

## Supplementary information

# **Bifunctional Pt/Au Janus electrocatalysts for simultaneous oxidation/reduction of furfural with bipolar electrochemistry**

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## Materials

All chemicals were of analytical grade and used as received without further purification. Hexachloroplatinic (IV) acid hydrate ( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ , Sigma-Aldrich,  $\geq 99\%$ ), and Chloroauric acid trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , Sigma-Aldrich,  $\geq 99\%$ ) were used as metal precursors for Pt and Au electrodeposition, respectively. Glassy carbon beads (630 – 1000  $\mu\text{m}$ , type 2, Alfa Aesar) were used as a support material for the Pt/Au Janus particles. Graphite rods were used as feeder electrodes for the bipolar electrochemical experiments. Potassium hydroxide (KOH, Sigma-Aldrich,  $\geq 85\%$ ) was employed as supporting electrolyte. Furfural (Sigma-Aldrich,  $\geq 99\%$ ) was the starting compound for the electrochemical synthesis. Milli-Q water (18.2  $\text{M}\Omega \text{ cm}$ ) was used for all electrochemical experiments.

## Instrumentation and experiments

### *Conventional three-electrode system*

All electrochemical characterization experiments were performed with a potentiostat (AUTOLAB) with a conventional three-electrode system. A Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. Prior to all the experiments, the working electrodes were cleaned by ultrasonication in isopropanol and Milli-Q water for 15 min and then dried under  $\text{N}_2$  flow. Four commercial electrodes were tested, including Pt, Au, Ni, and Cu (0.25  $\text{cm}^2$ ). All the performance tests for electrochemical furfural conversion were carried out at room temperature (25  $^\circ\text{C}$ ) using 50 mM KOH solution in the absence or presence of 15 mM furfural as a starting substrate. Cyclic voltammetry was performed to examine the electrocatalytic performance using a scan rate of 20 mV/s.

### *Janus particle preparation using bipolar electrodeposition*

Bipolar electrodeposition was used to synthesize Janus particles modified with Pt and Au at the opposite extremities employing a KEITHLEY model 2450 power supply. Glassy carbon beads were positioned at the bottom of a homemade bipolar cell with a distance of 30 mm between two feeder electrodes in a 1 mM solution of the metal precursor. Different potentials (20, 40, 60, and 80V) were applied to identify optimized deposition conditions for a fixed electrodeposition time of 10 min. In the bipolar cell, various numbers of Janus particles (12, 24, 48 and 96) have been modified simultaneously. In the case of Pt/Au Janus particles, Pt was synthesized first on one hemisphere of the particles that were positioned at the bottom of the bipolar cell, and subsequently Au deposition was performed on the opposite side by switching the polarity of the feeder electrodes. Then, the obtained particles were rinsed with water and dried under  $\text{N}_2$  flow.

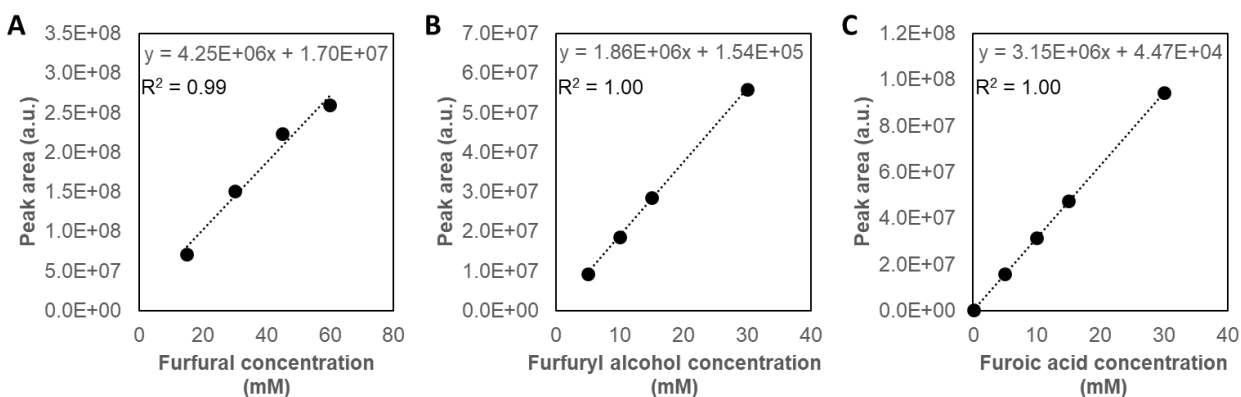
### *Electrochemical furfural conversion using bipolar electrochemistry*

To investigate the electrochemical activity of the Janus particles with respect to the electrochemical conversion of furfural, a certain number of Pt/Au particles (12, 24, 48 and 96) were positioned in the central compartment of the bipolar cell, which is separated from the electrode compartments by Nafion membranes (N115, thickness 0.005 in.). Attention was paid to the orientation of the Janus particles with respect to the electric field lines to make sure that the Pt hemisphere is facing the feeder cathode and the gold hemisphere the feeder anode. The bipolar

reaction was performed by applying the appropriate potential for 30 min in a 50 mM of KOH solution containing 15 mM of furfural. The voltage difference that needs to be applied between the feeder electrodes ( $\Delta V$ ) is proportional to the difference in potential between the reduction and oxidation of furfural ( $\Delta E$ ), determined by cyclic voltammetry, as well as the distance between the feeder electrodes ( $d$ ). It also inversely scales with the characteristic dimension of the bipolar electrode ( $l_e$ ).  $\Delta V$  is calculated by the following equation:<sup>1</sup>

$$\Delta V = \frac{\Delta E}{l_e} \times d$$

Quantitative analysis of the reaction products was performed by high-performance liquid chromatography (HPLC) on a Shimadzu LC-2030C3D equipped with a sugar HPLC column (SP0810, 300×8 mm inner diameter) and using Milli-Q water as a mobile phase at 80 °C with a flow rate of 1 ml/min and a photodiode array (PDA) detection at 211, 245, and 276 nm for furfuryl alcohol, furoic acid, and furfural, respectively. The absorption peak areas of the products were integrated using Lab Solution software. Calibration curves (see Fig. S1) obtained from integrated peak areas were used to calculate the electrocatalytic conversion.



**Fig. S1** Calibration curves based on the integrated peak area obtained from HPLC measurements for (A) Furfural, (B) Furfuryl alcohol, and (C) Furoic acid.

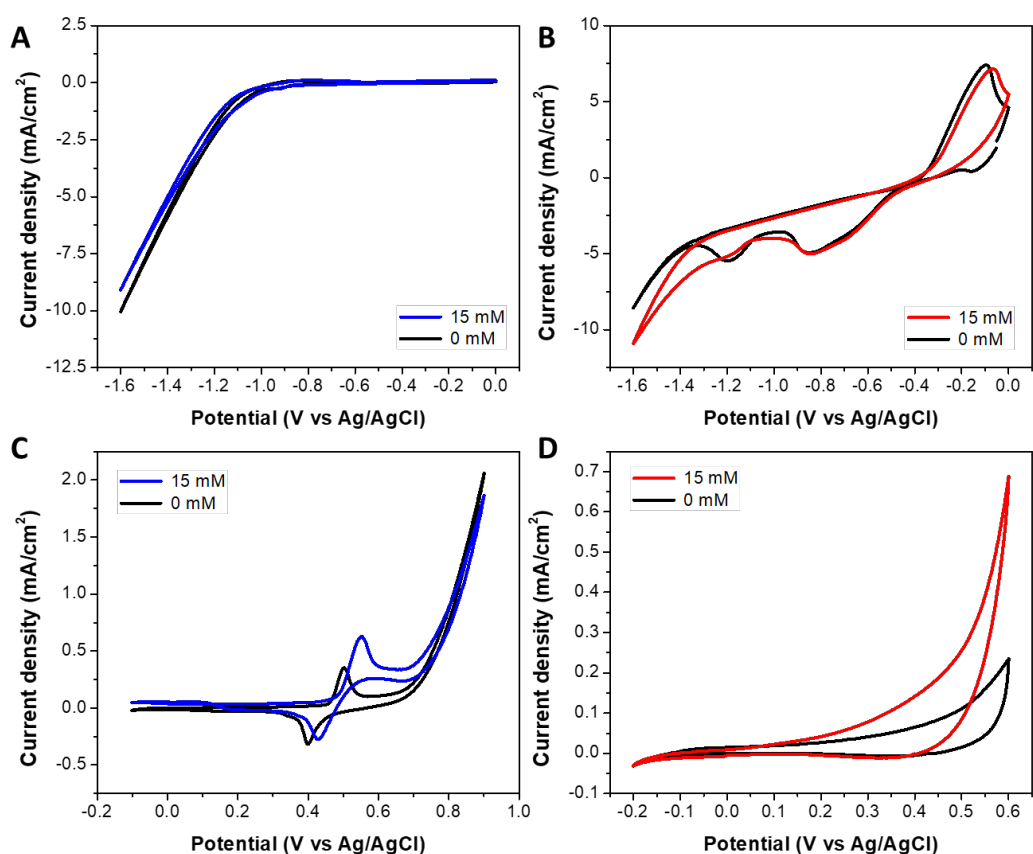
Subsequently, the total conversion of furfural ( $X_{FAL}$ ) and the product selectivity ( $S_i$ ) were estimated by the following equations:

$$X_{FAL} = \frac{(n_{FAL})_0 - (n_{FAL})_t}{(n_{FAL})_0} \times 100\%$$

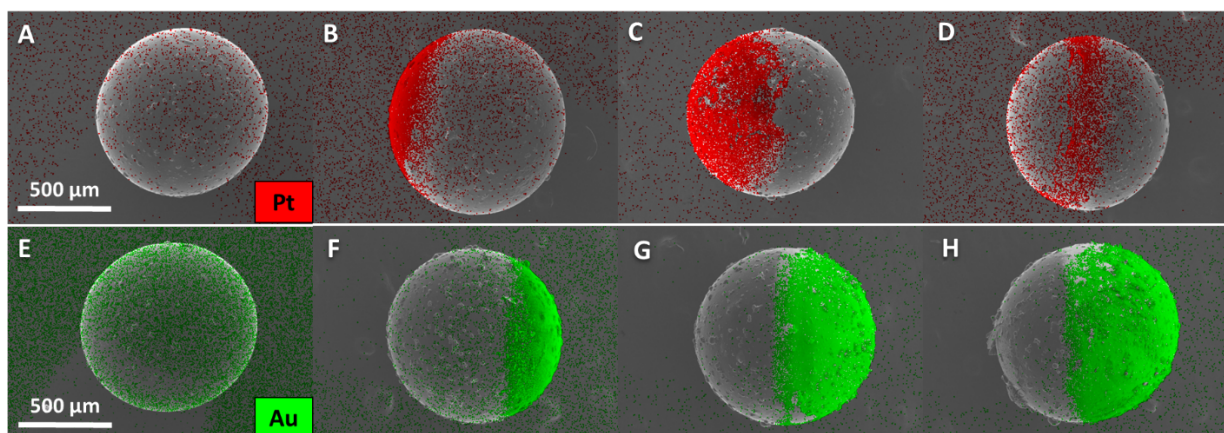
$$S_i = \left( \frac{n_i}{(\sum n)_t} \right)$$

where  $(n_{FAL})_0$ ,  $(n_{FAL})_t$ ,  $n_i$ , and  $\sum n$  are the initial moles of furfural, the moles of furfural at a certain time, the moles of the desired product  $i$ , and the total moles of all the products, respectively. The mass balance was estimated for all experiments to be around  $91.5 \pm 8.5\%$ .

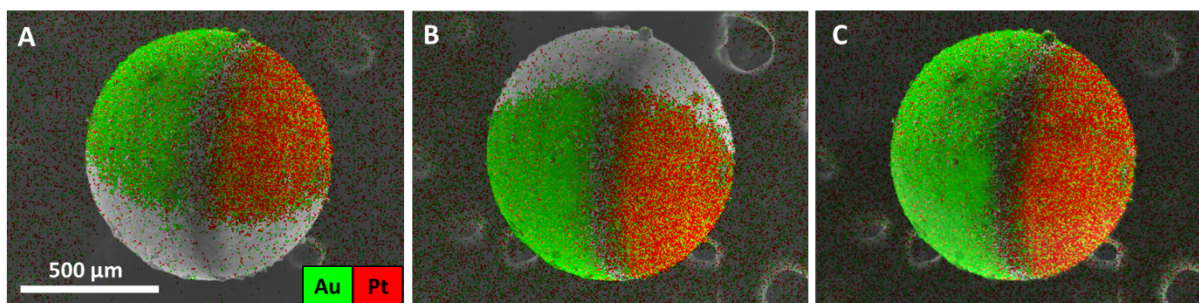
Additionally, scanning electron microscopy (SEM) images were recorded with a JEOL JSM-7610F microscope to study the morphology of the catalyst layers. Elemental mapping has been performed with an SEM equipped with Energy Dispersive X-ray spectrometry (SEM-EDS) on a JEOL JSM-7610F microscope. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-ARM200F microscope at 200 kV and the elemental distribution was studied by energy dispersive spectroscopy (EDS). To prepare the sample for TEM measurements, Pt/Au Janus particles were sonicated in ethanol and the solution was dropped onto a carbon film supported copper grid at room temperature. The oxidation states of Pt and Au were characterized by using X-ray photoelectron spectroscopy (XPS) using a JEOL JPS-9010 equipped with nonmonochromatic Mg K $\alpha$  X-rays (1486.6 eV). Moreover, proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectra were recorded by a BRUKER AVANCE III HD operating in  $\text{CDCl}_3$  at 600 MHz to further identify the different products.



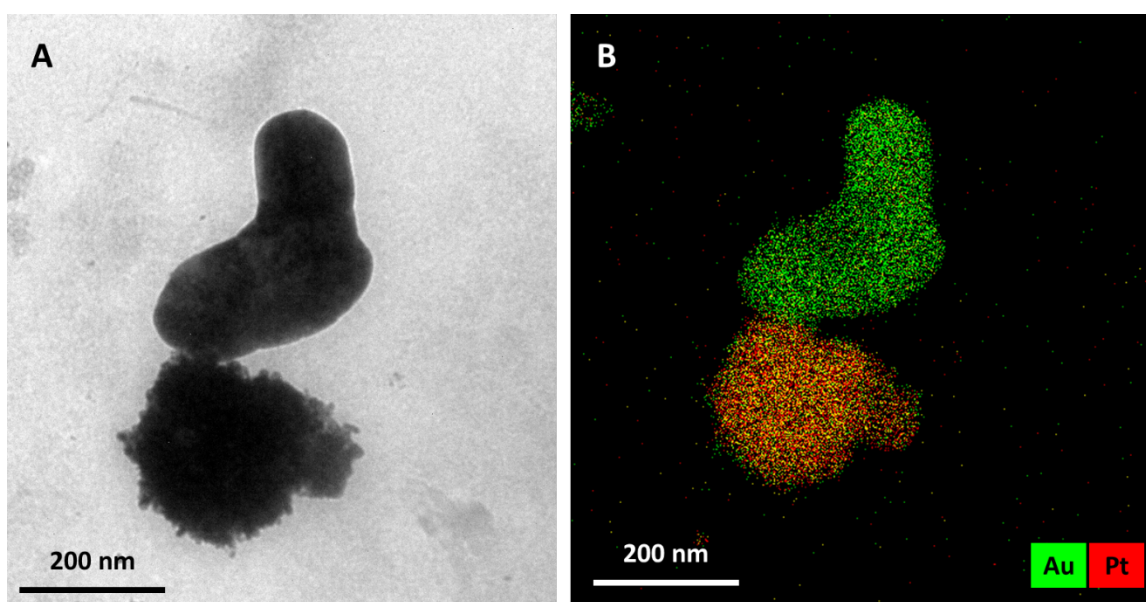
**Fig. S2** Cyclic voltammograms of furfural electroreduction (A, B) and furfural electrooxidation (C, D) with a Ni electrode (A,C) and a Cu electrode (B,D), respectively, in 50 mM KOH in the absence and in the presence of 15 mM of furfural using a scan rate of 20 mV/s.



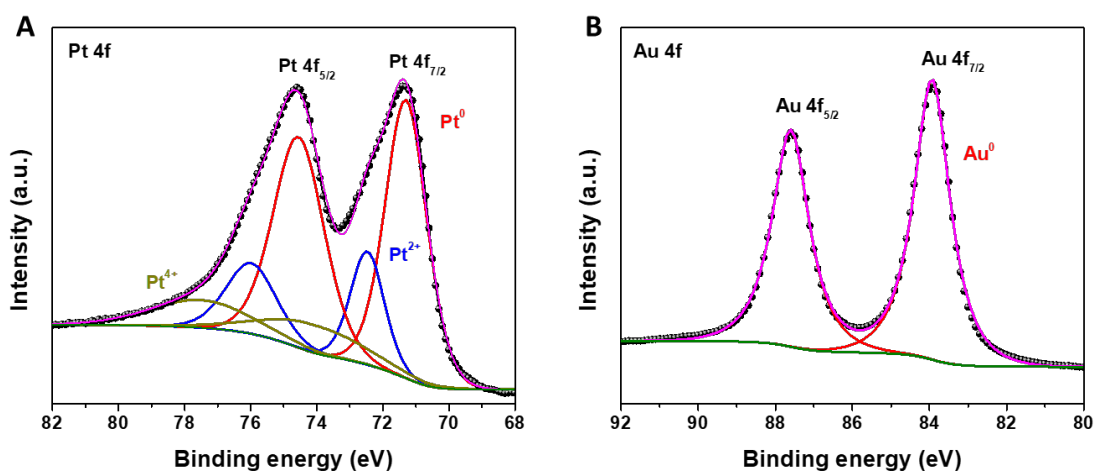
**Fig. S3** SEM-EDS images of (A-D) Pt electrodeposition at various potential differences between the feeder electrodes: (A) 20 V, (B) 40 V, (C) 60 V, (D) 70 V for 10 min, and (E-H) Au electrodeposition at various potential differences: (E) 20 V, (F) 40 V, (G) 60 V and (H) 80 V for 10 min.



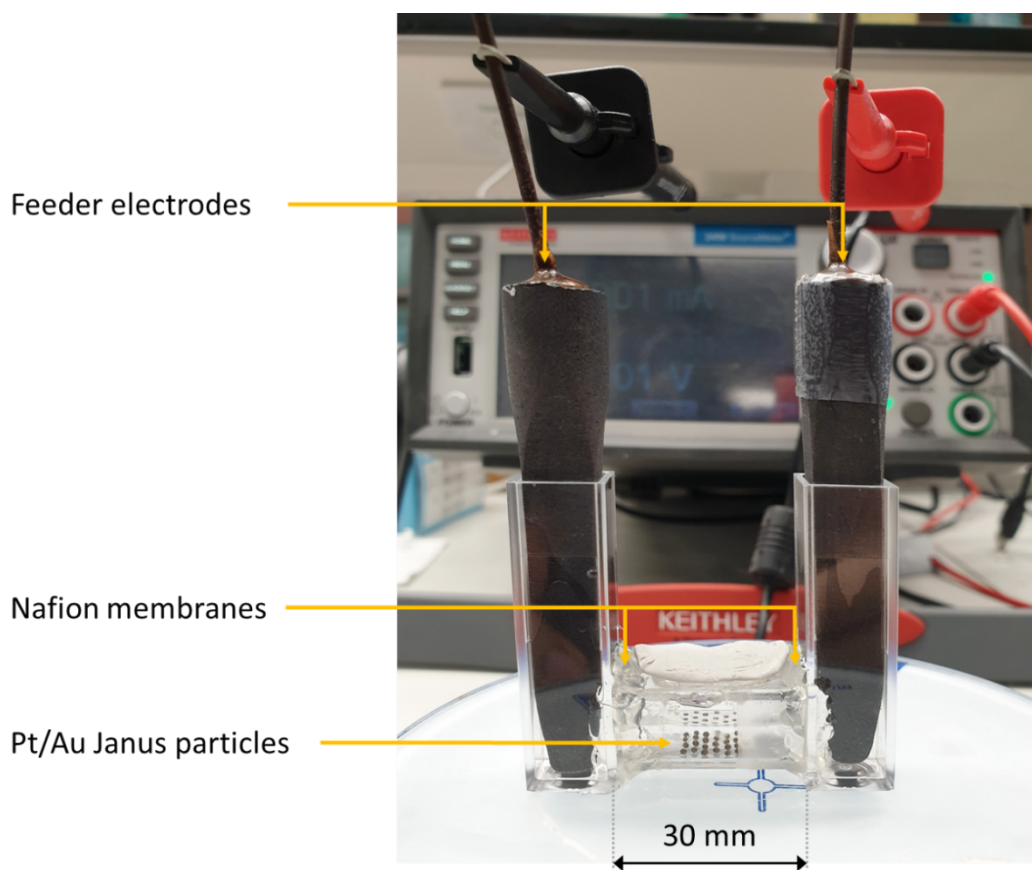
**Fig. S4** SEM-EDS images of Pt/Au Janus particle obtained from A) Top view, B) Bottom view and C) Superimposed images of the top and bottom views.



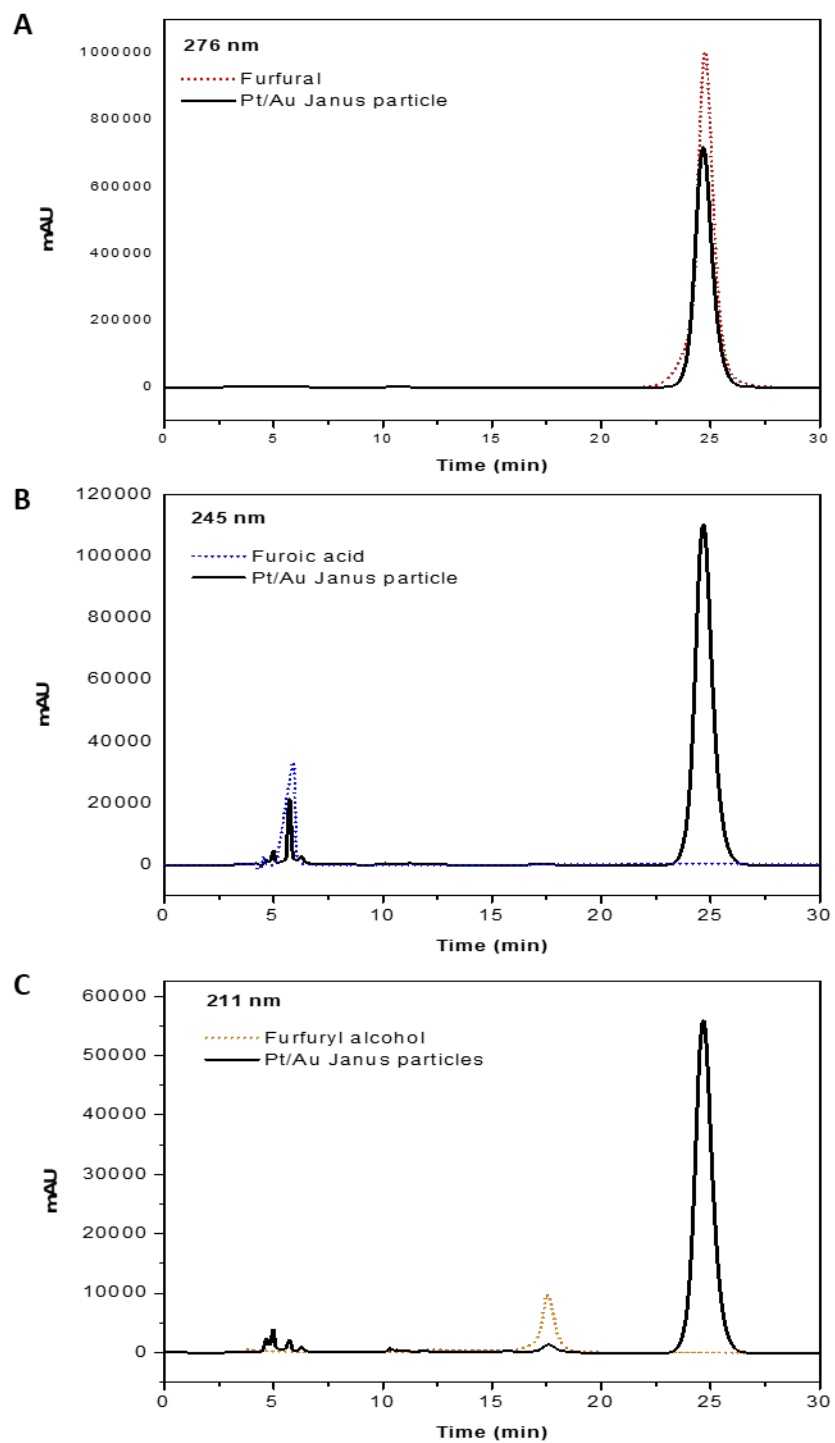
**Fig. S5** TEM-EDS images (A, B) of fractions of the Pt and Au deposit recovered from the Pt/Au Janus particle surface.



**Fig. S6** XPS spectra of (A) Pt 4f and (B) Au 4f of the Pt/Au Janus particle surface at the two hemispheres.

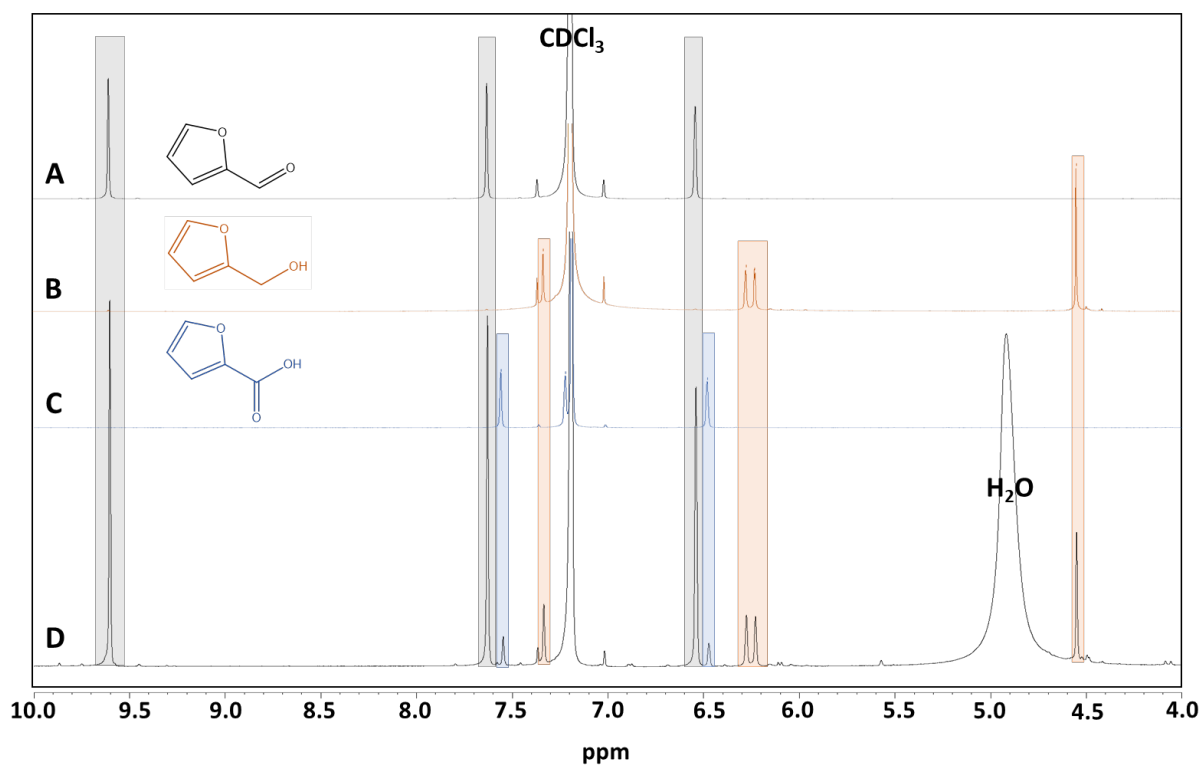


**Fig. S7** Experimental set-up for the bipolar electrochemical furfural conversion

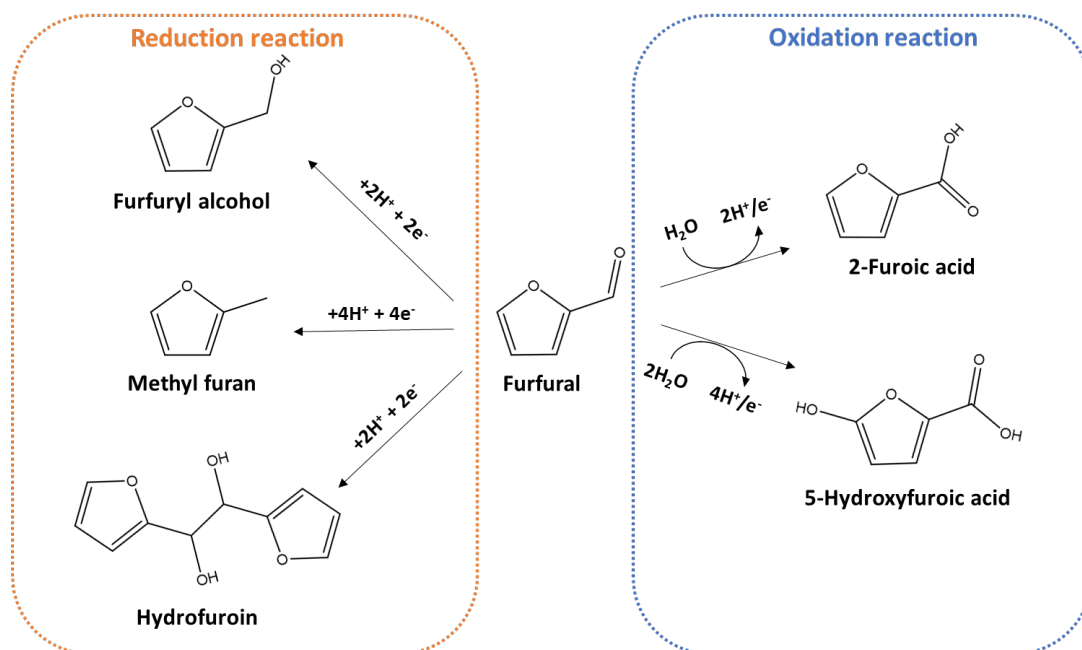


**Fig. S8** HPLC chromatograms of the product solution of the conversion of furfural using 24 Pt/Au Janus particles in 50 mM KOH with 15 mM of furfural in a bipolar electrochemical cell with an applied potential of 48 V for 30 min, compared with the standards of (A) Furfural at 276 nm, (B) Furoic acid at 245 nm and (C) Furfuryl alcohol at 211 nm.

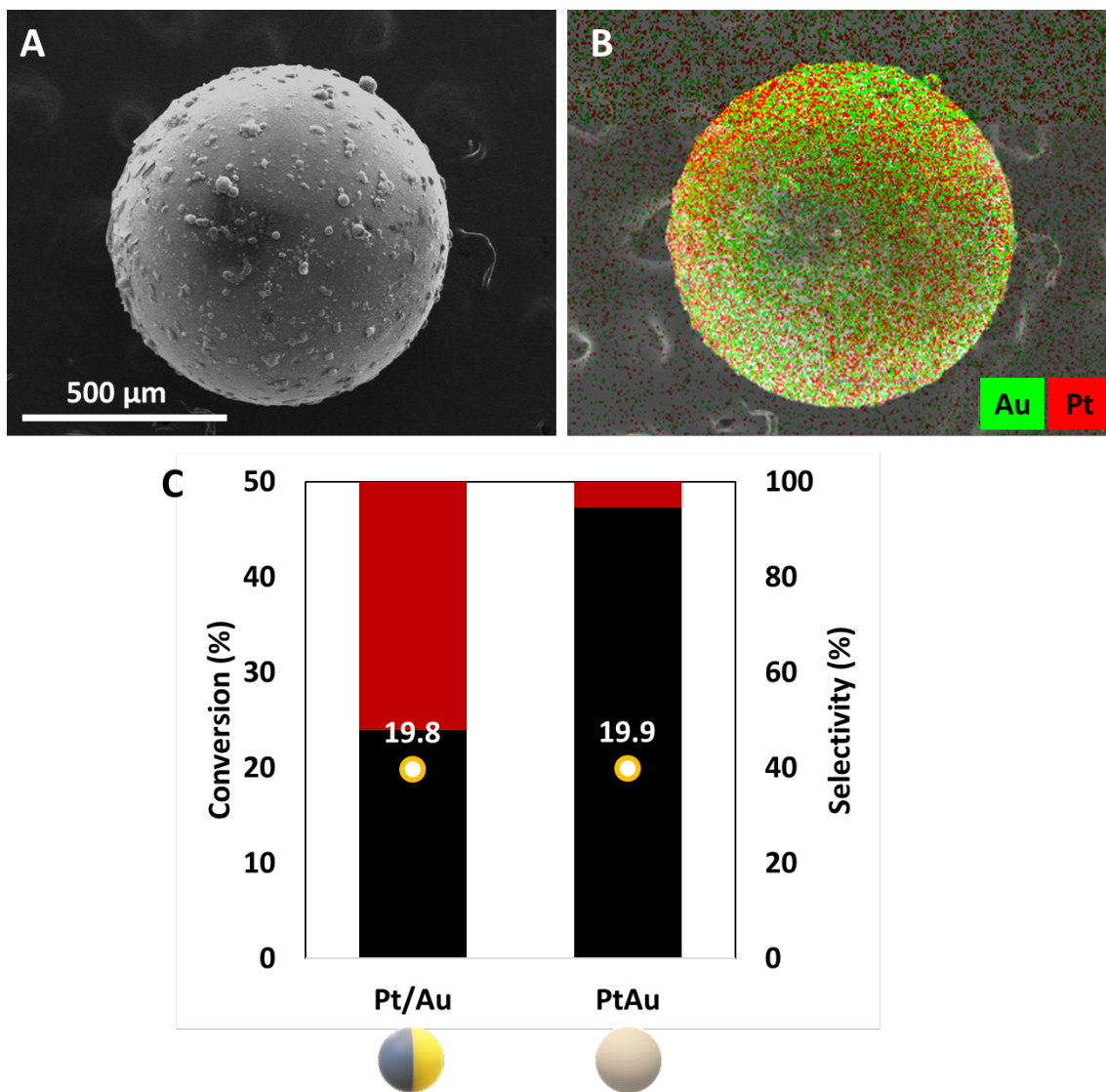




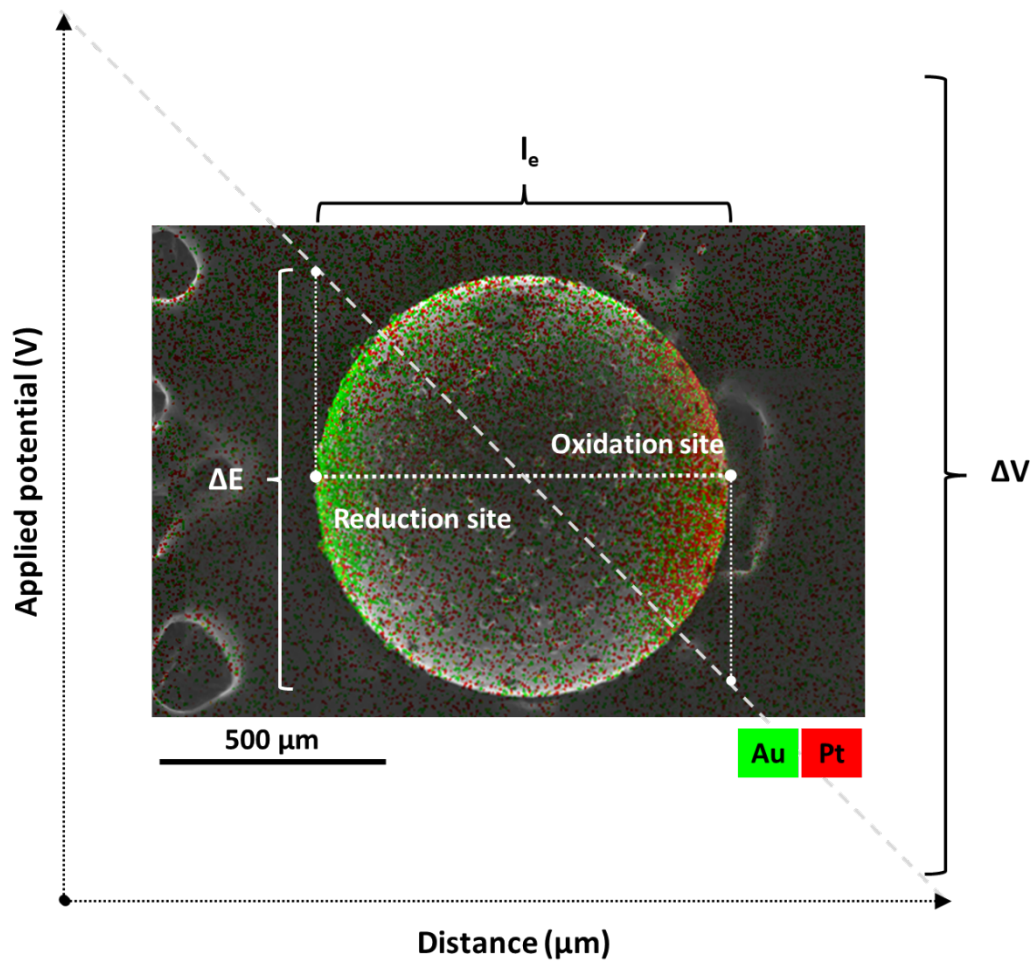
**Fig. S9**  $^1\text{H-NMR}$  spectra (600MHz,  $\text{CDCl}_3$ ) of standard references of A) furfural, B) furfuryl alcohol, C) furoic acid, and D) a sample taken from the electrochemical conversion of furfural using 24 Pt/Au Janus particles in 50 mM KOH with 15 mM of furfural in a bipolar electrochemical cell with an applied potential of 48 V for 30 min.



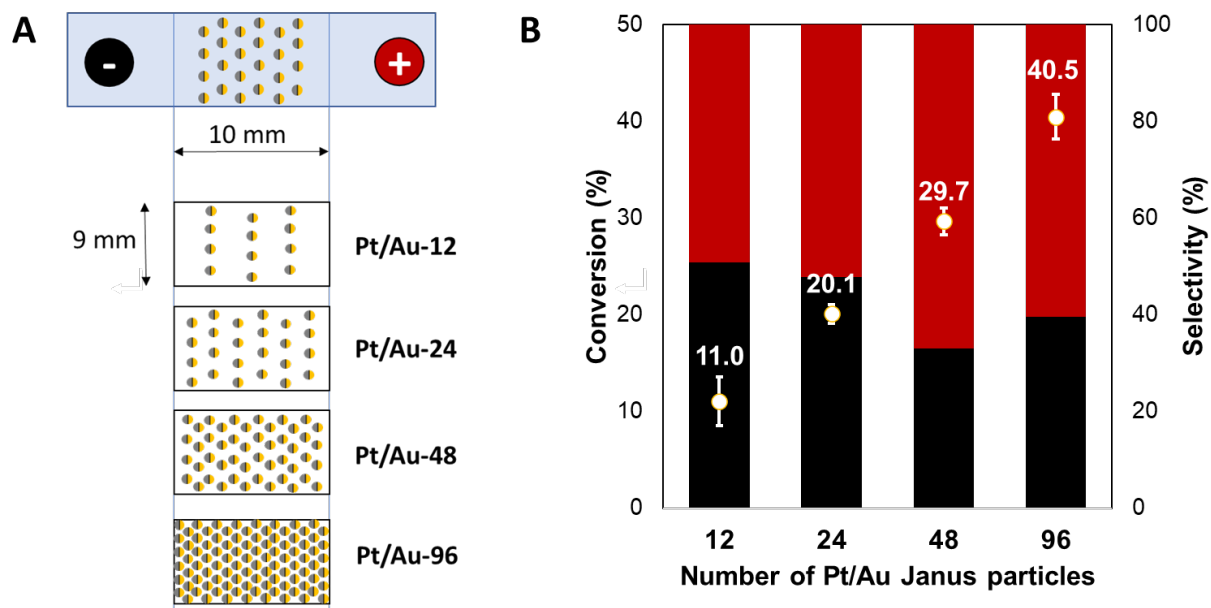
**Fig. S10** Different possible reaction mechanisms of furfural reduction and oxidation with the corresponding products.<sup>2,3</sup>



**Fig. S11** SEM-EDS images (A-B) of a PtAu particle obtained by Pt-Au co-electrodeposition using a mixture of 1 mM Pt precursor and 1 mM Au precursor at 60 V for 10 min deposited homogeneously on the entire particle surface, and (C) Electrocatalytic conversion of furfural with PtAu particles compared to bifunctional Pt/Au Janus particles in 50 mM KOH with 15 mM furfural in a bipolar electrochemical cell with an applied potential of 48 V for 30 min. Red and black bars represent the furoic acid and fufuryl alcohol selectivity, respectively, while the white circle refers to the total furfural conversion.



**Fig. S12** Schematic representation of polarization potential for a partially covered Pt/Au Janus particle using bipolar electrodeposition at 40 V for 10 min on each side.



**Fig. S13** A) Schematic illustration of bipolar cell with varying numbers of the Pt/Au Janus particles, and B) Electrocatalytic conversion of furfural with an increasing number of bifunctional Pt/Au Janus particles in 50 mM KOH with 15 mM of furfural in a bipolar electrochemical cell with an applied potential of 48 V for 30 min. Red and black bars represent furoic acid and furfuryl alcohol selectivity, respectively, and the white circles refer to total furfural conversion.

## References

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