

## Electronic Supplementary Information

# Spontaneous deposition of Ir nanoparticles on 2D siloxene as high-performance HER electrocatalyst with ultra-low Ir loading

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### List of Contents:

- 1. Experimental section: materials, preparation of siloxene sheets and Ir NPs/Siloxene, and characterization.**
- 2. Material characterization and electrochemical data.**
- 3. References**

## 1. Experimental section

**Materials** Calcium silicide ( $\text{CaSi}_2$ ) was purchased from Sigma-Aldrich (USA). Hexachloroiridium acid hydrate ( $\text{H}_2\text{IrCl}_6 \cdot x\text{H}_2\text{O}$ , Ir 35% in HCl) was purchased from Shanghai Macklin Biochemical Co. Ltd, China. Hydrochloric acid was supplied by Sinopharm Chemical Reagent Co. Ltd., China. The commercial Pt/C catalyst (20 wt. % Pt) was obtained from Alfa Aesar (USA).

**Preparation of siloxene sheets and Ir NPs/Siloxene** 2D siloxene sheets were prepared via topotactic transformation of layered  $\text{CaSi}_2$ .<sup>1</sup> Before the synthetic procedure,  $\text{CaSi}_2$  was pretreated with NaOH aqueous solution to remove impurity of crystalline silicon.  $\text{CaSi}_2$  powder (2 g) was dispersed into ice-cold concentrated hydrochloric acid (HCl, 200 mL) under vigorous stirring for 4 days. With the deintercalation of calcium from  $\text{CaSi}_2$ , the color of the dispersion transformed from black to yellowish green. The product was purified with acetone and water for several times, and then collected via centrifugation. Finally, the obtained siloxene sheets were freeze-dried under vacuum.

The Ir NPs/Siloxene catalyst was synthesized via a green and facile hydrothermal approach. Firstly, 2D siloxene sheets (60 mg) were added into deionized water (30 mL), followed by ultrasonic treatment to form a homogeneous dispersion. Subsequently, 20  $\mu\text{L}$   $\text{H}_2\text{IrCl}_6 \cdot x\text{H}_2\text{O}$  was dissolved into above mixture under continuous stirring for 30 min. The mixed solution was then transferred into a Teflon-lined autoclave and heated at 180 °C for 12 h. Finally, the product of Ir NPs/Siloxene catalyst was obtained after washing with deionized water and freeze-

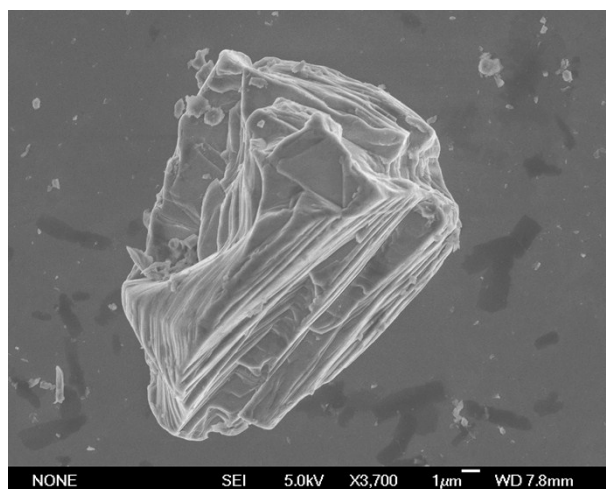
dried under vacuum. For comparative study, the sample of siloxene support was obtained by a similar hydrothermal treatment process without the addition of hexachloroiridium acid hydrate.

**Characterization** Scanning electron microscope (SEM) images and transmission electron microscope (TEM) images were obtained on Hitachi S-4800 (Japan) and Tecnai G2 F20 S-TWIN instruments (USA), respectively. Raman spectrum was collected on a Laser confocal inverted microraman spectrometer (invia-reflex, England). Powder X-ray diffraction (XRD) analysis was carried out on a D/MAX-RA instrument (Japan). Fourier transform infrared (FT-IR) spectroscopy measurements were performed on a Thermo Scientific FT-IR spectrometer (Nicolet 6700, USA). X-ray photoelectron spectroscopy (XPS) was recorded by ESCALAB250Xi spectrometer (USA). The loading mass of Ir in Ir NPs/Siloxene catalyst was measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

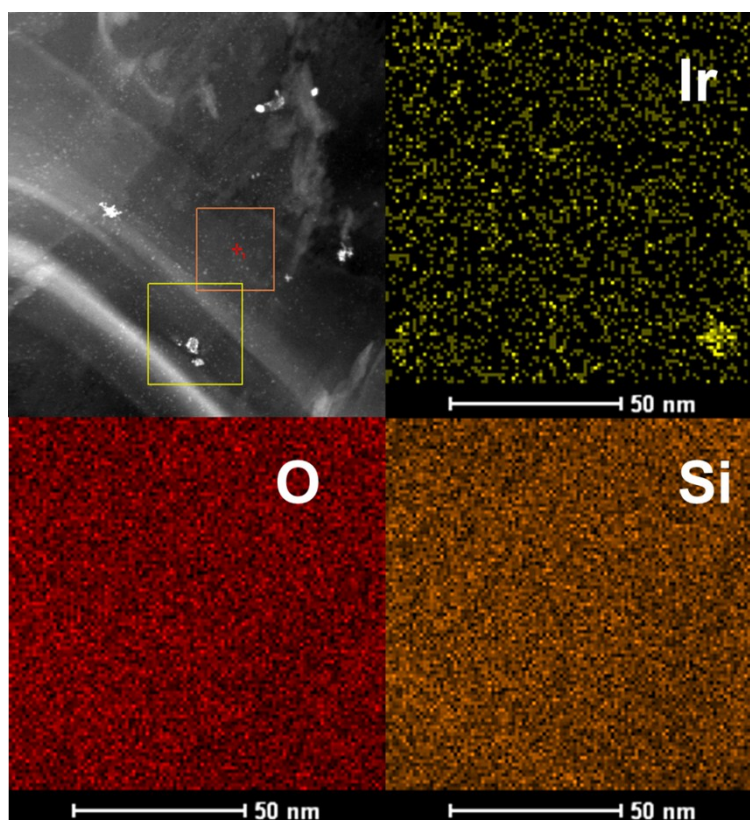
All electrochemical measurements were conducted on a CHI660D electrochemical workstation (Chenhua, China) at room temperature with a typical three-electrode configuration in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution. The modified glassy carbon (GC, 3 mm in diameter) electrode and saturated calomel electrode (SCE) were respectively employed as the working electrode and the reference electrode, and carbon rod was used as the counter electrode. To fabricate the working electrode, GC electrode was successively polished using 0.3 μm and 0.05 μm of alumina slurry, followed by rinsing with deionized water and ethanol alternately, and then dried for further use. The catalyst ink was prepared by ultrasonically

dispersing 5 mg of catalysts into 1 mL mixed solvent of ethanol/water with a volume ratio of 1:1. After that, 4  $\mu\text{L}$  of the catalyst slurry was pipetted onto the surface of GC electrode with a loading of  $0.2831 \text{ mg}_{\text{catalyst}} \cdot \text{cm}^{-2}$ . After dried at room temperature, 4  $\mu\text{L}$  of 0.5 wt.% Nafion ethanol solution was coated on the electrode. For the linear sweep voltammetry (LSV) measurements, the scan rate was set as 10 mV/s. The polarization curves were collected without iR compensation. Derived from the corresponding LSV curves, Tafel plots were obtained based on Tafel equation of  $\eta = a + b \log j$  ( $\eta$  is the overpotential,  $a$  is the Tafel constant,  $b$  is the Tafel slope and  $j$  is the current density). All the potentials reported are calibrated with respect to a reversible hydrogen electrode (RHE,  $E_{\text{vs.RHE}} = E_{\text{vs.SCE}} + 0.2415 + 0.0591 \times \text{pH}$ ). To show the hydrogen adsorption and desorption processes, the cyclic voltammetry (CV) measurements for the Ir NPs/Siloxene and Pt/C electrodes were conducted at  $50 \text{ mV s}^{-1}$  in the potential range of 0.01 V to 1.1 V vs RHE in 0.5 M Ar-saturated  $\text{H}_2\text{SO}_4$  aqueous solution. Electrochemical impedance spectroscopy (EIS) measurements were carried out with a frequency from 0.01 Hz to 100 kHz at amplitude of 5 mV. The electrical conductivity of siloxene was measured on a four-terminal configuration (Agilent 4339B) at room temperature and normal pressure.

## 2. Material characterization and electrochemical data

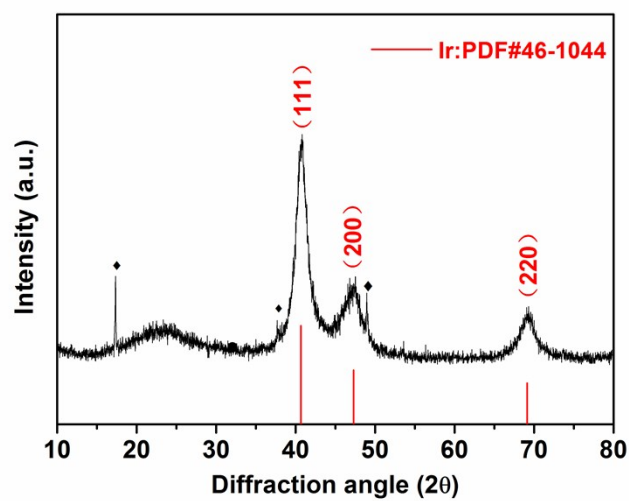


**Fig. S1** SEM image of the pristine  $\text{CaSi}_2$ .

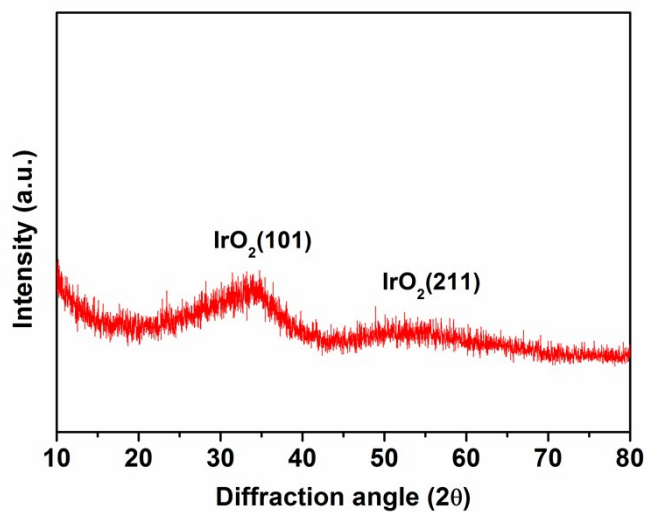


**Fig. S2** STEM image of Ir NPs/Siloxene and the corresponding EDX mapping of Ir,

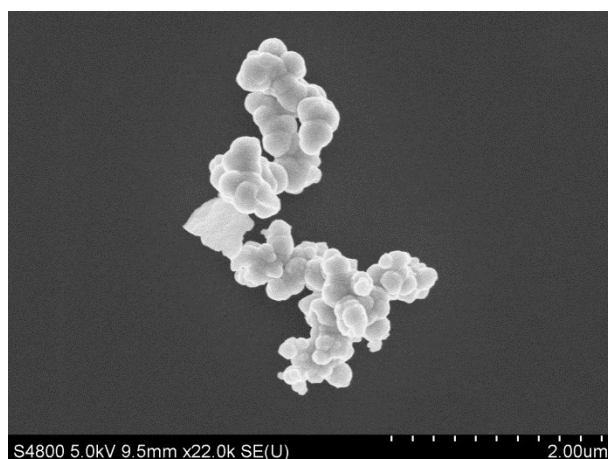
O and Si elements.



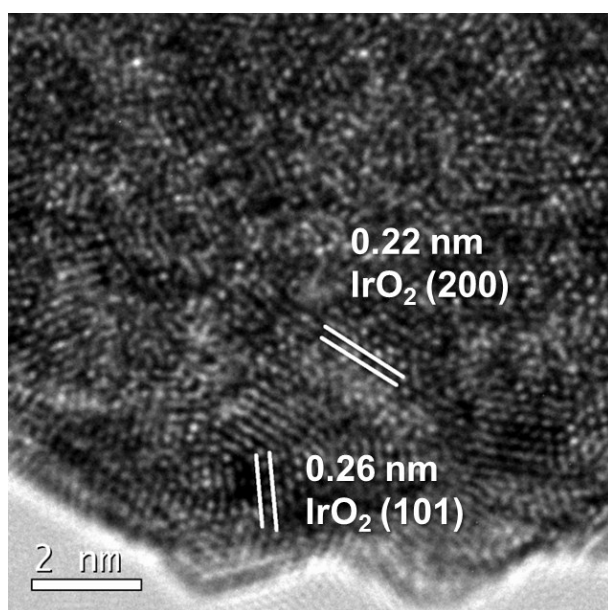
**Fig. S3** XRD pattern of Ir NPs/Siloxene (FeSi<sub>2</sub> impurity as marked by ◆ is often unavoidable in commercial CaSi<sub>2</sub> even after purification<sup>2, 3</sup>).



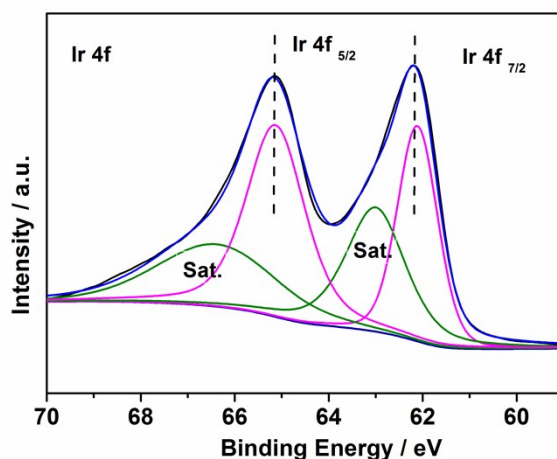
**Fig. S4** XRD pattern of the Ir-based sample synthesized by a similar procedure without the addition of siloxene.



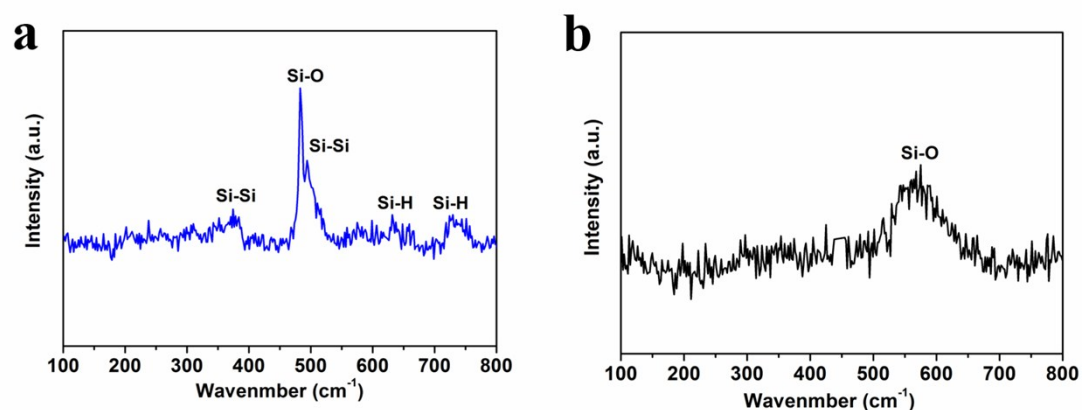
**Fig. S5** SEM image of the Ir-based sample synthesized by a similar procedure without the addition of siloxene.



**Fig. S6** HRTEM images of the Ir-based sample synthesized by a similar procedure without the addition of siloxene.



**Fig. S7** High-resolution Ir 4f XPS spectrum of the Ir-based sample synthesized by a similar procedure without the addition of siloxene.

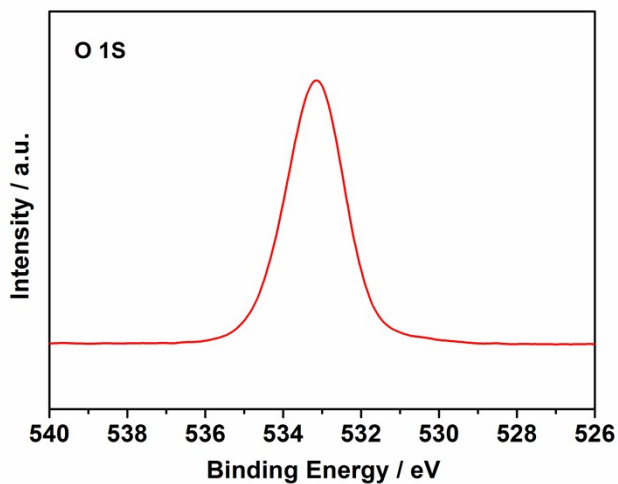


**Fig. S8** Raman spectra of (a) siloxene and (b) Ir NPs/Siloxene.

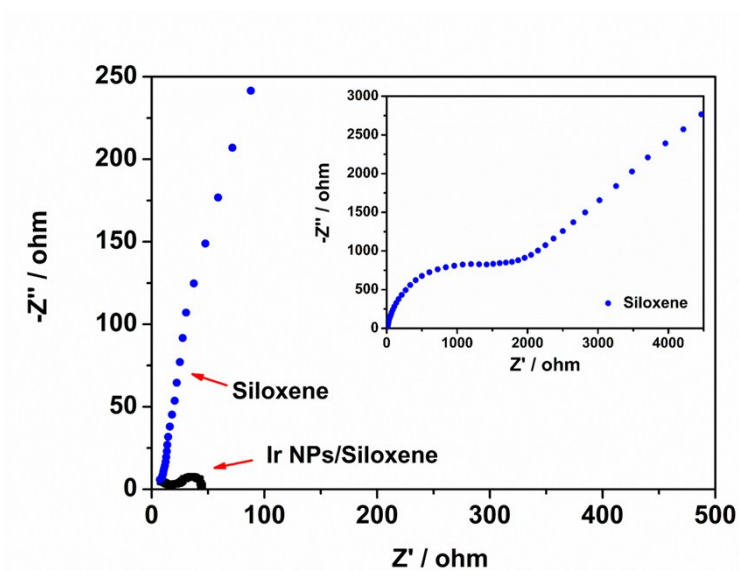
Raman spectrum in Fig. S8a indicates the successful preparation of siloxene with the presence of Si-Si vibrations ( $375\text{ cm}^{-1}$  and  $495\text{ cm}^{-1}$ ), Si-O vibrations ( $480\text{ cm}^{-1}$ ), and Si-H vibrations ( $640\text{ cm}^{-1}$  and  $735\text{ cm}^{-1}$ ).<sup>4, 5</sup> By contrast, the characteristic peaks of Si-H vibrations at  $640\text{ cm}^{-1}$  and  $735\text{ cm}^{-1}$  disappear for Ir NPs/Siloxene (Fig. S8b), further confirming the depletion of Si-H groups on siloxene during the reduction of



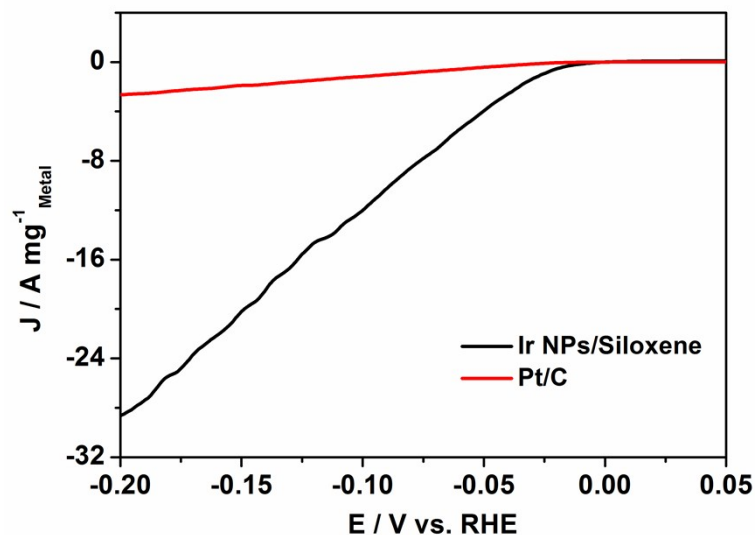
$\text{IrCl}_6^{2-}$ . The weakening of Si-Si vibrations for Ir NPs/Siloxene is potentially attributed to the slight oxidation of siloxene during the hydrothermal treatment,<sup>1</sup> resulting in the dominant Si-O vibrations at  $\sim 575 \text{ cm}^{-1}$ .<sup>6</sup>



**Fig. S9** High-resolution O 1s XPS spectrum of Ir NPs/Siloxene.



**Fig. S10** Nyquist plots of siloxene and Ir NPs/Siloxene at 25 mV overpotential. The insert plot is the whole EIS pattern of siloxene.

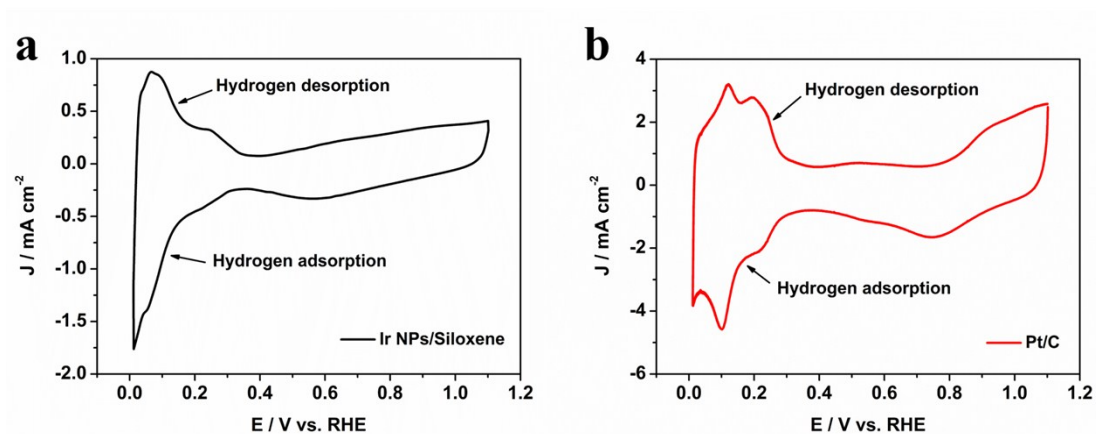


**Fig. S11** The mass activity of the Ir NPs/Siloxene and Pt/C catalysts.

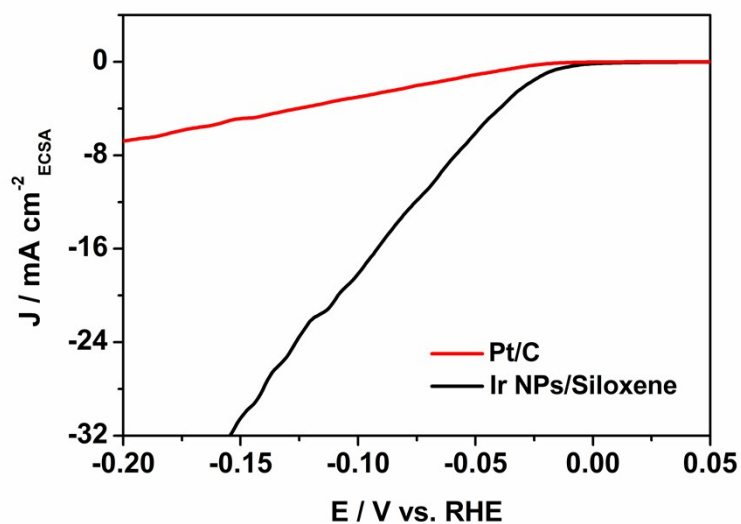
The mass activity of Ir NPs/Siloxene and Pt/C catalysts were calculated by normalizing to noble metal loading based on the ICP results according to the following equation:<sup>7</sup>

$$\text{Mass activity} = \frac{J}{0.2831 * W} (\text{A} \cdot \text{mg}^{-1})$$

Where J and W respectively represent the current density ( $\text{A} \cdot \text{cm}^{-2}$ ) and noble metal loading mass (wt.%) on the catalysts. And  $0.2831 \text{ mg}_{\text{catalyst}} \cdot \text{cm}^{-2}$  is the catalyst loading mass on the surface of the glassy carbon electrode.



**Fig. S12** CV curves of Ir NPs/Siloxene and Pt/C catalysts in Ar-saturated 0.5 M  $H_2SO_4$  aqueous solution.



**Fig. S13** Specific activity of the Ir NPs/Siloxene and Pt/C catalysts.

The specific activity of Ir NPs/Siloxene and Pt/C catalysts is further evaluated based on the electrochemically active surface areas (ECSA) estimated from the CV results in Fig. S12. By integrating and averaging the amount of Coulombic charge of hydrogen adsorption and desorption after subtracting the double-layer region,<sup>8</sup> the ECSA values of the Ir NPs/Siloxene and Pt/C catalysts are calculated to be 0.28 cm<sup>2</sup> and 1.57 cm<sup>2</sup> respectively according to the following equation:

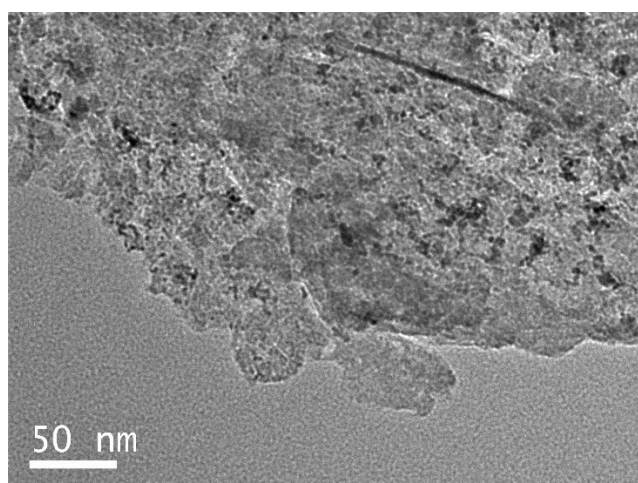
$$ECSA_{Ir} = \frac{Q_H}{2.18 \times 10^{-4}} cm^2$$

$$ECSA_{Pt} = \frac{Q_H}{2.10 \times 10^{-4}} cm^2$$

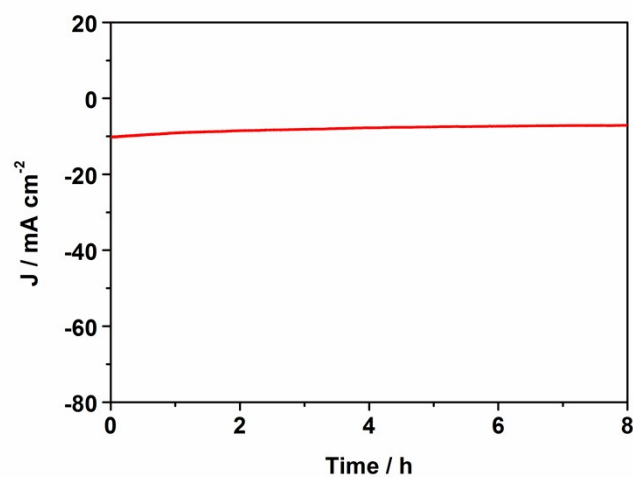
Where  $Q_H$  (C) presents the average charge of hydrogen adsorption and desorption;  $2.18 \times 10^{-4}$  (C cm<sup>-2</sup>) and  $2.10 \times 10^{-4}$  (C cm<sup>-2</sup>) are the surface charge density for a monolayer adsorption of H on Ir and Pt, respectively.<sup>9, 10</sup> Consequently, the specific

activities of the Ir NPs/Siloxene and Pt/C catalysts are obtained by normalizing the current of the HER polarization curves according to corresponding ECSA.<sup>11</sup>

The TOF values was calculated based on the resulted ECSA values according to the reported method.<sup>12, 13</sup>



**Fig. S14** TEM of Ir NPs/Siloxene after 1000 CV cycles.



**Fig. S15** Time-dependent current density of Ir NPs/Siloxene catalyst at a static overpotential of 31 mV for 8h.

### 3. References

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