Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Facile Synthesis of CoFe-B-P Nanochains as Efficient Bifunctional Electrocatalysts for Overall Water-splitting

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Experimental Section

Samples preparation

For the Co-Fe-B samples, 0.8 mmol of $CoCl_2 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ with different Co:Fe molar ratios (1:1; 1:3; 3:1) and 800 mg of polyvinyl Pyrrolidone (PVP) were dissolved into 200 mL deionized water in a beaker under stirred with Ar for 30 min to remove air in the solution. Then, 80 mL of deionized water containing 100 mg $NaBH_4$ was added into the above solution quickly. The PVP and $NaBH_4$ serve as surfactant and reducing agent. Then, the produced black products was obtained by vacuum filtration and washed several times with deionized water and alcohol, respectively. The obtained catalysts were named as were denoted as Co_1-Fe_1-B, Co_1-Fe_3-B and Co_3-Fe_1-B, respectively. The Co-B and Fe-B samples were prepared using the same procedure accordingly.

Phosphorous doped Co-Fe-B (Co-Fe-B-P) nanochains were synthesized via a low-temperature phosphorization procedure. Different mass ratio of Co-Fe-B and NaH_2PO_2 (1:10; 1:15; 1:20) were put into two seperated porcelain boats, and then annealed with a heating rate of 2 $^oC\ min^{-1}$ in Ar atmosphere to 300 ^oC for 2 h in a tube furnace and then cooling to room temperature naturally.

Physical Characterization

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) was performed on S-4800, Hitachi and JSM-2100, respectively, to research the morphology of the prepared catalysts. X-ray diffraction (XRD) was conducted on X'Pert PRO. X-ray photoelectron spectroscopy (XPS) was measured on AXIS-ULTRA DLD to confirm the chemical valence and composition.

Electrochemical Characterization

The electrocatalytic measurement for HER and OER were conducted in a typical three-electrode setup in 1 M KOH with carbon rod, Ni foam and reversible hydrogen electrode (RHE) as counter electrode, working electrode and reference electrode, respectively. The Ni foam was treated with diluted HCl solution and ethanol and dionized water

severl times before utilization. For the working electrode (working area1.5 cm^{-2}), the prepared catalysts with carbon black and polyvinylidene fluoride (7:2:1, mass ratio) were dispersed into *n*-methyl-pyrrolidone (NMP) to form homogenous ink. The prepared ink (100 μL) was pasted onto the Ni foam and dried at 80 ^{o}C in vacuum oven for 12 h (mass loading 0.46 mg cm^{-2}). The linear sweeping voltammograms (LSV) was obtained with a scanning rate of 5 mV s^{-1} for all the electrocatalytic process. Chronopotentiometric measurements were measured to evaluate the long-term durability of the as-prepared electrocatalysts. The electrochemical activity of the overall water splitting setup applied with Co_1-Fe_1-B-P as both the anode and cathode, similar with actual water decomposition, was performed in 1.0 M KOH through LSV with a scanning speed of 5 mV s^{-1}.

Figures

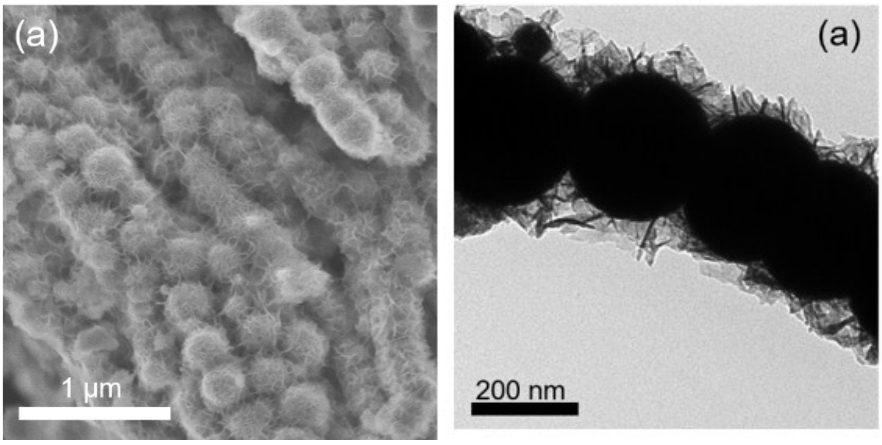

Figure S1. (a) SEM and (b) TEM images of Co_1-Fe_1-B nanochains.

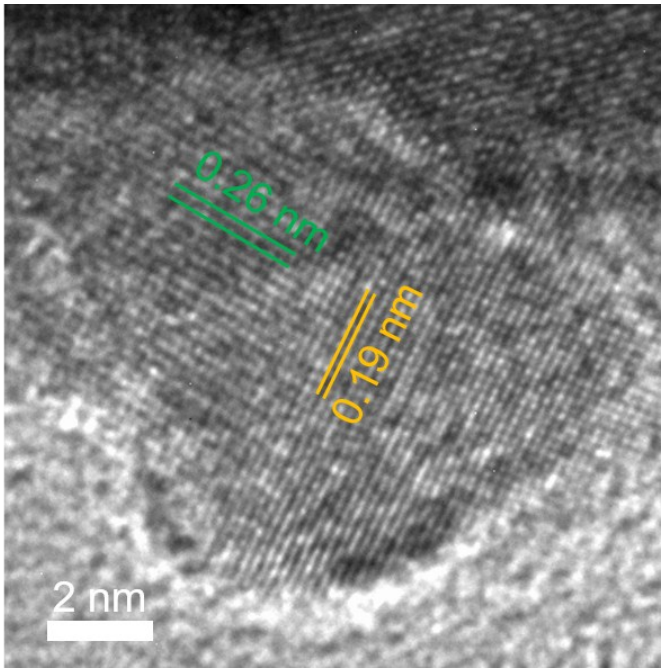

Figure S2. HRTEM image of Co_1-Fe_1-B nanochains at shell region.

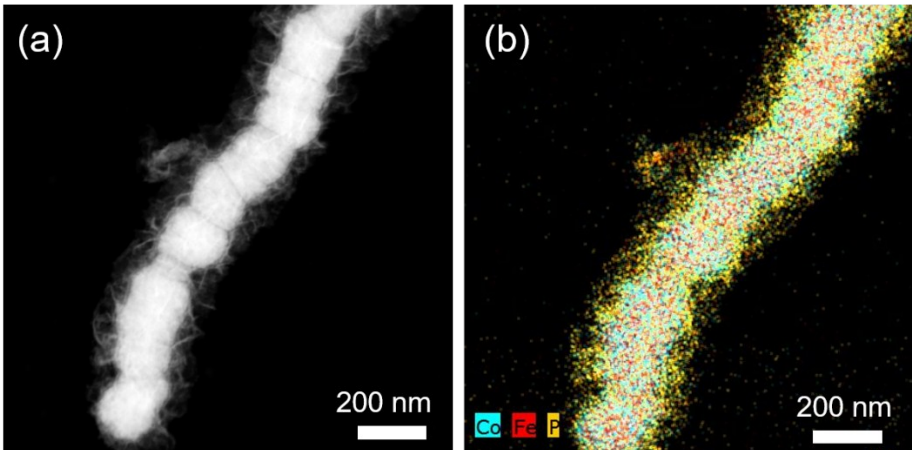

Figure S3. (a) S-TEM image of Co1-Fe1-B-P. (b) Overlay of Co, Fe and P.

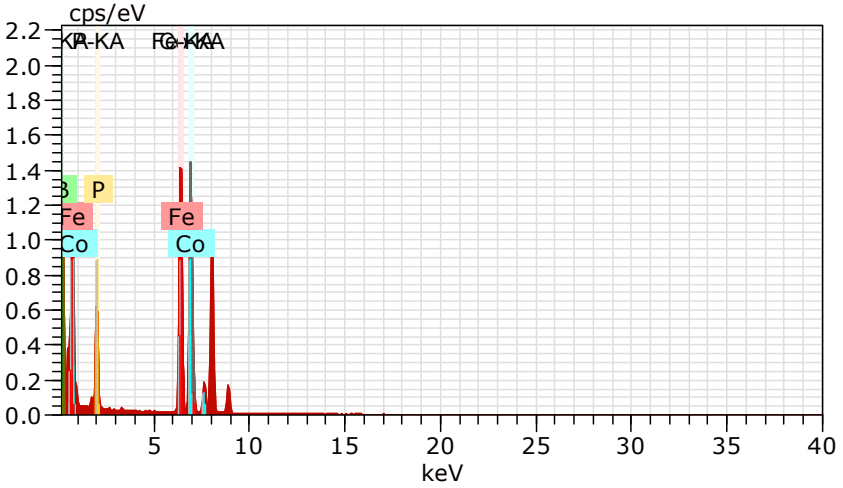

Figure S4. EDX spectrum of Co_1-Fe_1-B-P nanochains.

Figure S5. SEM images of (a) CoB and (b) FeB samples.

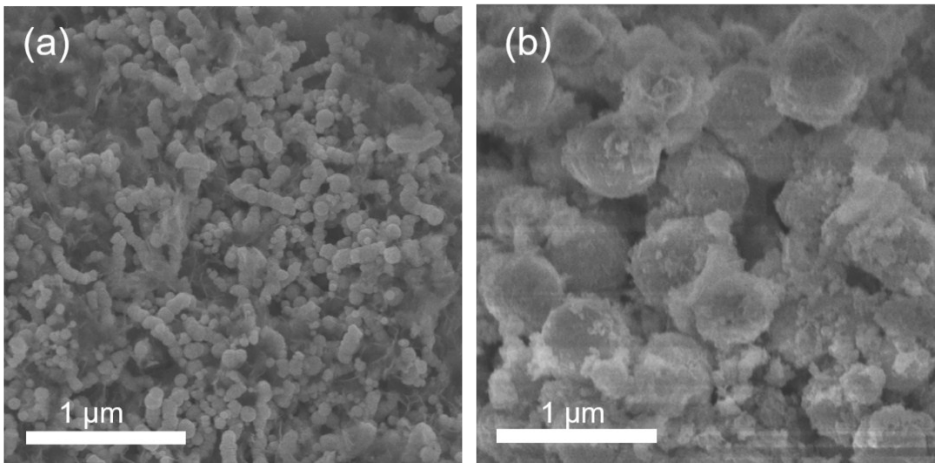

Figure S6. SEM images of (a) Co_3-Fe_1-B and (b) Co_1-Fe_3-B samples.

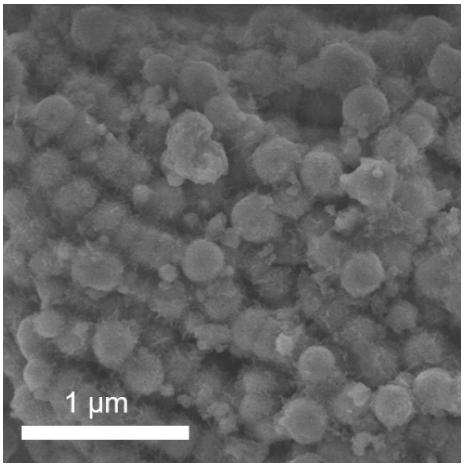

Figure S7. SEM image of Co_1-Fe_1-B-P after long-term OER measurement.

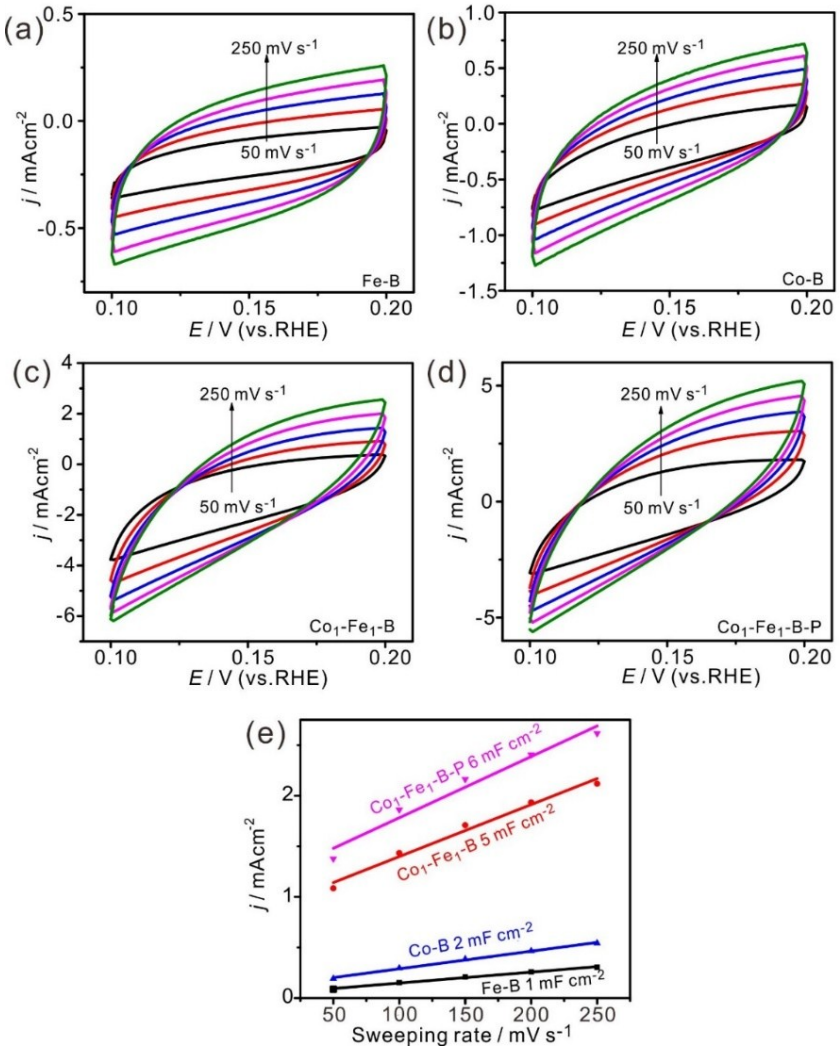

Figure S8. Cyclic voltammograms of (a) Fe-B, (b) Co-B, (c) Co_1-Fe_1-B and (d) Co_1-Fe_1-B-P; (e) Linear fitting of sweeping rates with capacitive current densities of catalysts.