Supporting Information

Hollow spherical Cu/CuO-Fe_3O_4 composite for high-efficiency photothermal co-catalysis of hydrogen evolution

Nan Lu,[a,b] Fozia Sultana,[b] Zhenyong Ying,[a] Xiaofan Zhang,[a] Tongtong Li,[b] Renhong Li,[*,b] Benxia Li,[*,a] Xiaoqing Yan[*,a]

[a] *Department of Chemistry, School of Chemistry and Chemical Engineering, Zhejiang Sci-Tech University, Hangzhou, 310018, PR China*

[b] *State Key Laboratory of Bio-based Fiber Materials, Department of Materials Science & Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, PR China*

*Corresponding Authors

E-mail: yanxiaoqing927@126.com *(X.Q. Yan)*

E-mail: libx@zstu.edu.cn (B.X. Li)

E-mail: lirenhong@zstu.edu.cn *(R.H. Li)*

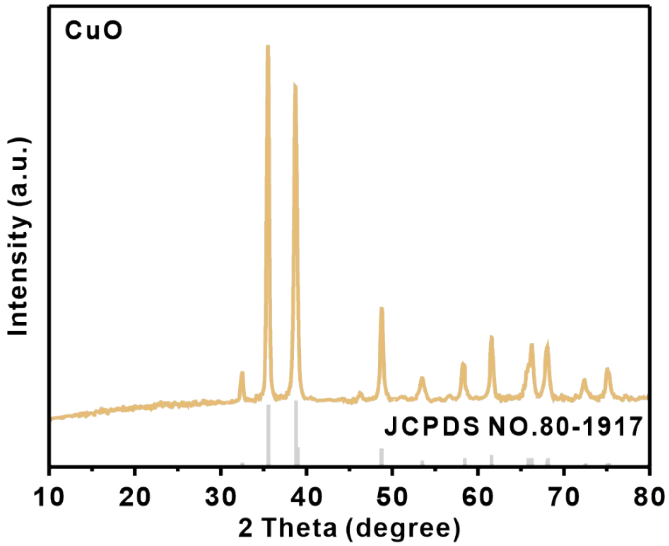

Fig. S1 XRD pattern of the synthesized CuO.

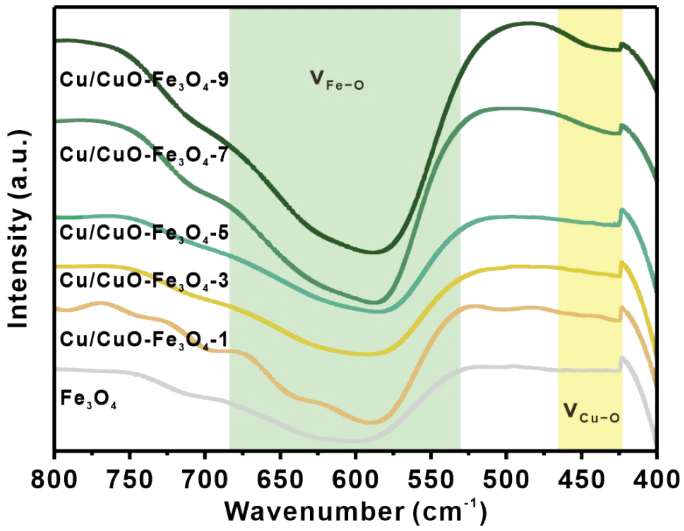

Fig. S2 FTIR spectrum of Cu/CuO-Fe_3O_4 catalysts with varying Cu contents at 400-800 cm^{-1}.

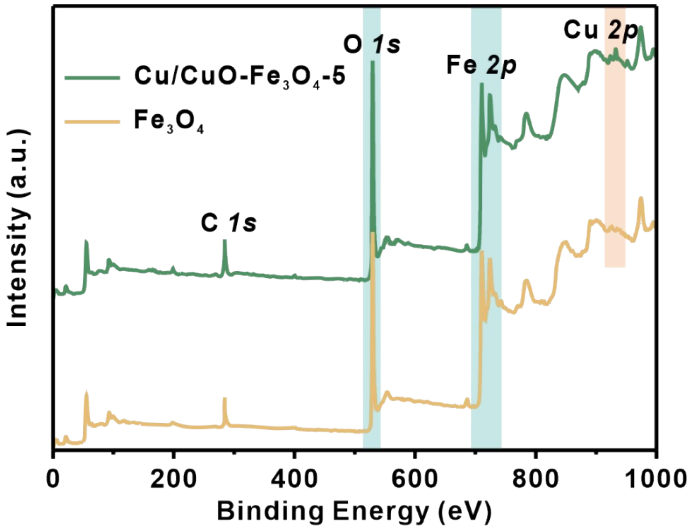

Fig. S3 XPS survey spectra of of Cu/Fe_3O_4-5 and Fe_3O_4.

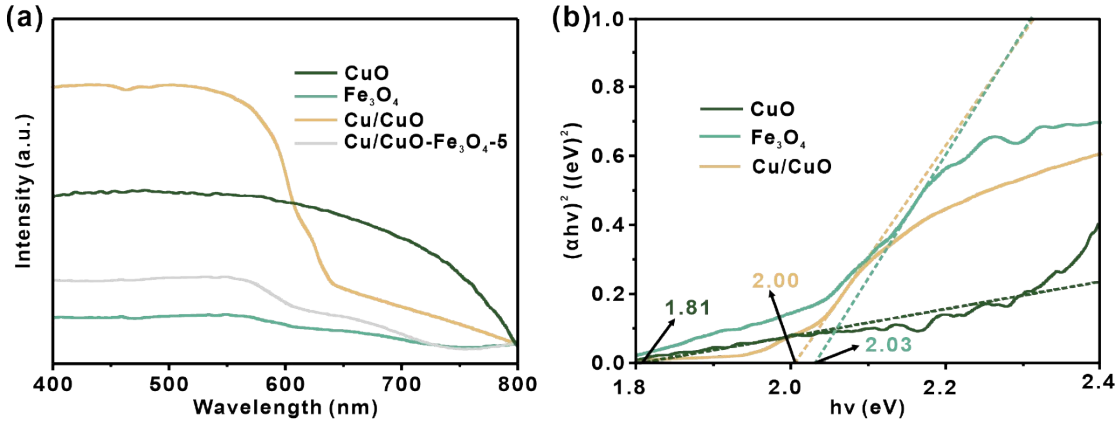

Fig. S4 (a) UV-visible diffuse absorption spectra of Cu/Fe_3O_4-5, Fe_3O_4, Cu/CuO and CuO. (b) Tauc plot of Cu/Fe_3O_4-5, Fe_3O_4 and CuO.

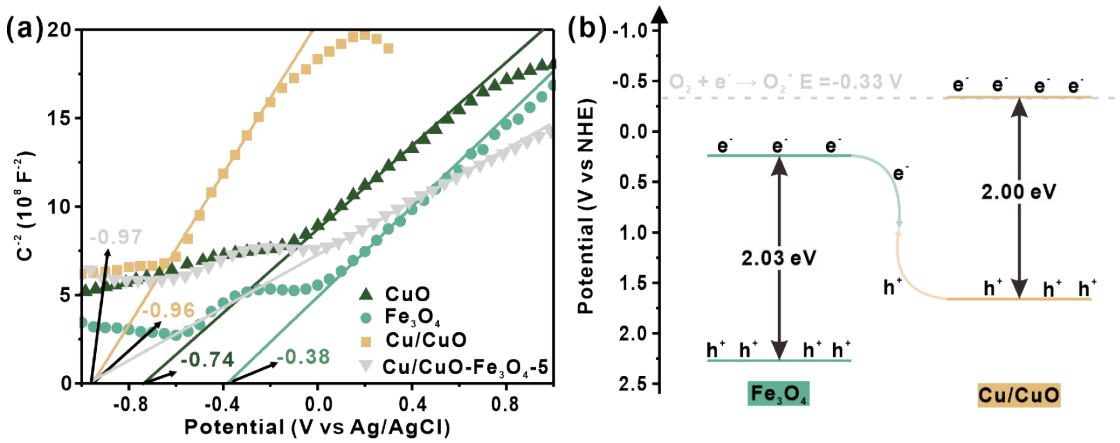

Fig. S5 (a) Mott-Schottky plots of CuO, Fe_3O_4, Cu/CuO and Cu/CuO-Fe_3O_4-5 (b) Mechanism diagram of the band structures of Cu/CuO-Fe_3O_4-5.

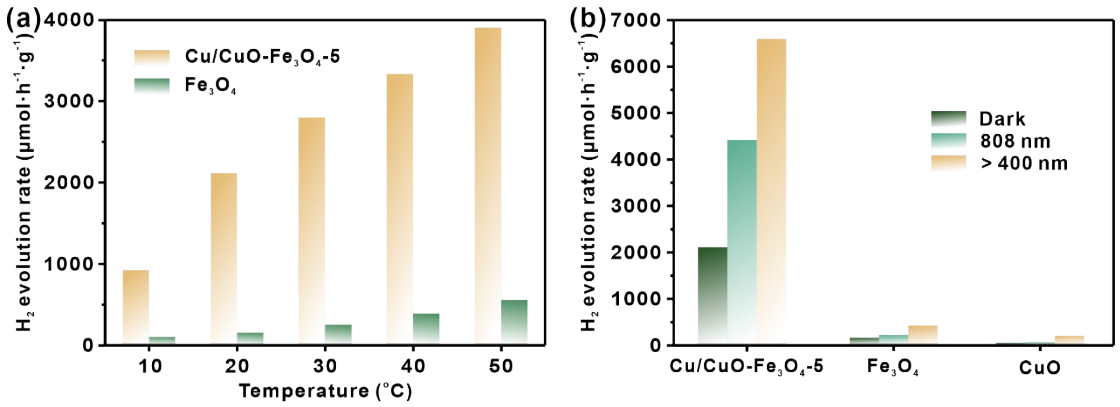

Fig. S6 (a) Catalytic H_2 evolution from alkaline formaldehyde solutions using Cu/CuO-Fe_3O_4-5 or Fe_3O_4 catalysts under air and dark conditions. (b) Catalytic H_2 evolution from alkaline formaldehyde solutions using Cu/CuO-Fe_3O_4-5, Fe_3O_4 or CuO catalysts under different illumination conditions. The concentrations of HCHO and NaOH are 1.0 mol·L^{-1} and 1.0 mol·L^{-1}, respectively.

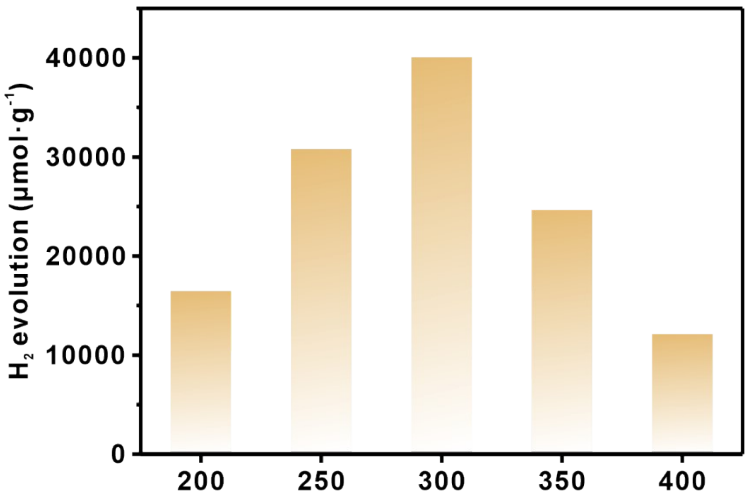

Fig. S7 The effect of the calcination temperature during catalyst preparation on the rate of H_2 evolution within 3 h of reaction in the alkaline HCHO solutions. The concentrations of HCHO and NaOH are 1.0 mol·L^{-1} and 1.0 mol·L^{-1}, respectively.

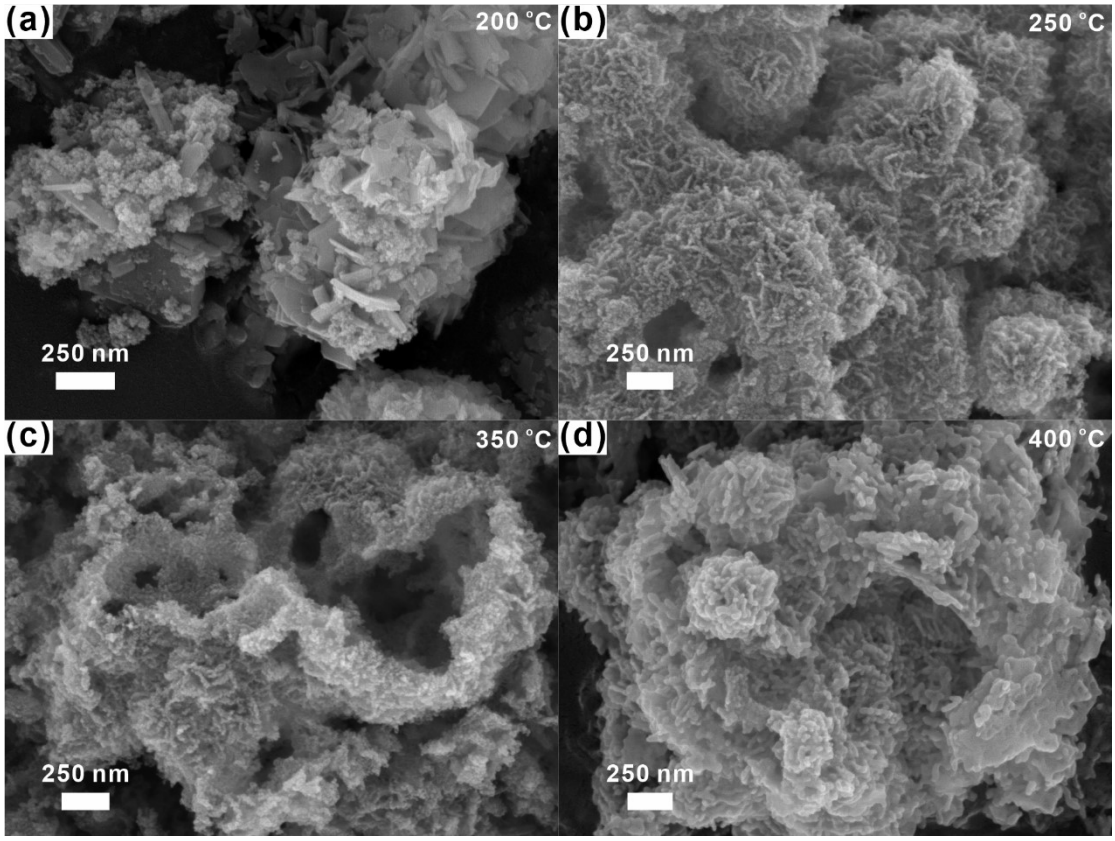

Fig. S8 SEM micrograph of Cu/CuO-Fe_3O_4-5 after calcination at (a) 200 ℃, (b) 250 ℃, (c) 350 ℃ and (d) 400 ℃.

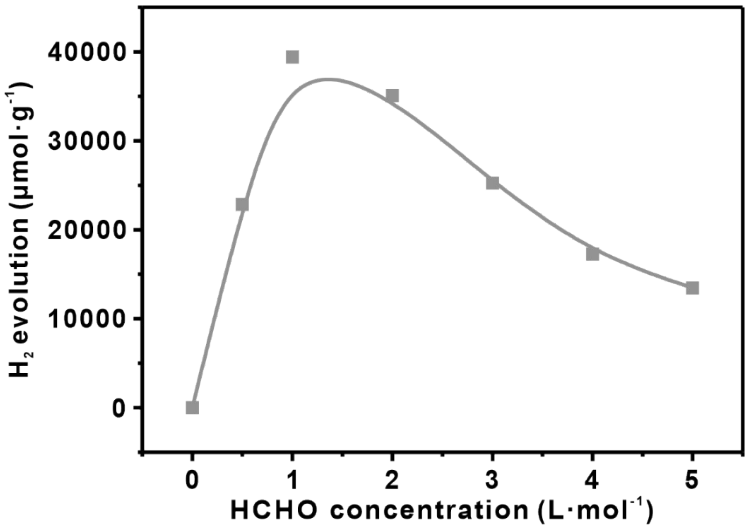

Fig. S9 The effect of HCHO concentration during catalyst preparation on the rate of H_2 evolution within 3 h of reaction in the alkaline HCHO solutions. The concentrations of NaOH are 1.0 mol·L^{-1}.

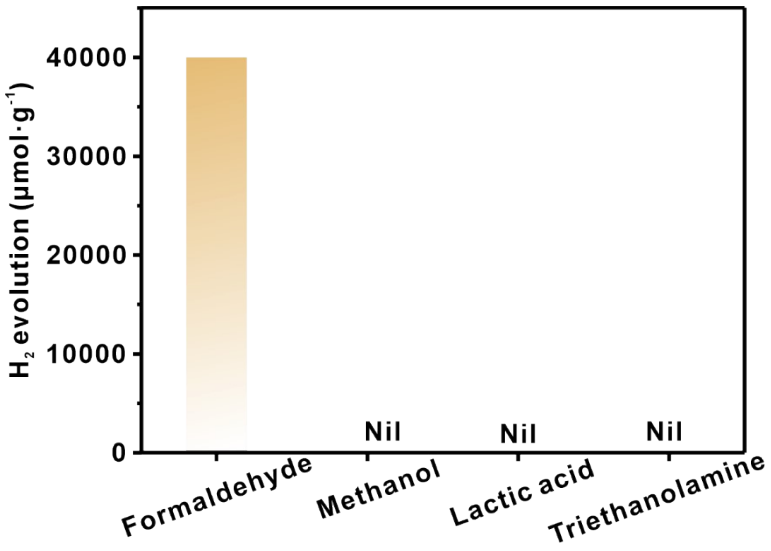

Fig. S10 Catalytic performance of Cu/CuO-Fe_3O_4-5 in different organic substrates.

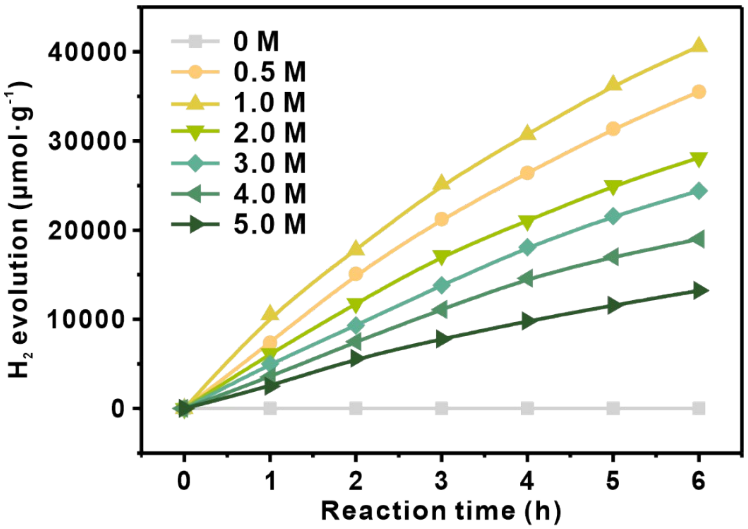

Fig. S11 The effect of NaOH concentration during catalyst preparation on the rate of H_2 evolution within 3 h of reaction in the alkaline HCHO solutions. The concentrations of HCHO are 1.0 mol·L^{-1}.

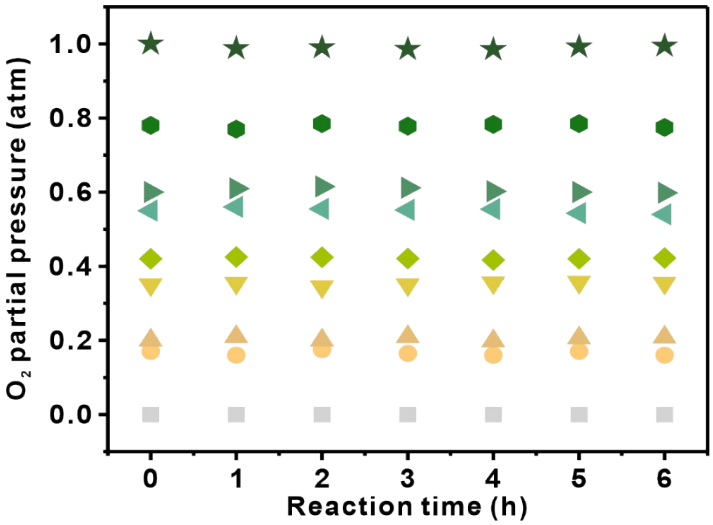

Fig. S12 The variation of p_{O2} over time in the alkaline HCHO solutions; Cu/Fe_3O_4-5 is employed as the photocatalyst.

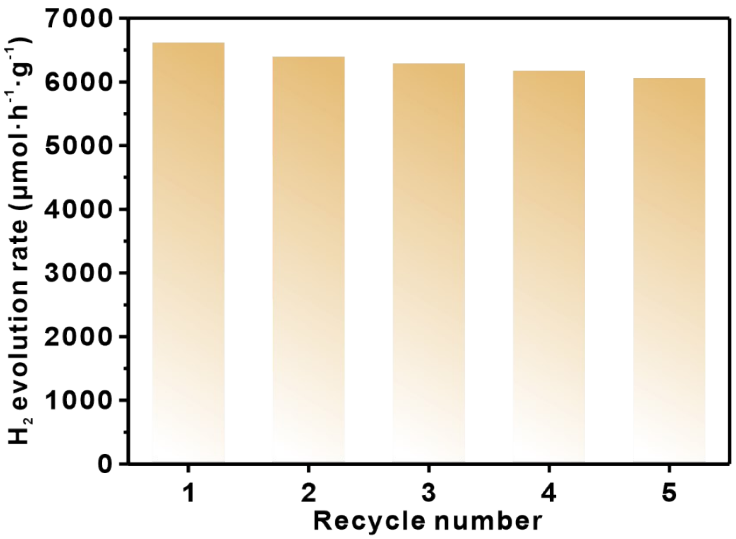

Fig. S13 Repeated photothermal co-catalytic H_2 evolution tests with recycled Cu/Fe_3O_4-5 by an external magnetic field. For each cycle, the concentrations of HCHO and NaOH are 1.0 mol·L^{-1} and 1.0 mol·L^{-1}, respectively.

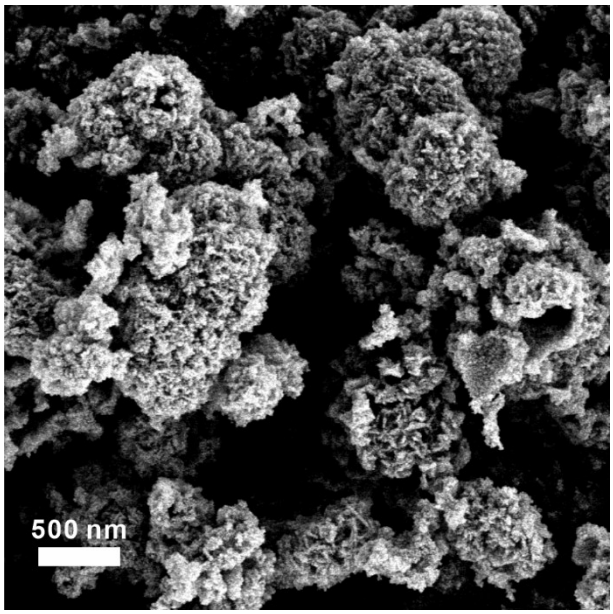

Fig. S14 SEM images of Cu/Fe_3O_4-5 after the photothermal co-catalytic reaction.

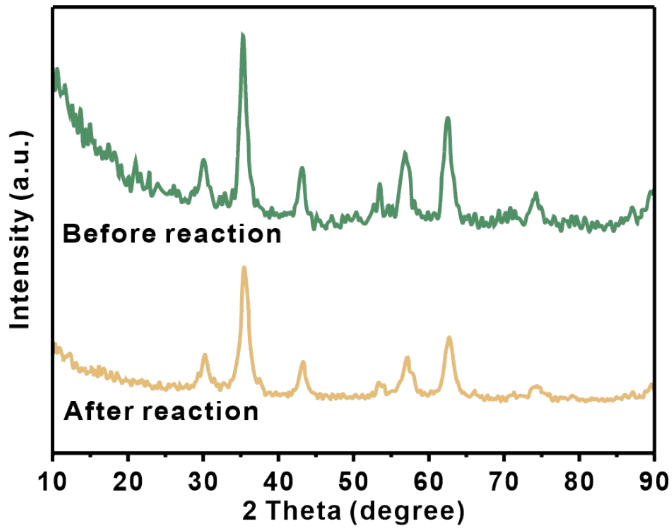

Fig. S15 XRD patterns of Cu/Fe_3O_4-5 before after the photothermal co-catalytic reaction.