

Electronic Supplementary Information

Experimental Information

Materials. 1,3,5-Phenyltriboronic acid tris(pinacol) ester (98%), 4,7-dibromobenzo[c]-1,2,5-thiadiazole (97%) and tetrakis(triphenylphosphine) palladium(0) (99%), were purchased from Aladdin. Potassium carbonate (K_2CO_3) and all other solvents were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals and solvents were used as directly.

Characterization

The UV-Vis diffuse reflection spectra were recorded at room temperature on Shimadzu UV-2600 UV-vis spectrometer. FT-IR spectra were recorded with the Bruker Alpha II Attenuated Total Reflection (ATR) FT-IR spectrometer. Solid State ^{13}C CP/MAS NMR spectroscopy was carried out using a Bruker Avance II solid state NMR spectrometer operating at 300 MHz equipped with a magic angle spinning (MAS) double resonance probe head. The nitrogen adsorption and desorption isotherms at 77.3 K was recorded by a ASAP2030 volumetric adsorption analyzers (Micromeritics, Norcross, GA, USA). Sample was pre-treated at 60 °C under vacuum before degassed at 120 °C for 12 h before analysis. The specific surface area calculation was based on the Brunauer-Emmett-Teller (BET) method. Pore size distributions and pore volumes were determined by Barrett-Joyner-Halenda (BJH) model and the adsorption amount obtained at $p/p_0 = 0.99$ respectively.

Scanning electron microscope (SEM) images were obtained by a Zeiss Gemini 300 (Carl Zeiss AG, Germany). Transmission Electron Microscopy (TEM) images were captured using JEOL JEM 2100F TEM instrument operated at 200 kV. Cyclic voltammetry (CV) measurements were performed on a CHI 660E electrochemical working station using a three-electrode system: glassy carbon working electrode, Hg/HgCl₂ reference electrode and platinum wire counter electrode. The samples were grounded into fine powder and then dispersed in 5 wt% Nafion IPA solution, the mixture was dropped cast on top surface of a glassy carbon electrode and dried under a NIR lamp. The degassed 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution as used as electrolyte. The measurement was carried out in the range of -2.0 V to 0.5 V with a scan rate of 100 mV s⁻¹. The equation $E_{NHE} = E_{SCE} - 0.24$ V was applied to convert Hg/HgCl₂ redox couple to the Normal Hydrogen Electrode (NHE).

The palladium-catalyzed Suzuki-Miyaura cross-coupling reaction was used to prepare the CMT-BT and GMPs series. Here is the typical prepare procedure for CMP-BT:

1,3,5-Phenyltriboronic acid tris(pinacol) ester (1 mmol), 4,7-dibromobenzo[c]-1,2,5-thiadiazole (1.5 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.05 mmol) were added into a 50 mL Schlenk tube and followed by dissolved in 30 mL DMF. Then, 5 mL 2M K₂CO₃ aqueous solution was added to the organic phase. The mixture was degassed by three freeze-thaw-pump cycles. The reaction was conducted at 120 °C for 72 h. Later, the resulted insoluble solids were collected by filtration followed by washed with 50 mL DI water for three times. The obtained solid was Soxhlet extracted by DCM, acetone and methanol 72 h to remove the unreacted matters. The final products were dried at 60 °C under vacuum. The preparation of GMPs series was similar to that of CMP-BT except adding designed amount RGO into the reaction mixture.

For photocatalytic hydrogen production test, 20 mg of photocatalyst was first dispersed to 100 mL MilliQ water under ultrasonication and then 10 mL TEOA as hole sacrificial agent was added. The reaction aqueous solution was evacuated to remove the air and then 3 wt% Pt was photo deposited onto the surface of photocatalysts under 300 W Xe lamp irradiation. Long-pass cut-off filters were used to achieve excitation light with designed wavelength. The amount of generated H₂ was determined by a gas chromatography.

The apparent quantum efficiency (AQE) for H₂ evolution was measured using 300 W Xe lamps with band pass filter of 420, 460, 520, 520 and 600 nm.

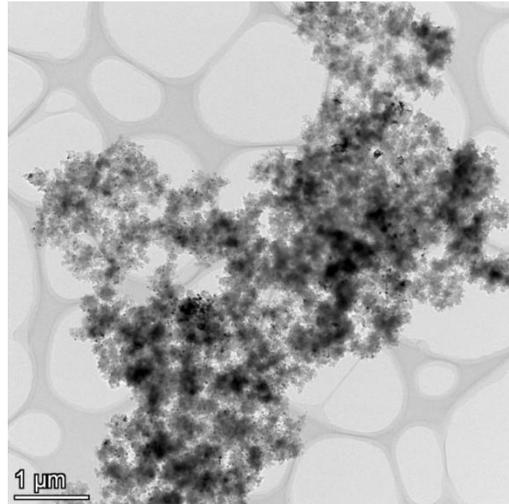


Fig. S1 TEM images of CMP-BT.

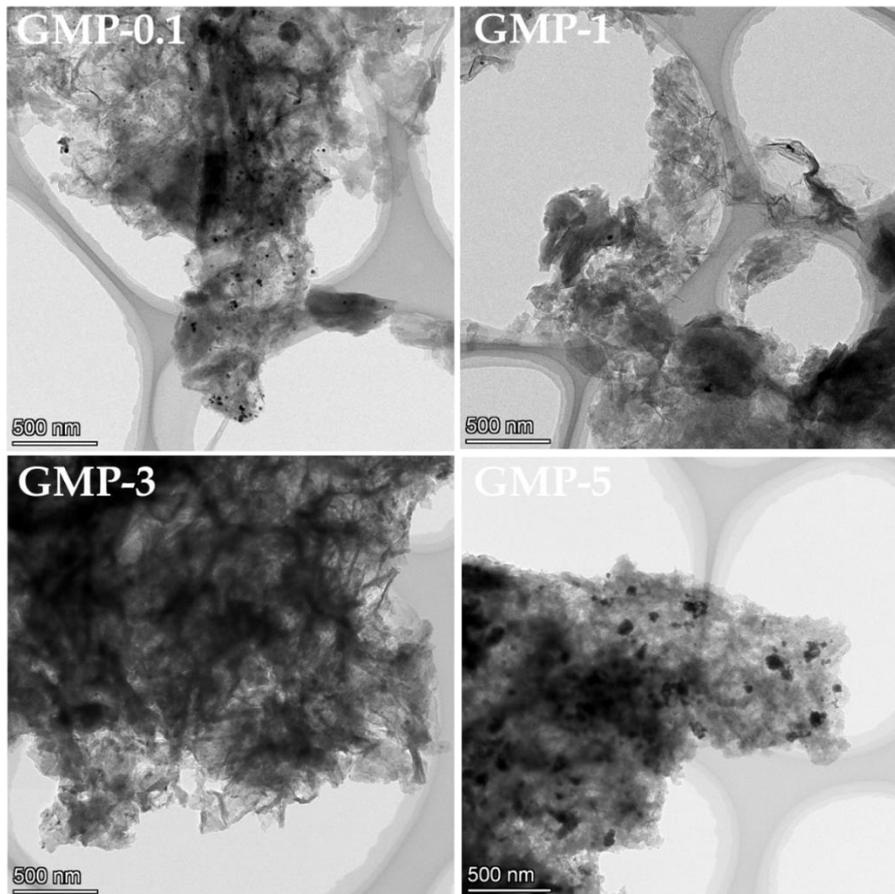


Fig. S2 TEM picture of GMP-0.1.

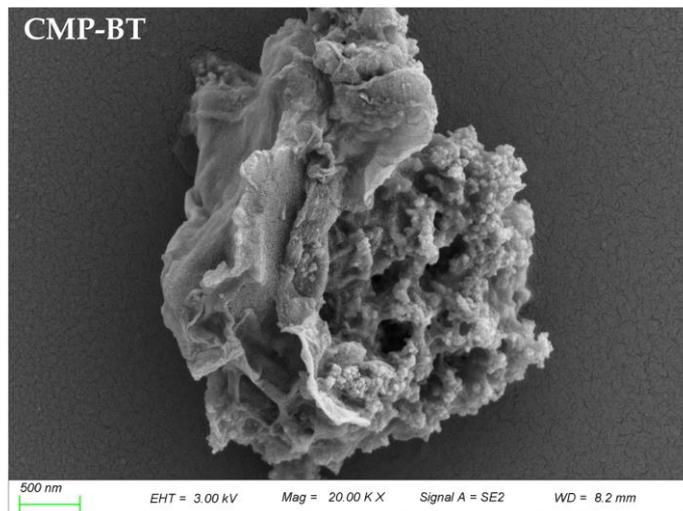


Fig. S3 SEM figure of CMP-BT.

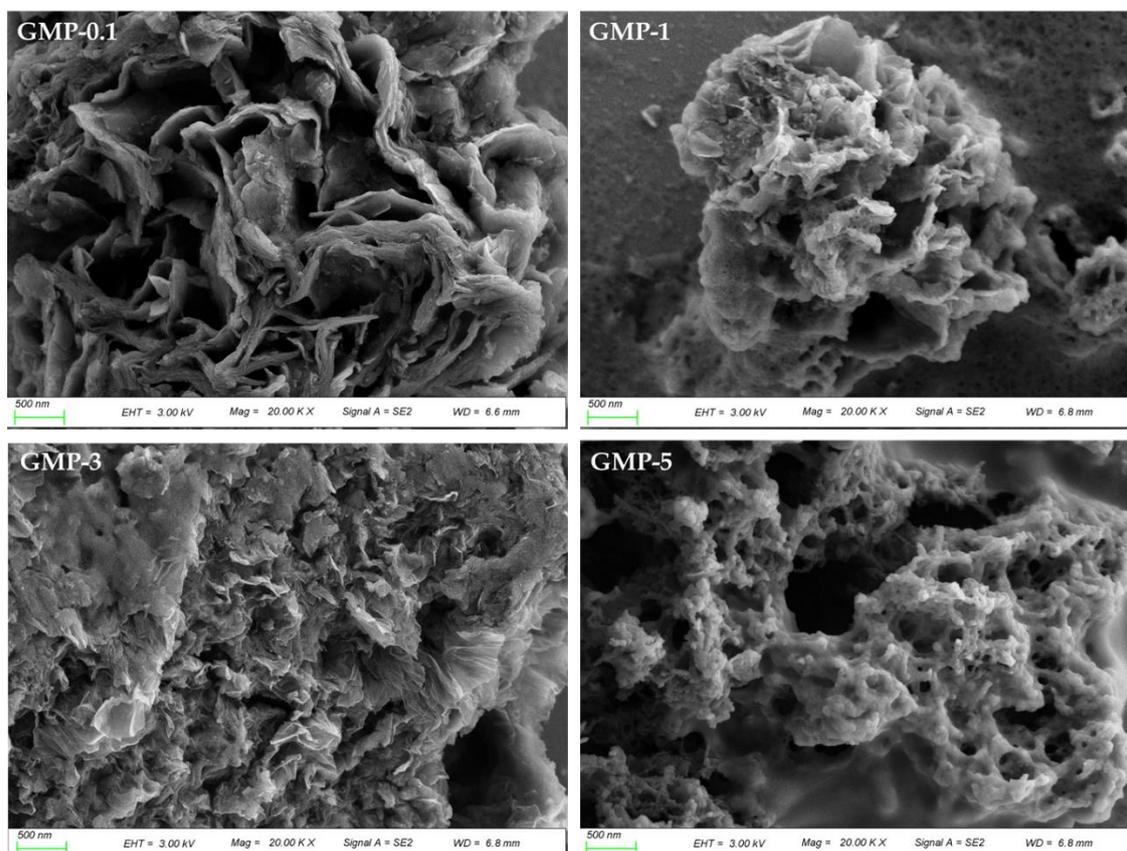


Fig. S4 SEM figures of GMPs.

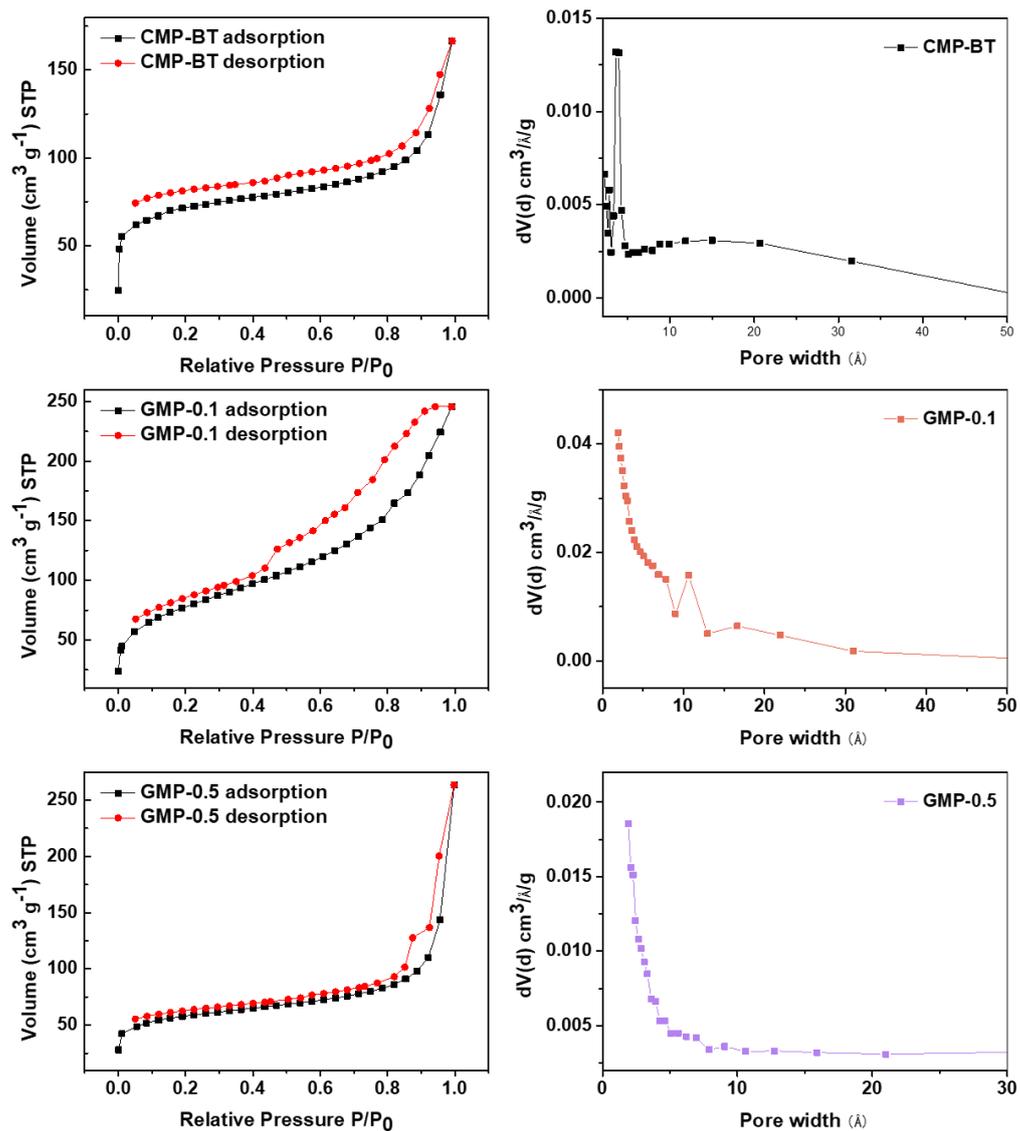


Fig. S5 N_2 Sorption isotherms and pore size distributions of GMPs.

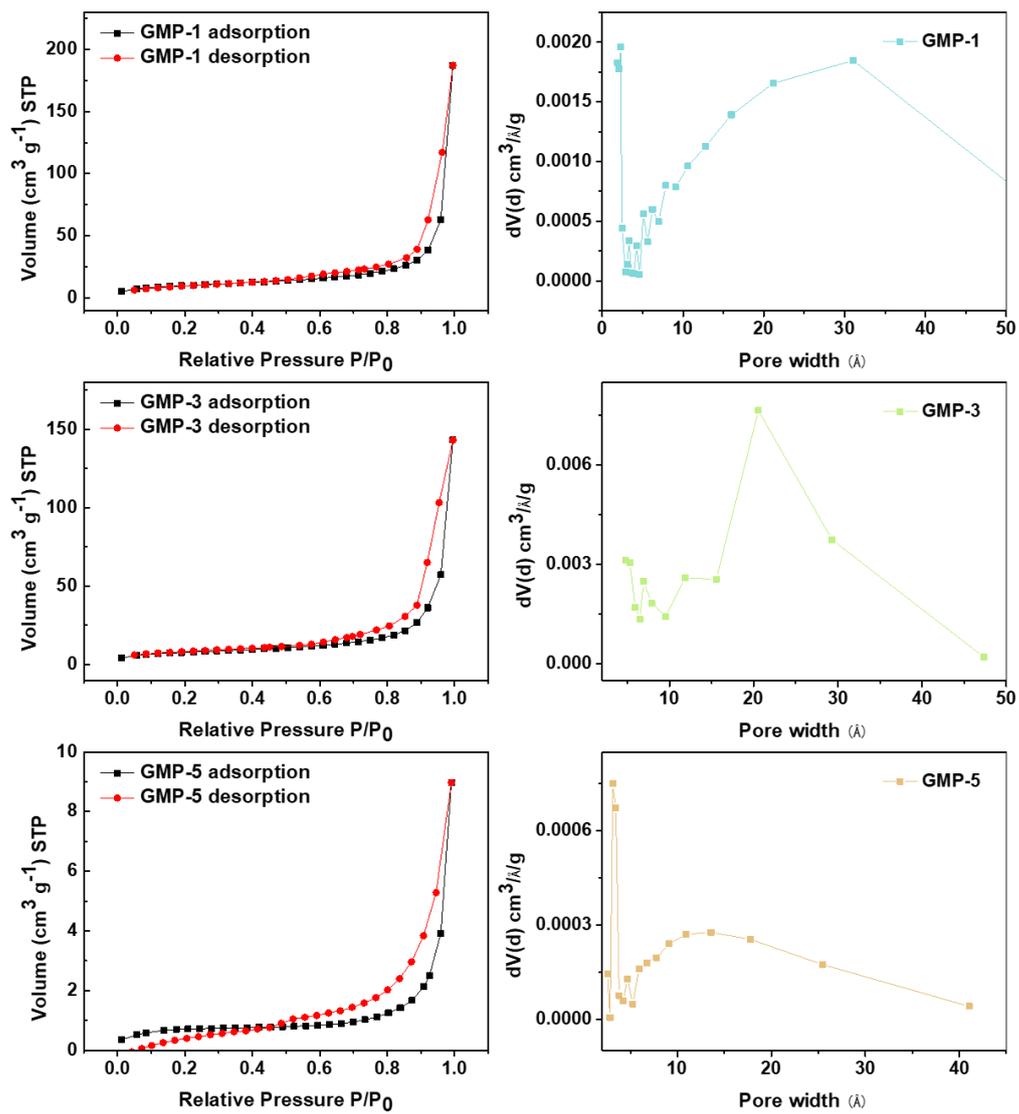


Fig. S6 N_2 Sorption isotherms and pore size distributions of GMP-1, GMP-3 and GMP-5.

CMP-BT

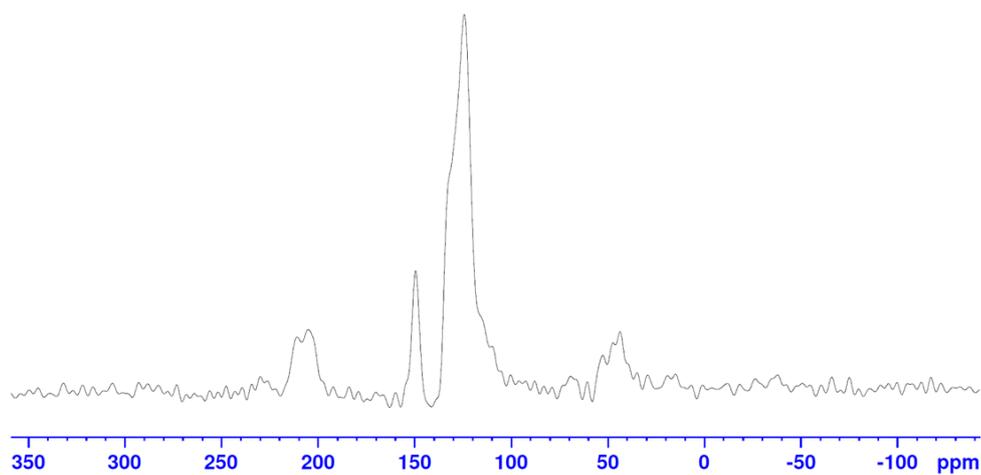


Fig. S7 Solid state ^{13}C CP/MAS NMR spectra of CMP-BT.

GMP-0.1

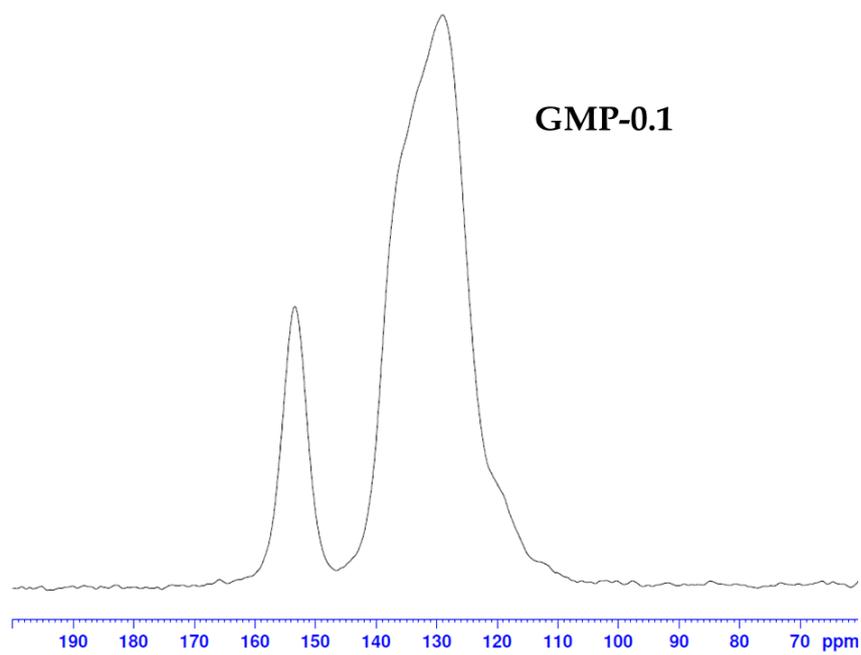


Fig. S8 Solid state ^{13}C CP/MAS NMR spectra of GMP-0.1.

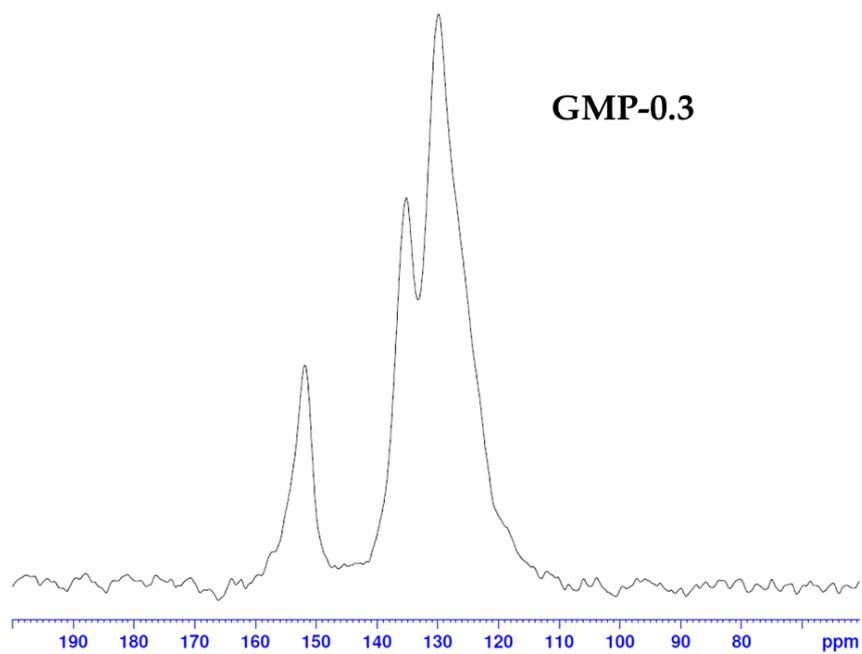


Fig. S9 Solid state ^{13}C CP/MAS NMR spectra of GMP-0.3.

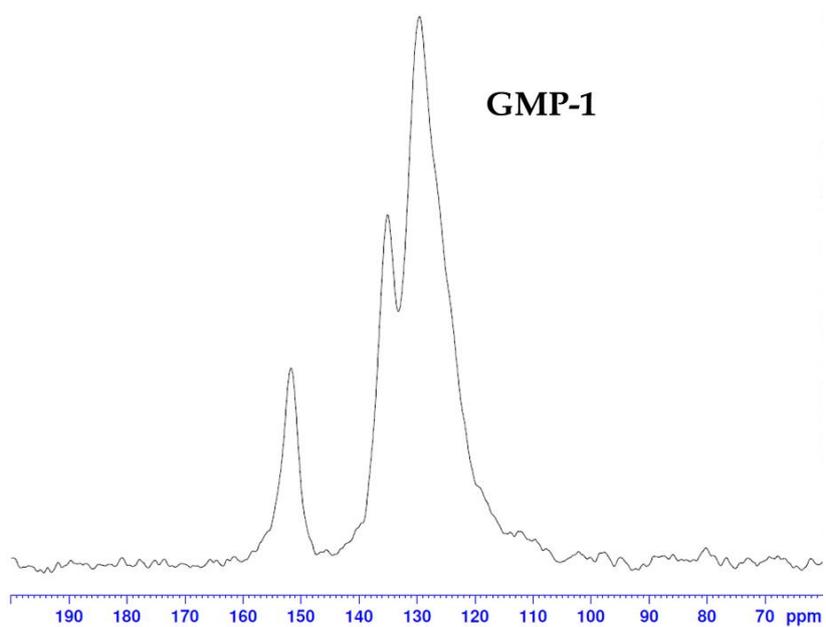


Fig. S10 Solid state ^{13}C CP/MAS NMR spectra of GMP-1.

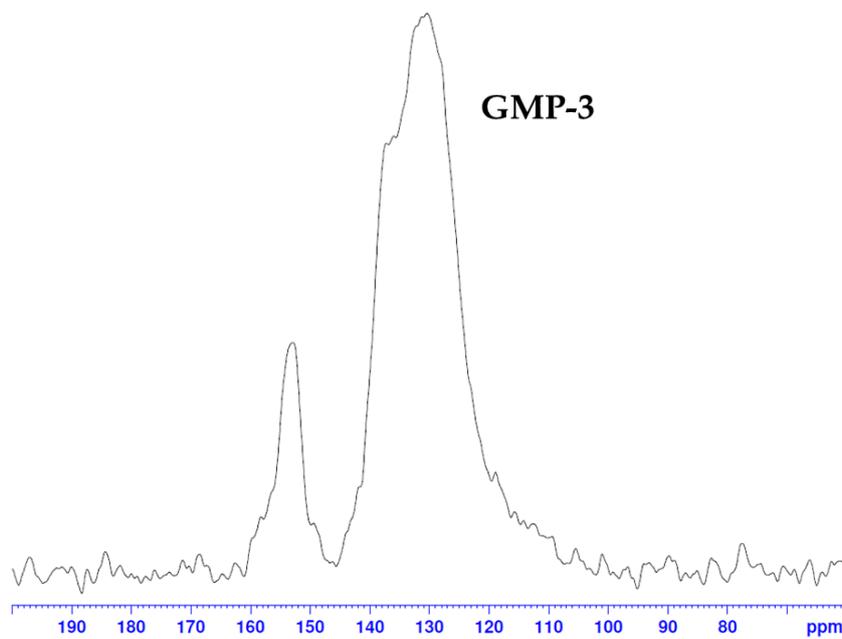


Fig. S11 Solid state ^{13}C CP/MAS NMR spectra of GMP-3.

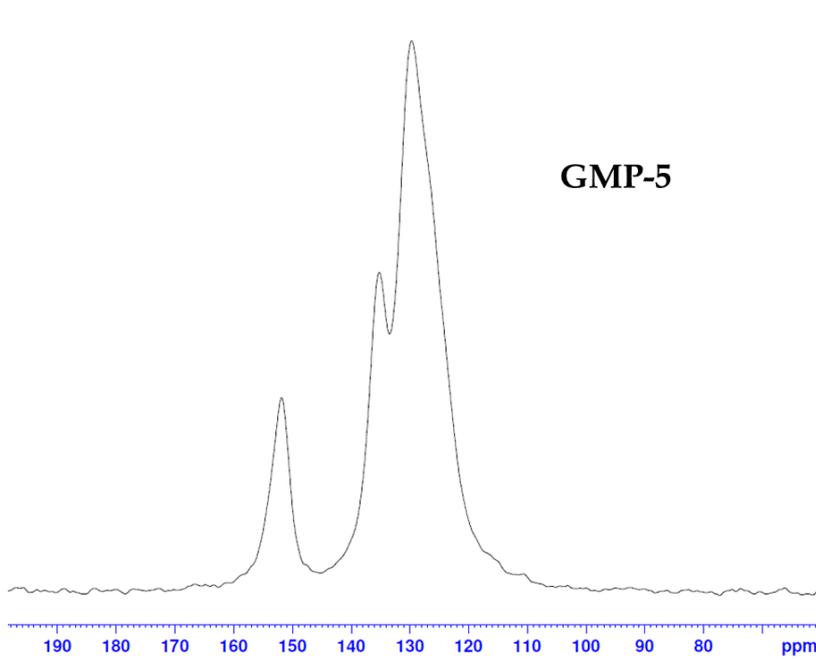


Fig. S12 Solid state ^{13}C CP/MAS NMR spectra of GMP-5.

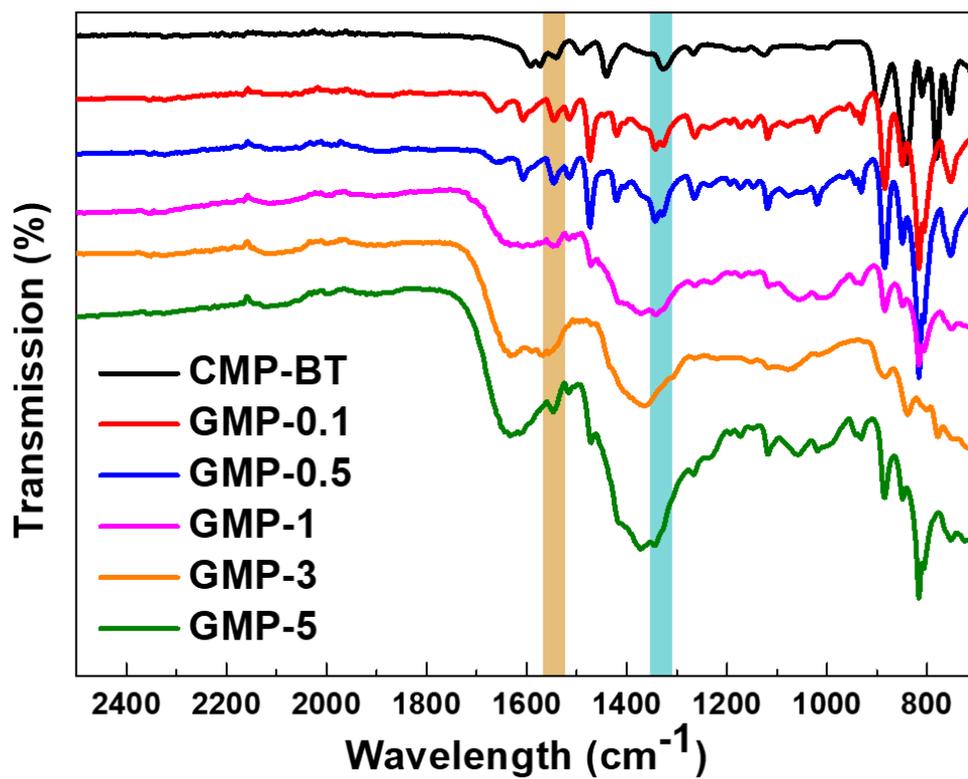


Fig. S13 FT-IR spectra of CMP-BT and GMPs.

Table S1 Calculated individual life and corresponded intensity of CMP-BT and GMPs based on TRPL spectrum.

Species	τ_1 lifetime (ns)	τ_2 lifetime (ns)	τ_{avg} (ns)
CMP	0.59	2.75	1.73
GMP-0.1	0.76	2.48	1.50
GMP-0.5	0.80	2.58	1.48
GMP-1	0.29	3.02	1.51
GMP-3	0.32	2.54	0.77
GMP-5	0.29	1.48	0.60

Table S2 Residual Pd content of CMP-BT and GMPs via ICP-MS measurements.

Sample	Pd content (ppm)
CMP	52
GMP-0.1	67
GMP-0.5	53
GMP-1	61
GMP-3	66
GMP-5	59

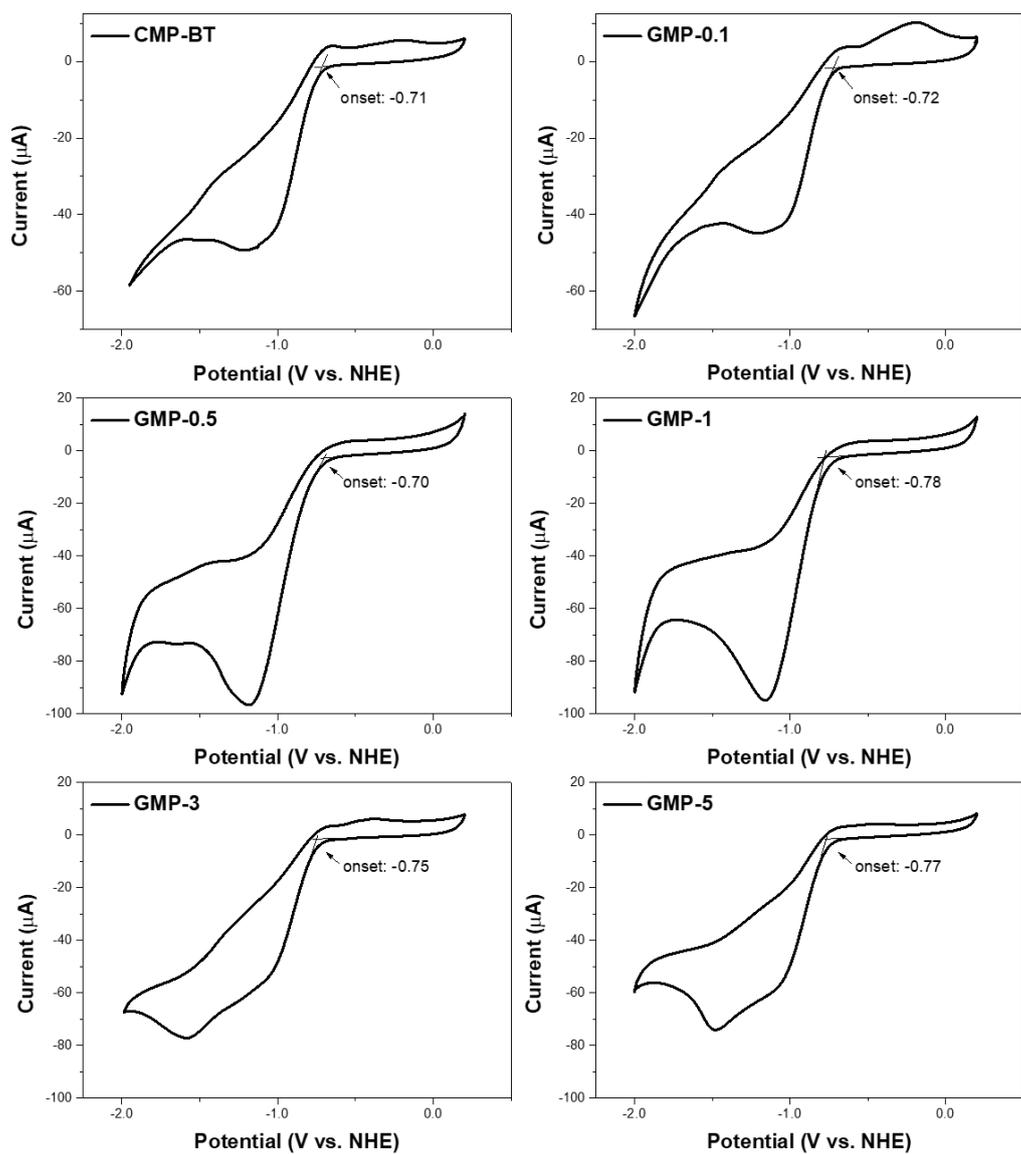


Fig. S14 Cyclic voltammety measurement for CMP-BT and GMPs.

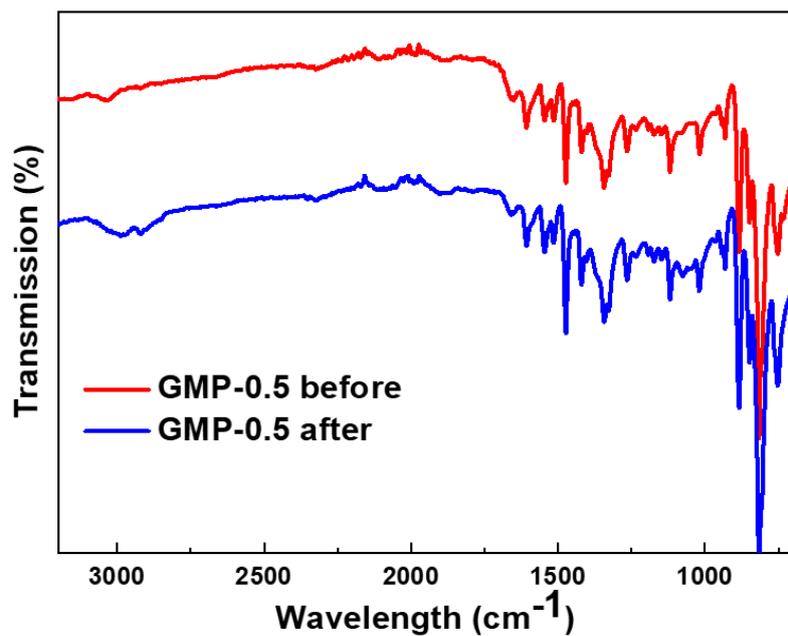


Fig. S15 The UV-vis spectra of GMP-0.5 before and after 25 h photocatalytic reaction.

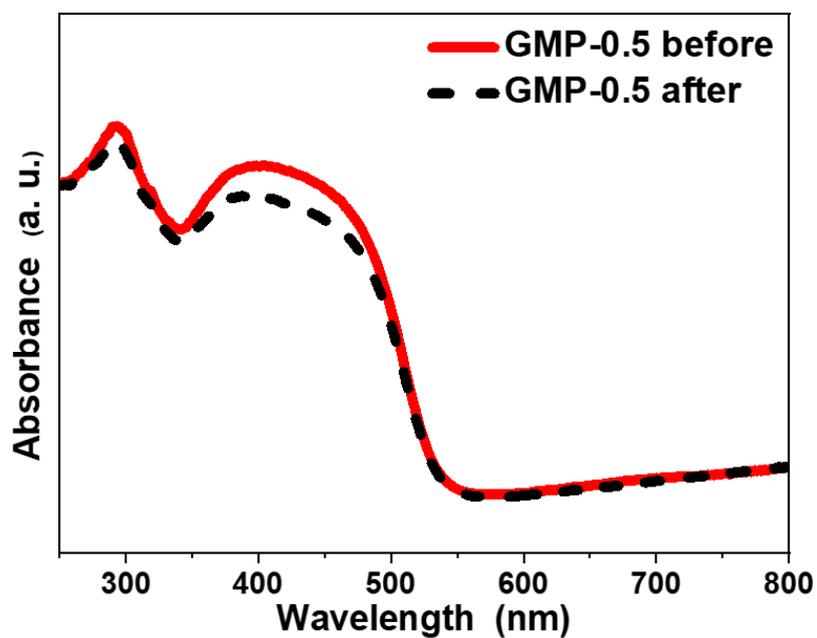


Fig. S15 The FT-IR spectra of GMP-0.5 before and after 25 h photocatalytic reaction.