Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Base-free hydrogen generation from formaldehyde and water catalyzed by copper nanoparticles embedded on carbon sheets

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The calculations of surface Cu contents in Cu-based catalysts.

$D = 5.19/r$ (r = radius of Cu, Å) [1]

For Cu@CS, the average size of Cu nanoparticles was 14.6 nm, r = 73 Å, D = 5.19/73=0.071, the Cu content was 52.8 wt% according to ICP result.

As for 5 mg catalysts used for every reaction, the content of surface Cu need to be identified.

n_{Cu}= 5 × 52.8 wt%/64 = 0.041 mmol

$S_{Cu} = 0.041 \times 0.071 = 2.93 \times 10^{-3}$ mmol

For Cu/C catalysts, the average size of Cu nanoparticles was 26.7 nm, r = 133.5 Å, D = 5.19/133.5 = 0.039, the Cu content was 9.57 wt% according to ICP result.

As for 20 mg catalysts used for reaction, the content of surface Cu identified as below.

$n_{Cu} = 20 \times 9.57\ \%/64 = 0.030$ mmol

$S_{Cu} = 0.030 \times 0.039 = 1.17 \times 10^{-3}$ mmol

Thus, the surface of Cu atom was 2.93×10^{-3} mmol in Cu@CS catalysts, and the surface of Cu atom was 1.17×10^{-3} mmol.

The calculations of gases generated in the reaction system.

$n_{H2} = S_{\text{area of GC}} * V_{\text{gas dispersed in reaction bottle}} / (a * 22.4 * 100 * 1000)$ (unit mmol, a was the slope of H_2 standard curve which identified by GC)

v_{H2} = slope of (n_{H2} / T) (mmol/h)

$v_{H2\ normalized} = v_{H2} / S_{Cu}$ (mol mol_{Cu}^{-1} h^{-1} or mmol $mmol_{Cu}^{-1}$ h^{-1})

$n_{H2} = S_{area\ of\ GC} * V_{gas\ dispersed\ in\ reaction\ bottle} / (b * 22.4 *100 *1000)$ (unit mmol, b was the slope of H_2 standard curve which identified by GC)

v_{CO2} = slope of (n_{CO2} / T) (mmol/h)

$v_{CO2\ normalized} = v_{CO2} / S_{Cu}$ (mol mol_{Cu}^{-1} h^{-1} or mmol $mmol_{Cu}^{-1}$ h^{-1})

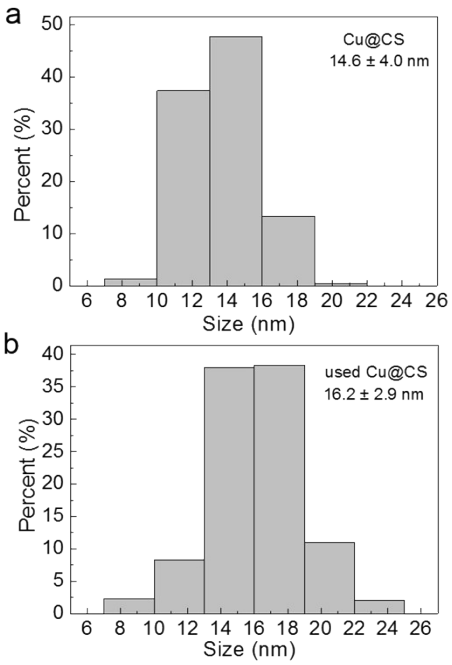

Figure S1. Size distribution of (a) Cu@CS catalysts and (b) used Cu@CS catalysts (300 nanoparticles were counted for each sample).

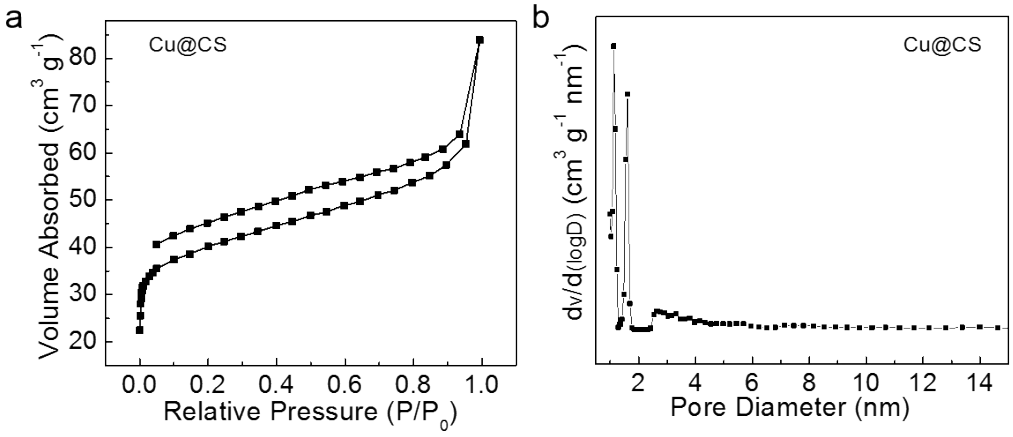

Figure S2. (a) Nitrogen adsorption−desorption isotherms and (b) porous size distribution of Cu@CS catalysts.

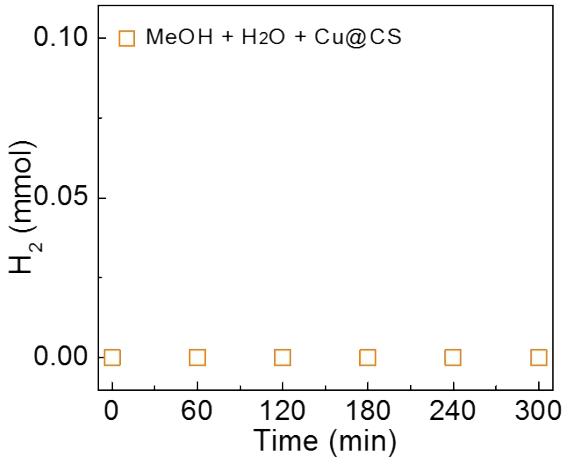

Figure S3. The reaction of MeOH and H_2O system catalyzed by the Cu@CS catalysts. **Reaction condition**: 5 mg of the Cu@CS catalysts, 4.3 mL of aqueous MeOH solution (0.70 M) and 120 °C, Ar.

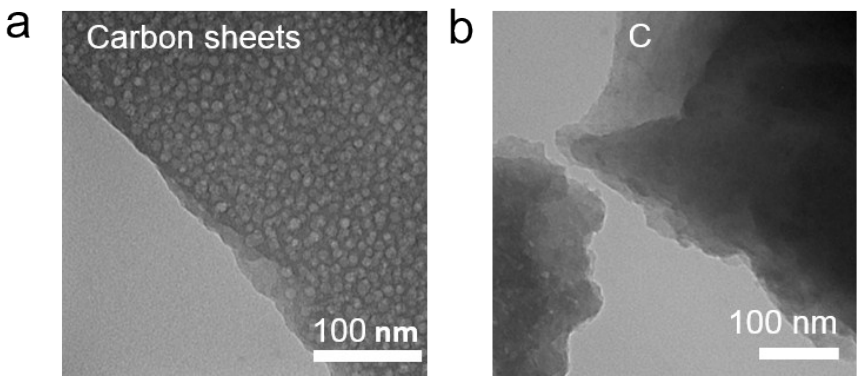

Figure S4. TEM images of (a) carbon sheets and (b) carbon particles catalysts.

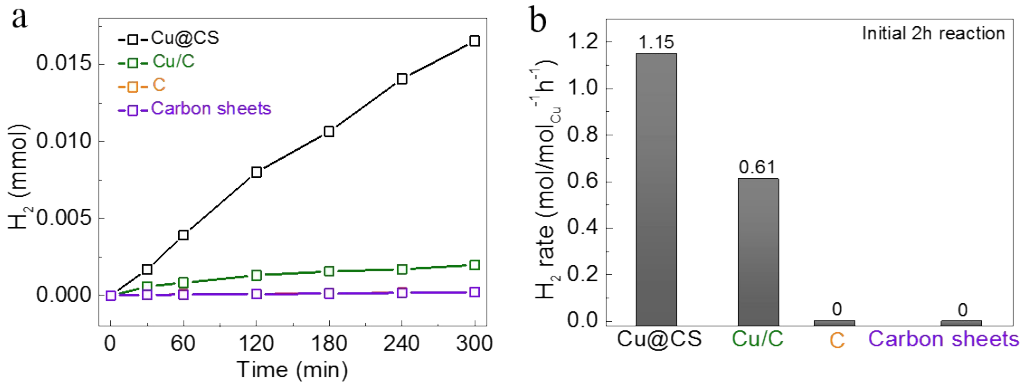

Figure S5. (a) H_2 production *vs* time and (b) H_2 production rates in formaldehyde solution catalyzed by different catalysts. **Reaction conditions:** Cu@CS (5 mg)/ Carbon sheets (20 mg) / C (20 mg) / Cu/C (20 mg), HCHO concentration of 0.70 M (4.3 mL), and 120 ^{o}C, Ar.

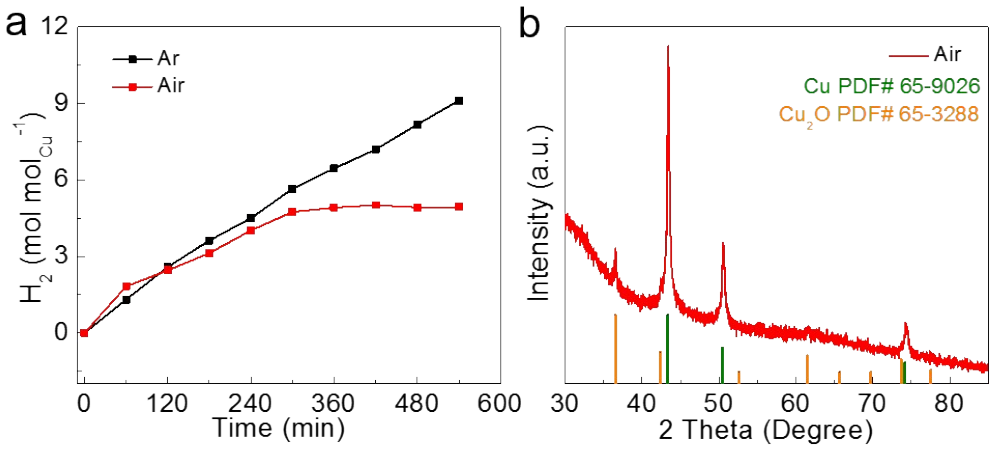

Figure S6. (a) The hydrogen production of formaldehyde and H_2O system under Ar/air atmosphere. **Reaction conditions:** Cu@CS (5 mg), HCHO (0.7M, 4.3 mL), 120 °C, Ar/air. (b) The XRD pattern of the used Cu@CS catalysts under air atmosphere.

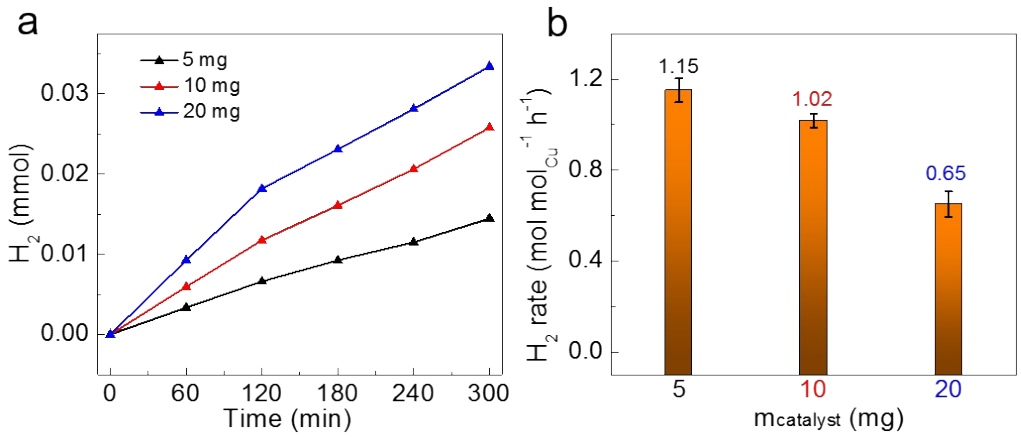

Figure S7. (a) The hydrogen production of formaldehyde/H_2O system and (b) The hydrogen production rate with various dosage of Cu@CS catalysts. **Reaction conditions**: Cu@CS (5 mg, 10 mg and 20 mg), HCHO (0.7M, 4.3 mL), 120 ^oC, Ar.

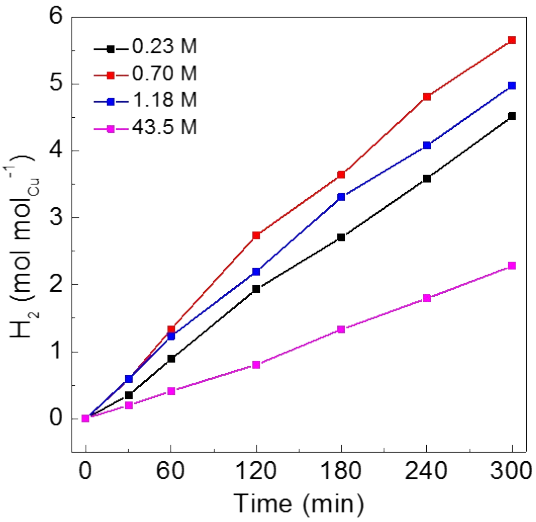

Figure S8. H_2 production in aqueous HCHO solution with various concentrations. **Reaction conditions**: Cu@CS (5 mg), various HCHO concentrations (4.3 mL), and 120 ^{o}C, Ar.

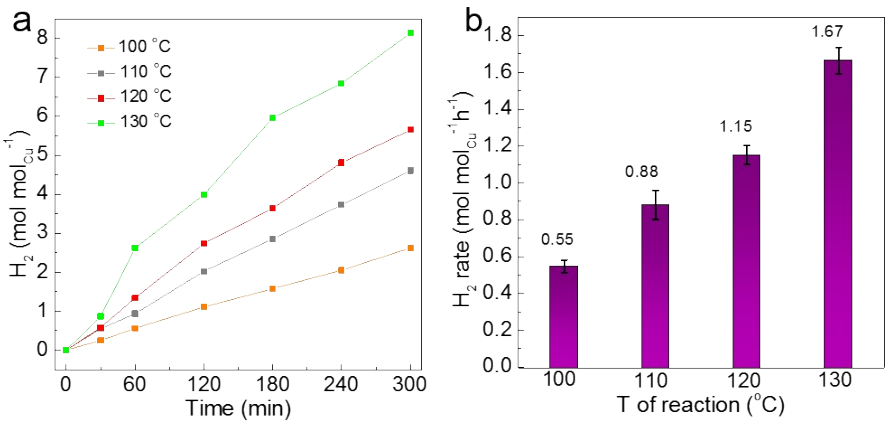

Figure S9. (a) H_2 production and (b) the H_2 production rates in aqueous HCHO solution under various reaction temperatures (100-130 °C) catalyzed by Cu@CS catalysts. **Reaction conditions:** Cu@CS (5 mg), HCHO concentration of 0.7 M, various reaction temperatures (100, 110, 120, and 130 °C), Ar.

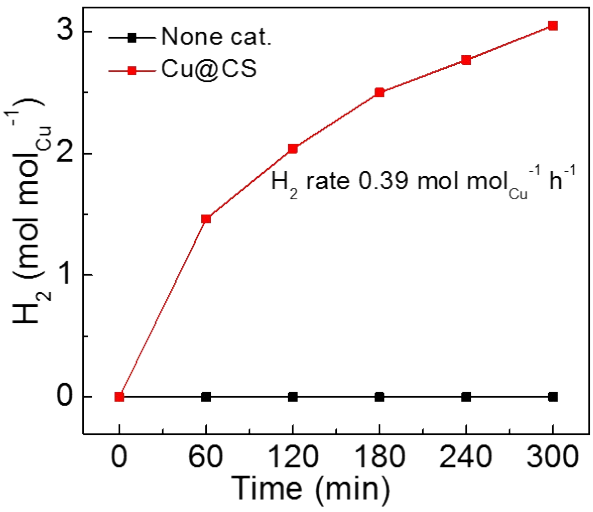

Figure S10. The catalytic hydrogen production and hydrogen production rate from formaldehyde and water system catalysed by Cu@CS catalysts under alkaline condition. **Reaction conditions:** Cu@CS (0 mg / 5 mg), aqueous HCHO solution (4.3 mL, 0.7M) contains 0.1 M NaOH, 30 ^{o}C, Ar.

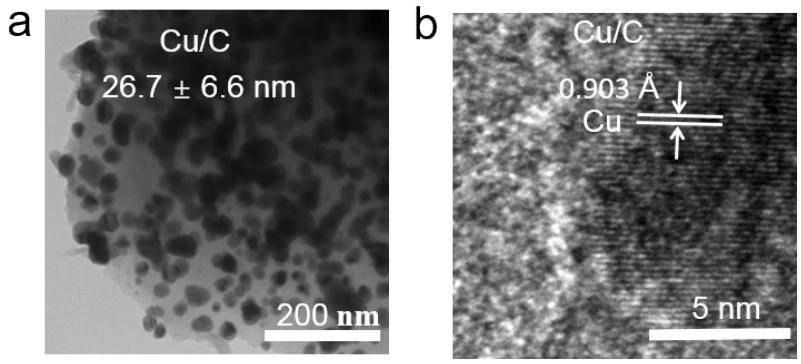

Figure S11. (a) TEM and (b) HRTEM images of Cu/C catalysts.

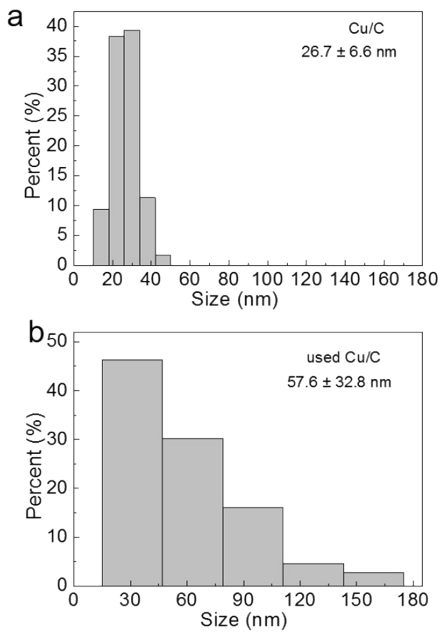

Figure S12. Size distribution of (a) Cu/C catalysts and (b) used Cu/C catalysts (300 nanoparticles were counted for each sample).

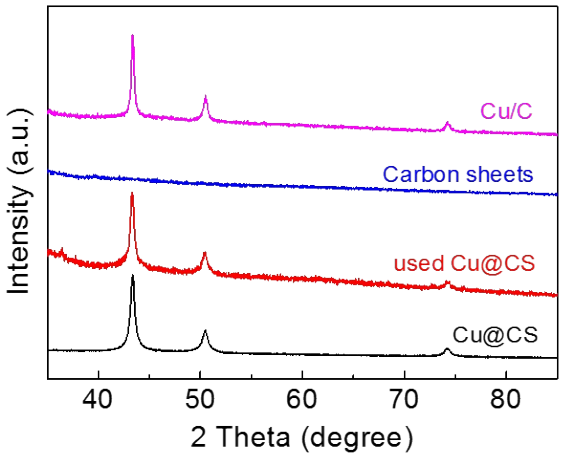

Figure S13. XRD patterns of catalysts used in the hydrogen production of formaldehyde and water system.

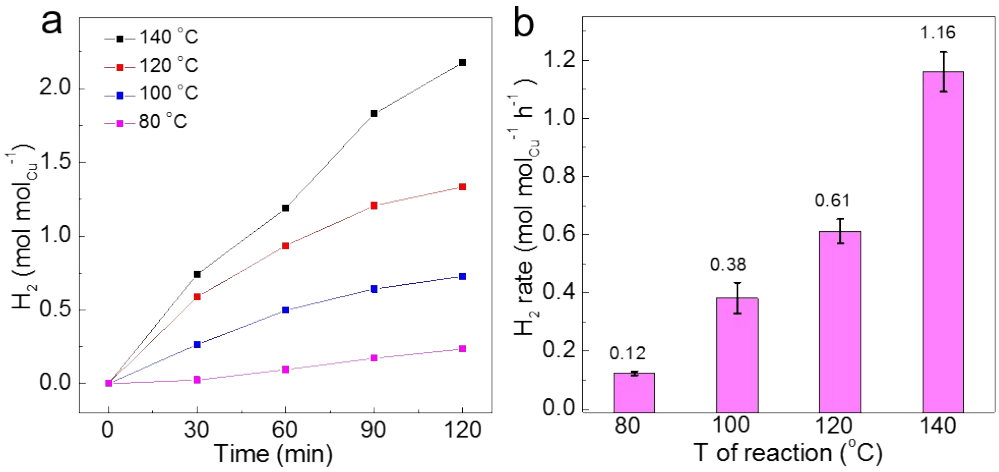

Figure S14. (a) H_2 production and (b) H_2 production rates with various reaction temperatures (80-140 °C) catalyzed by Cu/C catalysts. **Reaction conditions:** Cu/C (20 mg), HCHO concentration of 0.7 M, various reaction temperatures (80, 100, 120, and 140 °C), Ar.

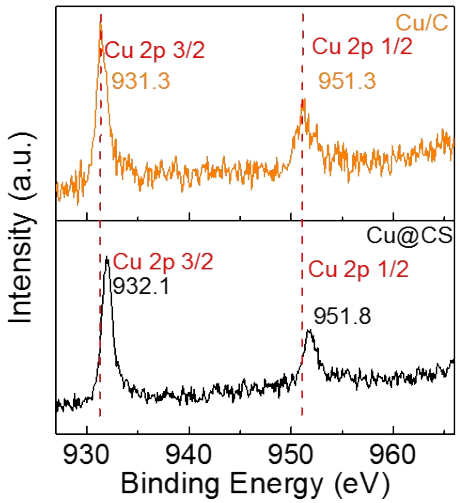

Figure S15. Cu 2p XPS spectra of Cu/C and Cu@CS catalysts.

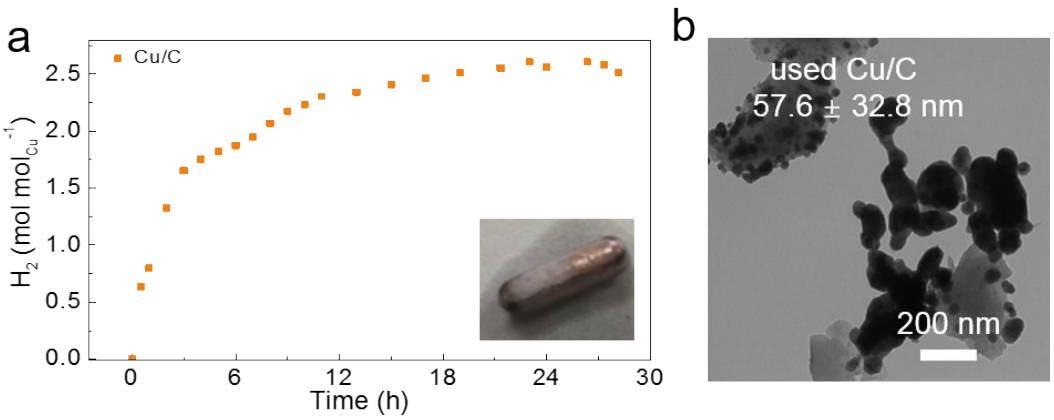

Figure S16. (a) The catalytic stability of H_2 production catalyzed by the Cu/C catalysts (the inset image was the Cu deposited on Stirring magneton after reaction), (b) TEM image of used Cu/C catalysts. **Reaction condition:** Cu/C (20 mg), HCHO concentration of 0.7 M, 120 ^{o}C, Ar.

References

1. J.R. Anderson, Structure of Metallic Catalysts. Acad. Press: London, **1975**.