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## **Electronic Supplementary Information**

**Fig. S1** (a) SEM, (b) TEM and (c) HAADF-STEM and corresponding elemental mapping images of the PdRu NAs.



Fig. S2 XPS survey pattern of the PdRuBP NAs.



Fig. S3 TEM image of the Pd black.



**Fig. S4** (a) SEM, (b) TEM, (c) HAADF-STEM and corresponding elemental mapping images and (d) XRD pattern of the PdRuB NAs.



Fig. S5 CV curves of the catalysts in a 0.5 M  $H_2SO_4$  solution with a scan rate of 50 mV s<sup>-1</sup>.



Fig. S6 TEM images of the PdRuBP NAs after electrocatalytic stability testing.

**Table S1** The comparisons of FAOR performance for the PdRuBP NAs and some other reportedPd-based electrocatalysts.

Catalysts	Electrolyte	Scan rate (mV s <sup>-1</sup> )	Mass activity (mA μg <sub>Pd</sub> <sup>-1</sup> )	Ref.
PdRuBP NAs	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	1.71	This work
PdRu nanospine assemblies	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	1.10	1
Pd/NP-Coal-CFs(DCD/TPP)	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	0.537	2
CuPd@Pd tetrahedra	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	0.502	3
Twisted PdCu nanochains	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	1.108	4
Core-shell Pd-P@Pt nanoparticles	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	0.502	5
Pd/PCNTs	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	0.695	6
PdBi nanodot	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	1.629	7
Pd-Ni <sub>2</sub> P/C -30%	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	1.425	8
Pd-P NNs	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	1.505	9
Pd-P <sub>85</sub> /C	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	0.877	10
PdNi/RGO	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	0.604	11
3D super-branched PdCu	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	0.808	12
flower-like Au@AuPd core-shell nanocrystals	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	1.250	13
Pd <sub>51</sub> Cu <sub>49</sub> alloy	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	0.517	14
Cu <sub>3</sub> PdN nanoparticles	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M HCOOH	50	0.870	15

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