Supporting Information

Ir oriented nanocrystalline assemblies with high activity for hydrogen oxidation/evolution reactions in alkaline electrolyte

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Experimental Section:

Materials:

Iridium chloride ($IrCl_3$, 99.0 %) was purchased from Changcheng Chemical Co., Ltd. Cetyltrimethylammonium bromide (CTAB, 99.0 %) was purchased from Boao Biotechnology Co., Ltd. Sodium borohydride ($NaBH_4$, 98.0 %), *n*-hexane (n-C_6H_{14}, 98.5 %), 1-hexanol (1-$C_6H_{13}OH$ 98.0 %), isopropanol (i-C_3H_7OH 99.5 %) and ethanol (C_2H_5OH 99.7 %) were purchased from Sinopharm Chemical Reagent Co., Ltd. Potassium hydroxide (KOH 99.99 %) was purchased from Aladdin Industrial Co.. Commercial Pt/C (Johnson Matthey Hispec 3600, 20 wt %) was purchased from Shanghai Hesen Electric Co., Ltd. Nafion solution (5 wt %) was purchased from Sigma-Aldrich Co.. All the raw materials were directly used without any further purification, and the water (18.25 MΩ cm^{-1}) prepared from ultrapure water system was used throughout the whole experiment.

Synthesis of Ir ONA:

Ir ONA was synthesized through a microemulsion process according to the preceding literature with a little change. Typically, CTAB (2 g) was first dissolved in a mixed solvent consisted of *n*-hexane (20 mL) and 1-hexanol (12 mL) at 40 °C. Next, $IrCl_3$ (20 mg) was added into this solution with continual stirring at least for 2 h. Subsequently, fresh $NaBH_4$ aqueous solution (5 mL, 2 mol L^{-1}) was added dropwise under vigorous stirring, and then kept for 12 h. After cooling down to room temperature, the final product was collected by centrifugation and washed with ethanol and water, and finally dried in a vacuum. Ir NPs was obtained in the same way only without the presence of CTAB. The yields of Ir ONAs and of Ir NPs are about 65 % and 57 %, respectively.

Characterization:

Powder X-ray diffraction (XRD) patterns were performed by a Bruker D8-Advance X-ray diffractometer using Cu Kα radiation source (λ = 0.154178 nm) with a velocity of 8° min^{-1}.The morphologies and sizes of the samples were observed by using a Tecnai G20 U-Twin transmission electron microscope (TEM) at an acceleration voltage of 200 KV.

Preparation of the working electrode:

In the first place, a certain amount of Ir ONAs/NPs and quintupled amount of XC-72 were mixed in 15 mL of *n*-hexane under sonication and then kept stirring for 12 h under N_2 atmosphere. After that, the catalyst was obtained by centrifugation before drying under a vacuum condition. To prepare the working electrode, 5 mg of the catalyst was dispersed in a solution of 0.98 mL of isopropyl alcohol mixed with 0.02 mL of 5 wt % Nafion solution and then sonicated for at least 1 h to obtain the 5 mg mL^{-1} catalyst ink. The glassy-carbon electrode (GCE, 5 mm in diameter) was polished successively with 1.0, 0.5, and 0.05 μm alumina powder to obtain a mirror-like surface and then washed with ultrapure water and ethanol by sonication. After dried in air, 6 μL of the ink was drop-casted on the surface of the GCE (loading 0.153 mg cm^{-1}) and dried in air before the electrochemical measurements.

Electrochemical Measurements:

A CHI 760E electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, People's Republic of China) was used to measure the electrochemical properties of all samples in a three-electrode system, with a modified GCE, Hg/HgO (0.1 M KOH) electrode, and graphite rod were used as the working electrode, reference electrode, and counter electrode, respectively. All operation was performed at the constant temperature at 303 K. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) curves were carried out to study the electrochemical properties of the working electrode after conducted with *i*R-compensation. For HOR, the catalysts were pre-treated under N2-saturated 0.1 M KOH through more than 40 CVs from ~ 0.02 to 1.0 V with the sweeping rate of 50 mV s^{-1} to obtain a stable voltammogram. After the electrolyte was H_2-saturated, a linear sweep voltammogram was recorded in the potential range from about -0.08 to 1.0 V vs. RHE at a scan rate of 5 mV s^{-1} under 1600 rpm of the RDE rotation rate. For HER, the same preconditioning process of the catalysts were carried out, and then a linear sweep voltammogram was recorded in the potential range from about 0.1 to - 0.4 V vs. RHE in H_2-saturated electrolyte with the scan rate of 5 mV s^{-1} under 1600 rpm of the RDE rotation rate. Accelerated durability test (ADT) was operated via a 1000 CVs from -0.25 V to 0.25 V under N_2-saturated electrolyte on the scan speed of 100 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was carried out at the open circuit potential from 200 kHz to 0.1 Hz after the HOR/HER measurement. Faraday efficiency of H_2 evolution was measured via the chronopotentiometry test with a piece of carbon cloth (1 × 1 cm) decorated by Ir ONA/C catalyst (~ 0.15 mg cm^{-2}) using as a 3D working electrode in order to eliminate the effect of the H_2 bubble at such a high-current of 100 mA.

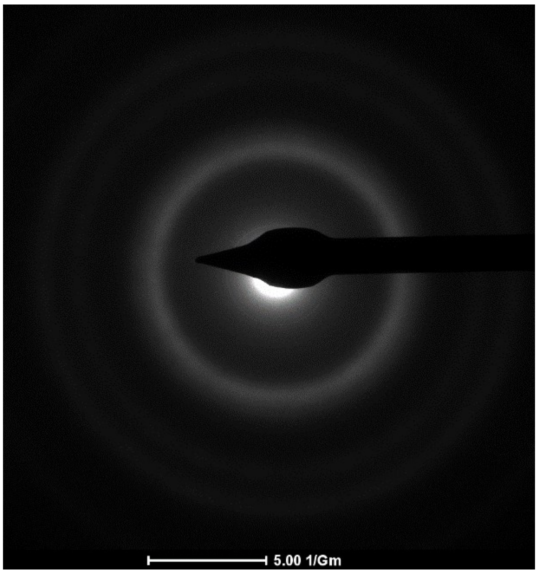

Fig. S1 SAED pattern of Ir ONA.

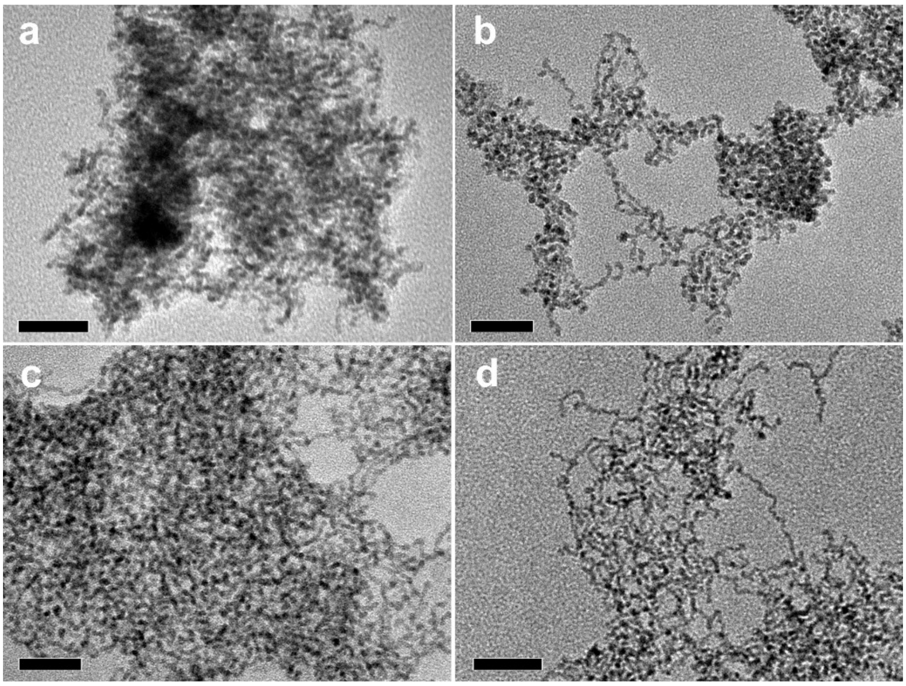

Fig. S2 TEM images of Ir nanocrystalswith different amounts of CTAB: (a) 0.1 g, (b) 0.5 g, (c) 1.0 g and (d) 3.0 g. (the scale is 20 nm)

Different amounts of CTAB was used during the preparation of Ir ONAs, and the morphologies of these samples were characterized by TEM and shown in Fig. S2. As observed, dominating nanoparticles with a small quantity of oriented assembled nanorods were observed in Fig. S2a when only 0.1 g CTAB was used. When the content of CTAB was increased to 0.5 g, more quasi 1D nanostructures appear with longer length (Fig. S2b). Dominating ONAs with a few nanoparticles could be seen in Fig. S2c once increasing the amount of CTAB to 1.0 g. However, the morphologies of the Ir nanostructures with using 2.0 g and 3.0 g CTAB (Fig. 2a,b and Fig. S2d) are similar. We deduce that the morphologies of Ir nanostructures would change from 0D to (quasi-)1D when the amounts of CTAB increased till saturation concentration.

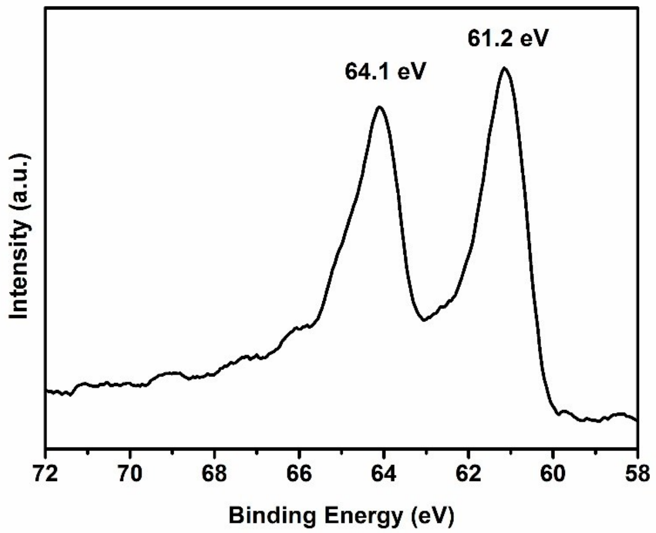

Fig. S3 High resolution XPS of Ir 4f for Ir ONA.

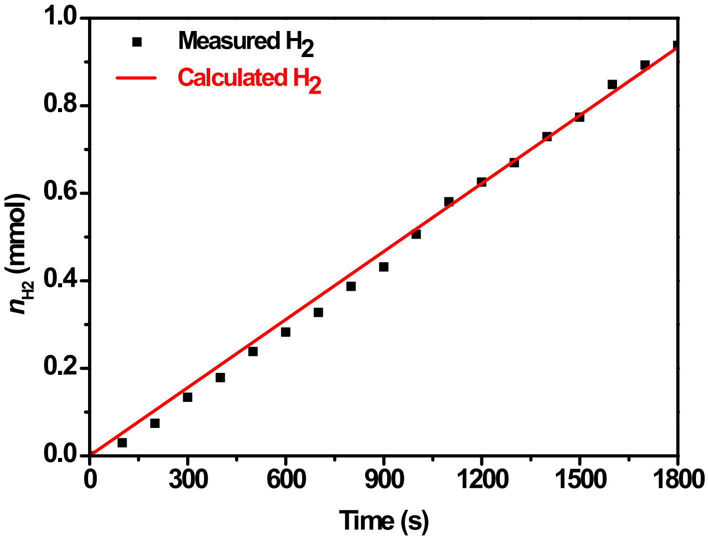

Fig. S4 Faraday efficiency of H_2 evolution.

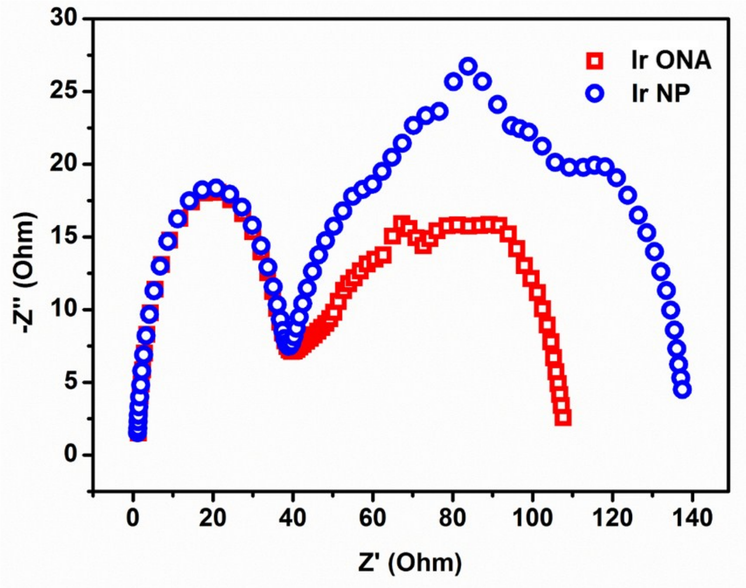

Fig. S5 Nyquist plots of Ir ONA and Ir NP.

Table S1 HOR property of Ir ONA, Ir NP and commercial Pt/C.

	ECSA (cm_{metal}^{2} μg_{metal}^{-1})	Loading (μg_{metal} cm_{geo}^{-2})	Exchange current density		current density @10 mV		current density @50 mV	
			SA (mA cm_{metal}^{-2})	MA (mA μg_{metal}^{-1})	SA (mA cm_{metal}^{-2})	MA (mA μg_{metal}^{-1})	SA (mA cm_{metal}^{-2})	MA (mA μg_{metal}^{-1})
Ir ONA	0.155	30	0.518	0.080	0.877	0.135	2.507	0.387
Ir NP	0.164	30	0.399	0.066	0.724	0.119	2.103	0.345
Pt	0.291	30	0.352	0.103	0.591	0.172	1.486	0.433

Table S2 HER properties of the noble-metal-based catalysts reported in recent literatures.

Sample	Loading ($\mu g_{noble\text{-}metal}$ cm^{-2})	Electrolyte	Overpotential at 10 mA cm-2 (mV)	Ref
Pt_3Ni_2-NWs-S/C	15 (Pt)	0.1 M KOH	45	Nat. Commun., 2017, 8, 14580
		1.0 M KOH	42	
$Ni(OH)_2$ modified Ir surface	/	1.0 M KOH	64	Angew Chem. Int. Ed., 2012, 124, 12663
$Ni(OH)_2$ modified Pt surface			75	
Pt@2D-$Ni(OH)_2$	1.13 (Pt)	0.1 M KOH	> 150	Nano Energy, 2017, 31, 456
		0.1 M LiOH	> 100	

Ru-MoO$_2$	285 (Cat.)	1.0 M KOH	29	J. Mater. Chem. A, 2017, 5, 5475
Ultrafine Ru/N-graphene	~ 21 (Ru)	1.0 M KOH	44	Sustainable Energy Fuels, 2017, 1, 1028
RuP$_2$@NPC	233 (Ru)	1.0 M KOH	69	Angew. Chem. Int. Ed. 2017, 56, 1
Pt$_9$Rh-WC/C	250 (Cat.)	0.1 M KOH	> 80	Int. J. Hydrogen Energy, 2017, 42, 5993
Pt$_9$Rh/C			> 100	
RuCo@NC	275 (Ru)	1.0 M KOH	28	Nat. Commun., 2017 8, 14969
Pt$_{13}$Cu$_{73}$Ni$_{14}$/CNF @CF	/	1.0 M KOH	> 148	ACS Appl. Mater. Interfaces, 2015, 7, 28148
Pd-CN$_x$	28 (Pd)	0.5 M KOH	> 180	ACS Catal., 2016, 6, 1929
Ir-OMC-Ni foam	/	0.1 M KOH	80	J. Energ. Chem., 2017, 10.1016/j.jechem.2017.05.004
Ir-OMC-NF on GC	0.6 (Ir)		130	
Ir ONA/C	30 (Ir or Pt)	0.1 M KOH	47	This work
Ir NP/C			79	
Commercial Pt/C			48	