

1 **Electrocatalytic hydrogenation of furfural paired with photoelectrochemical oxidation**
2 **of water and furfural in the batch and flow cells**

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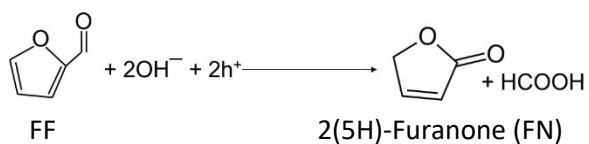
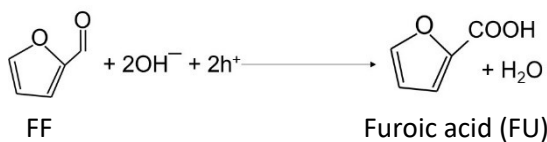
Supplementary information



2 Cathode: Furfural (FF) Furfuryl alcohol (FA)

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4 Photoanode:



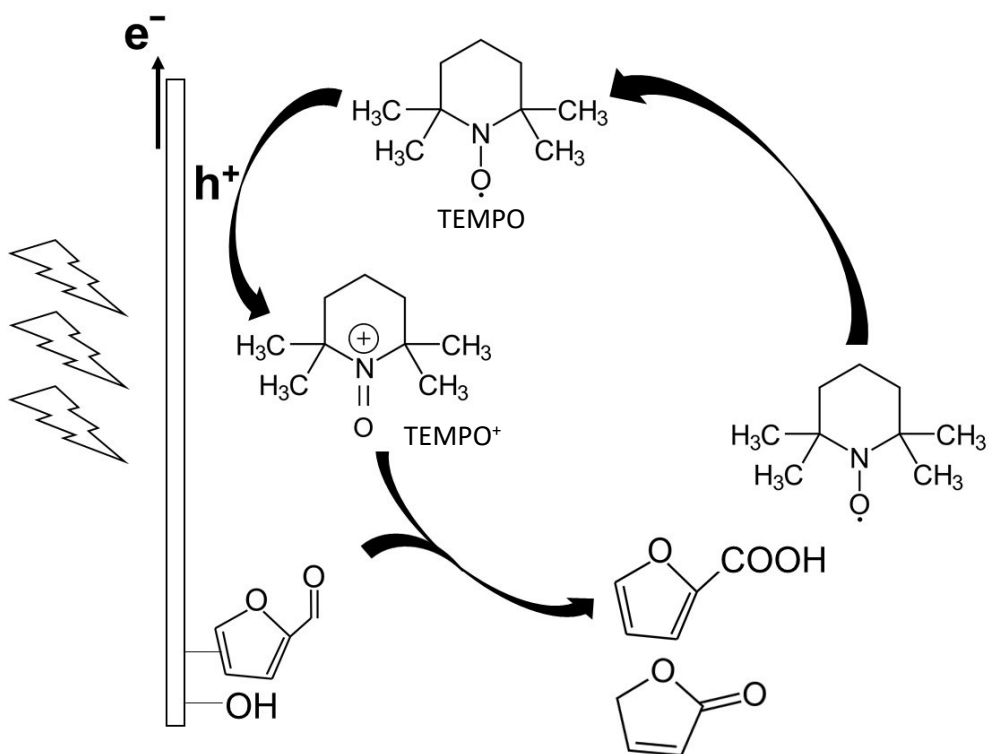
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8 **Scheme S1.** Half-cell reactions at the Cu-Ni/NF cathode and TiO₂ NTs photoanode.

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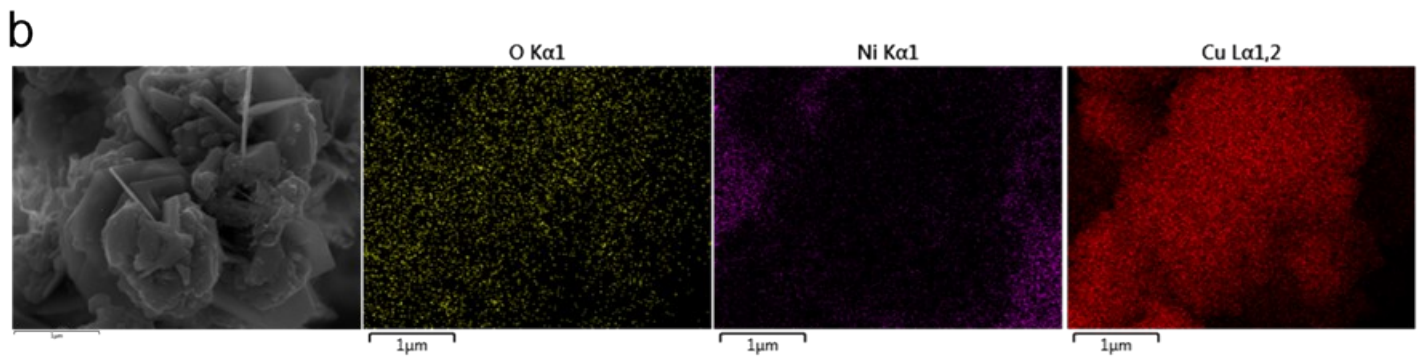
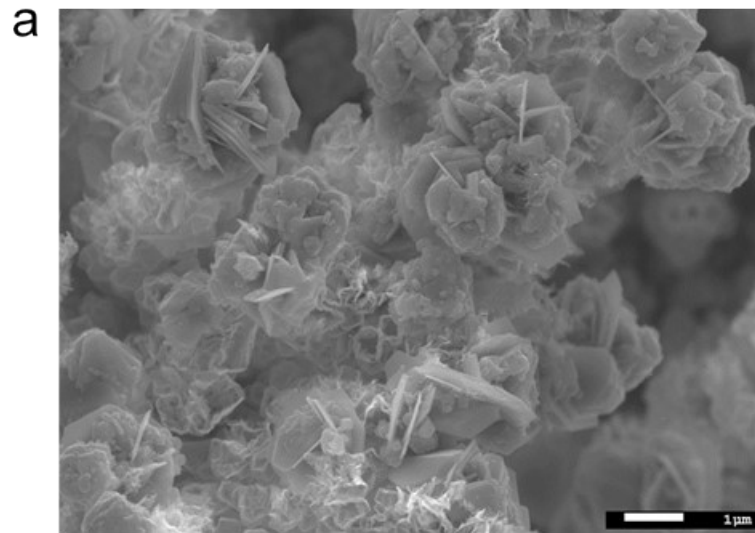


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1 **Scheme S2.** TEMPO mediated FF oxidation at the TiO₂ NTs photoanode surface.

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6 **Fig. S1. a.** SEM; **b.** EDX analysis of Cu-Ni/NF.

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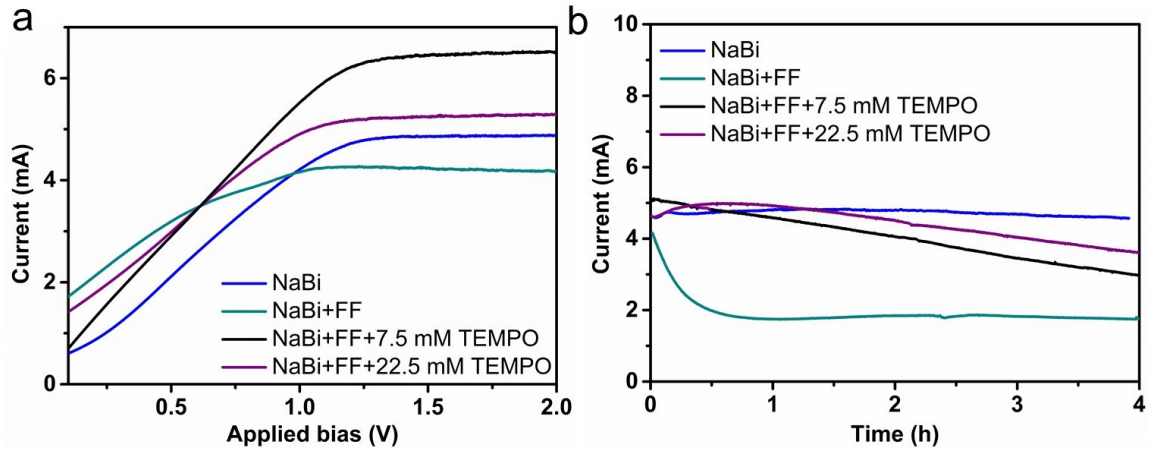
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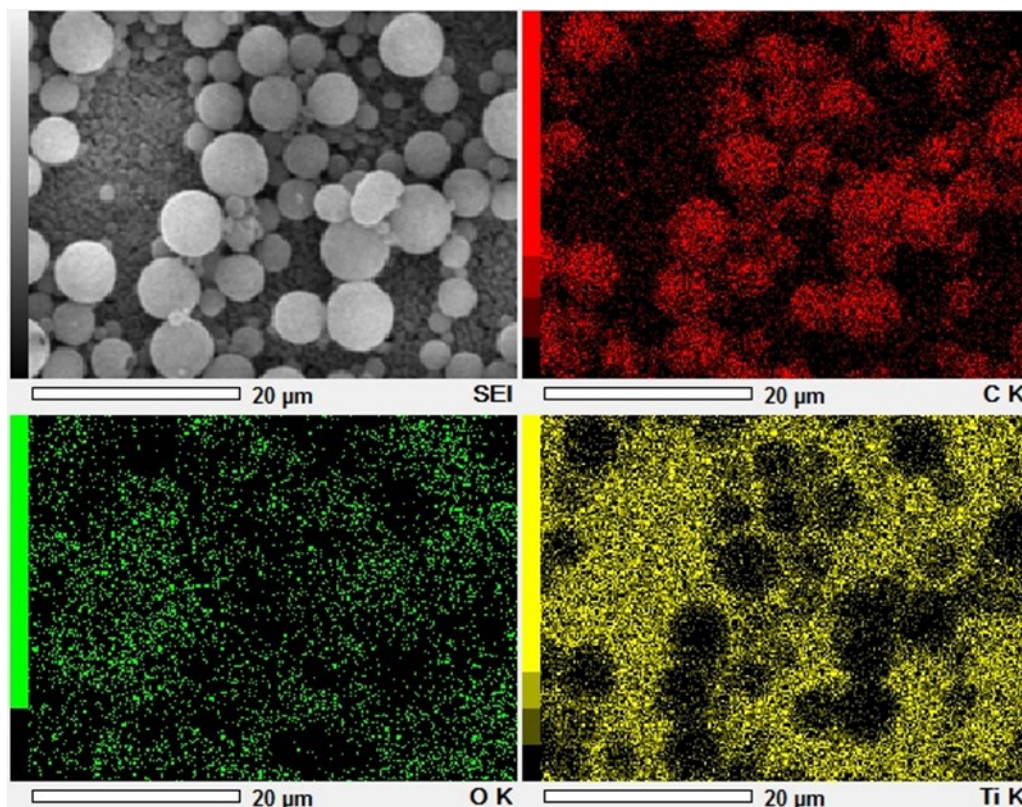


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6 **Fig. S2. Photoelectrochemical cell (PEC)** | a. Linear sweep voltammetry using analytes at the
7 scan rate of 20 mV sec^{-1} ; b. Chronoamperometry. Analytes: NaBi, NaBi+FF, and
8 NaBi+FF+7.5 mM TEMPO, NaBi+FF+22.5 mM TEMPO. Catholyte: NaBi+FF. Reaction
9 condition: applied bias of 1 V for 4 h for chronoamperometry. PEC: Cu-Ni/NF cathode with
10 TiO_2 NTs photoanode.

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3 **Fig. S3.** SEM and EDX of photoanode after paired reaction (furfural electrocatalytic
4 hydrogenation paired with photoelectrochemical oxidation) using NaBi+FF anolyte at 1 V for
5 4 h in PEC. Catholyte: NaBi+FF, PEC: Cu-Ni/NF cathode and TiO₂ NTs photoanode.

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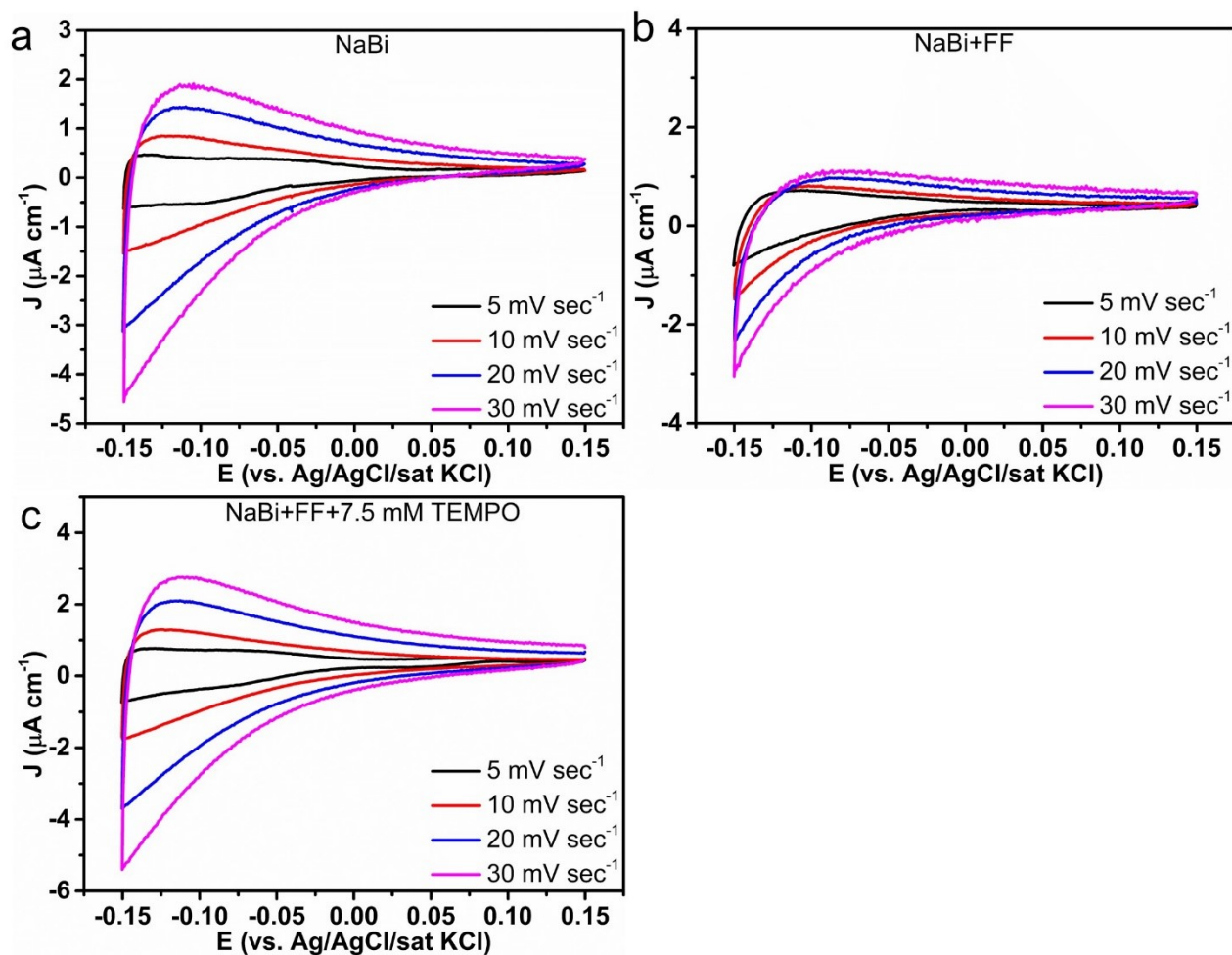
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2 **Fig. S4.** CV in a 3-electrode undivided PEC under dark condition at the scan rate of 5, 10, 20,
 3 30 mV sec⁻¹ using **a.** NaBi; **b.** NaBi+FF; **c.** NaBi+FF+7.5 mM TEMPO electrolytes.

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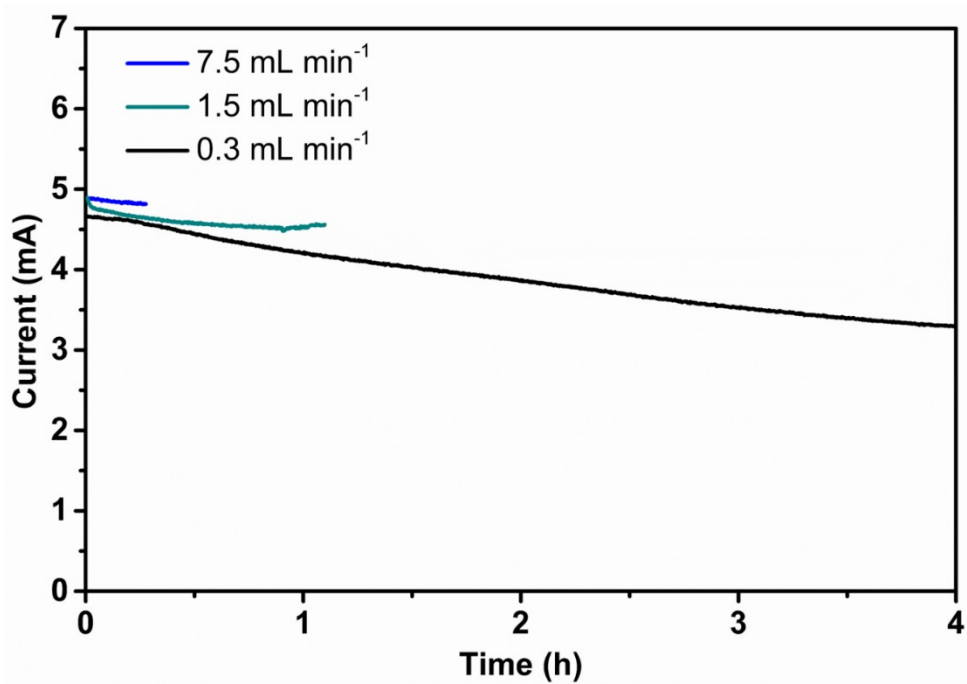
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3 **Fig. S5.** Chronoamperometry in a flow PEC at the flow rate of 0.3, 1.5, 7.5 mL min⁻¹.

4 Catholyte: NaBi+FF, anolyte: NaBi+FF+7.5 mM TEMPO. Reaction condition: applied bias of

5 1 V. PEC: Cu-Ni/NF cathode and TiO₂ NTs photoanode.

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