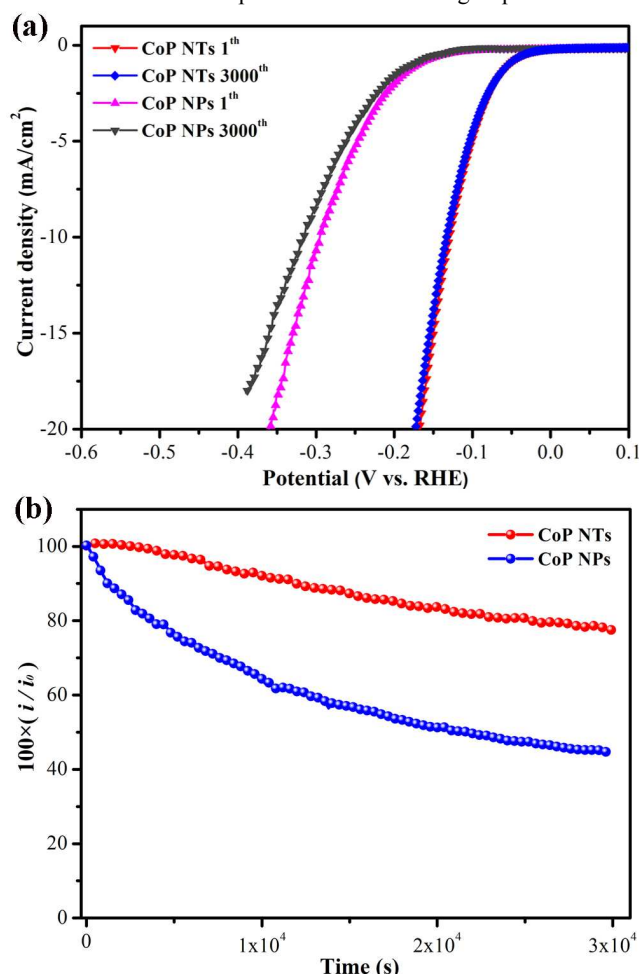
negative. In addition, to achieve current densities of 2 and 10 mA/cm<sup>2</sup>, the former only needs overpotentials of 72 and 129 mV, respectively, but the latter requires overpotentials of 200 and 297 mV, respectively. These results indicate that CoP NTs catalyst has much higher electroactivity toward HER. The achieving performance of our catalyst in an acidic electrolyte is much better than those reported Mo-based catalysts including double-gyroid MoS<sub>2</sub>,<sup>6c</sup> metallic MoS<sub>2</sub> nanosheets,<sup>6d</sup> MoS<sub>3</sub> particles,<sup>6f</sup> MoS<sub>2</sub>/MoO<sub>3</sub>,<sup>6h</sup> bulk MoB,<sup>6j</sup> Mo<sub>2</sub>C nanocrystals,<sup>6k</sup> MoSe<sub>2</sub>/RGO,<sup>6l</sup> NiMoN<sub>x</sub>,<sup>6o</sup> Co<sub>0.6</sub>Mo<sub>1.4</sub>N<sub>2</sub>,<sup>6p</sup> it's also better than FeP nanosheets<sup>12c</sup> and TaCN nanoparticle,<sup>16</sup> those values are shown in Table S1.



**Fig. 2** (a) Polarization curves of CoP NTs, CoP NPs, Pt/C and bare GCE. (b) Tafel plots of CoP NTs, CoP NPs and Pt/C.

Fig. 2b shows the Tafel plots of CoP NTs, CoP NPs and Pt/C. The linear regions of the Tafel plots were fit to the Tafel equation ( $\eta = b \log j + a$ , where  $j$  is the current density and  $b$  is the Tafel slope), yielding Tafel slopes of 60, 82 and 30 mV/dec for CoP NTs, CoP NPs and Pt/C catalyst, respectively. The Tafel slope of CoP NTs is smaller than that of some non-noble metal catalysts like bulk MoS<sub>2</sub> (94 mV/dec),<sup>6b</sup> amorphous MoS<sub>2</sub> (60 mV/dec),<sup>6c</sup> MoSoy/RGO (62.7 mV/dec),<sup>6g</sup> bulk Mo<sub>2</sub>C (87.6 mV/dec),<sup>6j</sup> Mo<sub>2</sub>C nanocrystals (110–235 mV/dec),<sup>6k</sup> MoSe<sub>2</sub>/RGO (101 mV/dec),<sup>6l</sup> TaCN nanoparticles (103–158 mV/dec)<sup>15</sup> and NiSe nanofiber assemblies (64 mV/dec).<sup>17</sup> It is also comparable to that of MoO<sub>3</sub>/MoS<sub>2</sub> nanowires (50–60 mV/dec)<sup>6h</sup> and Mo<sub>2</sub>C/XC (59.4 mV/dec)<sup>6m</sup> etc. Tafel slopes of 30, 40 and 120 mV/dec can be achieved if the Tafel, Heyrovsky or Volmer step is the rate-determining step,

respectively.<sup>18</sup> The experimentally observed Tafel slopes of 60 and 82 mV/dec for CoP NTs and CoP NPs reveal that the Volmer-Heyrovsky HER mechanism presumably takes effect in the HER and the electrochemical desorption is the rate limiting step.<sup>6b</sup>

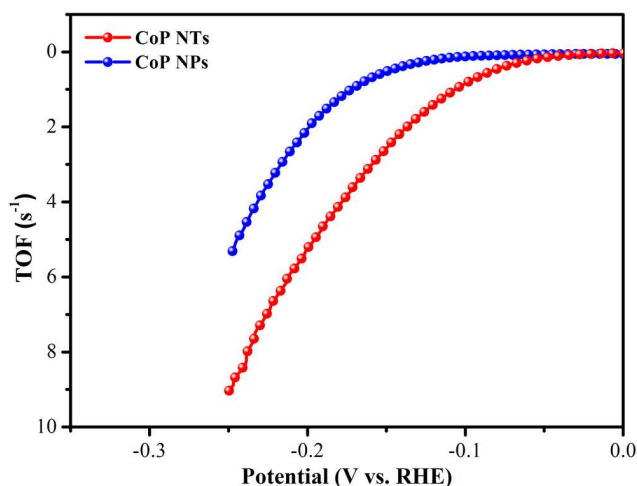


**Fig. 3** (a) Polarization curves of CoP NTs and CoP NPs initially and after 3000 CV scans between -0.2 and +0.2 V. (b) Time-dependent current density curves of CoP NTs and CoP NPs under static overpotential of 150 mV.

We further probed the durability of CoP NTs and CoP NPs in an acidic media by a long-term cycling test. Fig. 3a shows the comparison of polarization curves measured before and after 3000 cyclic voltammetry (CV) cycles ranging from -0.2 to 0.2 V at a scan rate of 100 mV/s. At the end of cycling, only negligible current loss is observed in the polarization curves of CoP NTs. However, CoP NPs shows obvious current loss up to 3000 cycles. Fig. 3b shows the time-dependent current density curves of CoP NTs and CoP NPs under static overpotential of 150 mV. After a long period of 30000 s, around 80% of the current intensity for CoP NTs can still be maintained but only 45% for CoP NPs is maintained. These observations indicate that CoP NTs have superior stability in a long-term electrochemical process over CoP NPs.

To gain further insights into the intrinsic catalytic activity of CoP NTs and CoP NPs, the turnover frequency (TOF) for each active site was estimated using the reported methods.<sup>19</sup> The number of active sites was examined by CVs at a scan rate of 50 mV/s over a range of -0.2 to 0.8 V in phosphate buffer (pH = 7) (Fig. S1). There is no apparent redox peak was observed, indicating one electron transfer

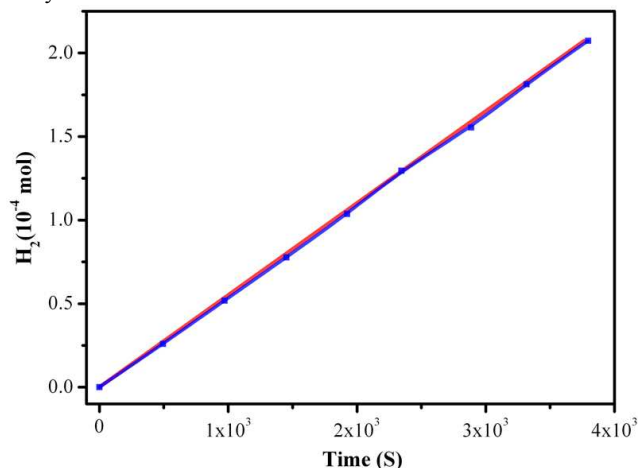
process, and thus the integrated charge over the whole potential range should be proportional to the total number of active sites. The calculated number of the active sites for CoP NTs and CoP NPs are  $3.79 \times 10^{-9}$  and  $1.60 \times 10^{-10}$  mol, respectively. Fig. 4 shows the polarization curves (measured in 0.5 M H<sub>2</sub>SO<sub>4</sub>) normalized by the active sites and expressed in terms of TOF. To accomplish a TOF value of 1.00 s<sup>-1</sup>, CoP NTs and CoP NPs need overpotentials of 106 and 172 mV, respectively. The TOF value of CoP NTs is comparable to that of the reported several non-noble metal-based catalysts.<sup>12a,20</sup> The superior catalytic performance of the CoP NTs catalyst could be attributed to its 1D tubular nanostructure. On one hand, the high aspect ratio of CoP NTs effectively improves the catalytic activity per geometric area;<sup>6c</sup> while on the other hand, both the inner and outer surface of CoP NTs can be accessed by electrolyte thus providing more exposed active sites.



**Fig. 4** Calculated TOFs for CoP NTs and CoP NPs in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

MoP has been recently reported to possess better catalytic ability than Mo<sub>3</sub>P towards HER due to more favorable H-binding on P sites of MoP,<sup>21</sup> indicating that catalytic ability of Molybdenum phosphide is strongly affected by its constitution. We can also reasonably expect that the cobalt phosphide could have the similar constitution effect on its catalytic ability towards HER. Fig. S2 shows the X-ray photoelectron spectroscopy (XPS) 2p spectra in the Co (2p) and P (2p) regions of CoP NTs. One obvious peak appears at 779.1 eV in the Co (2p) region along with two peaks at 134.0 and 129.9 eV in the P (2p) region. The observed two peaks at 779.1 and 129.9 eV can confirm the formation of CoP.<sup>22</sup> The peak at 134.0 eV in the P (2p) can be assigned to the oxidized species arising from superficial oxidation due to air contact.<sup>23</sup> The positive shift of Co (2p) binding energy (779.1 eV) from Co metal (778.1-778.2 eV) and the negative shift of P (2p) binding energy (129.9 eV) from elemental P (130.2 eV)<sup>24</sup> suggest that the Co and P in CoP have a partial positive and negative charge, respectively, which are resulted from the transfer of electron density from Co to P.<sup>25</sup> Indeed, calculations and electron density maps also suggest covalency for Co-P bonds with charge separation due to charge transfer from Co to P.<sup>26</sup> It is known that metal complex HER catalysts incorporate proton relays from pendant acid-base groups positioned close to the metal activation center where H<sub>2</sub> production occurs<sup>27</sup> and hydrogenases also use pendant bases proximate to the metal centers as the active sites.<sup>28</sup> Considering that CoP also features pendant base P close proximity to the metal Co, we may expect it share similar catalytic mechanism with the metal complex catalysts and hydrogenases toward the HER.

We further confirmed the gas generation by gas chromatography (GC) for quantitative measurement of the generated hydrogen, in which a calibrated pressure sensor is used to monitor the pressure change in the cathode compartment of an H-type electrolytic cell. Bulk cathodic electrolysis was carried out by maintaining CoP NTs-loaded glassy carbon plate under a static overpotential of 250 mV for a period of time. To calculate the FY of the electrocatalytic hydrogen evolution, we compared the amount of experimentally quantified hydrogen with theoretically calculated hydrogen (assuming 100% FY) as shown in Fig. 5. It suggests that the CoP NPs has a FY of nearly 100%.



**Fig. 5** The amount of theoretically calculated (red) and experimentally measured (green) hydrogen versus time of CoP NTs under a static overpotential of 250 mV.

In summary, CoP NTs have been successfully synthesized via the low-temperature phosphidation of Co salt inside a porous AAO template followed by dilute HF etching. Such CoP NTs as a novel HER catalyst show excellent activity and durability in an acidic media with a FY close to 100%. This work provides a general methodology to fabricate nanotubes of TMP for applications toward electrocatalysis and Li-ion batteries.<sup>9,10</sup>

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