# Supporting Information

## Highly efficient and durable PtCo alloy nanoparticles encapsulated in

### carbon nanofibers for electrochemical hydrogen generation

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#### Experimental

#### Materials.

Chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, 99.9%), sulfuric acid, and dimethylformamide (DMF, 99.5%) were procured from Shanghai Civi Chemical Technology Co., Ltd. Cobalt chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O) was supplied by Aladdin Co., Ltd. Polyacrylonitrile (PAN,  $M_w \approx 1.4 \times 10^5$ , copolymerized with 10 wt% methyl acrylate) was purchased from Sinopec Shanghai Petrochemical Co., Ltd. Ultrapure water (Milli-Q) was used throughout the experiments. All the reagents were used as received.

#### Fabircation of PtCo/CNFs composite nanofibers by electrospinning.

A common electrospinning method was chose to prepare the PtCo/PAN nanofibers (PtCo/PANFs). In a typical procedure, 3.0 g of PAN powder was dissolved in 22 mL of DMF to form a ca. 10 wt% solution by vigorously stirring of the mixture for 1 hour, then, 0.1 g CoCl<sub>2</sub>·6H<sub>2</sub>O was dropped into the PAN/DMF solution and the mixture was stirred at 80 °C for 1 hour. Subsequently, 0.15 g H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was immediately added to the above mixture and the mixture was stirred at 80 °C for over 6 hours to ensure the homogeneity of the three-component mixture, then the precursor solution was obtained. Thereafter, the resultant precursor was transferred into a 10 mL syringe with a stainless copper needle at the tip that was subsequently mounted onto a syringe pump controlled the flow rate of the precursor solution to 0.6 mL h<sup>-1</sup>. The needle was connected to a high voltage power supply to get a voltage of 15 kV, and the collector was vertically positioned at ca.10 cm away from the needle. Under these conditions, the homogeneous nanofibers were obtained and formed the films of networks at room temperature. For carbonization, the as-spun PtCo/PANFs were first stabilized in air at 280 °C for 6 hours in a home-built chemical vapor deposition (CVD) technique in a tube furnace with heating rate of 2 °C min<sup>-1</sup> from room temperature to 280 °C, and then the brown films were carbonized under Ar gas flow (100 sccm) at a temperature ramp of 5 °C per minute to optimal temperature of 1000 °C and kept at the temperature for 8 hours to generate a high graphitization. Finally, the products were cooled to room temperature under Ar atmosphere. For reliable comparison, the Pt/CNFs and Co/CNFs were prepared similarly by replacing PtCo with Pt and Co, respectively. As a control, the precursor was prepared without using metallic salt solution to prepare the blank CNFs. Physicochemical characterization.

The samples were characterized by different analytic techniques. Field-emission scanning electron microscopy (FE-SEM) images were recorded on the JSM-6700F (JEOL, Japan) at high vacuum with an accelerating voltage of 3 kV. Transmission electron microscopy (TEM), high-

resolution TEM (HRTEM), high-angle annular dark field scanning TEM (HAADF-STEM), STEM mapping, and line-scan energy dispersive X-ray spectroscopy (EDX) were carried out using a STEM (Tecnai G2 F30S-Twin, Philips-FEI) operating at 300 kV. Particle size distribution was determined by analyzing about 200 particles in TEM image using the Image-Pro Plus 6.2 software. The X-ray diffraction (XRD) analysis was carried out on a Bruker AXS D8 DISCOVER X-ray diffractometer with Cu K<sub> $\alpha$ </sub> radiation ( $\lambda$ =1.5406 A°) at a scanning rate of 0.02° 20 s<sup>-1</sup> in the 20 range of 10-90°. X-ray photoelectron spectra (XPS) were performed on an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) with an aluminum (mono) K<sub> $\alpha$ </sub> source (1486.6 eV). The aluminum K<sub> $\alpha$ </sub> source was operated at 15 kV and 10 mA. *Electrochemistry*.

All electrochemical measurements were performed on an Autolab potentiostat/galvanostat (Model PGSTAT302N) workstation with a standard three-electrode system composed of the modified glassy carbon electrode (GCE, 3 mm diameter, 0.071 cm<sup>2</sup>) as working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Prior to surface modification, GCE was polished with 1.0, 0.3 and 0.05  $\mu$ m alumina slurry, and thoroughly washed ultrasonically in ultrapure water and ethanol before use. Then, 3 mg of the catalyst powder was dispersed in 1 mL of 4:1 (v/v) DIW/isopropanol mixed solvent with 40  $\mu$ L of Nafion solution (5 wt%) by at least 30 min ultrasonication to form a homogeneous ink, and thereafter, 5  $\mu$ L of the catalyst ink was carefully transferred onto the GCE and dried at room temperature. Moreover, the catalyst loading on the GCE was 212.3  $\mu$ g cm<sup>-2</sup>. After solution evaporation, the electrodes prepared were stored in a desiccator at room temperature before use.

Experimentally, the H<sub>2</sub>SO<sub>4</sub> solution was degassed by bubbling Ar for at least 15 min to remove the dissolved oxygen, and then, cyclic voltammetry was carried out with a continuous Ar flow at a scan rate of 50 mV s<sup>-1</sup> until the curves were stable. For HER measurements, the linear sweep voltammetry was obtained at a scan rate of 2 mV s<sup>-1</sup>, and the corresponding polarization curve was obtained after iR-compensation. The electrochemical impedance spectroscopy measurement was performed at-0.25 *versus* reversible hydrogen electrode (RHE) over a frequency range from 100 kHz to 0.1 Hz. The accelerated stability test was performed by potential cycling between 0 and 1.2 V vs. RHE at a sweep rate of 100 mV s<sup>-1</sup> for 1000 cycles. At the end of the cycles, the resulting electrodes were used for polarization curves at a scan rate of 2 mV s<sup>-1</sup>. PtCo/CNFs membrane (1 cm<sup>2</sup>) was used as working electrode to collect chronoamperometry data at the applied potential of -0.056 V vs. RHE for up to 10 h. All measurements were performed at room temperature. Meanwhile, the measured potentials *versus* the SCE were converted to RHE. In 0.5 M H<sub>2</sub>SO<sub>4</sub>, E<sub>RHE</sub> = E<sub>SCE</sub> + 0.218 V. Supplementary figures.



Fig. S1. Comparison of mass activity (the current is normalized by Pt mass) for the catalyst.



Fig. S2. SEM image of PtCo/CNFs after stability testing.