

Immobilized Iridium Complexes for Hydrogen Evolving from Formic Acid Dehydrogenation

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SI-1. The Preparation of the Immobilized Iridium Catalysts in Table 1.

The FTIR data of $[\text{Cp}^*\text{IrCl}_2]_2$ were collected by Nicolet iS10 (Nicolet Instrument Co. USA). As exhibited in the **Figure S 1**, the 2992 cm^{-1} and 2912 cm^{-1} are the asymmetric stretching vibration of the $-\text{CH}_3$. The 1626 cm^{-1} is the $\text{C}=\text{C}$ stretching vibration. The 1451 cm^{-1} and 1378 cm^{-1} are the $\text{C}-\text{H}$ bending vibration absorption peaks. The 451 cm^{-1} is the characteristic absorption peak of $[\text{Cp}^*\text{IrCl}_2]_2$, it belongs to the $\text{Ir}-\text{Cl}$ bond in the complex.

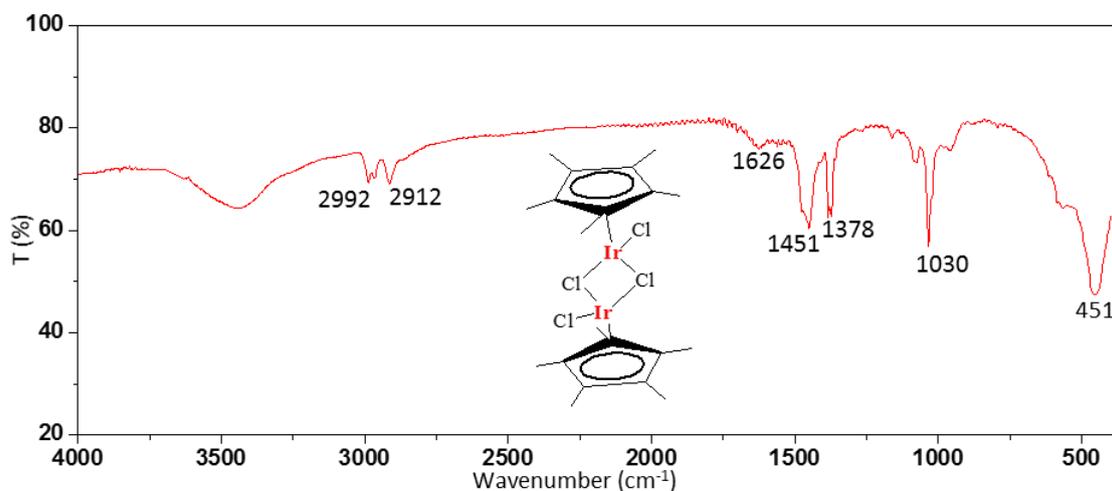
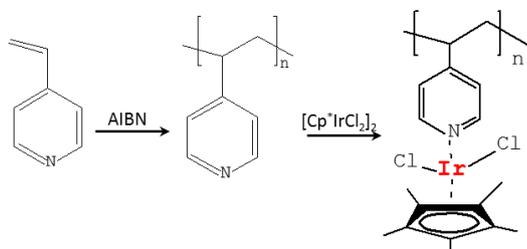


Figure S 1. The FTIR Spectrum of the $[\text{Cp}^*\text{IrCl}_2]_2$.

The detailed process to prepare the immobilized iridium complexes **a** is exhibited in **Scheme S 1**. Firstly, we use 4-vinylpyridine to prepare the polyvinylpyridine at 90 °C. AIBN are employed as the initiator, the water and ethanol are used as the mixing solvent. The polyvinylpyridine could immobilize the iridium complex through the complexation between the pyridine and iridium.



Scheme S 1. Detailed Process to Prepare the Immobilized Iridium Complex **a** in **Table 1**.

The FTIR data of the immobilized iridium complex **a** were collected by Nicolet iS10. As exhibited in the **Figure S 2**, the 3024 cm^{-1} , 2922 cm^{-1} and 2850 cm^{-1} are the C-H asymmetric stretching vibration of the pyridine ring, methyl and methylene in the catalyst. The 1592 cm^{-1} and 1557 cm^{-1} are the C=N stretching vibration and the C=C stretching vibration of pyridine ring respectively. The 451 cm^{-1} is the Ir-Cl characteristic absorption peak, indicate the Cp^*IrCl_2 have been immobilized on the poly (vinyl pyridine).

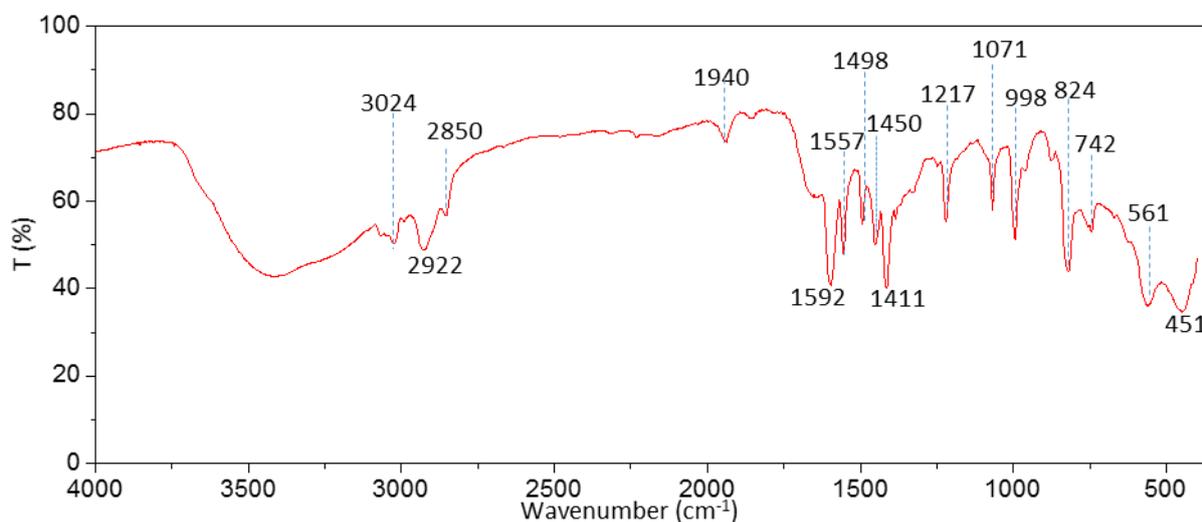
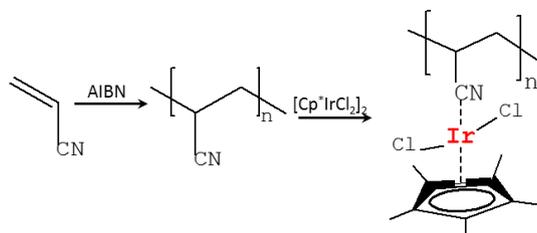


Figure S 2. the FTIR Spectrum of the Immobilized Iridium Complex **a** in **Table 1**.

The detailed process to prepare the immobilized iridium complex **b** is exhibited in **Scheme S 2**. Firstly, we use acrylonitrile to prepare the polyacrylonitrile at 90 °C. AIBN is employed as the initiator, the water and ethanol are used as the mixing solvent. The polyacrylonitrile could immobilize the iridium complex through the complexation between the nitrile group and iridium.



Scheme S 2. Detailed Process to Prepare the Immobilized Iridium Complex **b** in **Table 1**.

The FTIR data of the immobilized iridium complex **b** were collected by Nicolet iS10. As exhibited in the **Figure S 3**, the 2939 cm⁻¹ is the C-H asymmetric stretching vibration in the catalyst. The 2245 cm⁻¹ is the C≡N stretching vibration in the catalyst. The 1462 cm⁻¹ is the in-plane bending vibration of -CH₃ in the catalyst. The 451 cm⁻¹ is the Ir-Cl characteristic absorption peak, indicate the Cp*IrCl₂ have been immobilized on the polyacrylonitrile. These characteristic absorption peaks indicate the immobilized iridium catalyst own the Cp*IrCl₂ group and nitrile group, and the catalyst is the target product.

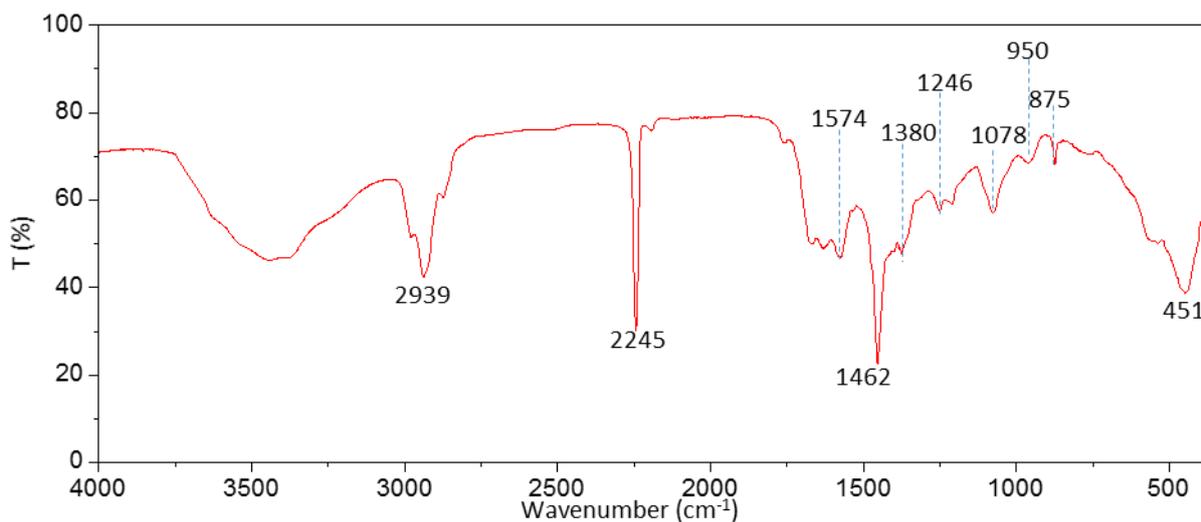
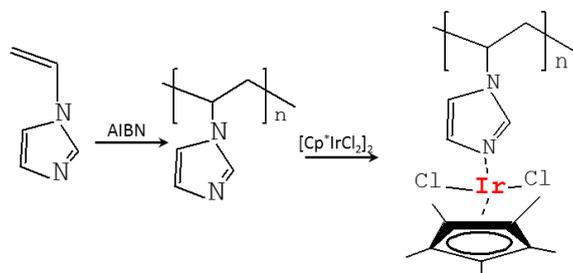


Figure S 3. the FTIR Spectrum of the Immobilized Iridium Complex **b** in **Table 1**.

The detailed process to prepare the immobilized iridium complex **c** is exhibited in **Scheme S 3**. Firstly, we use 1-vinylimidazole to prepare the polyvinylimidazole at 90 °C. AIBN is employed as the initiator, the water and ethanol are used as the mixing solvent. The polyvinylimidazole could immobilize the iridium complex through the complexation between the imidazole group and iridium.



Scheme S 3. Detailed Process to Prepare the Immobilized Iridium Complexes **c** in **Table 1**.

The FTIR data of the immobilized iridium complex **c** were collected by Nicolet iS10. As exhibited in the **Figure S 4**, the 3109 cm^{-1} and 2950 cm^{-1} are the C-H asymmetric stretching vibration of methyl and methylene in the catalyst. The 1665 cm^{-1} is the stretching vibration of C=N bond in the catalyst, which is belong to imidazole group. The 1496 cm^{-1} is the stretching vibration of C=C bond in the catalyst, which is also belong to imidazole group. The 451 cm^{-1} is the Ir-Cl characteristic absorption peak, indicate the Cp^*IrCl_2 have been immobilized on the polyvinylimidazole. These characteristic absorption peaks indicate the immobilized iridium catalyst own the Cp^*IrCl_2 group and imidazole group, and the catalyst is the target product.

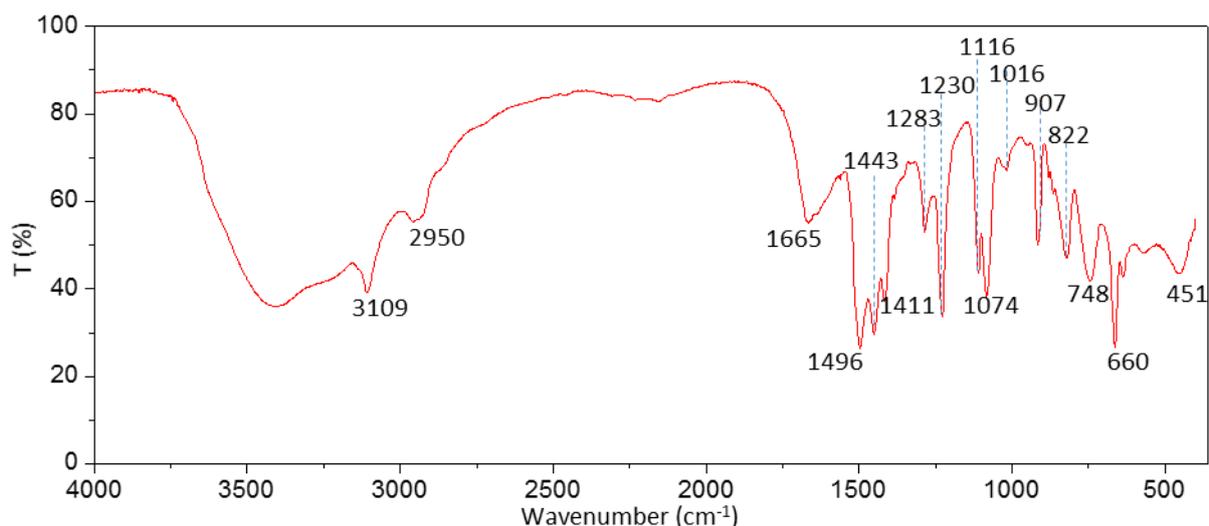
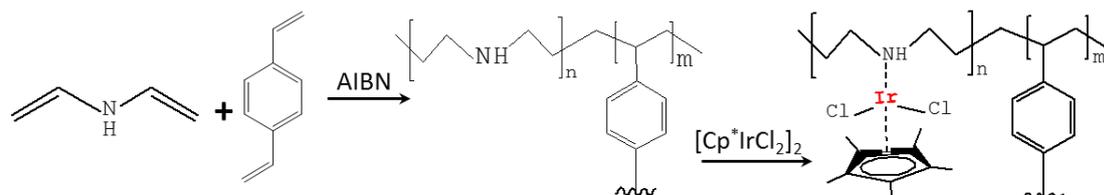


Figure S 4. The FTIR Spectrum of the Immobilized Iridium Complex **c** in **Table 1**.

The detailed process to prepare the immobilized iridium complex **e** is exhibited in **Scheme S 4**. Firstly, 1mL diallylamine and 0.8mL divinylbenzene were mixed in the water-ethanol solvent at 90 °C. Then 50mg AIBN were added in the solution. The diallylamine and divinylbenzene are the frequently used cross linking agent. After 8 hours, we gained the insoluble polydiallylamine. It is insoluble in most solvent. The polydiallylamine could immobilize the iridium complex through the complexation between the imino group and iridium.



Scheme S 4. Detailed Process to Prepare the Immobilized Iridium Complex **e** in **Table 1**.

The FTIR data of the immobilized iridium complex **e** were collected by Nicolet iS10. As exhibited in the **Figure S 5**, the 3022 cm^{-1} and 2920 cm^{-1} are the C-H asymmetric stretching vibration of methyl and methylene in catalyst. The 1631 cm^{-1} is the N-H stretching vibration in the catalyst. The 1597 cm^{-1} is the C=C stretching vibration in benzene ring. The 451 cm^{-1} is the Ir-Cl characteristic absorption peak, indicate the Cp^*IrCl_2 have been immobilized on the polydiallylamine. These characteristic absorption peaks indicate the immobilized iridium catalyst own the Cp^*IrCl_2 group and imine group, and the catalyst is the target product.

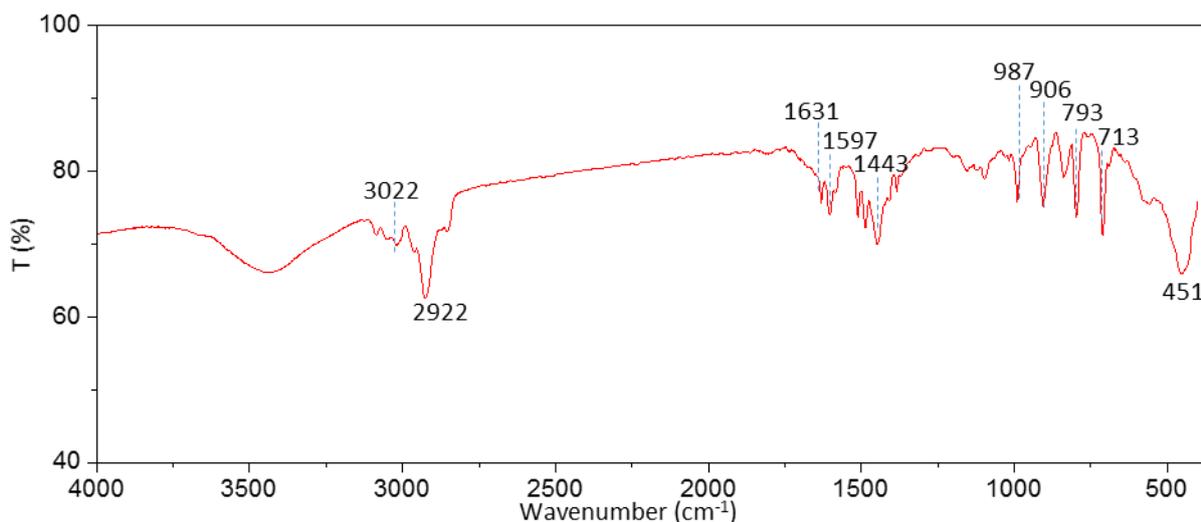
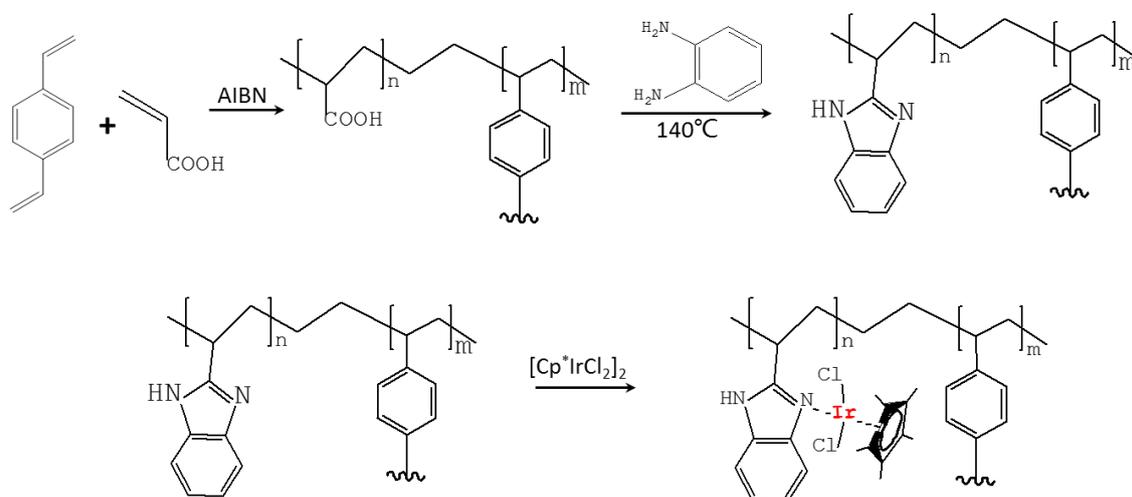


Figure S 5. The FTIR Spectrum of the Immobilized Iridium Complex **e** in **Table 1**.

The detailed process to prepare the immobilized iridium complex **f** is exhibited in **Scheme S 5**. Firstly, 1 mL acrylic acid and 0.8 mL divinylbenzene were mixed in the water-ethanol solvent at 90 °C. Then 50 mg AIBN were added in the solution. The divinylbenzene is the frequently used cross linking agent. After 8 hours, the insoluble polyacrylic acid could be filtered from the solution. At last, transferred 1 g insoluble polyacrylic acid in hydrothermal reactor, reacted with 300 mg o-phenylenediamine in ethanol at 140 °C for 12 hours. The benzimidazole group could form through the reactions between carboxyl and o-phenylenediamine. After being filtered, washed with water and dried under vacuum, the insoluble polybenzimidazole was prepared. The polybenzimidazole could immobilize the iridium complex through the complexation between the imidazole group and iridium.



Scheme S 5. Detailed Process to Prepare the Immobilized Iridium Complex **f** in **Table 1**.

The FTIR data of the immobilized iridium complex **f** were collected by Nicolet iS10. As exhibited in the **Figure S 6**, the 3062 cm⁻¹, 3029 cm⁻¹, 2920 cm⁻¹ and 2841 cm⁻¹ are the C-H asymmetric stretching vibration in methyl, methylene and benzene ring of the catalyst. 1702 cm⁻¹ is the C=O stretching vibration in the catalyst. 1627 cm⁻¹ is the C=N stretching vibration of benzimidazole in the catalyst. 1503 cm⁻¹ is the in-plane bending vibration of N-H in the catalyst. The 1455 cm⁻¹ and 1387 cm⁻¹ are C-H bending vibration absorption peaks of benzimidazole and methyl. The 451 cm⁻¹ is the Ir-Cl characteristic absorption peak, indicate the Cp*IrCl₂ have been immobilized on the polybenzimidazole. These characteristic absorption peaks indicate the immobilized iridium catalyst own the Cp*IrCl₂ group and benzimidazole group, and the catalyst is the target product.

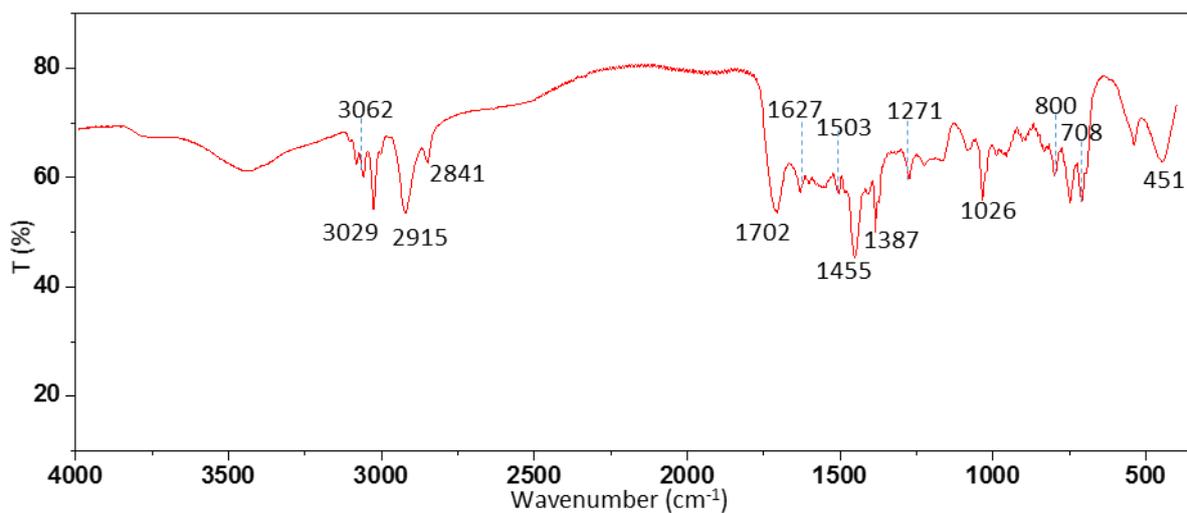


Figure S 6. The FTIR Spectrum of the Immobilized Iridium Complex **f** in **Table 1**.

SI-2. Characterization of Two Representative Polymers.

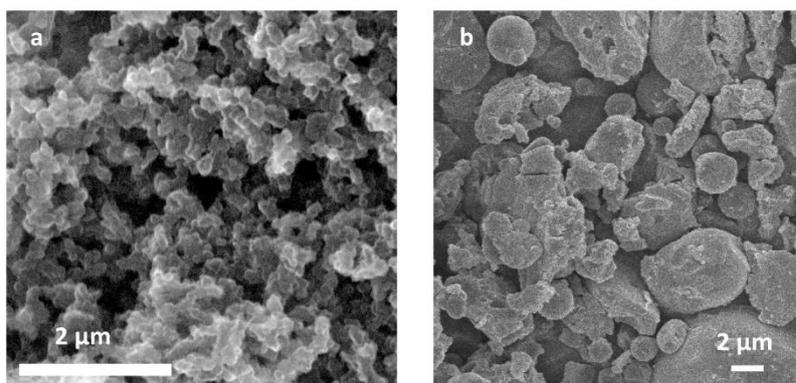


Figure S 7. (a) and (b) SEM Images of Polypyrrole and the Poly(benzimidazole) Respectively.

The samples were lay on the conductive glass. The SEM images were recorded on Quanta 400 FEG, FEI. As exhibited in the **Figure S 7**, the polypyrrole have the porous structure and big surface area. The poly(benzimidazole) don't own the porous structure.

As exhibited in the **Figure S 8**, the bending energy of C 1s and N 1s in polypyrrole are 284.6 eV and 399.4 eV respectively.

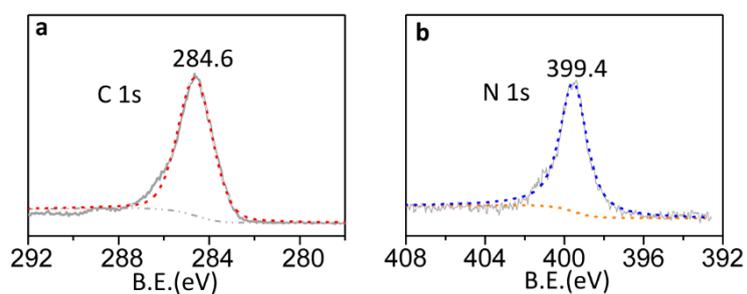


Figure S 8. XPS Spectra of C 1s and N 1s in Polypyrrole.

SI-3. Characterization and Catalytic Activity of the $[\text{Cp}^*\text{IrCl}_2]_2$.

As exhibited in the **Figure S 9**, the binding energy of Ir 4f in $[\text{Cp}^*\text{IrCl}_2]_2$ is 64.6 eV and 61.6 eV, the binding energy of C 1s in $[\text{Cp}^*\text{IrCl}_2]_2$ is 284.6 eV.

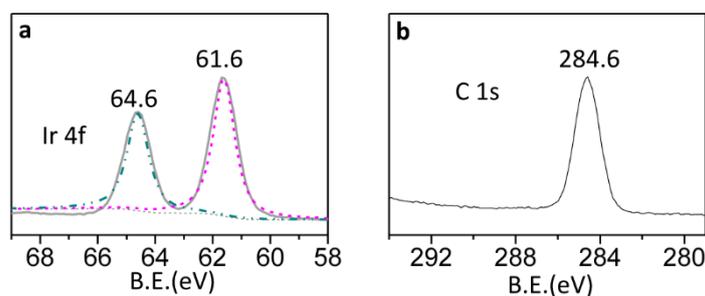


Figure S 9. XPS Spectra of C 1s and N 1s in $[\text{Cp}^*\text{IrCl}_2]_2$.

As exhibited in the **Figure S 10**, the $[\text{Cp}^*\text{IrCl}_2]_2$ has low catalytic activity for hydrogen generation from the formic acid dehydrogenation. The catalytic stability is not well, the gas evolving rate decrease during the formic acid dehydrogenation.

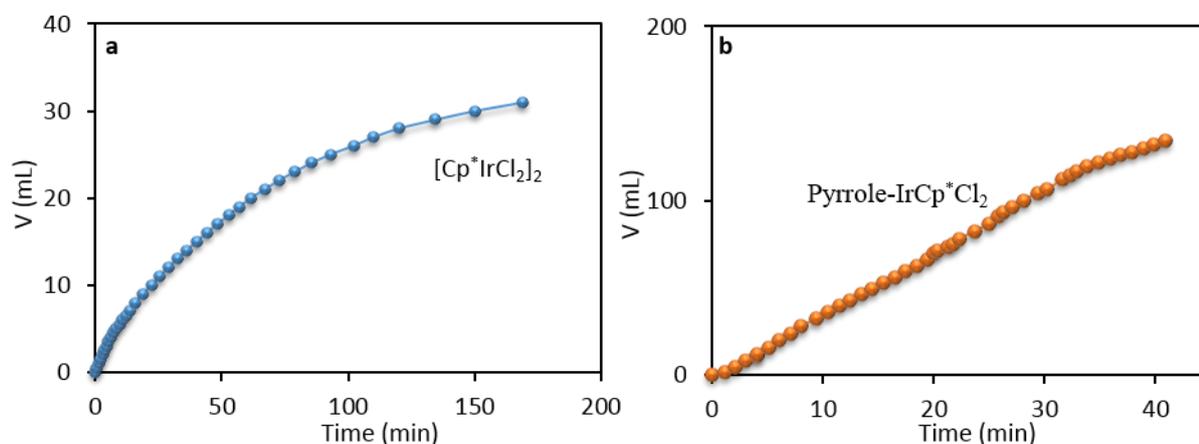


Figure S 10. Formic Acid Dehydrogenation. (a) Gas Evolved From 1M Formic Acid Dehydrogenation Catalyzed by 3mg $[\text{Cp}^*\text{IrCl}_2]_2$ at 30 °C in water. (b) Gas Evolved From 1M Formic Acid Dehydrogenation Catalyzed by pyrrole- IrCp^*Cl_2 at 30 °C in water, the solution contain 3 mg $[\text{Cp}^*\text{IrCl}_2]_2$ and 100 μ L pyrrole.

The pyrrole- IrCp^*Cl_2 catalytic system shows more catalytic activity and stability for the formic

acid dehydrogenation.

SI-4.Characterization and Catalytic Activity of the Cp*IrCl₂ (ppy).

As exhibited in the **Figure S 11**, the bending energy of N 1s in Cp*IrCl₂ (ppy) is 399.0 eV, the bending energy of Ir 4f in Cp*IrCl₂ (ppy) is 64.5 eV and 61.5 eV. ¹

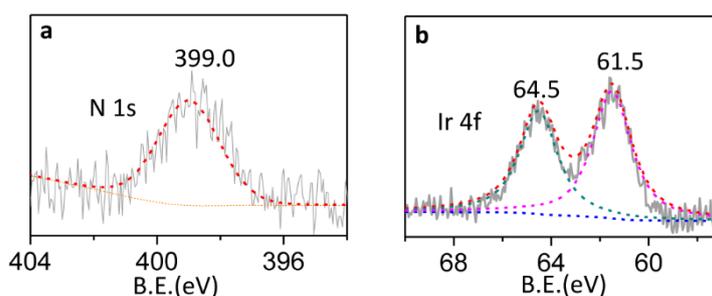


Figure S 11. XPS Spectra of C 1s and N 1s in Cp*IrCl₂ (ppy).

The particle size distribution of the Cp*IrCl₂(ppy) is analyzed by Malvern Instruments Zetasizer Nano ZS90. As exhibited in the **Figure S 12**, the particle size distribution is among 300 nm to 700 nm. The small particles could well disperse in the reaction solution and catalyze formic acid dehydrogenation.

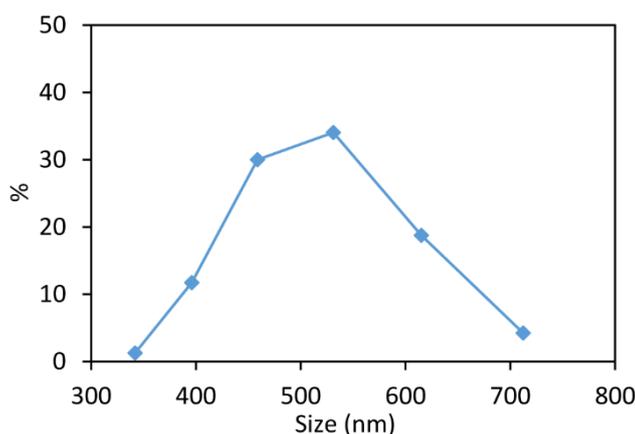


Figure S 12. Particle Size Distribution of the Cp*IrCl₂(ppy).

The surface areas of the polypyrrole and Cp*IrCl₂(ppy) were determined by the Brunauer-Emmett-Teller (BET) method, based on the amount of N₂ adsorbed at pressures 0.05 < P/P₀ < 0.3. The pore size distributions and average pore diameter of the catalyst were analyzed by the BJH nitro-gen

adsorption and desorption method (ASAP 2020, Micromeritics, USA). As exhibited in the **Figure S 13**, the specific surface areas of the $\text{Cp}^*\text{IrCl}_2(\text{ppy})$ was $51.0 \text{ m}^2 \text{ g}^{-1}$.

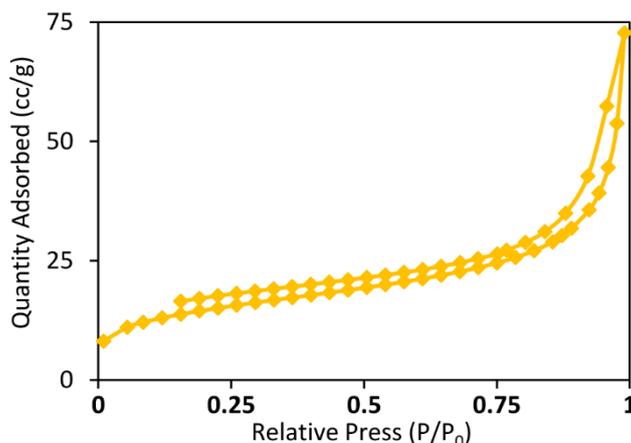


Figure S 13. N_2 BET Adsorption/Desorption Isotherms for the $\text{Cp}^*\text{IrCl}_2(\text{ppy})$.

The hydrogen could evolve from formic acid dehydrogenation catalyzed by $\text{Cp}^*\text{IrCl}_2(\text{ppy})$. As exhibited in the **Figure S 14**, when we added the HCl in the formic acid solution, the gas evolving rate will decrease although the H^+ concentration increase in the solution. So we think stronger acidity would lower the catalytic activity of IrCp^* group for formic acid dehydrogenation.

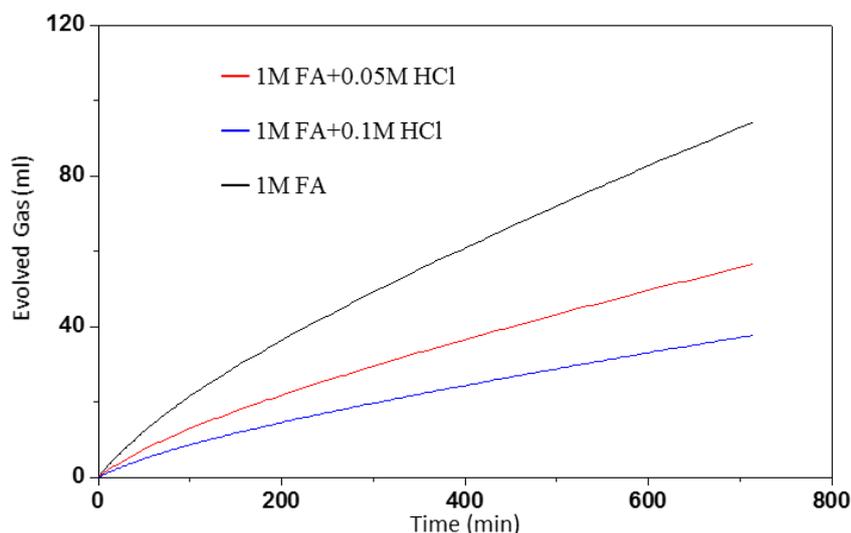


Figure S 14. Hydrogen Evolving from 1M Formic Acid Dehydrogenation Catalyzed by 3mg $\text{Cp}^*\text{IrCl}_2(\text{ppy})$ at 30°C in water under Different Condition.

The $\text{Cp}^*\text{IrCl}_2(\text{ppy})$ have high catalytic stability for the formic acid dehydrogenation. As exhibited in the **Figure S 15**, the gas will generate from the formic acid dehydrogenation catalyze by

$\text{Cp}^*\text{IrCl}_2(\text{ppy})$. The reaction rate is decreasing during the total process due to the formic acid consumption. Because the formic acid concentration will have great influence on its dehydrogenation.

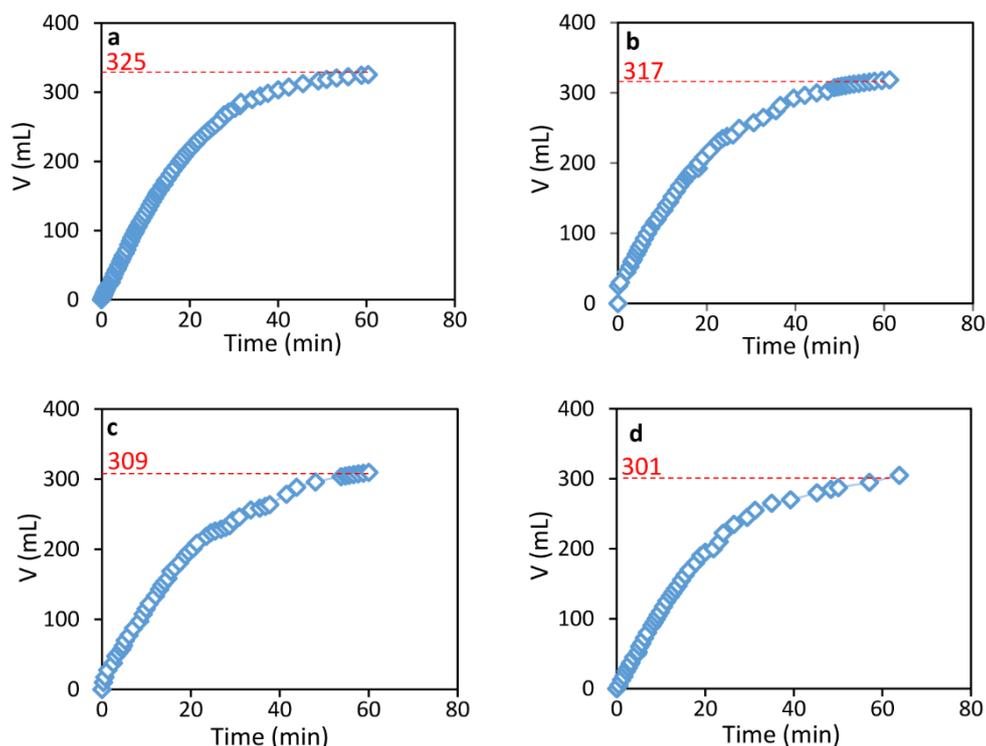


Figure S 15. The catalytic stability of the $\text{Cp}^*\text{IrCl}_2(\text{ppy})$. (a),(b),(c) and (d) The gas generation from formic acid dehydrogenation in water at 30 °C catalyzed by freshly-prepared $\text{Cp}^*\text{IrCl}_2(\text{ppy})$, first recycled $\text{Cp}^*\text{IrCl}_2(\text{ppy})$, second-recycled $\text{Cp}^*\text{IrCl}_2(\text{ppy})$ and third-recycled $\text{Cp}^*\text{IrCl}_2(\text{ppy})$ respectively. Reaction conditions: 8 mL solution contain 1 M formic acid and 1M sodium formate, 100 mg $\text{Cp}^*\text{IrCl}_2(\text{ppy})$.

The 8 mL solution will generate 384 mL gas according to the chemical equation. As exhibited in **Figure S 15a**, we will get 325 mL gas after 60 minutes when the freshly-prepared $\text{Cp}^*\text{IrCl}_2(\text{ppy})$ is employed, 84.6% of the formic acid could decompose during 60 minutes. Then we recycle the $\text{Cp}^*\text{IrCl}_2(\text{ppy})$ by filter membrane, and employed the first-recycled $\text{Cp}^*\text{IrCl}_2(\text{ppy})$ for the formic acid dehydrogenation. As exhibited in the **Figure S 15b**, 317 mL gas will generate during 60 minutes when we employed the first recycled $\text{Cp}^*\text{IrCl}_2(\text{ppy})$. When we recycle the $\text{Cp}^*\text{IrCl}_2(\text{ppy})$ secondly and employed the second-recycled $\text{Cp}^*\text{IrCl}_2(\text{ppy})$ for formic acid dehydrogenation, 309 mL gas will generate during 60 minutes (**Figure S 15c**). When we recycle the $\text{Cp}^*\text{IrCl}_2(\text{ppy})$ thirdly and employed the third-recycled $\text{Cp}^*\text{IrCl}_2(\text{ppy})$ for formic acid dehydrogenation, 301 mL gas will generate during 60 minutes (**Figure S 15d**).

SI-5. Characterization of the Cp*IrCl₂(pbi).

The XPS measurements were employed via Escalab 250Xi spectrometer. The binding energy of C 1s are 285.1 eV, 284.1 eV and 283.8 eV respectively, indicating the C originate from benzene ring, benzimidazole group and methyl. The binding energy of O 1s are 530.9 eV and 531.9 eV respectively, indicating the O originate from carboxyl in the catalyst.

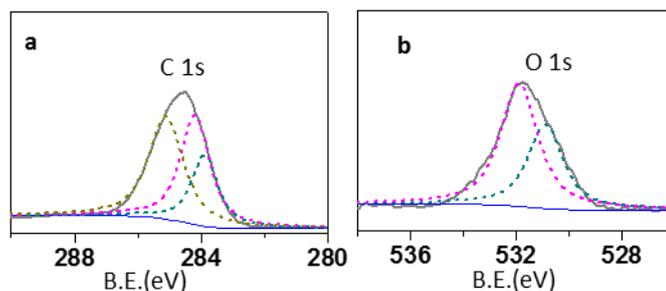


Figure S 16. XPS Spectra of C and O in Cp*IrCl₂(pbi).

N₂ adsorption/desorption measurements for the Cp*IrCl₂(pbi) were carried out on Quantachome iQ 2 Instrument at 77 K after the catalyst pretreated at 373 K for 8 hours. The specific surface areas of the Cp*IrCl₂(pbi) were determined by t-plot method and Brunauer-Emmett-Teller (BET) method. The specific surface area of the catalyst was 13.2 m²/g.

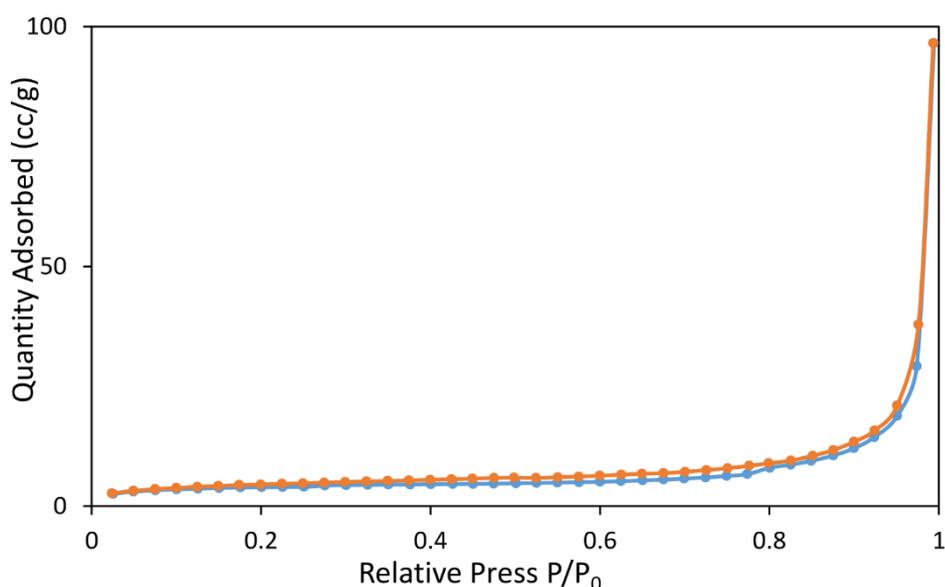


Figure S 17. N₂ BET Adsorption/Desorption Isotherms for the Cp*IrCl₂(pbi).

The particle size distribution of the $\text{Cp}^*\text{IrCl}_2(\text{pbi})$ is analyzed by Malvern Instruments Zetasizer Nano ZS90. The particle size distribution is among 400 nm to 900 nm. The small particles could well disperse in the reaction solution and catalyze formic acid dyhydrogenation.

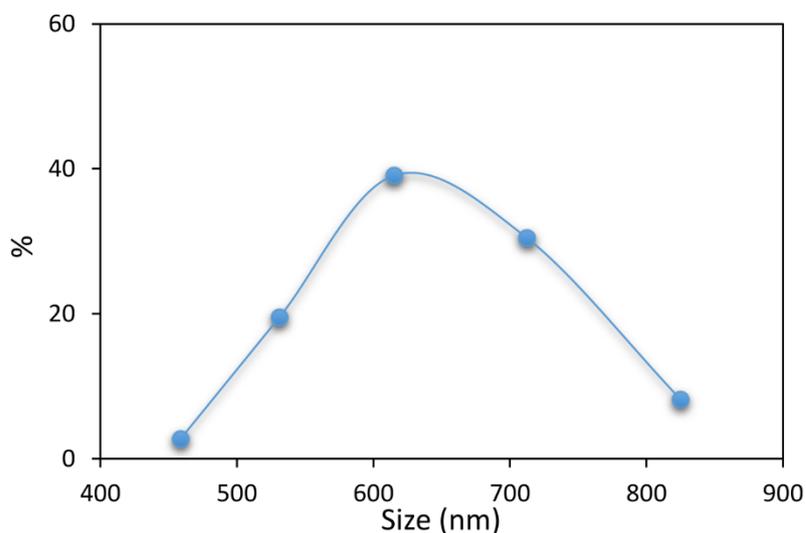


Figure S 18. Particle Size Distribution of the $\text{Cp}^*\text{IrCl}_2(\text{pbi})$.

Powder X-ray diffraction (XRD) patterns of the $\text{Cp}^*\text{IrCl}_2(\text{pbi})$ were recorded with Bruker D8 X-ray diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV and 40 mA). No crystal phase could be found in the $\text{Cp}^*\text{IrCl}_2(\text{pbi})$.

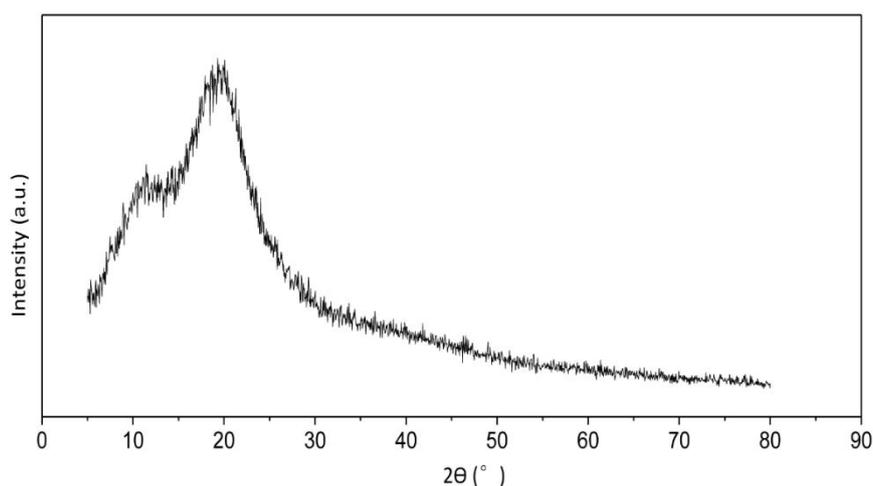


Figure S 19. XRD Analysis of the $\text{Cp}^*\text{IrCl}_2(\text{pbi})$.

SI-6 Conversion of Hydrogen Energy to Electric Energy

The energy density of the hydrogen is 142 kJ/g. The gas flow rate of the fixed bed reactor is 11.2 mL/min, 50% of the evolved gas is hydrogen.

Then the hydrogen flow rate is 0.09333 mL/s, which is equal to 7.778×10^{-6} g/s. So the hydrogen could generate 1.1 W electricity theoretically. The calculation process is as follows.

$$H_{H_2} = 142 \text{ kJ/g}$$

$$Q_{v,H_2} = 7.778 \times 10^{-6} \text{ g/s}$$

$$P = H_{H_2} \times Q_{v,H_2} = 142 \text{ kJ/g} \times 7.778 \times 10^{-6} \text{ g/s} = 1.1 \text{ J/s} = 1.1 \text{ W}$$

SI-7. Characterization and Catalytic Activity of Ir@ppy.

The iridium nanoparticles could also be immobilized on the polypyrrole. **Figure S 20a** exhibits a typical iridium nanoparticles immobilized on the polypyrrole. **Figure S 20b and c** show the HRTEM and EDX pattern of these particles respectively, the Cu and C signals originate from the TEM grid, and a little Fe signal originate from FeCl₃ residue during synthesizing the polypyrrole. We can determine these particles are Ir nanoparticle. The HRTEM image reveals the crystalline of the particles. The lattice spacing is 0.220 nm, which is similar to that of the (111) plane of the iridium nanoparticles.

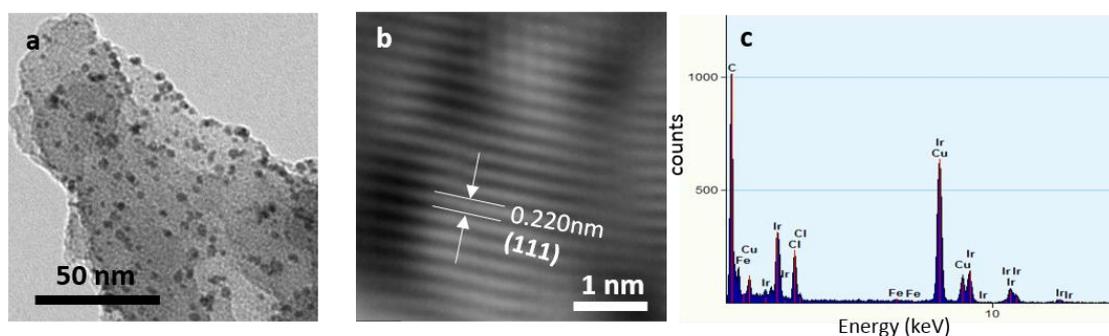


Figure S 20. (a) TEM Image of Iridium Nanoparticles Immobilized on the Polypyrrole (b) High-Resolution Iridium Nanoparticles (c) EDX Pattern of the Iridium Nanoparticles .

Figure S 21 shows the activity of iridium nanoparticles immobilized on the surface of polypyrrole in 1.0 M formic acid solution at 35°C. 3 mL gas was generated after reaction for 800 min by 2 mg catalyst. The catalytic activity is very low.

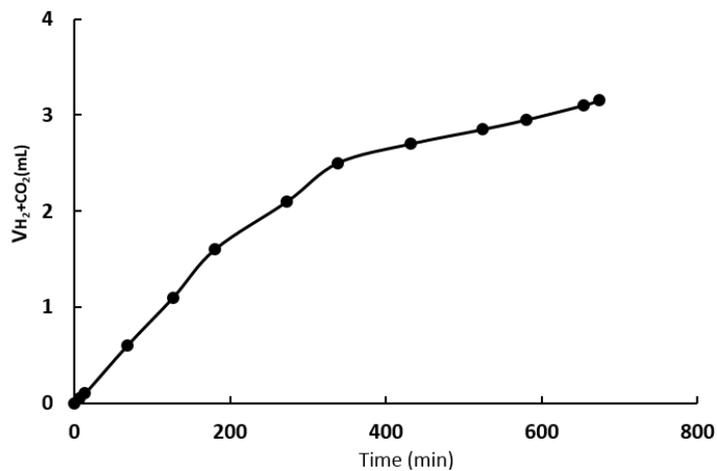


Figure S 21. Volume of the Generated Gas (CO_2+H_2) versus Time for 1.0 M FA Dehydrogenation catalyzed Ir nanoparticles at 35 °C. TOF = 16 h^{-1} .

Reference

1. Y. Shen, Y. Zhan, S. Li, F. Ning, Y. Du, Y. Huang, T. He and X. Zhou, *Chem. Sci.*, 2017, **8**, 7498-7504.