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► **To cite this version:**

Marisa Ketkaew, Sunpet Assavapanumat, Sorasak Klinyod, Alexander Kuhn, Chularat Wattanakit. Bifunctional Pt/Au Janus electrocatalysts for simultaneous oxidation/reduction of furfural with bipolar electrochemistry. *Chemical Communications*, 2022, 58 (27), pp.4312-4315. 10.1039/D1CC06759A . hal-03989945

HAL Id: hal-03989945

<https://cnrs.hal.science/hal-03989945v1>

Submitted on 15 Feb 2023

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

Marisa Ketkaew,^{a,b} Sunpet Assavapanumat,^a Sorasak Klinyod,^a Alexander Kuhna,^{b,*} and Chularat Wattanakit^{*,a}

The sustainable conversion of biomass-derived compounds into high added-value products is a very important contemporary scientific challenge. In this context, we report here the simultaneous electro-oxidation/-reduction of a biomass-derived compound in a one-pot approach using bipolar electrochemistry. Bifunctional Pt/Au Janus electrocatalysts are employed for a selective conversion of furfural into both, furfuryl alcohol and furoic acid, which can't be achieved when using non-Janus particles. The results emphasize the benefits of bipolar electrochemistry in the frame of electrosynthesis processes.

The conversion of renewable biomass-derived compounds to commercially valuable chemicals is one of the most interesting current research topics due to an increasing energy demand, the gradual depletion of petroleum resources, and severe environmental problems.^{1, 2} Therefore, the development of alternative processes using renewable resources instead of fossil-based supplies attracts an increasing interest of scientists. Among various biomass-based-derived compounds, furfural is one of the most promising ones, as it can be converted into several fine chemicals.³ In this context, the synthesis of chemicals including furfuryl alcohol and furoic acid using furfural as a unique starting compound merits special attention.¹ Indeed, as it is in an intermediate oxidation state between the corresponding alcohol and acid, it can be converted either into furfuryl alcohol or furoic acid via electroreduction or electrooxidation, respectively.⁴ This allows benefitting from the intrinsic advantages of electroorganic synthesis, emphasized by the current trend to reconsider chemical processes and explore more sustainable concepts.^{5, 6}

Furfural reduction to furfuryl alcohol, the key monomer for the synthesis of furan resins, has been widely studied because these polymers are used in various applications ranging from composites to coatings and adhesives. In addition, furfuryl alcohol is also known as an important synthesis intermediate for various types of other molecules, such as dyes, pharmaceutical compounds and agricultural chemicals.⁷ In a typical procedure of furfuryl alcohol synthesis, furfural hydrogenation has been carried out with heterogeneous catalysts under rather severe conditions such as high temperature and pressure and using an expensive external H₂ source.⁸ In contrast, furfural electroreduction allows hydrogenation under very mild conditions.⁹ Therefore, the electrochemical process is an attractive alternative pathway, because it can be carried out at room temperature and atmospheric pressure without requiring an external source of H₂.^{10, 11}

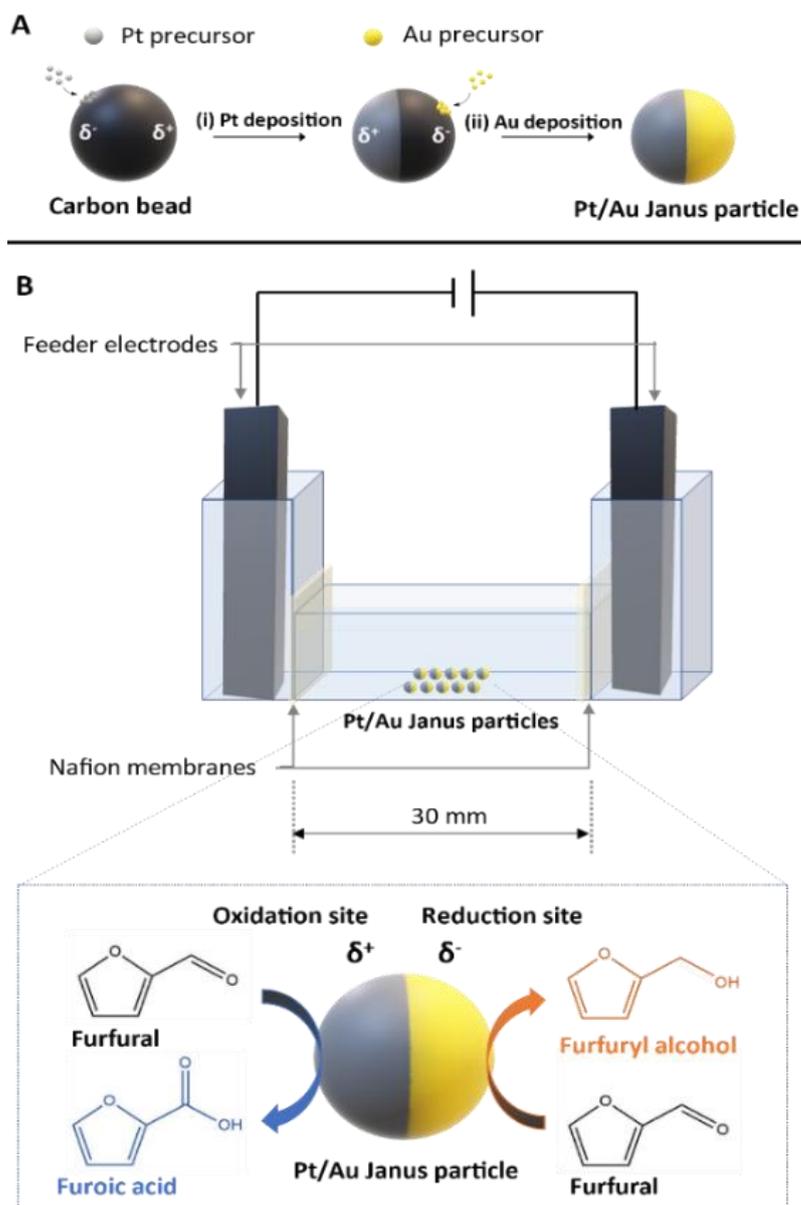
On the other hand, furfural oxidation to furoic acid and its derivatives, generally used as pharmaceuticals, fungicides, and as precursors for other molecules, has also been extensively investigated.¹ Moreover, furoic acid is considered as one of the most interesting alternative biomass-derived precursors to produce 2,5-furan-dicarboxylic acid (FDCA), a promising renewable monomer for bioplastic manufacturing. Indeed, the electrocatalytic oxidation of furfural offers several advantages, such as low operating temperatures and pressures, as well as an easy control of the product distribution by fine-tuning the electrode potential.^{2, 12}

Typically, the electro-reduction/-oxidation is achieved at an individual cathode or anode, respectively, with a three-electrode set-up using electrocatalysts, which have been widely developed by various techniques.¹³⁻¹⁵ Recently, the electrochemical conversion of furfural at both the anode and the cathode has been reported in a classic electrochemical set-up.¹ For example, Cu₃P (Cu₃P/CFC) and Ni₂P (Ni₂P/CFC) deposited on carbon fiber cloth (CFC) by a vapor-phase

hydrothermal method have been employed as modifiers for cathode and anode, respectively, for the simultaneous reduction and oxidation of furfural. This indicates the potential benefits which would result from a set-up where both catalytic reactions could be carried out simultaneously on a single particle. However, to the best of our knowledge, the development of bifunctional electrocatalysts on a single material for the simultaneous reduction and oxidation of furfural has not been demonstrated so far.

Due to their intrinsic bifunctionality, so-called Janus particles might be eventually employed as electrocatalysts for this purpose, thus allowing the transformation of a given molecule simultaneously by oxidation and reduction at the opposite sides of the particle. However, in classic electroorganic synthesis, catalysts need to be immobilized on the individual electrode surfaces and therefore can be only used for accelerating either an oxidation or a reduction, but not both at the same time. It is therefore necessary to circumvent this important roadblock by activating the electrochemical transformation in a wireless way. This can be achieved by using the concept of bipolar electrochemistry, which allows the electrochemical addressing of conducting particles that are not physically connected to a power supply.

In general, Janus particles have been synthesized by following various approaches.^{16, 17} One interesting possibility is to use also for this task bipolar electrochemistry.¹⁸ It is based on the fact that when a conducting material is positioned in a solution between two feeder electrodes, it experiences an asymmetric polarization due to the electric field.¹⁹⁻²³ This allows eventually triggering electroreduction and electrooxidation simultaneously at the opposite extremities of the object. The resulting micro- and nanosized bifunctional particles exhibit different anisotropic properties leading to asymmetric features combined on a single particle.²⁴⁻²⁶ Thus, the concept can also be used to generate bifunctional electrocatalysts with different metals at the two faces of the resulting Janus particle. In the present contribution, we have followed this approach to elaborate Janus electrocatalyst for the simultaneous furfural reduction and oxidation at the cathodic and anodic poles, respectively, in order to produce these two value-added compounds in a well-controlled way.



Scheme 1 (A) Schematic illustration of the electrodeposition process to synthesize Pt/Au Janus particles (B) Bipolar cell for simultaneous furfural conversion into furfuryl alcohol and furoic acid on Pt/Au Janus particles.

Pt and Au have been combined on the same particle, but at opposite sides, in order to benefit simultaneously from their superior catalytic activity.²⁷ The stepwise procedure is illustrated in Scheme 1A. When applying an appropriate potential to the bipolar cell, carbon beads placed at the bottom of the cell get polarized and the electrochemical reduction of the metal precursor occurs at the cathodic pole. Pt was first deposited on one side of the support material and the polarity of the electric field was subsequently switched for Au deposition at the other side, leading to uniform Pt/Au Janus particles. It should be noted that the Pt and Au deposition sequence can be changed, because these elements are noble metals, providing a rather high stability against back oxidation when inverting the electric field direction.

To perform simultaneous electroreduction/electrooxidation of furfural, the synthesized Pt/Au Janus particles, positioned at the bottom of the bipolar cell, have been employed as electrocatalysts using Au and Pt for furfural reduction to furfuryl alcohol and oxidation to furoic acid, respectively (Scheme 1B). This choice has been made after an initial investigation of the individual catalytic performance of several metals (Ni, Cu, Pt, Au) for the reduction and oxidation of furfural by classic electrochemistry. Cyclic voltammetry (CV) was used to determine the onset potential for both reactions in order to estimate the necessary potential difference between the feeder electrodes in the bipolar electrocatalysis experiment. As can be seen in Fig. 1A, the Au electrode allows furfural reduction for potentials more negative than -1.3 V. In contrast, the Pt electrode (Fig. 1B) shows no significant additional currents in the same potential range when adding furfural.

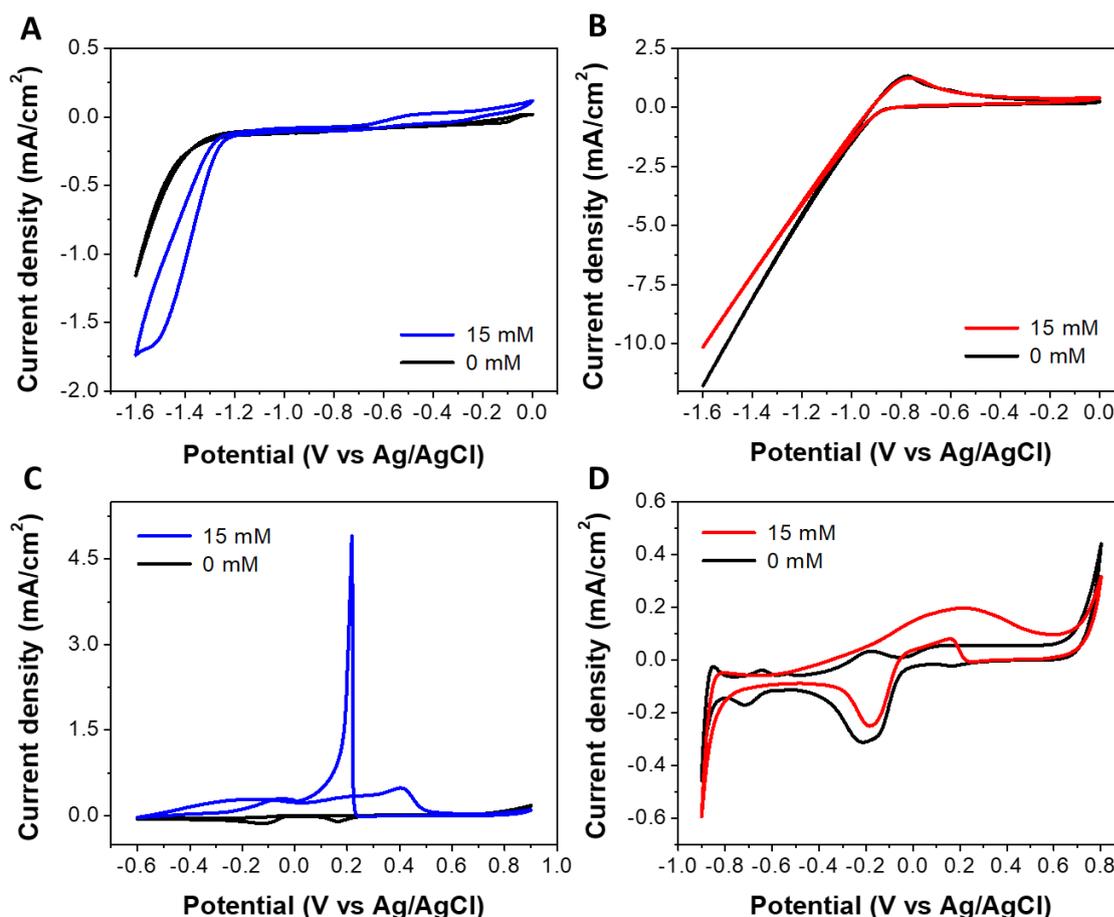


Fig. 1 Cyclic voltammograms of furfural electroreduction (A, B) and furfural electrooxidation (C, D) with an Au electrode (A,C) and a Pt electrode (B,D) in 50 mM KOH in the absence (black) and in the presence of 15 mM of furfural (blue or red) using a scan rate of 20 mV/s at 25 °C.

Furfural electrooxidation was also investigated with these two electrodes. The Au electrode exhibits an anodic peak at 0.4 V (Fig. 1C) and for the Pt electrode, a broad peak related to furfural oxidation can be observed around 0.3 V (Fig. 1D). The other metals, Ni and Cu, show no significant activity in the reduction regime and, most importantly, get oxidized before furfural oxidation can occur, as can be seen in Fig. S2.28,29 Based on these observations, it is reasonable to conclude that the most suitable candidate for furfural reduction is Au electrode, whereas the oxidation is possible with Pt.

Therefore, Pt/Au Janus particles seem to be the most promising combination of materials and were generated by using bipolar electrodeposition. In order to optimize the experimental parameters, the potentials required for metal deposition at the cathodic pole of carbon beads were investigated. As can be seen in Fig. S3, the most appropriate potential difference between the feeder electrodes in the given set-up was approximately 60 V with a deposition time of 10 min for both Pt and Au. It should be noted that potentials above 60 V are not suitable. In the case of Pt deposition, they typically lead to bubble generation due to hydrogen evolution,³⁰ hindering or completely preventing Pt deposition. In contrast, Au deposits cover more than half of the bipolar object for high potential values, and therefore an equilibrated coverage of both faces with the two metals cannot be achieved. Thus, Pt/Au Janus particles are typically obtained by depositing first Pt on one side of the carbon beads, followed by Au deposition on the other side after switching the orientation of the electric field direction, using 60 V for 10 min in each step.

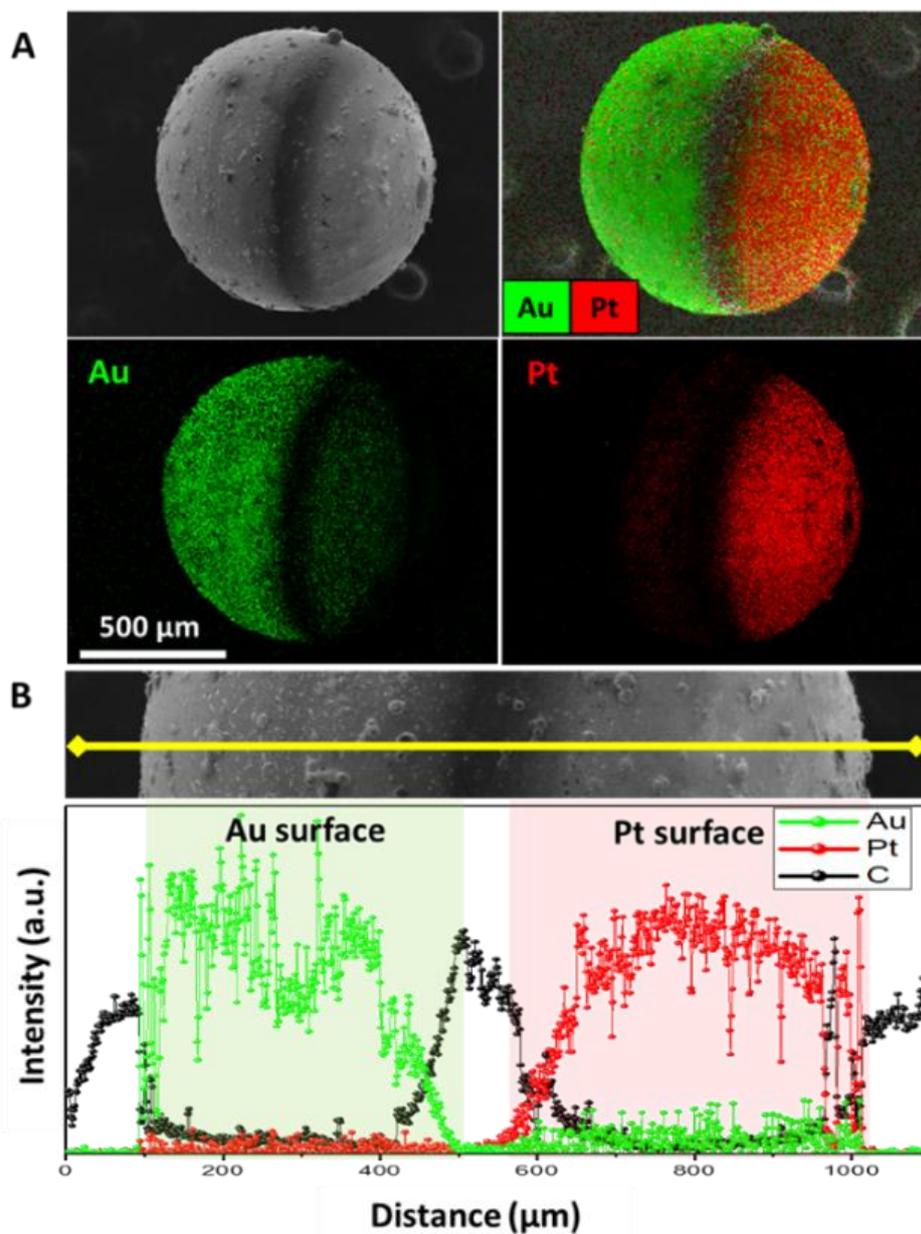


Fig. 2 (A) SEM-EDS images and (B) SEM-EDS line scan profiles of a Pt/Au Janus particle obtained by bipolar electrodeposition at 60 V for 10 min on each side.

Fig. 2 illustrates scanning electron microscopy images and energy-dispersive X-ray spectroscopy (SEM-EDS) measurements together with the EDS line scan profiles of the successfully prepared Janus particles. A lack of EDS signal at the bottom part of SEM-EDS images (see Fig. S4) originates from the orientation of the EDS detector, which cannot record signals generated behind the carbon bead. Thus, the entire elemental map is obtained by superposing SEM-EDS images of the two individual measurements carried out at two different angles (Fig. 2A). SEM-EDS line scan profiles indicate the presence of the individual metals without any overlap (Fig. 2B). The Pt and Au surfaces were further

analysed by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) to confirm the presence of the metallic form of Pt and Au as the predominant phase (see Fig. S5-S6)

The activity and the synergy effect of the Pt/Au Janus particles has been tested by electrochemical furfural conversion in a rather simple bipolar electrochemical set-up to produce both furfural alcohol and furoic acid simultaneously at the Au and Pt face, respectively (Scheme 1B and Fig. S7). For carrying out the electrocatalytic reactions on the particles generated with bipolar electrochemistry, an appropriate potential difference must be applied between the feeder electrodes to polarize the bipolar object.²¹ The calculated potential of 48 V was obtained considering the potential difference between furfural electrooxidation on Pt (+0.3 V) and furfural electroreduction on Au (-1.3 V), as well as taking into account the distance between the feeder electrodes (30 mm) and the diameter of the particles (1 mm).

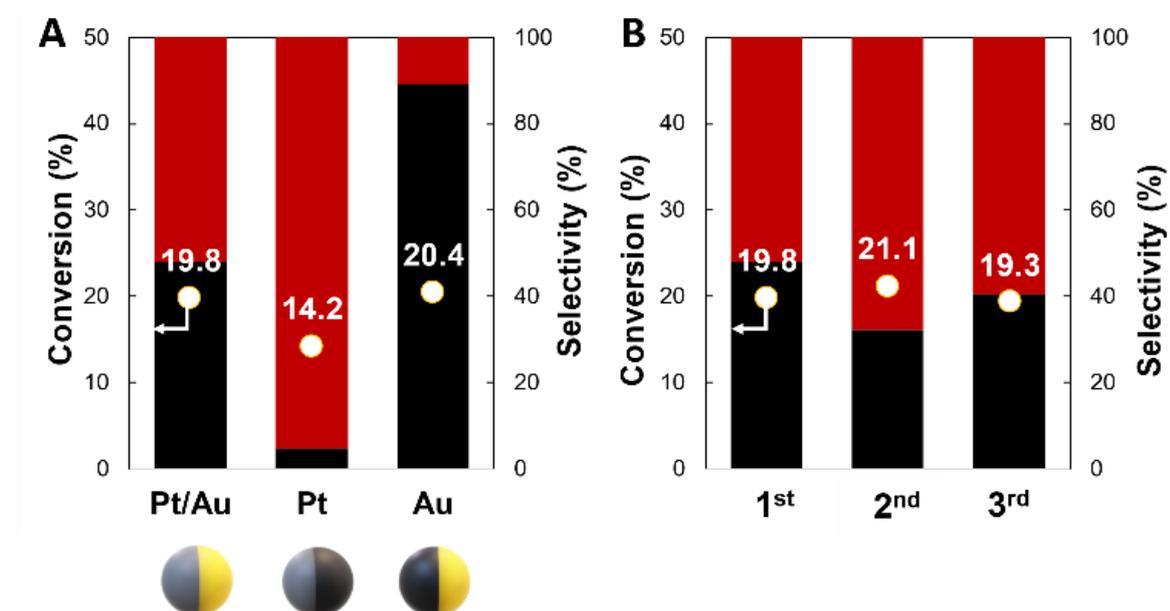


Fig. 3 (A) Electrocatalytic performance of different Janus particles in 50 mM KOH with 15 mM of furfural in a bipolar cell at an applied potential of 48 V for 30 min and (B) Reusability test of Pt/Au Janus particles for 3 cycles. Red and black bars represent furoic acid and furfuryl alcohol selectivity, respectively, while the white circle symbol refers to total furfural conversion.

Initially, a control experiment, in which the reaction proceeded at 48 V for 30 min without the presence of bipolar objects, was carried out, and no reaction products could be detected, because the feeder electrode compartments are protected by Nafion membranes. In strong contrast to this, the reaction in the presence of 24 Pt/Au Janus particles produces equivalent amounts of both furfuryl alcohol and furoic acid verified by HPLC and ¹H-NMR results as illustrated in Fig. S8-S9. As can be seen in Fig 3A (left bar), the selectivity of furfuryl alcohol and furoic acid are approximately 47.8 and 52.2%, with a total yield of 9.5 and 10.3% of the products, respectively. In order to deconvolute the contribution of the individual metals, the performance of Janus particles with only one metal present on one half-sphere has been tested separately (Fig 3A, middle and right column). Furoic acid is, as expected, the main product when using the Pt Janus particles, whereas the furfuryl

alcohol can be obtained quite selectively with Au Janus particles. The product distribution can be controlled by optimizing the experimental conditions to minimize undesired products⁶ with respect to the reaction mechanisms shown in Fig. S10. To verify the unique features of the Janus Pt/Au particles, we also tested the performance of a homogeneous PtAu deposit on carbon beads (Fig. S11). Such particles don't allow the simultaneous reduction and oxidation of furfural, but lead to the formation of only furfuryl alcohol. This underlines the benefits of the Janus character for the simultaneous reduction and oxidation of furfural. Particles with fully covered hemispheres have the highest efficiency, due to the possibility to apply a stronger polarization potential difference (see Fig. S12). Although the present overall conversion of furfural is moderate (19.8%), the efficiency can be enhanced by adjusting various factors. For example, furfural conversion increases linearly with the number of bimetallic particles and reaches almost half-conversion with less than a hundred Janus particles as shown in Fig. S13.

An important aspect in terms of potential practical application is the reusability of the catalyst particles. Therefore, additional tests were carried out using 24 Pt/Au Janus particles for several experiments (Fig. 3B). After each catalytic cycle, the Pt/Au Janus particles were recovered without any regeneration process. The results confirm that the particles can be reused for several cycles without a significant variation of the total furfural conversion and only slight changes in terms of selectivity. It should be noted that although a mixture of furfuryl alcohol and furoic acid is obtained after the electrochemical reaction, these two compounds can be easily separated due to their different boiling points.

In summary, the simultaneous electrochemical conversion of furfural via both oxidation and reduction has been achieved using specifically designed Pt/Au Janus particles as bifunctional electrocatalysts following a bipolar electrochemical approach. This work opens up interesting perspectives for bipolar electrochemistry as a strategy allowing an easy control of the catalytic activity for various types of reactions, including even bioelectrochemical transformations.^{5,31} In addition, the bifunctional particles can be reused and, although only a limited number of particles have been employed in the present proof-of-principle study, one might imagine a large-scale synthesis of high added-value molecules based on this strategy, especially with biomass-derived starting compounds.

Acknowledgments

This work was supported by the Vidyasirimedhi Institute of Science and Technology and the bilateral PICS and the IRP ChiraChem program of CNRS. M.K. is grateful to Campus France and the French Embassy in Thailand for a co-tutelle PhD scholarship. C. W. thanks the Mid-Career Research Grant 2020 from National Research Council of Thailand (NRCT5-RSA63025-03) and funding support from the NSRF via the Program Management Unit for Human Resources & Institutional Development, Research and Innovation (B05F640207). The project has also been partially funded by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement no 741251, ERC Advanced grant ELECTRA).

Conflicts of interest

There are no conflicts to declare.

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