

Electronic Supplementary Information (ESI)

Amorphous ultrathin iridium/carbon catalyst realizing efficient electrochemical hydrogen evolution

Jie Hou, Hao Jing, Hehe Wei*, Zixiang Su, Hui Li, Longtao Zhang, Xueqing Gong

School of Chemistry and Molecular Engineering, East China University of Science and

Technology, 130 Meilong Road, Shanghai 200237, China

*Correspondence to: weihh@ecust.edu.cn

Experimental Section

Materials.

Hexachloroiridium acid hydrate ($\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$), boric acid and potassium borohydride were purchased from Sinopharm Chemical Reagent Co. Ltd. Vulcan XC72R was purchased from Cabot Corporation. Commercial Pt/C (20 wt.%) was purchased from Johnson Matthey. All chemical materials were used without further pretreatment.

Synthesis of amorphous Ir/C catalyst.

The amorphous Ir/C catalyst was prepared by one-step hydrothermal process. Firstly, pure carbon (XC72R) was washed with 50 ml hydrochloric acid solution (0.5 mol L^{-1}), 200 ml deionized water, and 200 ml ethanol under ultrasonication for 30 minutes, respectively, to remove the possible impurities. Then, 0.036 mol L^{-1} hexachloroiridium acid hydrate solution (385 ml), 100 mg active carbon, 10 ml deionized water, 10 ml ethanol, and 850 mg boric acid were mixed, followed by ultrasonication for 30 minutes and magnetic stirring for 1 hour to obtain homogeneous dispersion. And then the uniform dispersion was placed into a 50 mL autoclave, sealed and maintained 160°C for 5 hours in an oven. After naturally cooling down from 160°C to room temperature, the solids were collected, filtrated, entirely cleaned with deionized water, filtrated, dried and collected to obtain amorphous Ir/C catalyst.

Synthesis of carbon-supported Ir/NP catalyst without boric acid.

Firstly, pure carbon (XC72R) was washed with 50 mL hydrochloric acid solution (0.5 mol L^{-1}) and ethanol under ultrasonication for 30 minutes, respectively, to remove the possible impurities. Then, 0.036 mol L^{-1} hexachloroiridium acid hydrate solution (385

ml), 100 mg active carbon, 10 ml deionized water, and 10 ml ethanol were mixed, followed by ultrasonication for 30 minutes and magnetic stirring for 1 hour to obtain homogeneous dispersion. And then the uniform dispersion was placed into 50 mL Taflon-autoclave, sealed and maintained 160°C for 5 hours in an oven. After naturally cooling down to room temperature, the solids were filtrated, cleaned, dried and collected to obtain carbon-supported Ir/NP catalyst.

Synthesis of carbon-supported Ir/NP catalyst with potassium borohydride.

Firstly, pure carbon (XC72R) was washed with 50 mL hydrochloric acid solution (0.5 mol L⁻¹) and ethanol under ultrasonication for 30 minutes, respectively, to remove the possible impurities. Then, 0.036 mol L⁻¹ hexachloroiridium acid hydrate solution (385 ml), 100 mg active carbon, 10 ml deionized water, 10 ml ethanol, and 850 mg potassium borohydride were mixed, followed by ultrasonication for 30 minutes and magnetic stirring for 1 hour to obtain homogeneous dispersion. And then the uniform dispersion was placed into 50 mL Taflon-autoclave, sealed and maintained 160°C for 5 hours in an oven. After naturally cooling down to room temperature, the solids were filtrated, cleaned, dried and collected to obtain carbon-supported Ir/NP catalyst.

Characterizations.

The TEM, STEM and EDS mapping images were performed on ThermoFisher Talos F200X (FETEM) with the voltage of 200 kV. HAADF STEM images were recorded using a convergence semi angle of mrad and EDS was performed using 4 in-column Super-X detectors. XRD patterns was recorded on a Rotating Anode X-ray Powder Diffractometer (D/max2550VB/PC) with Cu K α radiation and a scan rate of 8° min⁻¹.

XPS spectra was obtained using an X-ray photoelectron spectrometer (ESCALAB 250Xi) with Al K α radiation exciting source. The obtained XPS spectra was corrected by C 1s (284.8 eV) to avoid the effect of charge and fitted using fitted XPSPEAK41 software. The Ir and B loadings of amorphous Ir/C catalyst was measured by the inductively coupled plasma optical emission spectrometer (ELAN DRC-e), showing the Ir loading of amorphous Ir/C catalyst was 0.76 wt.%.

Electrochemical test.

The performances of amorphous Ir/C catalyst, commercial Pt/C catalyst (20 wt%), and pure carbon (XC72R) were conducted in a three-electrode cell using an electrochemical workstation (CHI 760E) and Autolab potentiostat (MAC90646) in 0.5 M H₂SO₄. The amorphous Ir/C electrode was utilized as the working electrode, a graphite rod as the counter electrode and Ag/AgCl (KCl saturated) as the reference electrode.

For amorphous Ir/C catalyst, to prepare the working electrode, 4 mg catalyst and 50 μ L of 5 wt.% Nafion solution were dispersed in 950 μ L of mixed solution (4:17 v/v water/ethanol) by sonication until a homogeneous suspension was formed. Then 5 μ L of the above catalyst suspension was drop-cast onto a glassy carbon electrode (5 mm in diameter). As for commercial Pt/C catalyst with the Pt loading of 20 wt.%, 2 mg catalyst and 50 μ L of 5 wt.% Nafion solution were dispersed in 950 μ L of mixed solution (10:11 v/v water/ethanol) by sonication until a homogeneous suspension was formed, and then 5 μ L of the above catalyst suspension was also drop-cast onto a glassy carbon electrode. Moreover, the iR drops of amorphous Ir/C catalyst, commercial Pt/C

catalyst and pure carbon from the solution resistance during HER experiments were corrected. All potentials measured were calibrated to the RHE according to the Nernst equation ($E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.199 + 0.059 * \text{pH}$). A total of 1000 and 5000 cyclic voltammetry scanning was performed at the voltage range from 0.1 to -0.1 V versus RHE with a scan rate of 100 mV s⁻¹ in 0.5 M H₂SO₄, and the i-t stability measurements were carried out at the overpotential of 42 mV versus RHE.

The Faradic efficiency of the amorphous Ir/C catalyst in electrochemical hydrogen evolution was defined as the ratio of the amount of hydrogen gas evolved during the electrochemical experiments to the expected theoretical amount of hydrogen evolution based on Faraday law. In order to obtain Faradic efficiency, the evolved hydrogen gas was collected during galvanostatic electrolysis, meanwhile, the purity of the generated hydrogen gas was confirmed by gas chromatography analysis and calculated the moles generated with an ideal gas law. Moreover, 100% current efficiency occurred during electrocatalytic hydrogen evolution was assumed as 100%, attributing to only existed HER process at the working electrode. The theoretically expected amount of hydrogen gas was calculated by applying the Faraday law, which demonstrated that the passage of 96485.4 C causes 1 equivalent of reaction.

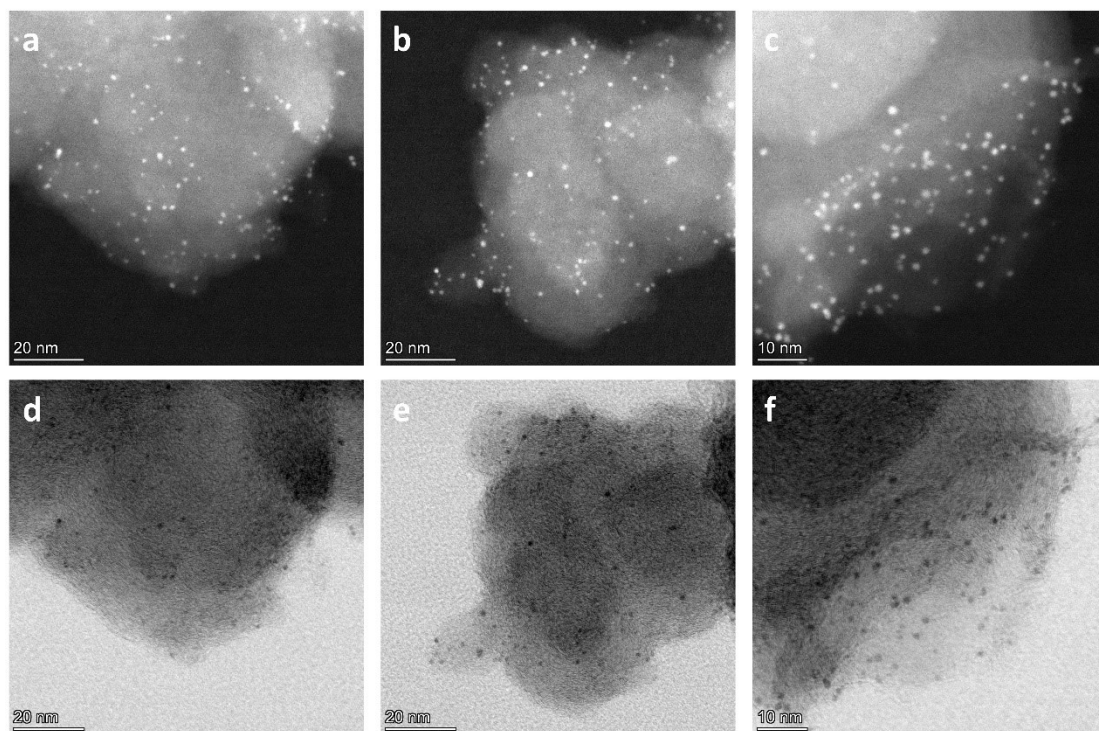


Figure S1. Extended STEM images of amorphous Ir/C catalyst.

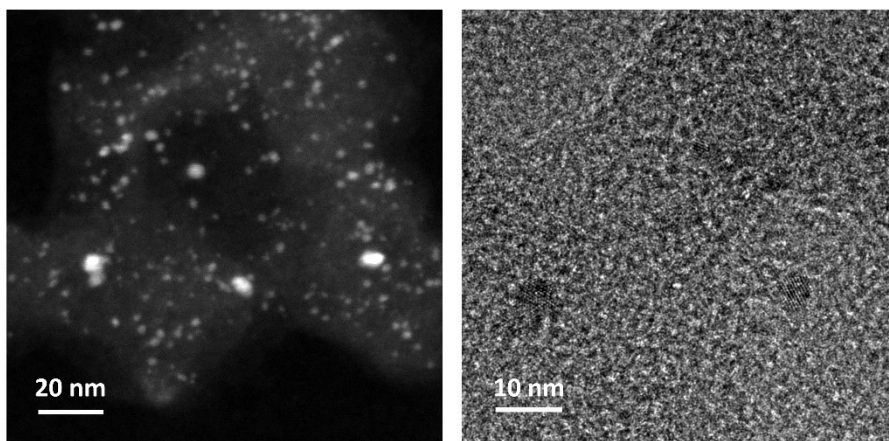


Figure S2. STEM images and HRTEM images of Ir NP/C catalyst, which synthesized via a hydrothermal method without the presence of boric acid.

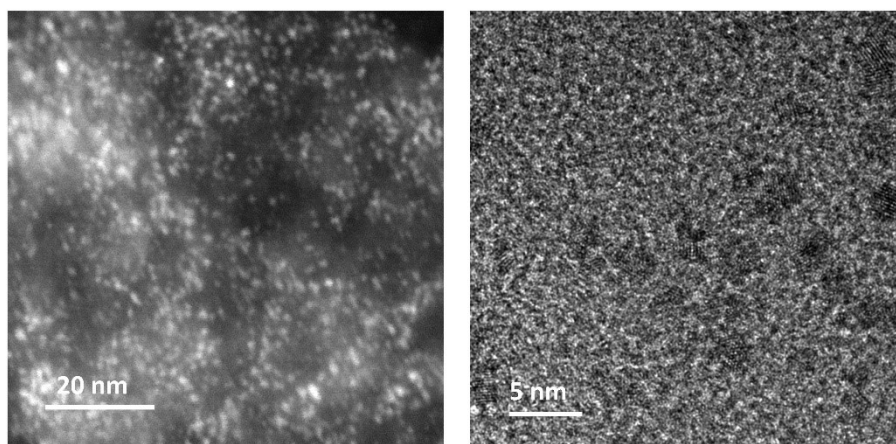


Figure S3. STEM images and HRTEM images of Ir NP/C catalyst, which synthesized via a hydrothermal method with the existence of potassium borohydride and without the presence of boric acid.

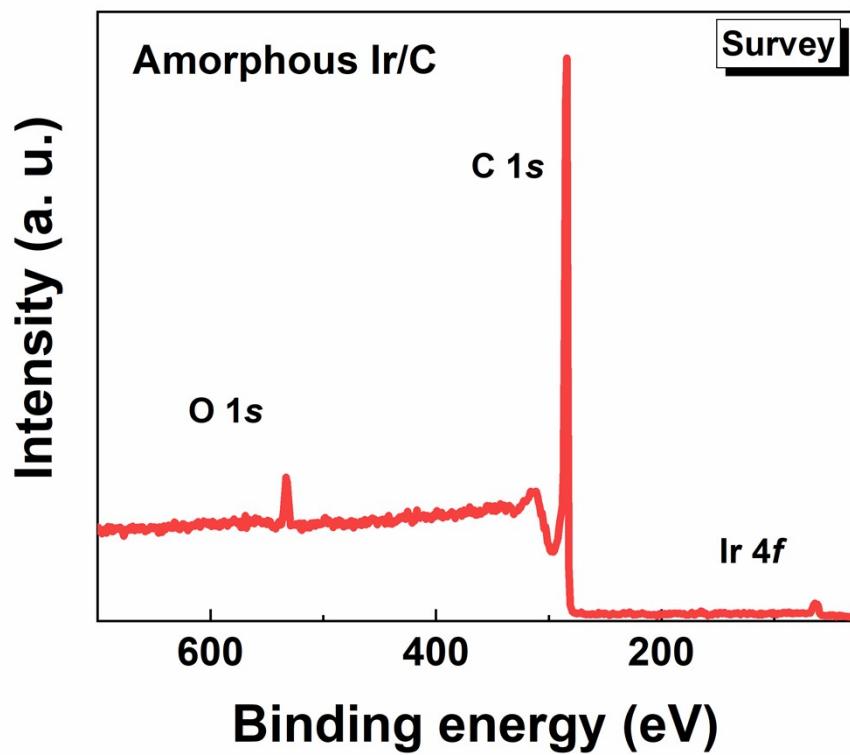


Figure S4. XPS survey of amorphous Ir/C catalyst. It indicated that no impurities were introduced.

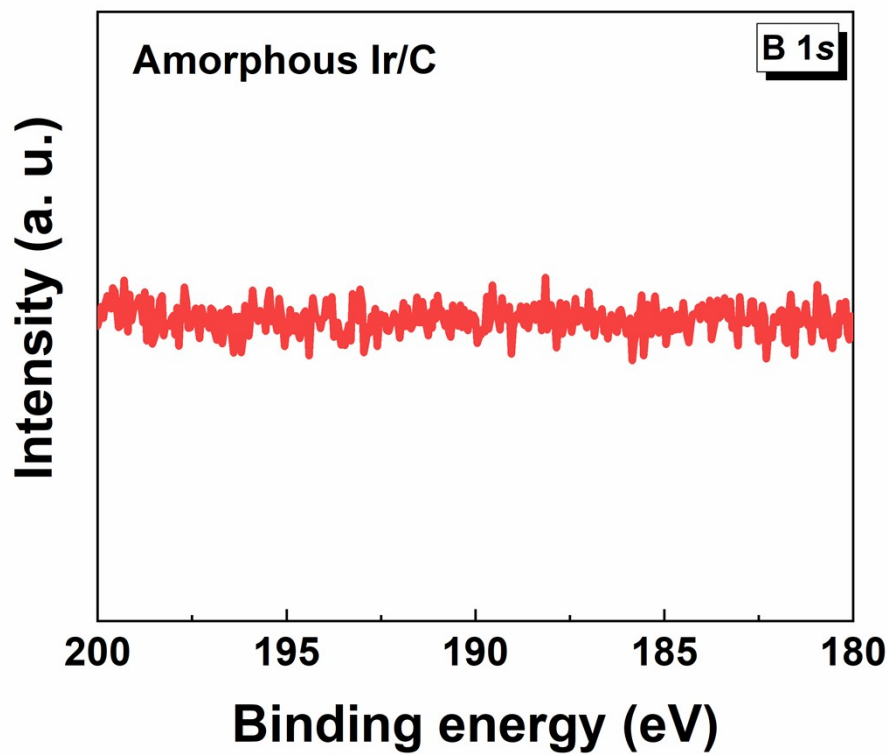


Figure S5. XPS spectrum of B 1s for amorphous Ir/C catalyst. It showed that no XPS signal of B 1s in amorphous Ir/C catalyst, indicative of almost no dopant of B element in amorphous Ir/C catalyst

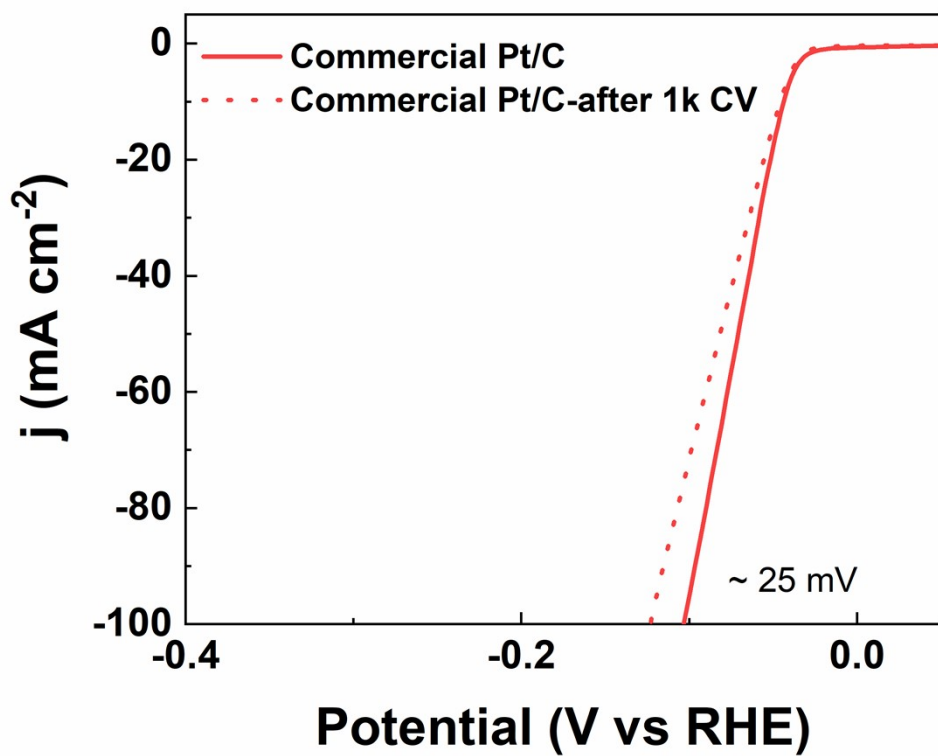


Figure S6. Polarization curves of fresh and used commercial Pt/C catalyst after 1000 CV cycles measurement. It showed that the polarization curve of the used commercial Pt/C catalyst exhibited an obvious decay of 25 mV after 1000 CV cycles.

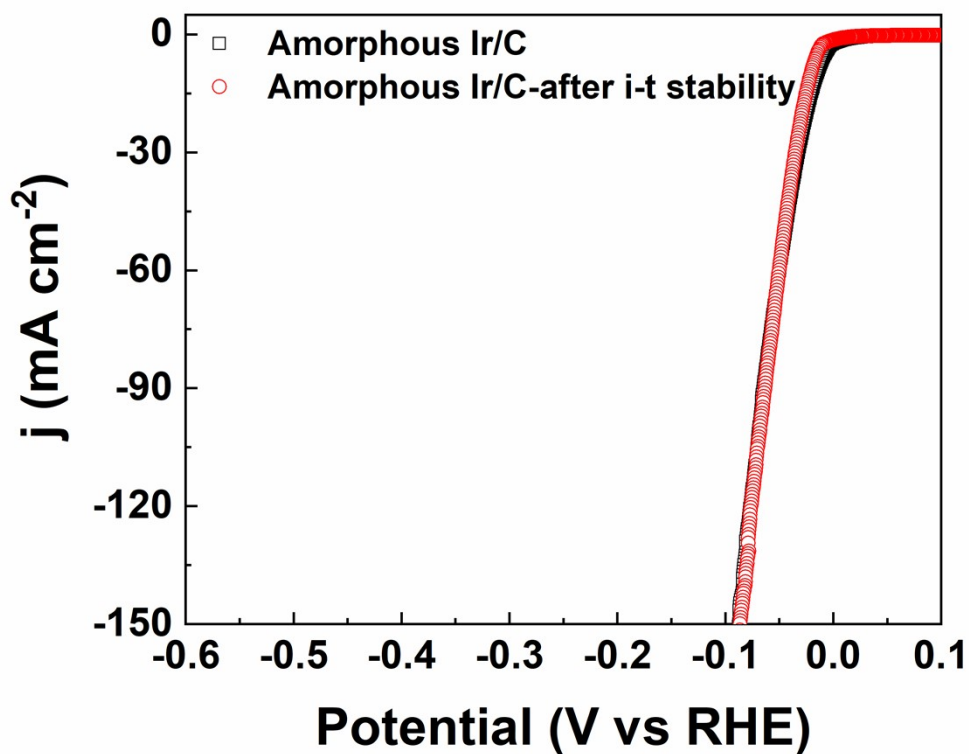


Figure S7. Polarization curves of fresh and used amorphous Ir/C catalyst after long-term i-t stability measurement. It showed that the polarization curve of the used amorphous Ir/C catalyst after long-term i-t stability test almost overlaid the curve of the fresh amorphous Ir/C catalyst with negligible loss in HER performance, indicating excellent durability of the amorphous Ir/C catalyst.

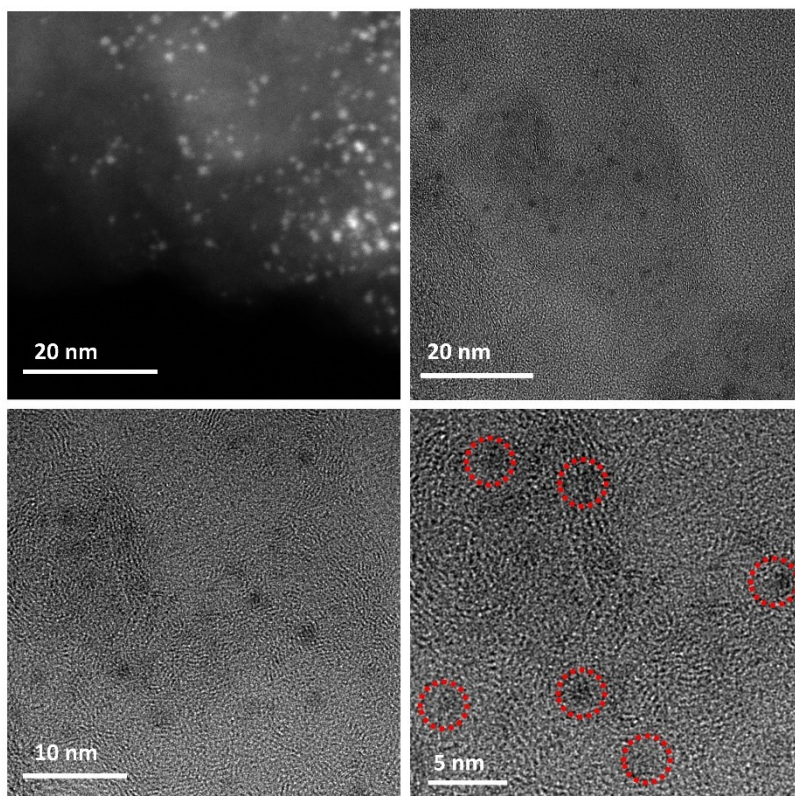


Figure S8. TEM and STEM images of amorphous Ir/C catalyst after i-t stability. It showed that the HER-post Ir/C catalyst still exhibited amorphous structure and almost unchanged Ir loading, indicative of its chemical stability.

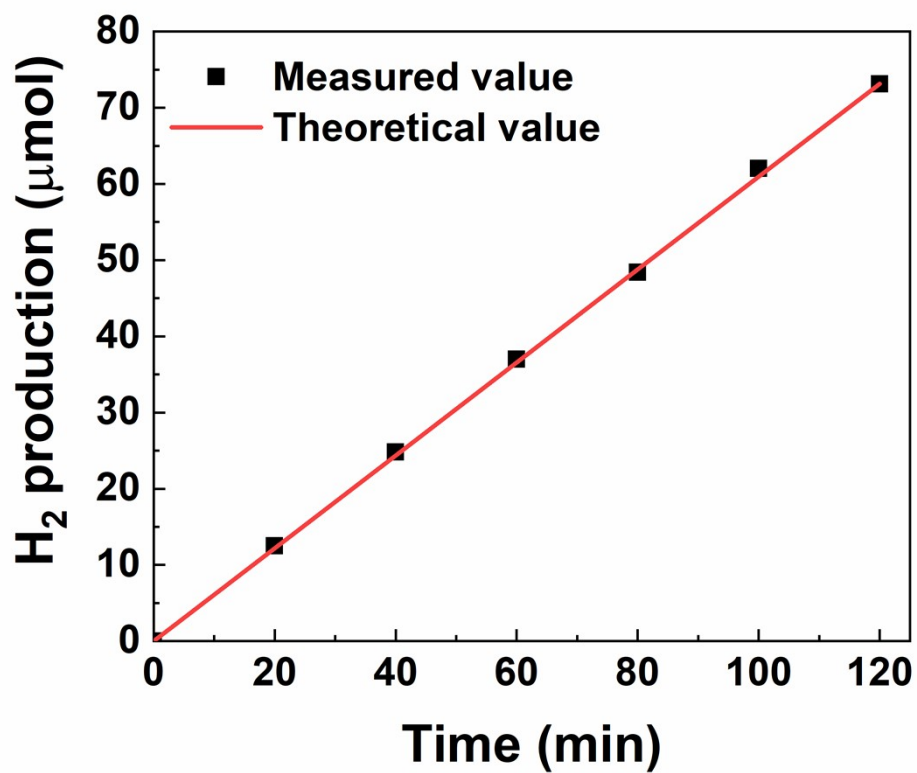


Figure S9. Electrochemical hydrogen production over amorphous Ir/C catalyst at a current density of 10 mA cm⁻².