



Supplementary Materials

## Enhanced Hydrogen Production from Ethanol Photoreforming by Site-Specific Deposition of Au on Cu<sub>2</sub>O/TiO<sub>2</sub> p-n Junction

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**Figure S1.** XRD patterns of (A) TiO<sub>2</sub>, (B) Cu<sub>2</sub>O/TiO<sub>2</sub>, (C) Au@TiO<sub>2</sub>, (D) Au@Cu<sub>2</sub>O/TiO<sub>2</sub>, (E) Au@TiO<sub>2</sub>/Cu<sub>2</sub>O@Au, (F) Au@TiO<sub>2</sub>/Cu<sub>2</sub>O.



Figure S2. GC-MS spectra of the products formed on Au@TiO<sub>2</sub>/Cu<sub>2</sub>O.



**Figure S3.** HRTEM photographs and Au particle size distribution of Au@TiO<sub>2</sub>/Cu<sub>2</sub>O after ethanol photoreforming.



Figure S4. Ti 2p, O 1s and Au 4f XPS spectra of Au@TiO2/Cu2O after ethanol photoreforming.



Figure S5. Cu 2p XPS and Cu LMM Auger spectra of Au@TiO2/Cu2O after ethanol photoreforming.



Figure S6. Bandgap estimation of TiO<sub>2</sub> nanorods.

Table S1. Ti 2p XPS analyses of Au@TiO2/Cu2O before and after ethanol photoreforming.

	B.E. in 2p <sub>3/2</sub> (eV)		<b>B.E. in 2p</b> <sub>1/2</sub> (eV)		Ti <sup>3+</sup> /Ti <sup>4+</sup>	
	Ti <sup>3+</sup>	Ti <sup>4+</sup>	Ti <sup>3+</sup>	Ti <sup>4+</sup>	ratio <sup>a</sup>	
Before	457.9	458.3	463.3	464.2	0.96/1	
After	457.9	458.3	463.3	464.2	0.97/1	

<sup>a</sup> The value refers to the ratio of the respective integral peak area. B.E. refers to binding energy.

	<b>B.E.</b> (eV)			Ov/OL
	OL	Ov	Oc	ratio <sup>a</sup>
Before	530.0	532.0	533.5	0.71
After	530.0	532.0	533.5	0.70

Table S2. O 1s XPS analyses of Au@TiO2/Cu2O before and after ethanol photoreforming.

<sup>a</sup> The value refers to the ratio of the respective integral peak area. B.E. refers to binding energy.

Table S3. Au 4f XPS analyses of Au@TiO2/Cu2C	before and after ethanol photoreforming.
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	<b>B.E.</b> (eV)	$\triangle$ <b>B.E.</b> (eV) <sup>a</sup>
Before	83.4	-
After	83.5	+0.1

<sup>a</sup> The value refers to the shift compared to that of Au@TiO<sub>2</sub>/Cu<sub>2</sub>O before the reaction. B.E. refers to binding energy.

photocatalysts	light source	$\begin{array}{c} H_2 \ (\mu mol \\ g_{cat}^{-1} \ h^{-1}) \end{array}$	$\begin{array}{c} CH_{3}CHO \ (\mu mol \\ g_{cat}^{-1} \ h^{-1}) \end{array}$	ref.
1.0% Au/TiO <sub>2</sub>	simulated solar light (100 mW $cm^{-2}$ )	6151	6522	1
MWCNT/Pd@TiO2	Xe lamp (150 W)	1500		2
dye/Pt/TiO <sub>2</sub>	visible light ( $\lambda > 420$ nm)	4359		3
Si/Au/TiO <sub>2</sub>	Xe lamp (300 W)	5143		4
Pt <sub>0.5</sub> -Au <sub>0.5</sub> /TiO <sub>2</sub>	Xe lamp (150 W)	1800		5
Au@TiO <sub>2</sub> /Cu <sub>2</sub> O	simulated solar light (100 mW $cm^{-2}$ )	8548	8806	this work

Table S4. Comparisons of Photocatalysts for Ethanol Photoreforming.

## References

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