Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary information for

# Organically doped palladium: a highly efficient catalyst for electroreduction of $CO_2$ to methanol

Heng-Pan Yang, Sen Qin, Huan Wang* and Jia-Xing Lu**

*Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China.*
**Corresponding Author: Dr. Huan Wang (Tel: +8621-52134935, E-mail: hwang@chem.ecnu.edu.cn).*
***Corresponding Author: Prof. Jia-Xing Lu (Tel: +8621-62233491, E-mail: jxlu@chem.ecnu.edu.cn).*

## 1. Materials and Instruments

All reagents were used as received.

Potentiostatic electrolysis and cyclic voltammograms were performed using a CHI 660C electrochemical Station (Shanghai Chenhua Instruments Company).

$^1$H-NMR and $^{13}$C-NMR spectra were recorded on an AVANCE 500 (500 MHz, Bruker, Germany) or Ascend 400 (400 MHz, Bruker, Germany) spectrometer in $CDCl_3$ with $Me_4Si$ as an internal standard.

Liquid phase products were quantitative analyzed by Gas Chromatography-Flame Ionization Detector (GC-FID) (SHIMADZU, GC-2014C).

The dopant amount in filtrate were determined by a high performance liquid chromatography (HPLC) instrument (DIONEX Ultimate 3000 pump) equipped with a UV (RS Variable Wavelength) detector.

Microstructure and EDX mapping were analyzed using Hitachi S-4800 field emission Scanning Electron Microscope (FE-SEM) equipped with an energy dispersive X-ray fluorescence spectrometer (EDX, Oxford; UK).

X-ray diffraction (XRD) patterns were recorded by a Ultima IV X-ray powder diffractometer using Cu Kα radiation (k= 1.5406 Å).

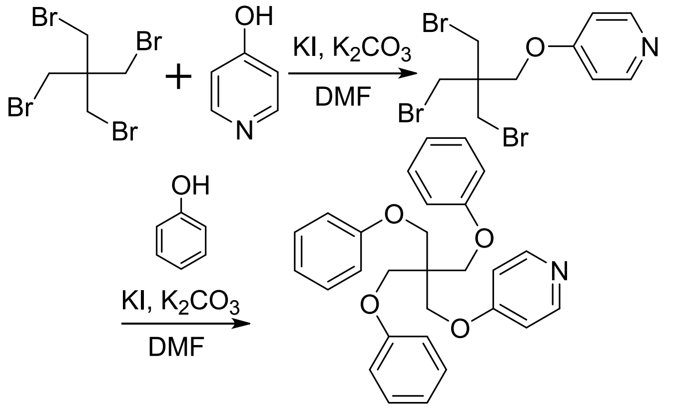
$N_2$ adsorption was carried out at 77 K on a BELSORP-MAX instrument after outgassing the samples for 10 h under vacuum at 573 K.

Infrared spectra were achieved by a Fourier transform infrared spectrometer (FT-IR, NEXUS 670, Nicolet).

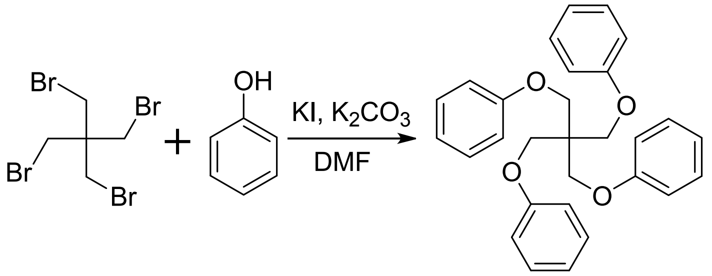
## 2. General methods

**Synthesis of PYD**: 1.96 g of pentaerythrityl tetrabromide, 0.47 g of 4-hydroxylpyridine, 2 g of $K_2CO_3$ and 0.1 g KI were mixed in 100 mL of DMF and refluxed at 95 °C for 2 days. Then 2.35 g phenol was added for another 2 days. After it was cooled, the mixture was poured into 1000 mL of water and stirred overnight. After separation white products was obtained.

**Synthesis of PHD**: 1.96 g of pentaerythrityl tetrabromide, 2.35 g of 4-hydroxylpyridine, 2 g of $K_2CO_3$ and 0.1 g KI were mixed in 100 mL of DMF and refluxed at 95 °C for 2 days. Post-treatment was same as PYD.



4-(3-phenoxy-2,2-bis(phenoxymethyl)propoxy)pyridine **PYD**



((2,2-bis(phenoxymethyl)propane-1,3-diyl)bis(oxy))dibenzene **PHD**

**Scheme S1**

**Characterization of PYD and PHD**:

**PYD**: $^{13}$C NMR (ppm, $CDCl_3$): 44.7, 66.4, 110.4, 114.7, 121.2，129.5，151.1，158.7，164.7 (Fig. S1). $^{1}$H NMR (ppm, $CDCl_3$): 4.42 (s, 6), 4.44 (s, 2), 6.84 (d, 2), 6.96 (d, 6), 7.27 (d, 9), 8.42 (d, 2).

**PHD**: $^{13}$C NMR (ppm, $CDCl_3$): 44.8, 66.6, 114.7, 121.0，129.5，158.9 (Fig. S2). $^{1}$H NMR (ppm, $CDCl_3$): 3.97 (s, 8), 6.96 (d, 8), 7.27 (d, 12).

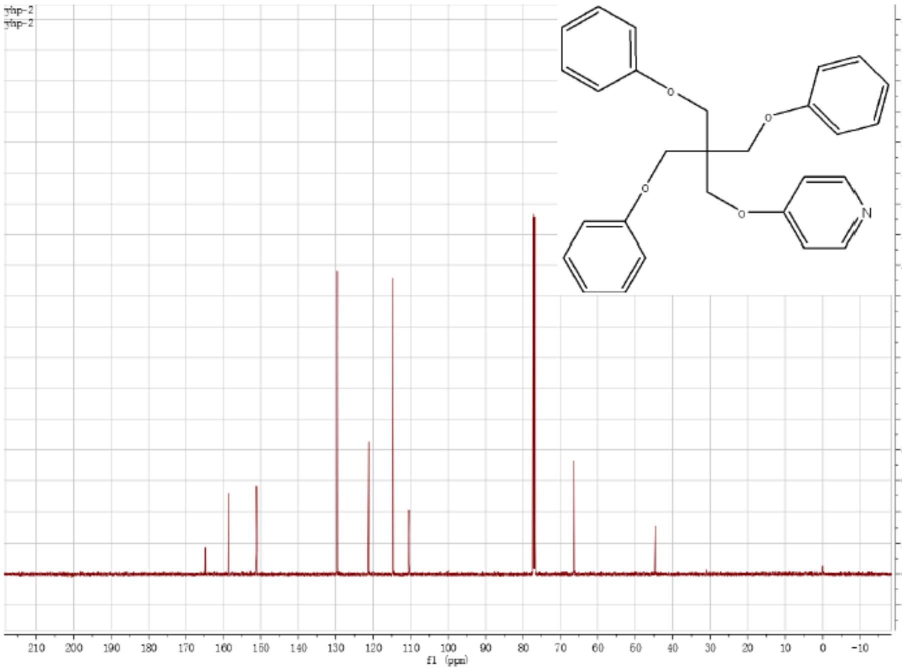


**Fig. S1** $^{13}$C spectrum of PYD

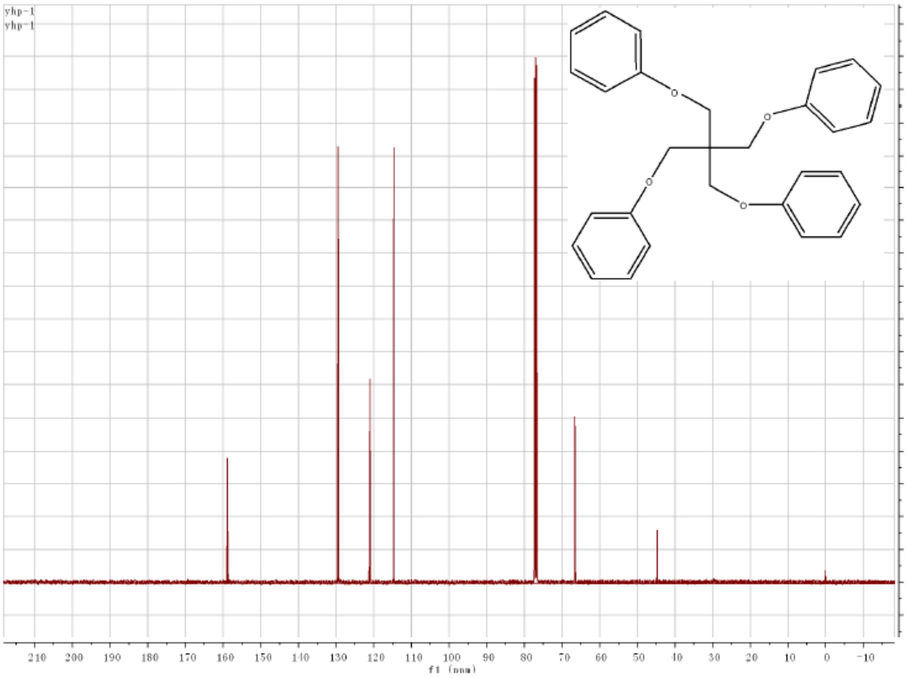


**Fig. S2** $^{13}$C spectrum of PHD

**Synthesis of [PYD]@Pd， [PHD]@Pd and pure Pd NPs**: For entrapment of PYD to produce [PYD]@Pd, 1.0 g of $PdCl_2$ (5.6 mmol) in 125 ml of distilled water was poured into a stirred solution of 0.9 g of sodium dodecyl sulfate (3.1 mmol) and 0.015 g of PYD (0.04 mmol) in 50 ml of water (molar ratio: Pd / PYD = 140). After 5 min stirring, 1.2 g of $NaH_2PO_2$ was slowly added, and the combined black slurry was stirred (500 rpm) at 25 °C for 2 h. Precipitation of [PYD]@Pd begins immediately. The precipitate was filtered, washed with 10 mL water 5 times, and dried over night at 30 ˚C under vacuum. Fine and dark powder was achieved after filtration and drying (Fig. S3). [PHD]@Pd was prepared the same method except for the utilization of PHD as dopant. Pure Pd NPs (Fig. S4) were prepared in the same way except for the absence of any dopant in reducing solution. Coarse and shine powder was obtained.

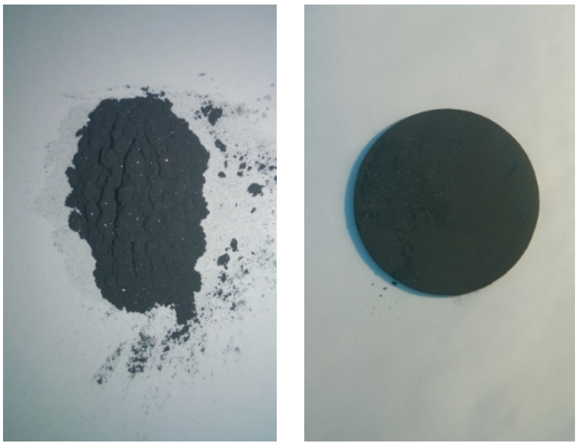


**Fig. S3** [PYD]@Pd before (left) and after (right) press.

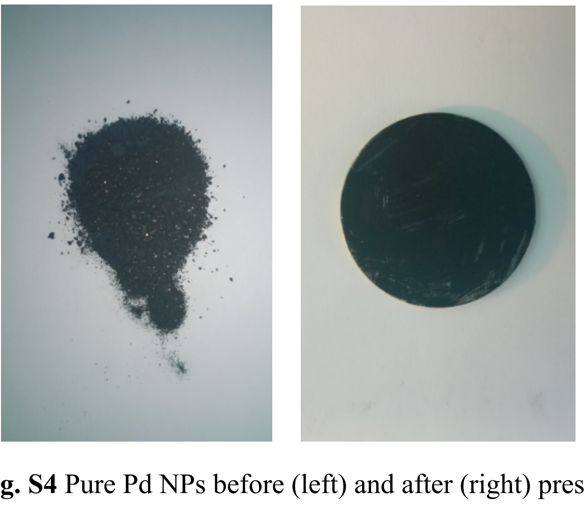


**Fig. S4** Pure Pd NPs before (left) and after (right) press.

**Potentiostatic $CO_2$ reduction procedure**: Powder of [PYD]@Pd was pressed into coin (D= 1cm，Fig. S3) and used as cathode to test the catalytic activity for $CO_2$ electroreduction. It was performed with a conventional three-electrode electrochemical H-type cell, in which a piece of Nafion®117 membrane was used as a separator. A saturated calomel electrode (SCE) saturated with KCl was the reference electrode, and a Pt foil (99.999% purity, 10 mm × 10 mm) was the counter electrode. An aqueous electrolyte of 10 mL 0.5 M KCl was used as electrolyte, which was bubbled with 1.0 atm $CO_2$ (99.995%) to be saturated with $CO_2$. The pH was preserved at 5.4. The potential was -0.6 V, and charge used was 50 C.

Cyclic voltammograms were recorded in an undivided cell. A saturated calomel electrode (SCE) saturated with KCl was the reference electrode, and a Pt foil (99.999% purity, 10 mm × 10 mm) was the counter electrode. An aqueous electrolyte of 10 mL 0.5 M KCl was used as electrolyte, which was bubbled with 1.0 atm $N_2$ or $CO_2$ (99.995%). The pH was preserved at 5.4. Scan rate was 0.1 V $s^{-1}$.

## 3. Differences between physical adsorption and entrapment

FT-IR further explored the difference between entrapment and adsorption. After physical adsorption in PYD solution, FT-IR spectra of pure Pd NPs (d) was almost identical to pure PYD (c). In [PYD]@Pd composite, PYD could not be detected by FT-IR spectra (a), but the presence of dopant could be confirmed by other characterization methods. If (d) was washed with MeCN, there was also no trace of PYD in FT-IR spectra (b), indicating that this adsorption is highly unstable. In summary, entrapment was fundamentally different from adsorption and much more stable.

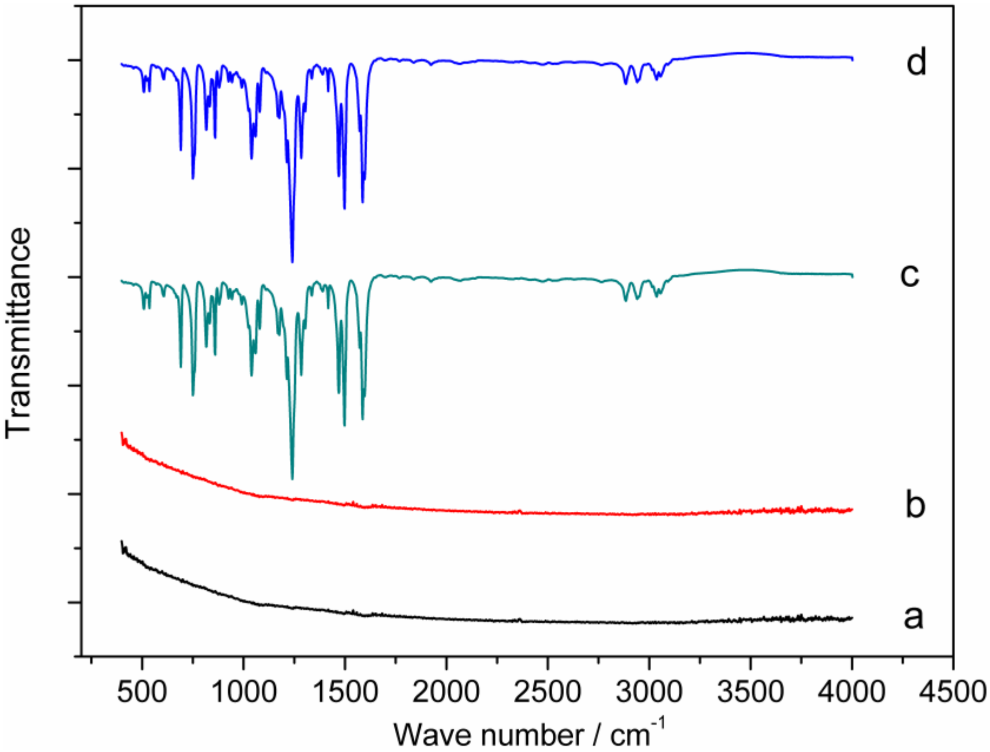


**Fig. S5** FT-IR spectra of [PYD]@Pd (a), pure PYD (c), pure Pd NPs after physical adsorption of PYD (d), (d) after washed with MeCN (b).

## 4. Characterization of pure Pd NPs.

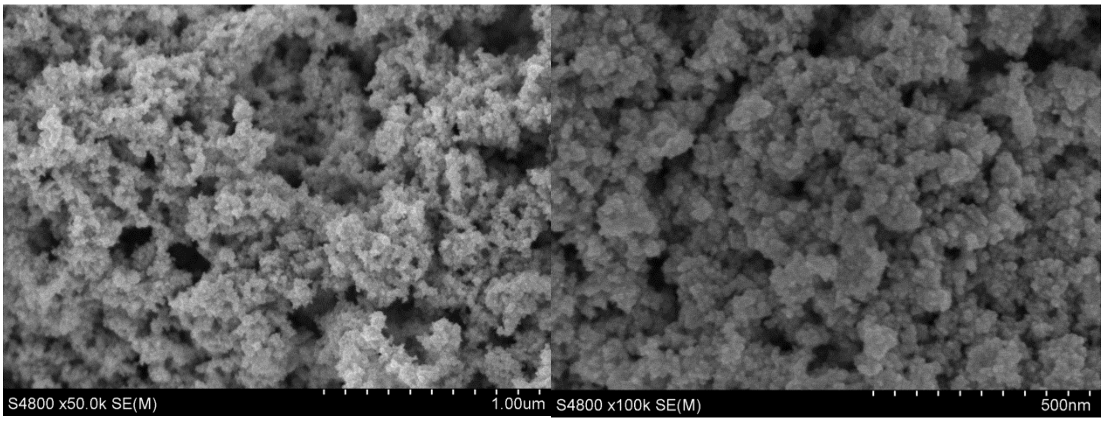


**Fig. S6** FE-SEM patterns of pure Pd NPs with different magnification, left (50k), right (100k).

According to Fig. S6, pure Pd NPs are in the ~40 nm size range, which is similar to [PYD]@Pd.

## 5. $N_2$ adsorption-desorption isotherm of [PYD]@Pd composite

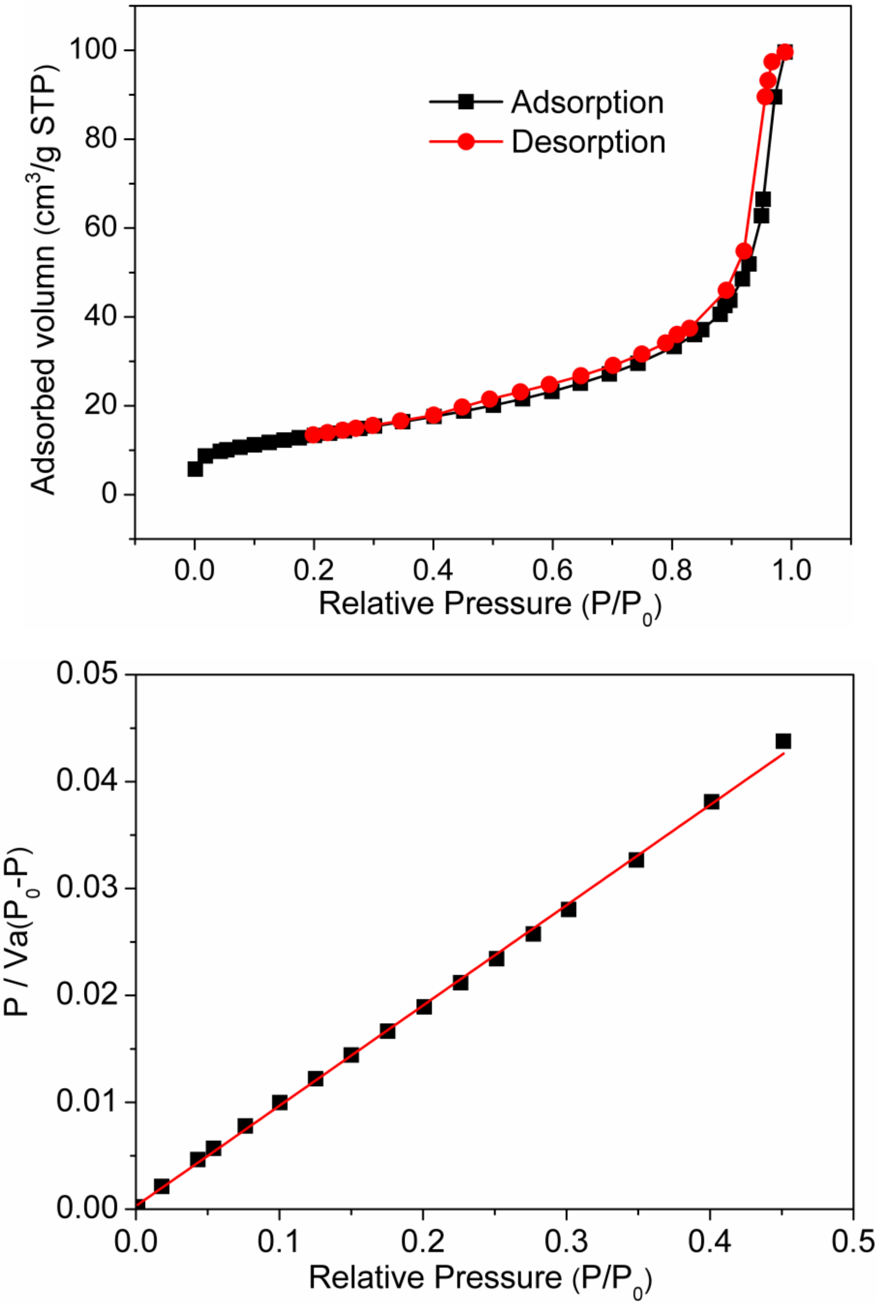


**Fig. S7** Adsorption-desorption isotherms of nitrogen reveal the mesopososity of [PYD]@Pd (up). The compliance to the BET equation is indicative of the homogeneity of the dopant (down)

## 6. Characterization of [PYD]@Pd after using.

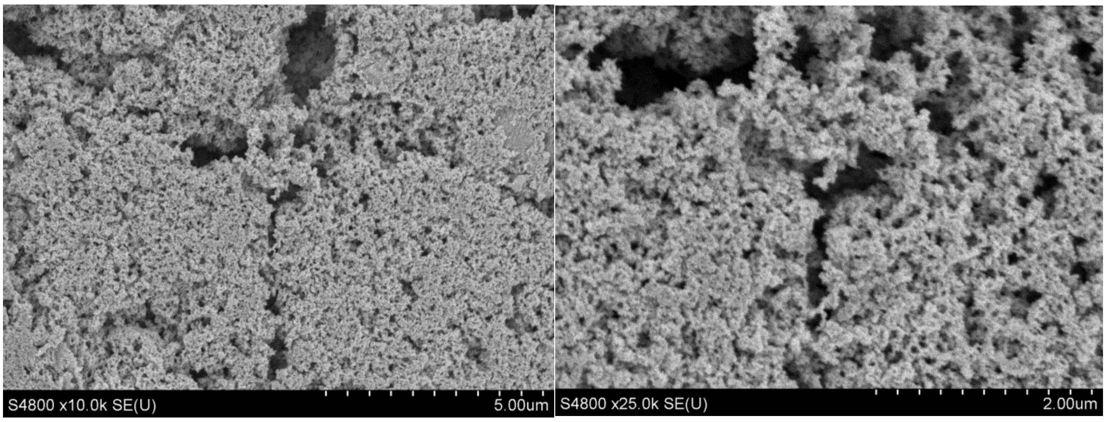
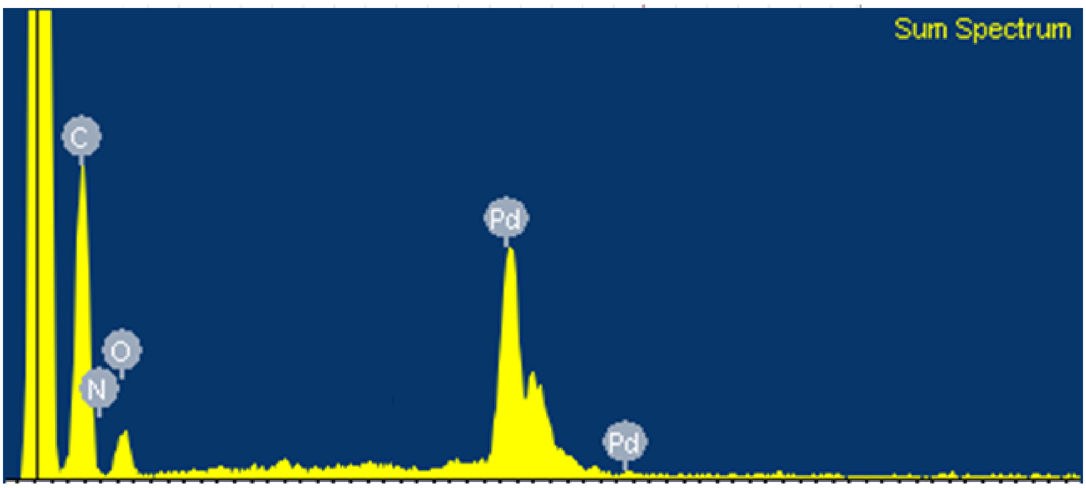


**Fig. S8** FE-SEM patterns of [PYD]@Pd after used for 15 times with different magnification, left (10k), right (25k).

According to SEM patterns, [PYD]@Pd remained its porous structure after used for 15 times.



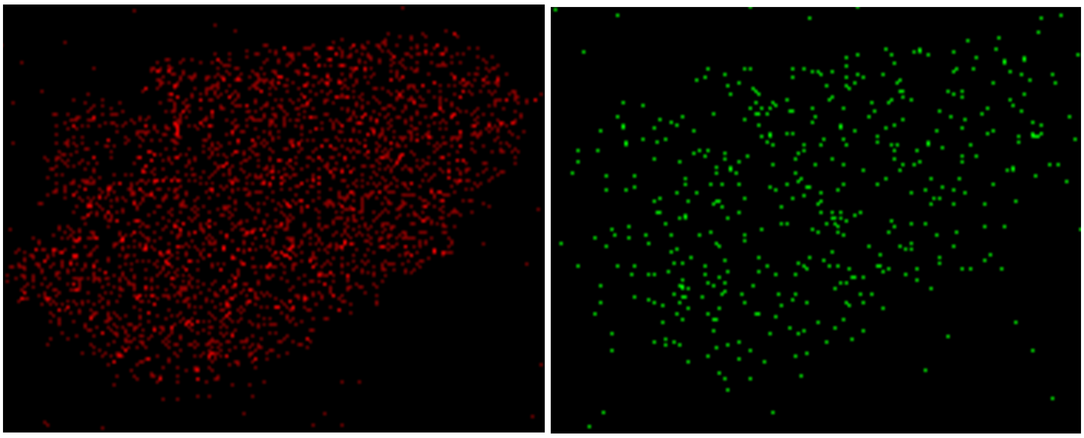


**Fig. S9** The EDX spectrum of [PYD]@Pd after used for 15 times (up); X-ray atomic mapping of the elements of the [PYD]@Pd (down), red and green colours represent Pd and C atoms, respectively.

## 7. Characterization of products

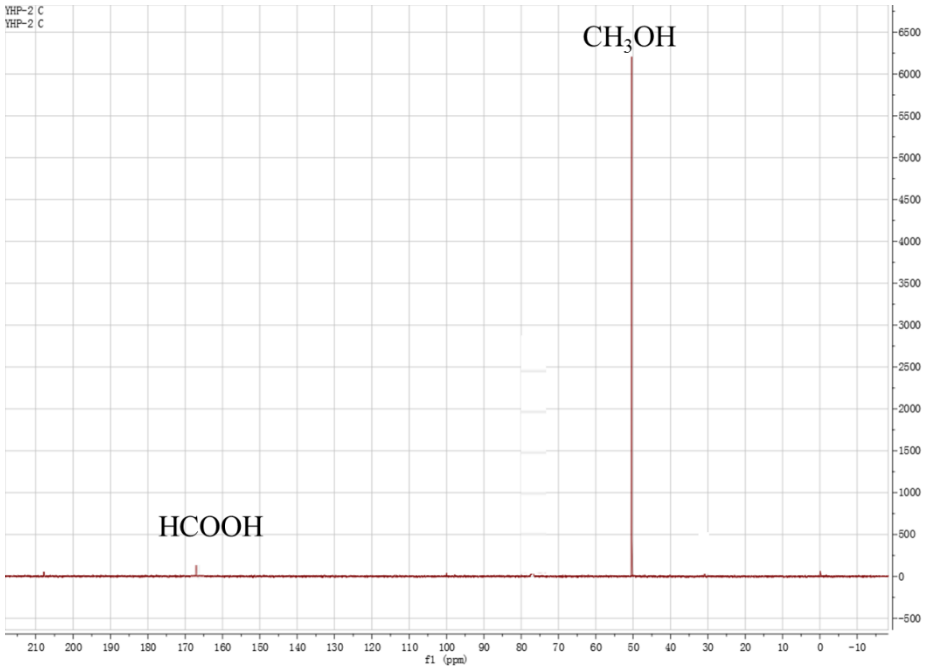


**Fig. S10** $^{13}C$ spectrum of products.