## **Supporting Information**

## Ultra-small nickel phosphide nanoparticles as an high-performance electrocatalysis for hydrogen evolution reaction

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Figure S1. Low-magnification TEM images of  $Ni_2P$  with different sizes synthesized at different temperatures without OAm: 100 °C (a) and 180 °C (b) The scale bar is 20 nm.



**Figure S2.** Low-magnification TEM images of  $Ni_2P$  with different sizes synthesized at different temperatures with 0.5 mL of OAm: (a) 8.1 nm and (b) 11.8 nm. The scale bar is 20 nm.



**Figure S3.** Wide area TEM image of 2.8 nm Ni<sub>2</sub>P nanoparticles after

high temperature annealing.



Figure S4. Wide area TEM image of 2.8 nm amorphous  $Ni_2P$  nanoparticles.



Figure S5. Wide area TEM image of 5.4 nm amorphous  $Ni_2P$  nanoparticles.



Figure S6. Wide area TEM image of 8.1 nm amorphous  $Ni_2P$  nanoparticles.



Figure S7. Wide area TEM image of 9.5 nm amorphous  $Ni_2P$  nanoparticles.



**Figure S8.** Low-magnification TEM images of  $Ni_2P$  with different sizes annealing at 450 °C for 2 hours: (a) 5.4 nm; (b) 8.1 nm; and (c) 9.5 nm. The scale bar is 20 nm.



Figure S9. Chronoamperometric stability measurements of 8.1 nm  $Ni_2P$  NPs (1.0 mg·cm<sup>-2</sup>) held at -150 mV vs. RHE for 5.6 hours in 0.5 M  $H_2SO_4$ .



**Figure S10.** (a) XRD patterns and (b) EDS spectrum of 8.1 nm  $Ni_2P$  NPs after long-term stability test.



Figure S11. SEM image of 8.1 nm  $Ni_2P$  NPs after long-term stability test.

Size (nm)	5.4 nm	8.1 nm	9.5 nm
Tafel slop (mV/decade)	41.4	44.9	46.7
Sg (cm²/mg)	1511	1020	960
Current Density at 150 mV (mA/cm <sup>2</sup> )	123.1	55.2	34.0
TOFs (s <sup>-1</sup> atom <sup>-1</sup> )	0.10	0.07	0.04

**Table S1.** Comparison of TOFs of  $Ni_2P$  NPs with different sizes from this report.