Supplementary information for

## Atomic Doping and Light Irradiation Promote Anodic Hydrogen Evolution through Furfural Oxidation on Cu<sub>2+1</sub>O/Cu Nano-Dendrites

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## **Figures**



Figure S1. Optimization of CuSO<sub>4</sub> concentration for optimum furfural oxidation. (a) Linear sweep voltammograms of copper nano-dendrites electrodeposited with different concentrations of CuSO<sub>4</sub>.
(b) Enlarged LSV curve in shadow region in (a). (c) Diagram of peak current density of furfural oxidation as a function of CuSO<sub>4</sub> concentration.



**Figure S2**. Optimization of  $K_2PdCl_4$  concentration. (a) Linear sweep voltammograms of copper nano-dendrites electrodeposited with different concentrations of  $K_2PdCl_4$  with fixed 50 mM CuSO<sub>4</sub>. (b) Enlarged LSV curve in the 0-0.5V region in (a). (c) Diagram of peak potential shift of furfural oxidation as a function of  $K_2PdCl_4$  concentration.



**Figure S3**. Optimization of deposition time. (a) Linear sweep voltammograms of copper nanodendrites electrodeposited at different times using electrolyte solution containing 100  $\mu$ M of K<sub>2</sub>PdCl<sub>4</sub> with fixed 50 mM of CuSO<sub>4</sub>. (b) Enlarged LSV curve in the 0-0.5V region in (a) showing furfural oxidation behavior. (c) Diagram of peak potential of furfural oxidation as a function of K<sub>2</sub>PdCl<sub>4</sub> concentration.



Figure S4. SEM image of a typical electrodeposit using the electrodeposition technique.



Figure S5. Energy dispersive spectrum of Pd@Cu<sub>2+1</sub>O/Cu NDs. Inset: ICP/MS result.



**Figure S6.** Comparison on current densities of furfural oxidation on  $Cu_{2+1}O/Cu$  and  $Cu_2O$ .  $Cu_2O$  was prepared by 2h electrooxidation by fixing potential at 0.55 V vs RHE in 1 M KOH.



Figure S7. The optical spectra of visible light produced by the light source.



Figure S8. (a) Full spectra of XPS for  $Cu_{2+1}O/Cu$  and  $Pd@Cu_{2+1}O/Cu$  NDs. (b) XPS spectra of Pd 3d for  $Cu_{2+1}O/Cu$  and  $Pd@Cu_{2+1}O/Cu$  NDs.



**Figure S9.** Cyclic voltammograms at different scan rates for  $Cu_{2+1}O/Cu$  (a) and Pd@Cu<sub>2+1</sub>O/Cu NDs (b). Potential range is set by OCP±50 mV.



**Figure S10.** LSV curves of Cu<sub>2+1</sub>O/Cu (a) and Pd@Cu<sub>2+1</sub>O/Cu (c) at different temperatures in 1 M KOH electrolyte containing 50 mM furfural; and their corresponding  $\log_{10} j \sim 1000/T$  curves for Cu<sub>2+1</sub>O/Cu (b), and Pd@Cu<sub>2+1</sub>O/Cu (d).