

## Electronic supplementary information

### One-pot conversion of biomass-derived xylose to furfuralcohol by a chemo-enzymatic sequential acid-catalyzed dehydration and bioreduction

Yucui He,<sup>\*a,b</sup> Yun Ding,<sup>a</sup> Cuiluan Ma,<sup>a,b</sup> Junhua Di,<sup>a</sup> Chunxia Jiang,<sup>a</sup> and Aitao Li<sup>\*,b,c,d</sup>

<sup>a</sup> *Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, College of Pharmaceutical Engineering and Life Science, Changzhou University, Changzhou, China. Email: [heyucui2001@163.com](mailto:heyucui2001@163.com); [yucuihe@cczu.edu.cn](mailto:yucuihe@cczu.edu.cn)*

<sup>b</sup> *Hubei Collaborative Innovation Center for Green Transformation of Bio-resources, Hubei Key Laboratory of Industrial Biotechnology, College of Life Sciences, Hubei University, Wuhan, China. [heyucui2001@163.com](mailto:heyucui2001@163.com); [aitaoli@163.com](mailto:aitaoli@163.com)*

<sup>c</sup> *Department of Biocatalysis, Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470, Mülheim an der Ruhr, Germany. Email: [aitaoli@163.com](mailto:aitaoli@163.com); [aitaoli@mpi-muelheim.mpg.de](mailto:aitaoli@mpi-muelheim.mpg.de)*

<sup>d</sup> *Department of Chemistry, Philipps-Universität Marburg, 35032, Marburg, Germany.*

## Figure captions

Table S1. Yields of furfural in the presence of  $\text{SO}_4^{2-}/\text{SnO}_2$ -APG or/and oxalic acid at 170 °C for 20 min.

Fig. S1. SEM images of fresh APG (a) and solid acid  $\text{SO}_4^{2-}/\text{SnO}_2$ -APG (b).

Fig. S2. FT-IR images of fresh APG and solid acid  $\text{SO}_4^{2-}/\text{SnO}_2$ -APG.

Fig. S3. XRD images of fresh APG and solid acid  $\text{SO}_4^{2-}/\text{SnO}_2$ -APG.

Fig. S4. Raman images of fresh APG and solid acid  $\text{SO}_4^{2-}/\text{SnO}_2$ -APG.

Fig. S5. MS for furfural (left) and FOL (right).

Fig. S6.  $^1\text{H}$  NMR for the prepared FOL.

Fig. S7 Recyclability and stability of  $\text{SO}_4^{2-}/\text{SnO}_2$ -APG solid catalyst for the conversion of corncob hydrolysate to furfural. Reaction conditions for the

recycling of the solid acid catalyst for the first step reaction: corncob pretreatment hydrolysate with a xylose concentration of 18.1 g/L, 3.6%  $\text{SO}_4^{2-}/\text{SnO}_2$ -APG solid catalyst in a 30 mL reaction system with magnetic stirrer (500 rpm) at 170 °C for 20 min.

Fig. S8 Recycling of immobilized *E. coli* CCZU-A13 cells for the conversion of furfural to FOL. Reaction conditions for the recycling of the biocatalyst for the the second step: 10.0 g immobilized cells (corresponds to 0.51 g dry cell weight), glucose (1 mol glucose/mol furfural) and 18.1 g/L furfural in a 30 mL reaction system with magnetic stirrer (300 rpm) at 30 °C for 3 h.

Table S1. Yields of furfural in the presence of  $\text{SO}_4^{2-}/\text{SnO}_2\text{-APG}$  or/and oxalic acid at 170 °C for 20 min.

Entry	Substrate	Catalyst	Yield of furfural
1	Biomass-derived xylose	Residual oxalic acid (pH 1.9) <sup>a</sup>	15%
2	Biomass-derived xylose	Residual oxalic acid plus $\text{SO}_4^{2-}/\text{SnO}_2\text{-APG}$ (pH 3.3) <sup>b</sup>	28%
3	Biomass-derived xylose	Oxalic acid plus $\text{SO}_4^{2-}/\text{SnO}_2\text{-APG}$ (pH 1.9) <sup>c</sup>	44%
4	Commercial xylose	$\text{SO}_4^{2-}/\text{SnO}_2\text{-APG}$ (pH 3.3) <sup>d</sup>	28%

<sup>a</sup> After the preparation of xylose-rich biomass hydrolysate (pH 1.9), residual oxalic acid in hydrolysate was used for the conversion of xylose into furfural.

<sup>b</sup> After the preparation of xylose-rich biomass hydrolysate (pH 1.9), the media was adjusted to pH 7.0, and  $\text{SO}_4^{2-}/\text{SnO}_2\text{-APG}$  (pH 3.3) was used for the conversion of xylose into furfural.

<sup>c</sup> After the preparation of xylose-rich biomass hydrolysate (pH 1.9), residual oxalic acid plus  $\text{SO}_4^{2-}/\text{SnO}_2\text{-APG}$  (pH 1.9) was used for the conversion of xylose into furfural.

<sup>d</sup> After the preparation of commercial xylose solution,  $\text{SO}_4^{2-}/\text{SnO}_2\text{-APG}$  (pH 3.3) was used for the conversion of xylose into furfural.

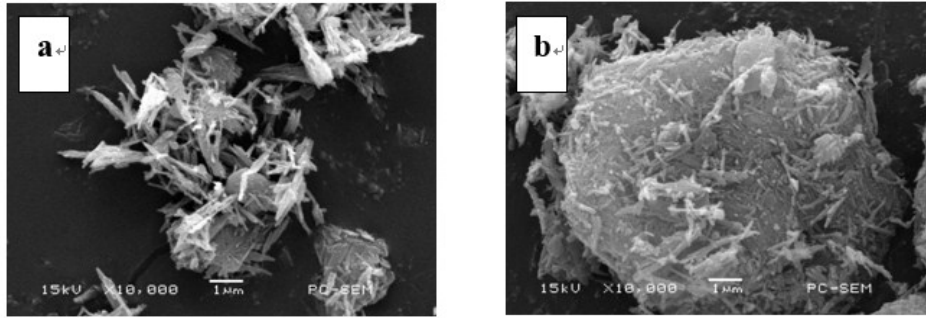


Fig. S1. SEM images of fresh APG (a) and solid acid  $\text{SO}_4^{2-}/\text{SnO}_2$ -APG (b).

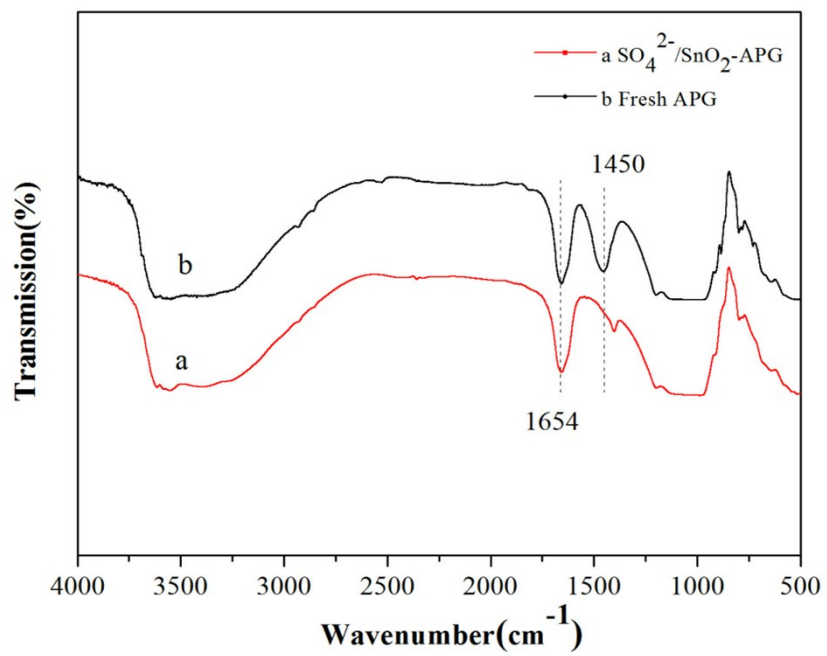


Fig. S2. FT-IR images of fresh APG and solid acid SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-APG.

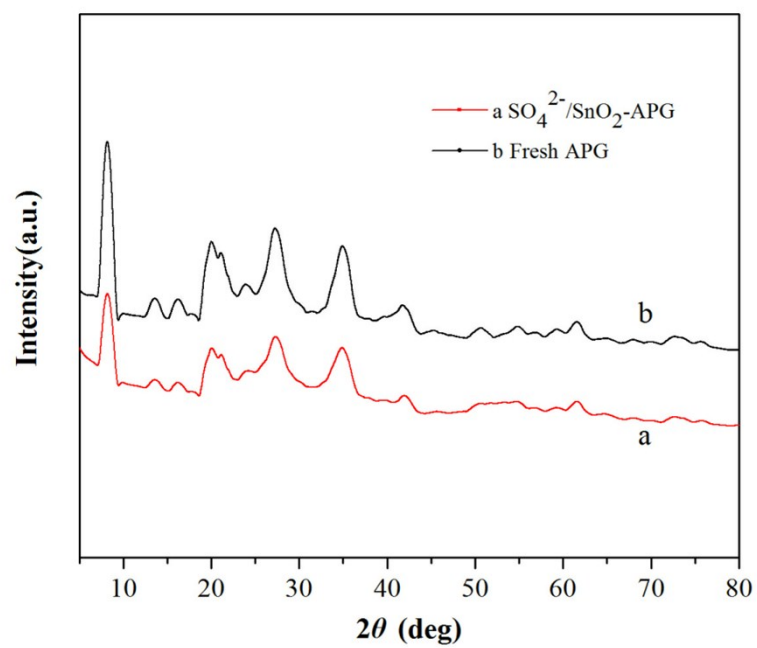


Fig. S3. XRD images of fresh APG and solid acid SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-APG.

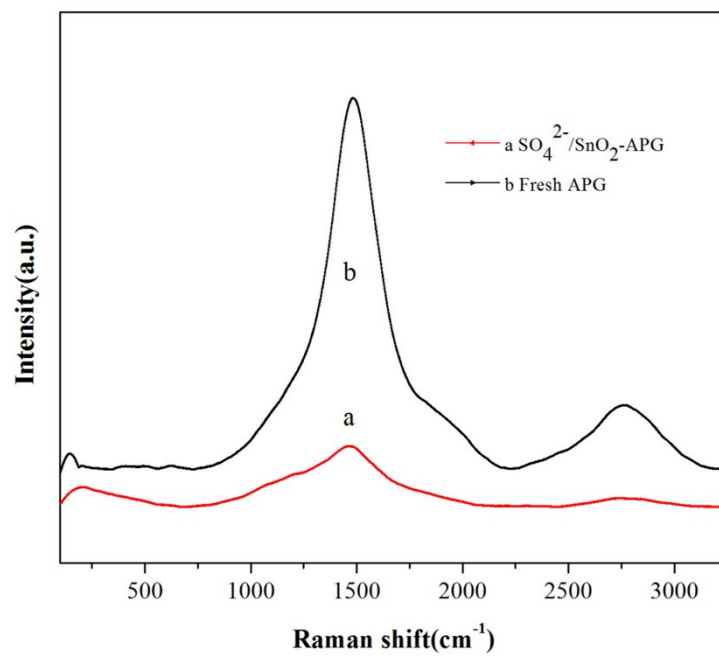


Fig. S4. Raman images of fresh APG and solid acid SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-APG.



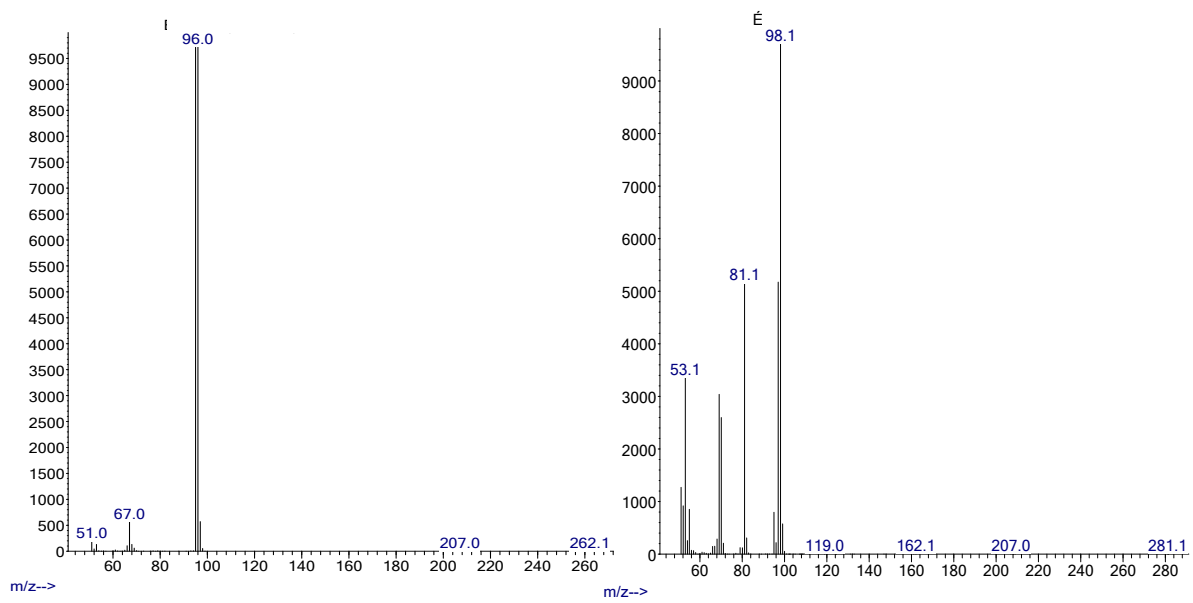


Fig. S5. MS for furfural (left) and FOL (right).

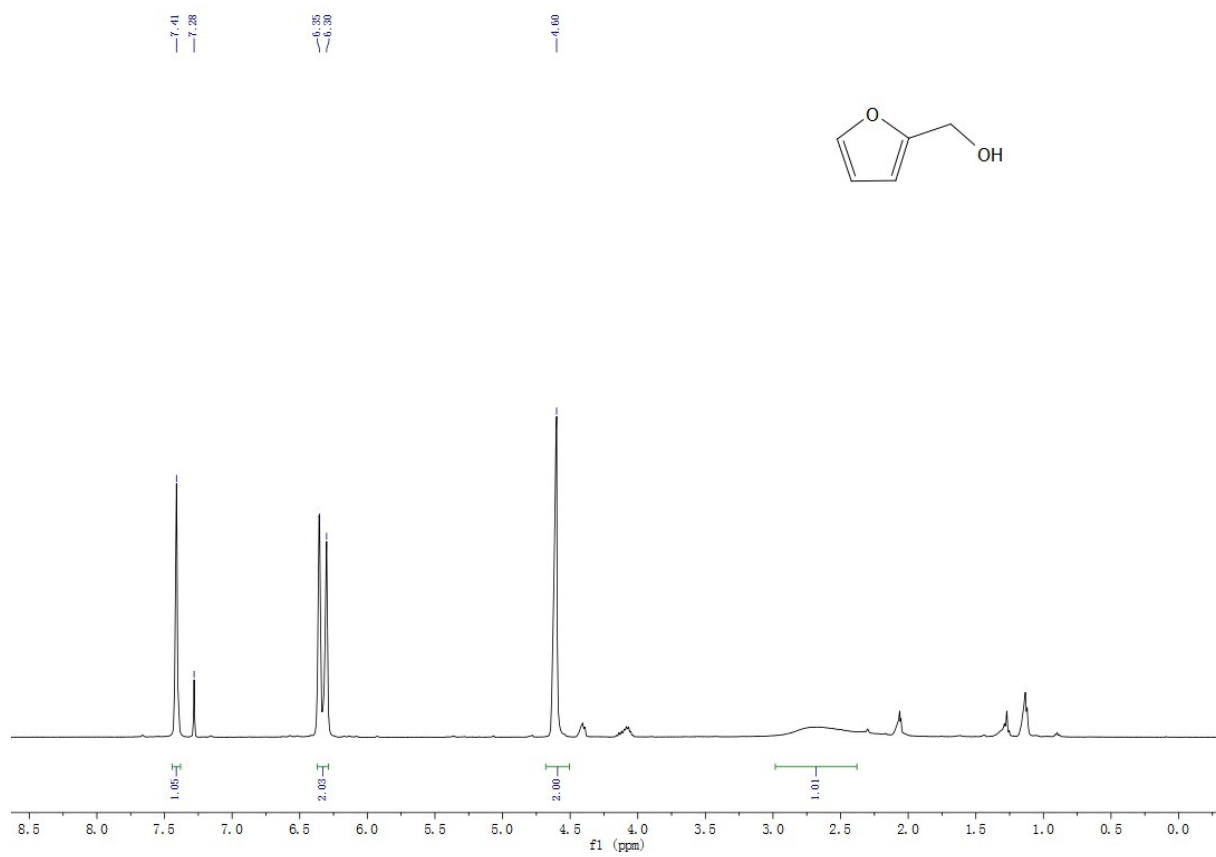


Fig. S6. <sup>1</sup>H NMR for the prepared FOL.

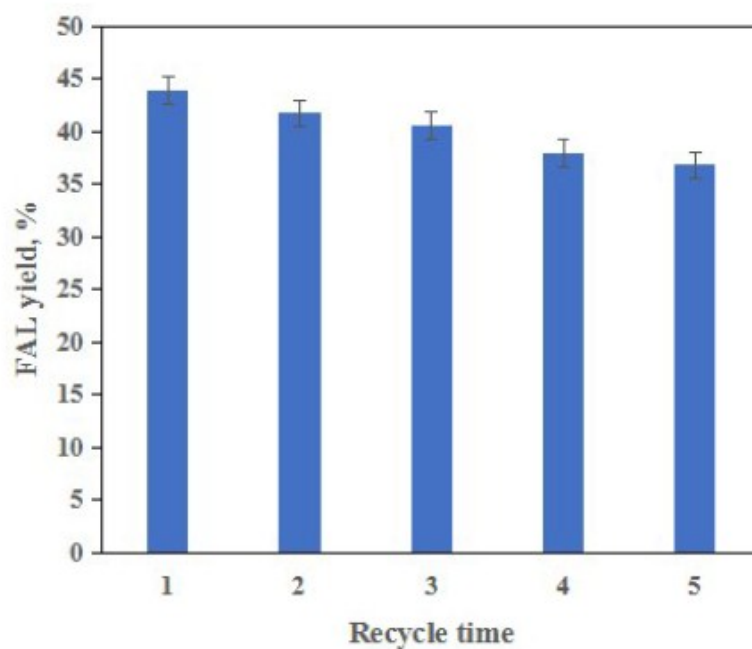


Fig. S7 Recyclability and stability of  $\text{SO}_4^{2-}/\text{SnO}_2$ -APG solid catalyst for the conversion of corncob hydrolysate to furfural. Reaction conditions for the recycling of the solid acid catalyst for the first step reaction: corncob pretreatment hydrolysate with a xylose concentration of 18.1 g/L, 3.6%  $\text{SO}_4^{2-}/\text{SnO}_2$ -APG solid catalyst in a 30 mL reaction system with magnetic stirrer (500 rpm) at 170 °C for 20 min.

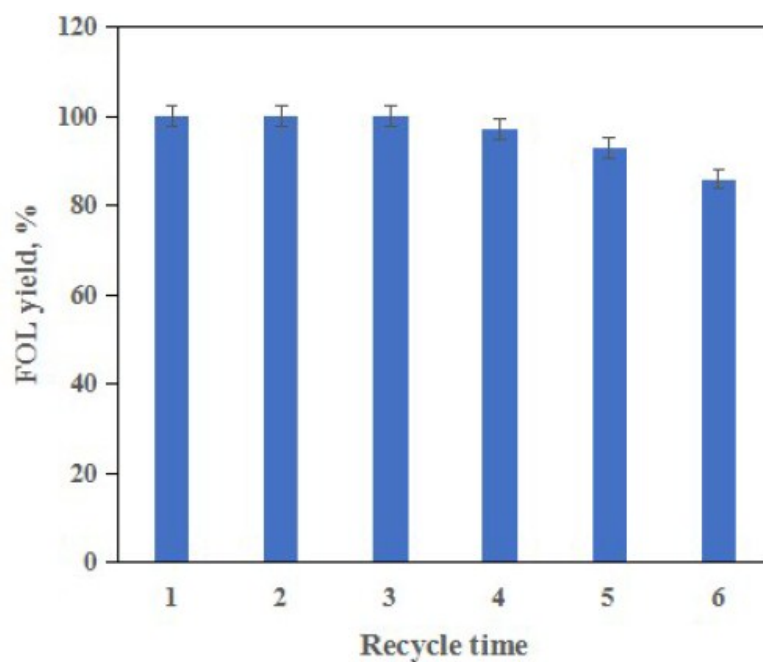


Fig. S8 Recycling of immobilized *E. coli* CCZU-A13 cells for the conversion of furfural to FOL. Reaction conditions for the recycling of the biocatalyst for the the second step: 10.0 g immobilized cells (corresponds to 0.51 g dry cell weight), glucose (1 mol glucose/mol furfural) and 18.1 g/L furfural in a 30 mL reaction system with magnetic stirrer (300 rpm) at 30 °C for 3 h.