

Hydrogen production from methane steam reforming using plasmonic photocatalysis

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Methane steam reforming (MSR) is accountable for half of the global hydrogen production. Thermal-driven MSR is dominant in the chemical industry as a mature technology, but challenges such as high operation temperature and coking formation remain persistent. Photocatalytic MSR provides a cleaner route without extra emission by directly converting photon energy to chemical energy. The main reaction for MSR is $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3 \text{H}_2$ ($\Delta H_r = 206$ kJ/mol), which can go further with the water gas shift (WGS) $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ($\Delta H_r = -41$ kJ/mol). The common side reactions include Boudouard reaction ($2 \text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$, $\Delta H_r = -173$ kJ/mol) and methane decomposition ($\text{CH}_4 \rightleftharpoons \text{C} + 2 \text{H}_2$, $\Delta H_r = 75$ kJ/mol). Literature indicates Ru-, Rh-, and Ni-based catalysts are among the best for MSR, but the challenges remain, including high temperature, sulfur, and coking. Here, we demonstrate highly reactive, selective, and stable photocatalytic MSR using a Cu-Rh antenna-reactor photocatalyst. The plasmonic antenna, Cu, absorbs photons and decays into hot carriers (HC) which drive the MSR on Rh reactors. The reactivity (H_2 production) reaches $\sim 50 \mu\text{mol/s/g}$, equivalent to $\sim 0.5 \text{ s}^{-1}$ turn-over-frequency on Rh reactor while the product selectivity ($\text{CO}:\text{CO}_2$ ratio) is as high as $\sim 10:1$ at 500 mW white light illumination without external heating and an equal amount of methane and water vapor at ambient condition. The stability profile in this reaction condition showed no decay of reactivity for 24 hours and no carbon deposition was detected.

We observed that the reactivity of PMSR is wavelength-dependent (Fig. 1A) but the trend is different than the optical absorption which peaked at ~ 570 nm (Fig. 1A, inset). The photothermal heating (Fig. 1B) follows the trend of optical absorption but its contribution to MSR is negligible otherwise the reactivity would follow the same trend. When doubling the illumination power at 700nm (the orange dot in Fig. 1A and 1B), the photothermal heating increased from 230 to 340 °C, but the corresponding reactivity is still near 0. Selectivity towards CO and CO_2 is also wavelength-depend, with blue light favoring CO (Fig. 1C) and red favoring CO_2 (Fig. 1D).

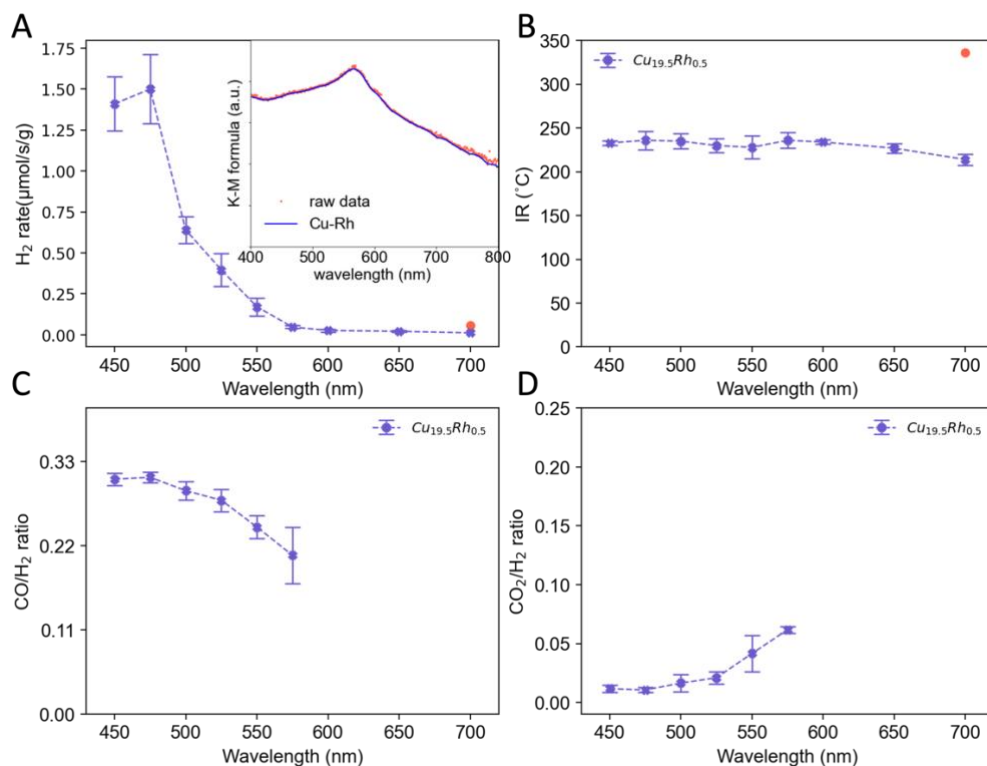


Fig. 1 The wavelength-dependence of the Cu-Rh photocatalyst. (A) H_2 production as a function of wavelength measured under different wavelengths measured by gas chromatography. (inset) optical absorption measured by diffuse-reflectance and plotted in the K-M formula. (B) The photothermal effect plotted as the maximum laser-induced heating temperature measured by an IR camera (2-10 μm). (C) Selectivity of CO plotted as CO to H_2 ratio, (D) selectivity of CO_2 as a function of wavelength. Reaction condition: 0.6 sccm CH_4 and 19.4 sccm of balancing He flows through water bubbler under ambient condition (3% of water vapor under equilibrium, resulting in $\text{CH}_4:\text{H}_2\text{O} = 1:1$) no external heating was applied, bandpass filters ($\pm 25\text{nm}$) were used for wavelength selection. Illumination power was kept at 100 mW ($\sim 13 \text{ W/cm}^2$).