



Electrolysis-driven propane dehydrogenation via bromine-mediated strategy for 6000 h of excellent performance at ambient temperature

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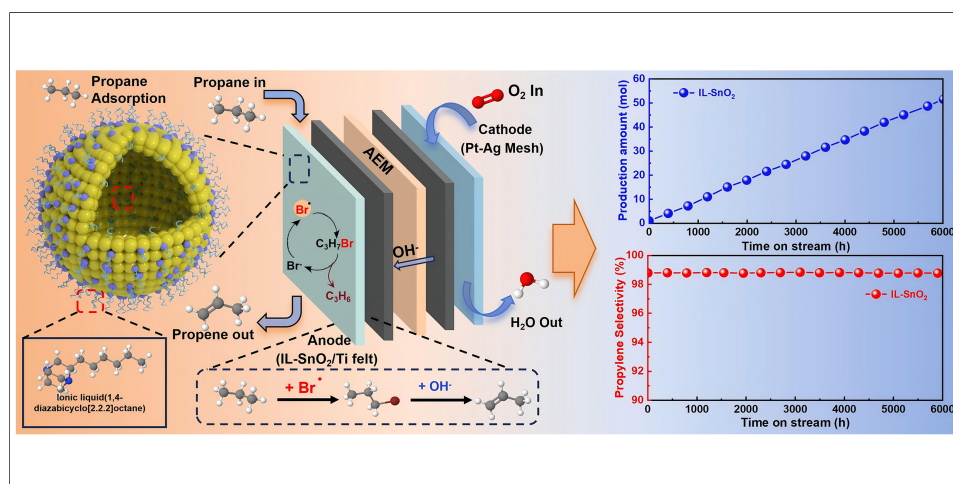
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Propene, as one of the most important light olefin feedstocks, is widely used for producing polymers and other chemicals, with a global market of over 217.74 billion dollars by the year of 2034^[1]. Currently, the propane dehydrogenation (PDH) to propene attracts significant attention owing to the low-cost propane from the success of the shale gas revolution^[2]. However, the activation of the C–H bond in propane requires harsh conditions up to 600 °C for reaching an industrially viable productivity. It not only causes serious energy consumption and rapid deactivation of the catalyst, but also induces various hydrocarbon by-products^[3]. Therefore, an innovative PDH strategy with high propane conversion, superior propene selectivity and long-term stability under mild conditions is highly desired^[4,5].

Promoting facile C–H activation in propane by sustainable electrochemistry for offering an efficient PDH shows great promise^[6], as it allows breaking the PDH equilibrium limitation and operating at ambient temperatures (AT). Bhadouria *et al.* found that propane (C₃H₈) can be spontaneously activated on platinum at 0.3 V [vs.

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reversible hydrogen electrode (RHE)] under AT, but with an “average” adsorbate of $C_3H_2^*$ ^[7]. Besides that, introducing O_2 gas as an oxidant, Liu *et al.* observed electrochemical PDH on a copper electrode, with a propane conversion rate of $11.6 \mu\text{mol}\cdot\text{cm}_{\text{Cu}}^{-2}\cdot\text{h}^{-1}$ and a propene selectivity of 86% at AT^[8]. However, the adsorption competition between propane and O_2 on Cu, as well as the low propane solubility in electrolytes, are identified as the rate-determining steps. Altering the oxidant to liquid H_2O_2 , the main product dramatically shifts to acetone (i.e., ~80% selectivity^[9]) as the electrogenerated $\cdot\text{OH}$ radicals directly convert propane to acetone via isopropanol. This indicates that electrolysis-driven PDH at AT is realizable, but with great challenges on developing efficient activators for C–H dissociation.

Recently, Yang *et al.* filled some of these gaps by proposing an innovative strategy, which uses electrogenerated bromine radicals ($\text{Br}\cdot$) as the mediator to activate the C–H bond and produces propene by a tandem bromination - Br elimination reaction at AT [Figure 1A]^[10]. Briefly, using ionic liquid-SnO₂ (IL-SnO₂) as the anodic catalyst, Br^- ions from the ionic liquid (IL; i.e., 1,4-diazabicyclo[2.2.2]octane/ $\text{Br}(\text{CH}_2)_n\text{CH}_3$) are electrochemically oxidized to bromine radicals ($\text{Br}\cdot$). The $\text{Br}\cdot$ attacks the C–H of propane for the formation of a hydrocarbon intermediate (i.e., $C_3H_7\cdot$), which spontaneously combines with the residual $\text{Br}\cdot$ to form $C_3H_7\text{Br}$. A further Br elimination of bromopropane with the hydroxide ions (OH^-) in electrolytes (i.e., 1M NaBr in NaOH aqueous, pH~10) appears on the catalyst, releasing propene as the sole gas product. It overcomes the limitation of C–H activation in both the thermocatalytic route and the electrocatalytic oxidation route.

A key finding of this work is developing an advanced catalyst (i.e., IL-SnO₂ hollow spheres), which allows an efficient electrosynthesis of bromine radicals ($\text{Br}\cdot$) to act as an initiator in PDH. Notably, $\text{Br}\cdot$ is an ideal species to activate the C–H bond, enabling spontaneous propane bromination ($\text{pK}_a \sim 4.92$; K_a is the acid dissociation constant) to bromopropane ($\text{pK}_a \sim 8.85$); however, keeping $\text{Br}\cdot$ radicals stable in alkaline electrolytes for reacting with propane is a challenge. They creatively proposed an IL decorated SnO₂ catalyst with a hollow sphere structure (i.e., 150 nm of outer diameter, 59 nm of inner cavity diameter and a 3.69 nm mesopore in SnO₂ skeleton) by a classical hydrothermal method [Figure 1B]. The ampholytic IL (i.e., a head of polar group of Br-N and a tail of non-polar group of alkyl chain) on SnO₂ induces a hydrophobic surface of IL-SnO₂ sphere, creating a water-deficient cavity for concentrating and stabilizing $\text{Br}\cdot/\text{Br}_2$ by preventing them from reacting with OH^- during the electrocatalysis. Contrarily, a commercial benchmark of dimensionally stable anode (i.e., RuIrO_x supported by Ti substrate) promotes hydroxyl radical ($\text{OH}\cdot$) formation from the OH^- electro-oxidation, instead of $\text{Br}\cdot$, under the same conditions. They further evaluate the effect of the alkyl chain length [i.e., from $-\text{CH}_3$ to $-(\text{CH}_2)_6\text{CH}_3$] in IL molecular on the stability of $\text{Br}\cdot$, revealing that a long alkyl chain (e.g., carbon number above 6) in IL intensively decreases the H_2O density from $1,000 \text{ mg}\cdot\text{cm}^{-3}$ (i.e., on the pristine SnO₂) to $\sim 800 \text{ mg}\cdot\text{cm}^{-3}$ [Figure 1C] and promote a facile Br^- oxidation to $\text{Br}\cdot$ at low over-potential of $\sim 12.7 \text{ mV}$. Additionally, the hydrophobic property of IL-SnO₂ also offers a high propane adsorption capacity above $65 \text{ mL}_{\text{propane}}\cdot\text{g}_{\text{IL-SnO}_2}^{-1}$ at 1 bar under AT [Figure 1D]. Here, the mesoporous hollow sphere of IL-SnO₂ acts as a concentrator for the electrogenerated Br radicals and the propane reactant, enabling a spontaneous PDH in alkaline solution.

Significantly, the feasibility of the Br-mediated PDH approach for practical use was verified by using a gas diffusion electrode (GDE) and membrane-electrode assembly (MEA) in Figure 1E. It shows a temperature-dependent propene (C_3H_6) production rate and selectivity [Figure 1F], with 0.32 and $0.8 \text{ mmol}_{\text{propane}}\cdot\text{h}^{-1}$ at room temperature and 90°C , respectively. High propene selectivity ($\sim 98.3\%$) with trace $C_3H_6\text{Br}_2$ (i.e., $\sim 0.2\%$) and $C_3H_7\text{Br}$ (i.e., $\sim 0.5\%$) was obtained, indicating that $> 99\%$ purity of propene could be obtained from the electrolyte chamber. Importantly, after 6,000 h of reaction at $800 \text{ mA}\cdot\text{cm}^{-2}$ [Figure 1G], the propene selectivity and the catalytic activity have negligible decrease, with a tiny increase rate ($3.16 \mu\text{V}\cdot\text{h}^{-1}$) of potential. It is superior to the commercial route (e.g., Oleflex from Honeywell UOP on Pt-Sn/ Al_2O_3 ^[2]) shows

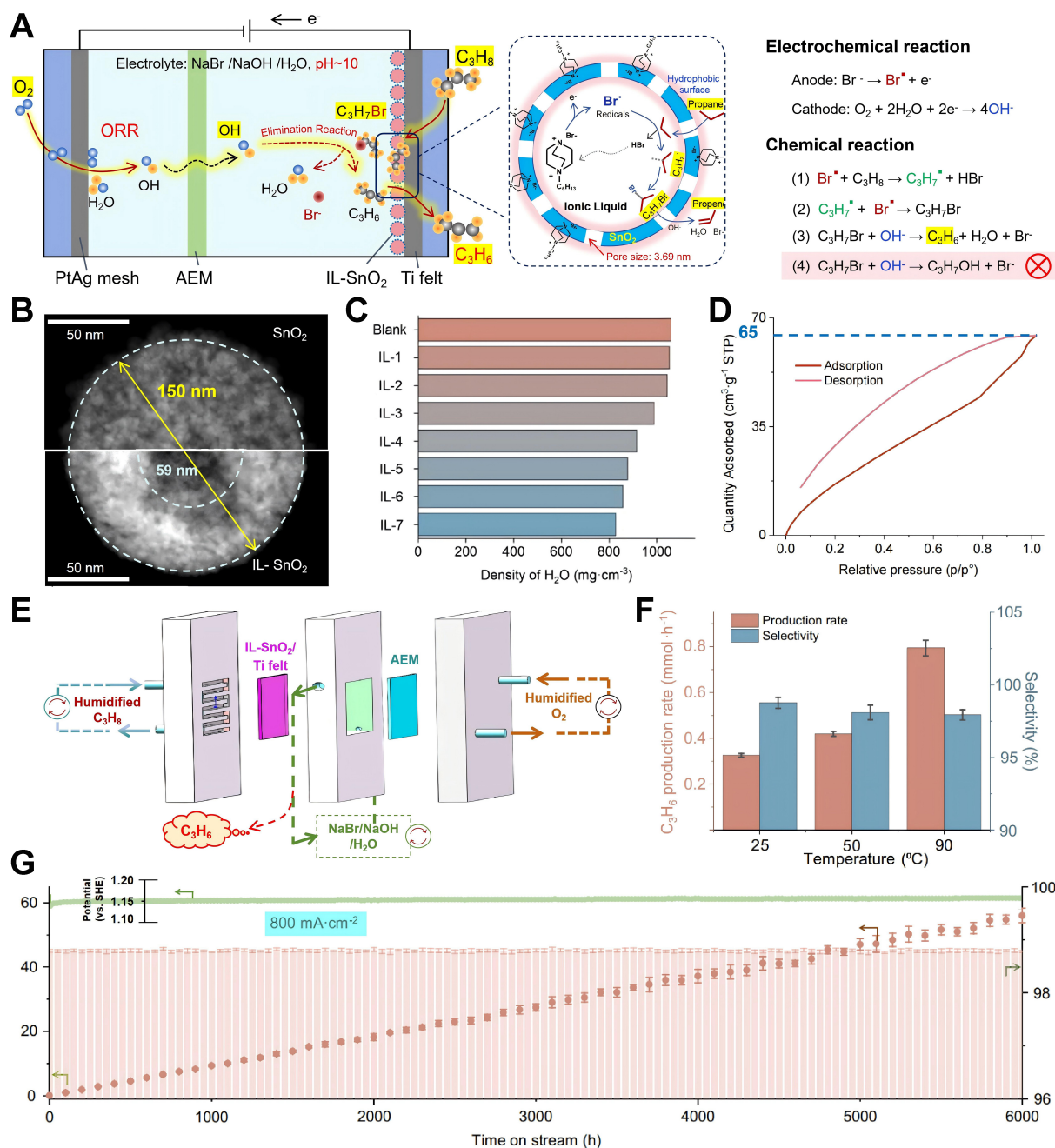


Figure 1. (A) Schematic diagram of the reaction process; (B) HAADF-STEM images of SnO₂ (upper) and IL-SnO₂ (bottom); (C) The calculated density of water on IL-SnO₂ with different lengths of the alkyl chain; (D) The BET adsorption and desorption curves of C₃H₈ on IL-SnO₂; (E) Schematic diagram of the flow reactor; (F) The production rate and selectivity of C₃H₆ at different temperatures in the flow reactor; (G) Stability test of IL-SnO₂ under the constant current density of 800 mA·cm⁻². (B-D) and (F and G) are reproduced with permission from Ref.^[10], © 2026 The American Association for the Advancement of Science. HAADF-STEM: High-angle annular dark-field scanning transmission electron microscopy; IL: ionic liquid; BET: Brunauer–Emmett–Teller; ORR: oxygen reduction reaction; AEM: anion exchange membrane; SHE: standard hydrogen electrode.

35%–45% propane conversion at above 600 °C with a catalytic stability below 10 h), revealing its high promise for acting as a next-generation PDH technology.

As comments and perspectives, Yang *et al.* innovated a Br-mediated strategy that enables electrocatalysis-driven PDH to have high value in industrial application^[10]. However, several questions remain open: (1) A few puzzles still remain in the catalytic mechanism; e.g., Br[−] elimination between bromopropane (C₃H₇Br) and OH[−] theoretically prefers to give C₃H₇OH as the main product. Interestingly, the selectivity here shifts toward propene (C₃H₆). So, the reaction kinetics of Br elimination reaction warrants in-depth calculations and verification. (2) One prefers to believe that the Br-mediator PDH reaction mainly occurs at the inner cavity of IL-SnO₂ hollow sphere, while further evidence of the Br[−] source for PDH reaction (e.g., isotopic labeling) and the rate-determining step of the reaction needs to be presented. (3) Partial Br₂ and by-products are identified, indicating a loss of Br mediator during catalytic reaction. The formation of Br₂, C₃H₆Br₂ and C₃H₇Br by-products is essentially due to both a lack of C₃H₈ reactant and the sluggish hydrolysis of bromopropane. Further optimization on the diameter of the inner cavity of IL-SnO₂ hollow sphere for concentrating C₃H₈ and on the thickness and pore size of SnO₂ skeleton for altering the bromopropane hydrolysis process are highly desired to avoid the necessary replacement of the electrolyte every 500 h during stability test. (4) For the scalability of this technology, in addition to the pilot-scale electrode manufacture, a cell assemble stack needs to be designed and built under the consideration of the effect of mass transfer in GDE and MEA. It may be strongly promoted by the construction of commercial fuel cells. All these questions are required to be addressed before reaching industrialization for sustainable PDH.

DECLARATIONS

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Authors' contributions

Made substantial contributions to conception and design of the study and performed data analysis and interpretation: Wang, Z.; Su, B. L.

Performed data acquisition and provided administrative, technical, and material support: Wang, Z.; Liu, X. L.; Wang, B. Y.; Cheng, B. C.

Availability of data and materials

Not applicable.

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Not applicable.

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Conflicts of interest

Su, B. L. is the Editor-in-Chief of the journal *Chemical Synthesis*. Su, B. L. was not involved in any steps of editorial processing, notably including reviewers' selection, manuscript handling, or decision-making. The other authors declare that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

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