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

In situ generated electron-deficient metallic copper as the catalytically active site for enhanced hydrogen production from alkaline formaldehyde solution

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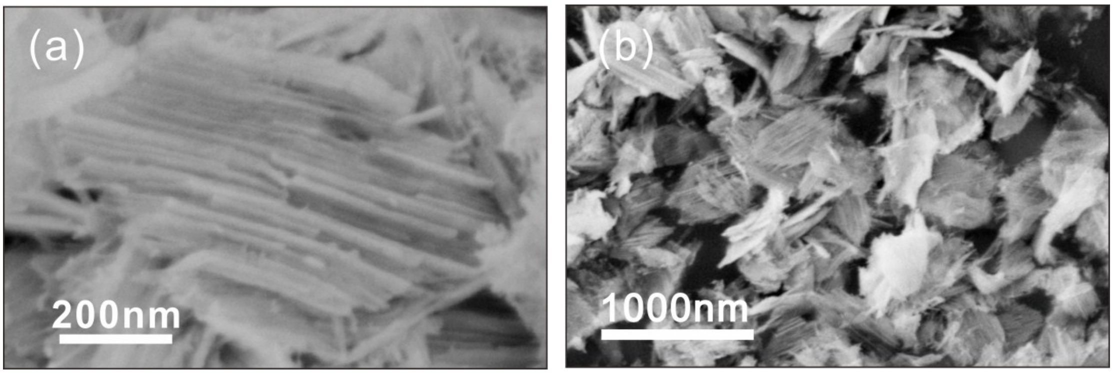

Fig. S1 SEM images of $Cu(OH)_2$ NRs precursor.

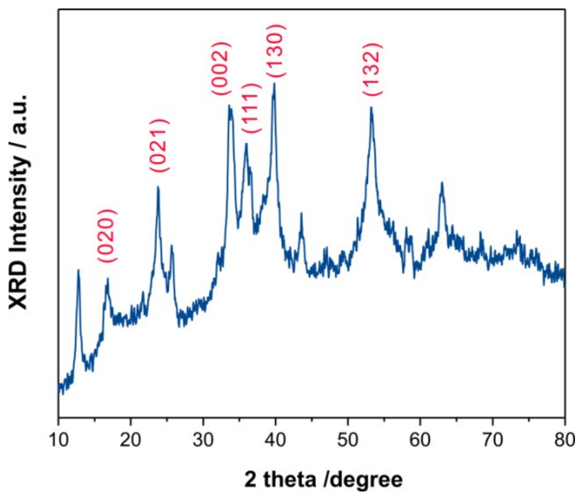

Fig. S2 XRD pattern of $Cu(OH)_2$ NRs precursor.

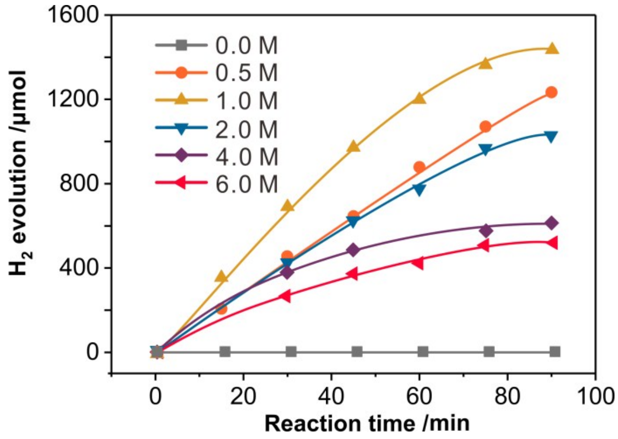

Fig. S3 The effect of formaldehyde concentration on the rate of H_2 evolution over CuO NPs.

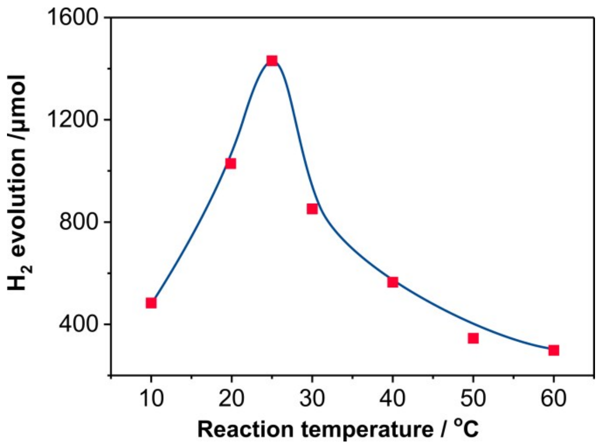

Fig. S4 The effect of reaction temperature on the rate of H_2 evolution over CuO NPs.

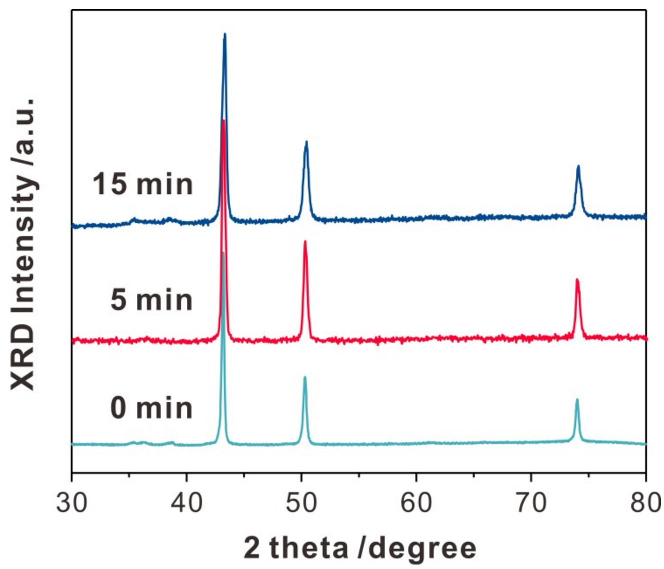

Fig. S5 *In–situ* XRD analysis of Cu NPs measured in 1M Na_2CO_3 solution before, after 5 min and 15 min of hydrogen production reaction.

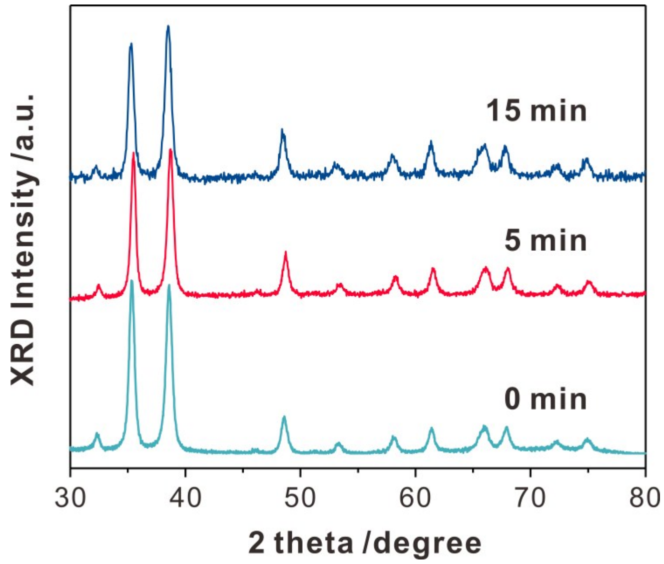

Fig. S6 *In–situ* XRD analysis of CuO NPs measured in 1M Na_2CO_3 solution before, after 5 min and 15 min of hydrogen production reaction.

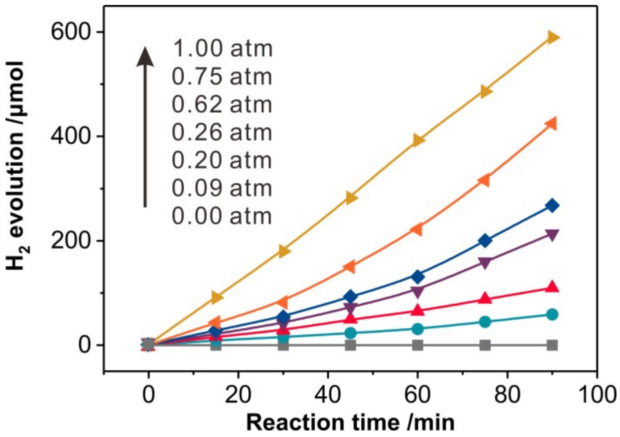

Fig. S7 The effect of oxygen partial pressure on the rate of H_2 evolution over Cu NPs.

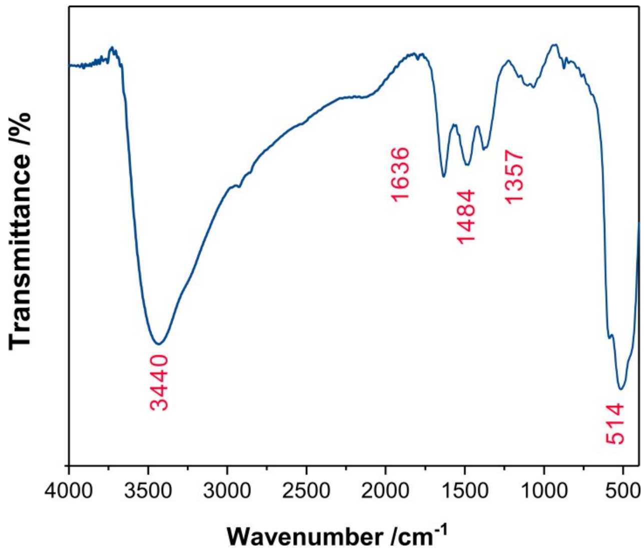

Fig. S8 FT-IR spectra of the reduced Cu after 15 min of hydrogen evolution reaction.

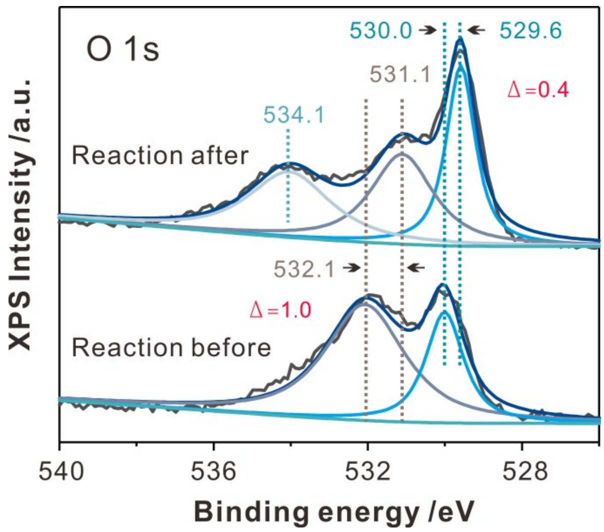

Fig. S9 O 1s XPS spectra of the reduced Cu before and after reaction.

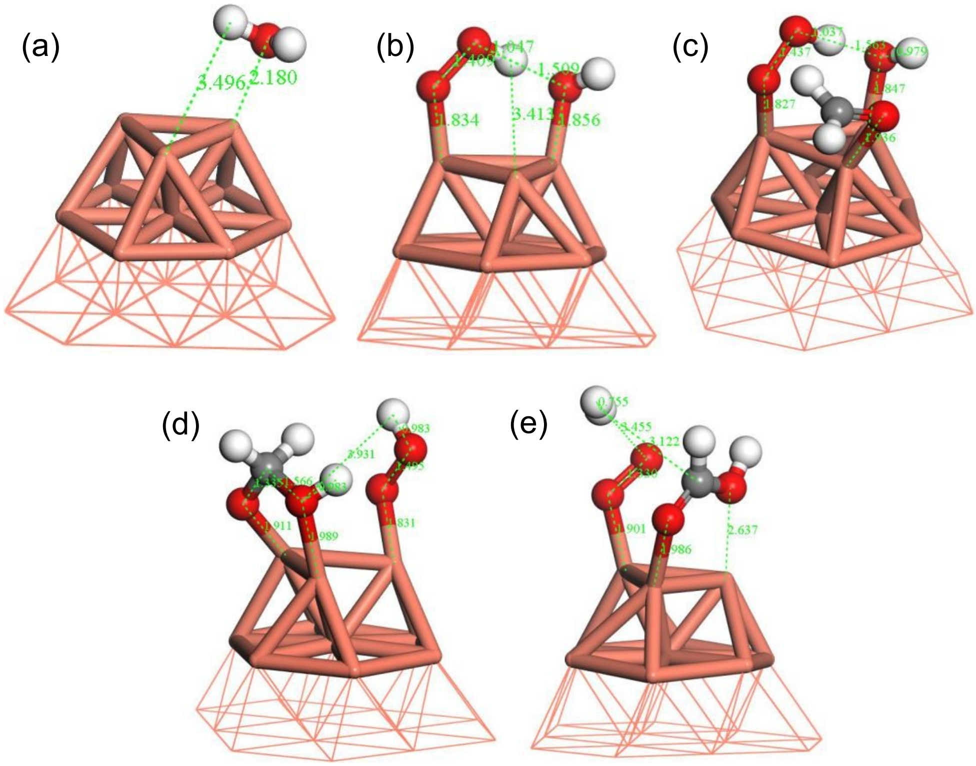

Fig. S10 (a) Optimized structures for Cu_{22}-H_2O (LM1). (b) Optimized structures for O_2 and H_2O co-adsorption on Cu_{22} cluster (LM2). (c) Optimized structures for O_2, H_2CO, and H_2O co-adsorption on Cu_{22} cluster (LM3). (d) Optimized structures for OOH-$H_2C(O)OH$ (LM4). (e) Optimized structures for O_2-H_2-HCOOH (LM5).

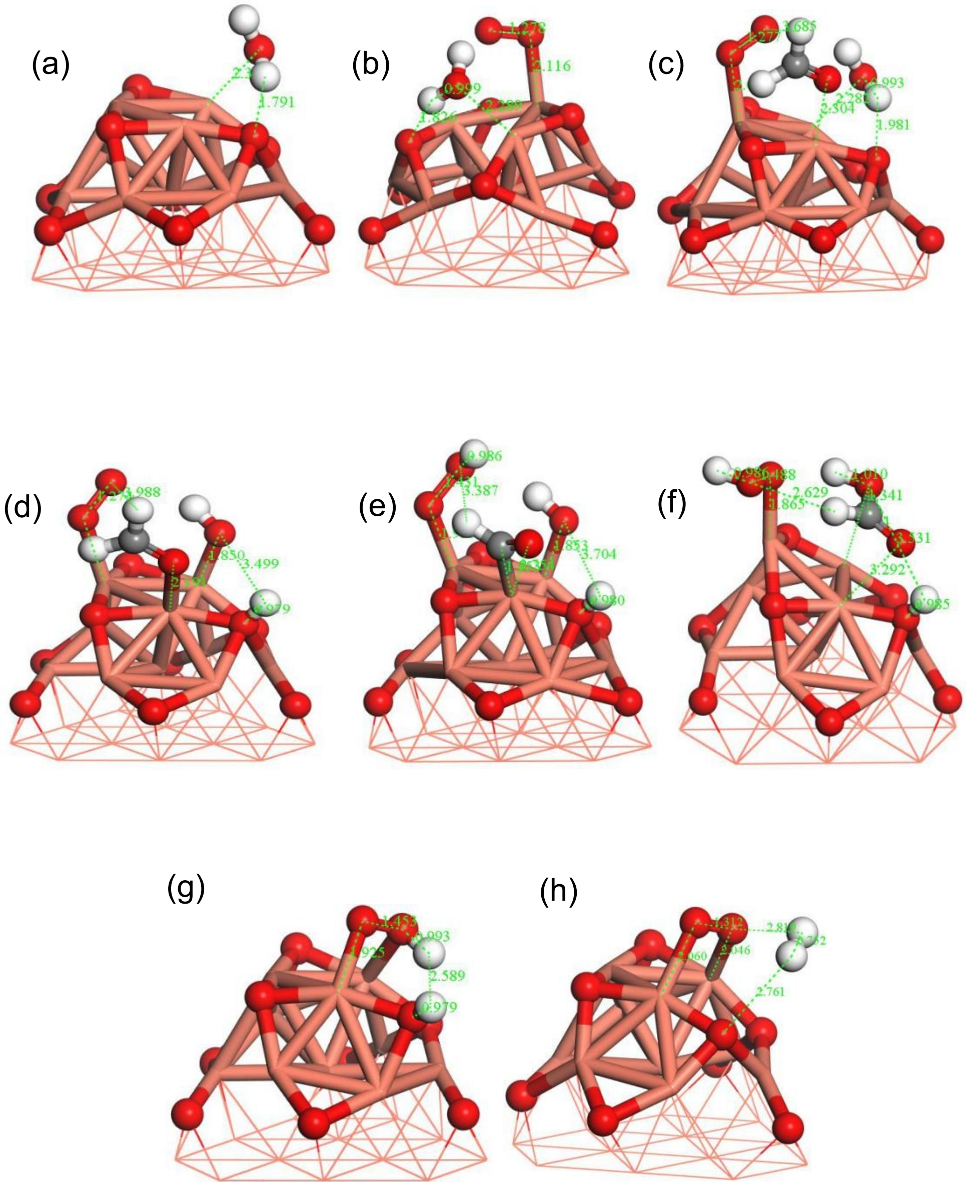

Fig. S11 (a) Optimized structures for $Cu_{22}O_9$-H_2O (LM1). (b) Optimized structures for co-adsorbed states of O_2+H_2O (LM2). (c) Optimized structures for co-adsorbed states of O_2+H_2O+H_2CO (LM3). (d) Optimized product structure for H_2O dissociation. (LM4). (e) Optimized structures for OOH-HCO. (f) Optimized product structure for HCOOH formation. (g) Optimized structures for OOH+H. (h) Optimized structures for O_2+H_2.

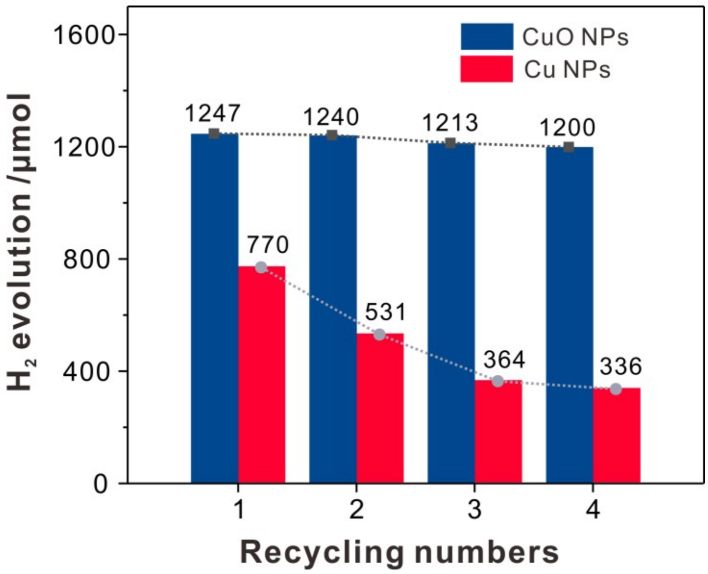

Fig. S12 The cycle performance of the CuO and Cu NPs catalyzes the hydrogen production of alkaline formaldehyde solution.

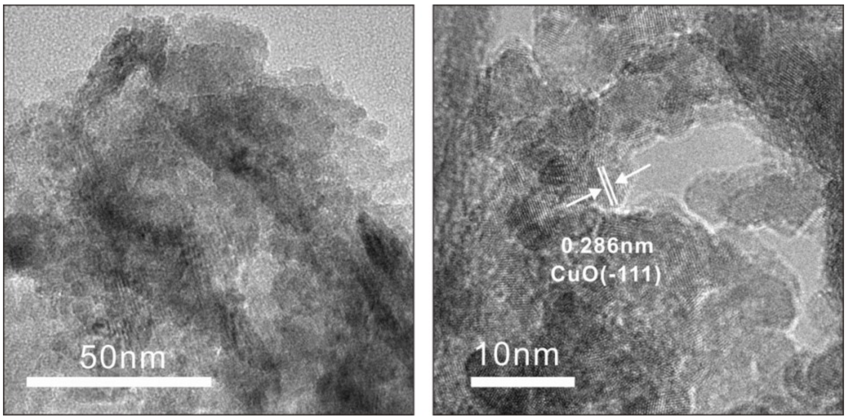

Fig. S13 TEM images of CuO catalyst after reaction.

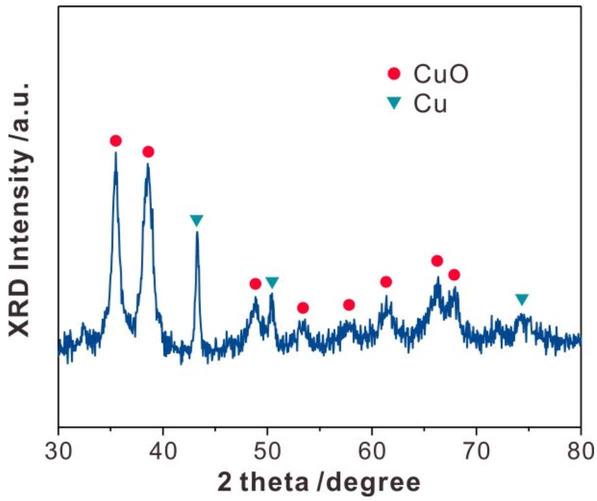

Fig. S14 XRD pattern of CuO catalyst after reaction.

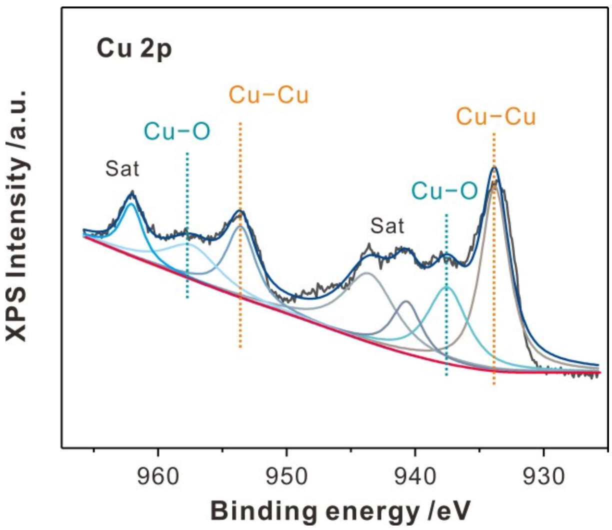

Fig. S15 Cu 2p XPS spectrum of CuO catalyst after reaction.