Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Carbon Capture and Storage Technique Using Gold Nanoparticles Coupling with Cu-based Composited Thin Film Catalysts

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Equations

- **Equations for CCS technique[1]**

$$CO_{2(g)} \rightleftarrows CO_{2(aq)} \quad \textbf{Eq. S1}$$

$$CO_{2(aq)} + H_2O_{(l)} \rightleftarrows {H^+}_{(aq)} + {HCO_3}^-{}_{(aq)} \cdots K1 \quad \textbf{Eq. S2}$$

$$K1 = \frac{\left[{HCO_3}^-\right]\left[H^+\right]}{\left[CO_{2(aq)}\right]} \quad \textbf{Eq. S3}$$

$${HCO_3}^-{}_{(aq)} \rightleftarrows {H^+}_{(aq)} + {CO_3}^{2-}{}_{(aq)} \cdots K2 \quad \textbf{Eq. S4}$$

$$K2 = \frac{\left[{CO_3}^{2-}\right]\left[H^+\right]}{\left[{HCO_3}^-\right]} \quad \textbf{Eq. S5}$$

- **Equations for CO_2RR[2]**

$$CO_{2(aq)} + 2{H^+}_{(aq)} + 2e^- \rightleftarrows CO_{(g)} + H_2O_{(l)} \quad \textbf{Eq. S6}$$

$$CO_{2(aq)} + 8{H^+}_{(aq)} + 8e^- \rightleftarrows CH_{4(g)} + 2H_2O_{(l)} \quad \textbf{Eq. S7}$$

$$CO_{2(aq)} + 2{H^+}_{(aq)} + 2e^- \rightleftarrows HCOOH_{(aq)} \quad \textbf{Eq. S8}$$

$$CO_{2(aq)} + 4{H^+}_{(aq)} + 4e^- \rightleftarrows HCHO_{(aq)} + H_2O_{(l)} \quad \textbf{Eq. S9}$$

$$2CO_{2(aq)} + 12{H^+}_{(aq)} + 12e^- \rightleftarrows C_2H_{4(g)} + 4H_2O_{(l)} \quad \textbf{Eq. S10}$$

$$2CO_{2(aq)} + 14{H^+}_{(aq)} + 14e^- \rightleftarrows C_2H_{6(g)} + 4H_2O_{(l)} \quad \textbf{Eq. S11}$$

$$2CO_{2(aq)} + 14{H^+}_{(aq)} + 14e^- \rightleftarrows C_2H_{6(g)} + 4H_2O_{(l)} \quad \textbf{Eq. S12}$$

$$2CO_{2(aq)} + 10{H^+}_{(aq)} + 10e^- \rightleftarrows CH_3COOH_{(aq)} + 2H_2O_{(l)} \quad \textbf{Eq. S13}$$

$$2CO_{2(aq)} + 12{H^+}_{(aq)} + 12e^- \rightleftarrows C_2H_5OH_{(aq)} + 3H_2O_{(l)} \quad \textbf{Eq. S14}$$

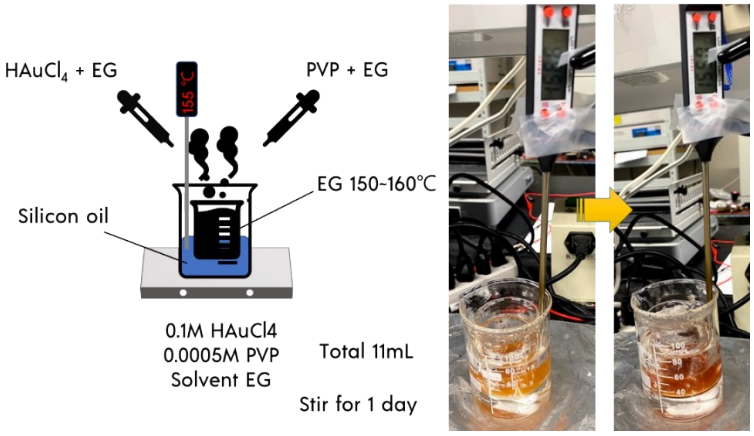
$$2CO_{2(aq)} + 16{H^+}_{(aq)} + 16e^- \rightleftarrows C_2H_5CHO_{(aq)} + 5H_2O_{(l)} \quad \textbf{Eq. S15}$$

$$2CO_{2(aq)} + 18{H^+}_{(aq)} + 18e^- \rightleftarrows C_3H_7OH_{(aq)} + 5H_2O_{(l)} \quad \textbf{Eq. S16}$$

Experimental Section

- **Synthesis of Au NPs reduced by $NaBH_4$ (0.1M) and ethylene glycol (EG)**

The other two reduction processes to form Au NPs were operated to compare the optical property with the synthesis of Au NPs reduced by $NaBH_4$ (0.5M) and ethylene glycol (EG). Similar to the reduction process in section 2.1.1, 0.5 M $NaBH_4$ powder as the reductant was inserted into 11 mL EG solution which also contained 0.1 M chloroauric acid (HAuCl4) and 0.0005 M polyvinylpyrrolidone (PVP). The reduction reaction was completed immediately. The Au NPs also can be obtained by heating the 11 mL EG solution which contained 0.1 M chloroauric acid ($HAuCl_4$) and 0.0005 M polyvinylpyrrolidone (PVP) in oil bath at 150℃~160℃ for 1 day (Scheme S1). The reduction reaction was completed immediately.



Scheme S1. Synthesis of Au NPs prepared from $HAuCl_4$, PVP, and EG solution.

Heating the EG solution could reduce the Au^{3+} ions in the solution and color could changed from yellow to purple.

Supporting Figures

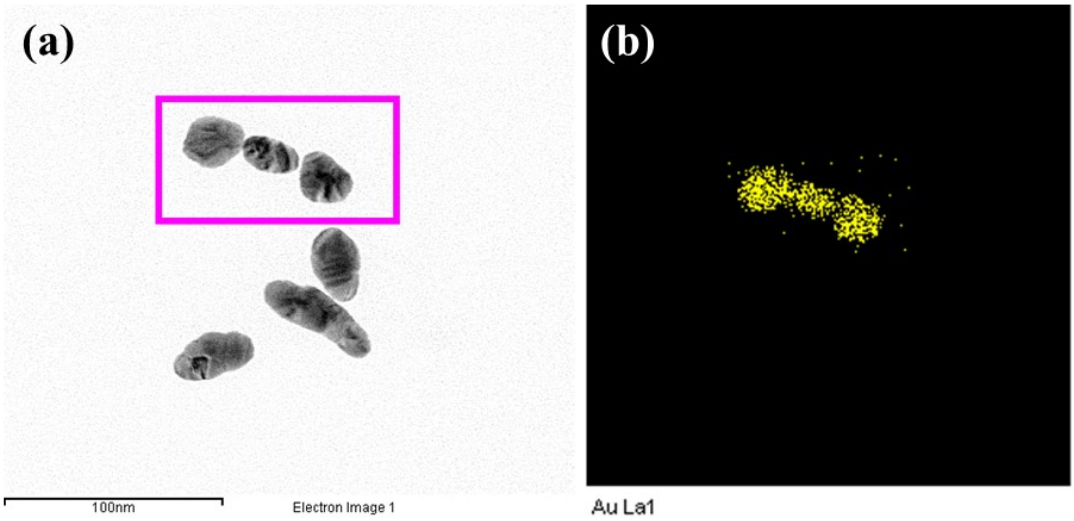


Figure S1. (a) TEM image of Au NPs prepared from $HAuCl_4$, PVP, $NaBH_4$, and EG solution. (b) The EDS analysis corresponding to the purple selection area, the yellow signal is the signal of the gold element.

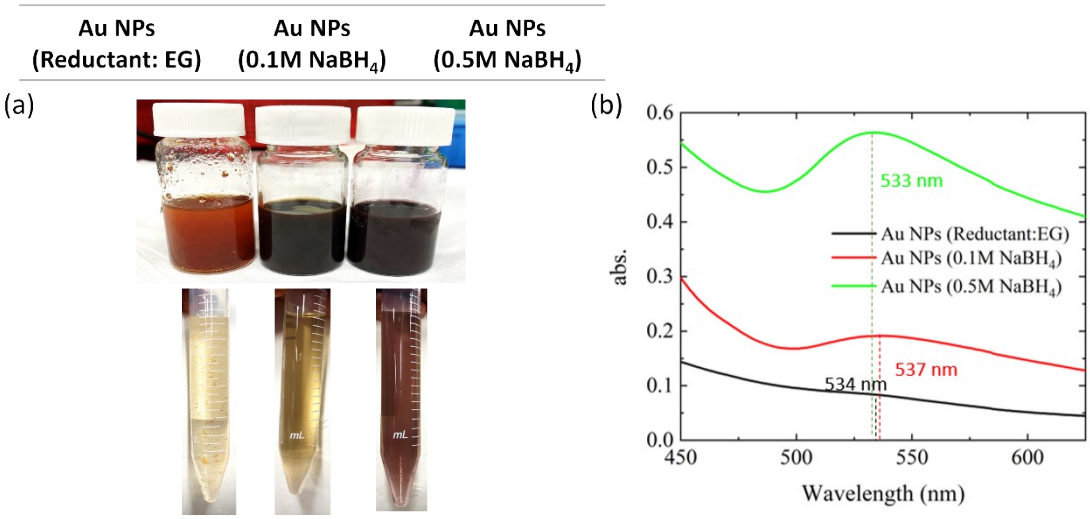


Figure S2. (a) The photographs of Au NPs which was reduce by ethylene glycol (EG) with 195℃ heated by oil bath, 0.1 M $NaBH_4$ and 0.5 $NaBH_4$. (b) UV-visible curve of Au nanoparticles in different reductants by the range of wavelength 450-650 nm.

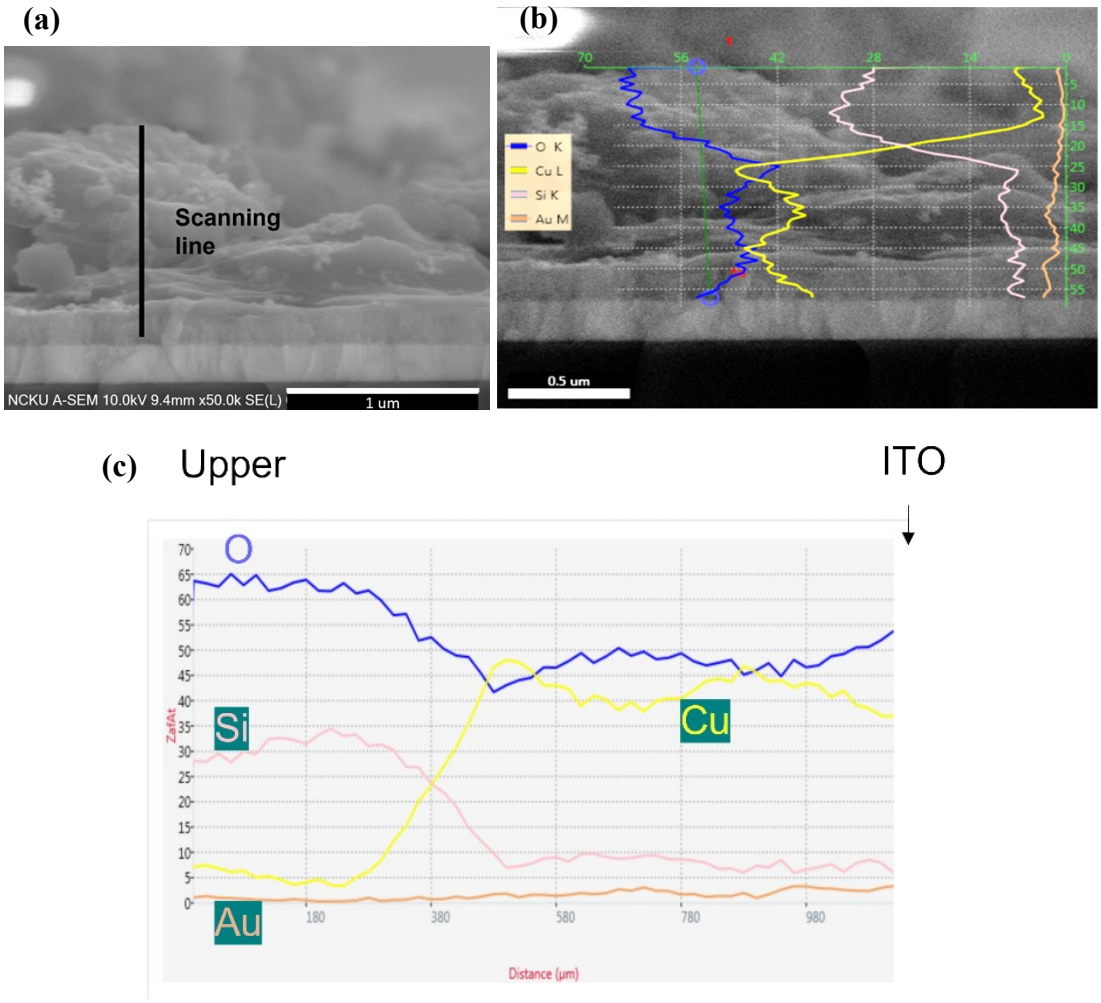


Figure S3. In-depth analysis of Au/Cu_2O composite films. (a)The indicated scanning area; (b) Composition analysis in depth of oxygen, copper, silicon, and gold signals with corresponding SEM image, the horizontal axis is the content (wt %), and the vertical axis is the depth from the surface to the glass substrate; (c) Depth analysis line chart of oxygen, copper, silicon and gold signals.

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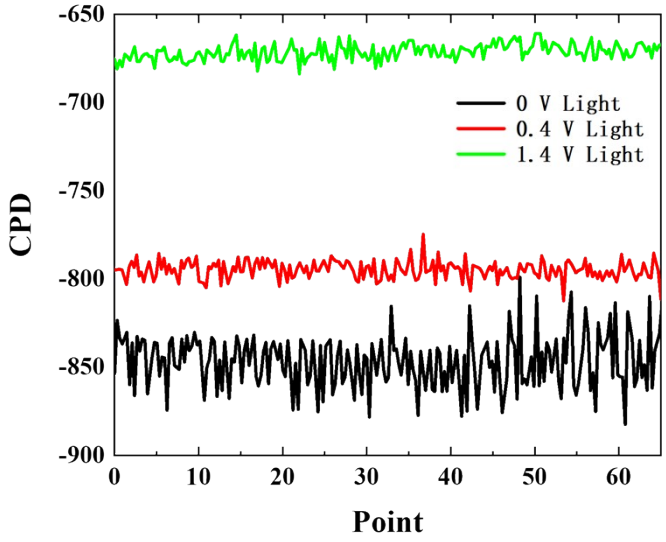


Figure S4. The Kelvin probe measurement of different voltage applied Au/Cu_2O thin film catalysts under AM 1.5 light illumination. The contact potential difference (CPD) between a sample and a tip could be detect and the work function of the sample can be calculated.

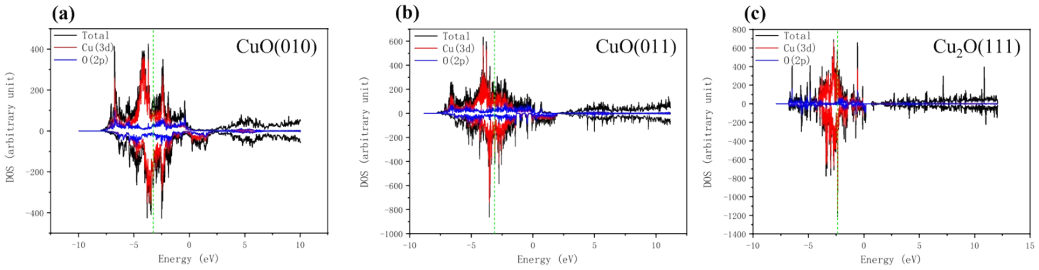
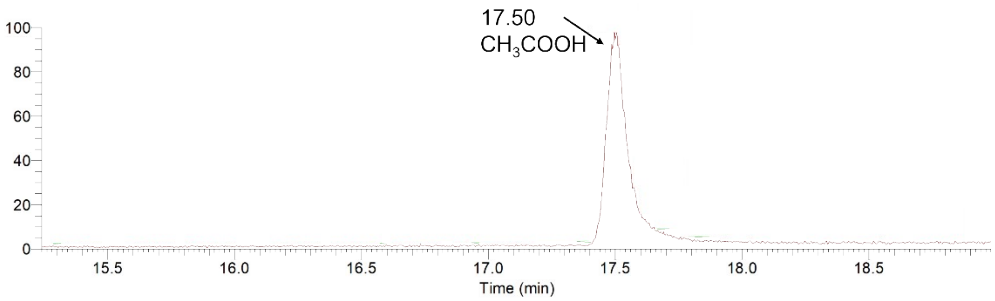


Figure S5. Density of states (DOS) and partial density of states (PDOS) of (a)CuO(110), (b)CuO(011) and (c) $Cu_2O(111)$. Note that the perpendicular green dashed line denotes the d-band center.

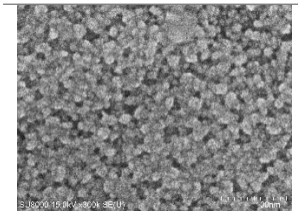


Supplementary Figure 2. GC-EID Chromatogram for the analysis of CO_2 reduction liquid product after potentiostaic electrochemical at 1.2V under light illumination for 1 hour. Related Compound was ethanol at the retention time 17.50 min.

Supporting Table

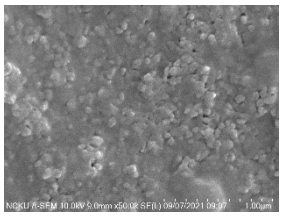
Supplementary Table 1.

Elemental composition result of the Cu_2O thin film which synthesized by electrodeposition process. The SEM image shows indicated area which EDS was analysis in.

Cu_2O	Element	Weight %	Atomic %
	**O K**	**27.53**	**60.14**
	Cu L	**72.47**	**39.86**

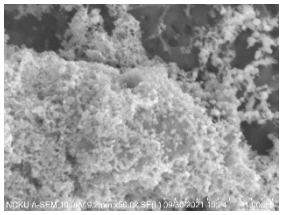
Supplementary Table 2.

Elemental composition result of the Cu2O modified by APTMS (0.1 wt%) mixed with Hexane. The SEM image shows indicated area which EDS was analysis in.

Cu_2O-modified by APTMS	Element	Weight %	Atomic %
	**O K**	**16.43**	**39.72**
	Cu L	**71.35**	**43.45**
	Si K	**12.22**	**16.83**

Supplementary Table 3.

Elemental composition result of the Au/Cu_2O thin film which combined Au NPs with modified Cu_2O by self-assembly process. The SEM image shows indicated area which EDS was analysis in.

Cu_2O-modified by APTMS	**Element**	**Weight %**	**Atomic %**
	**O K**	**10.22**	**45.27**
	Cu L	**23.29**	**25.97**
	Si K	**2.24**	**5.65**
	Au M	**64.24**	**23.11**

Reference

[1] Renforth, P. and G. Henderson, *Assessing ocean alkalinity for carbon sequestration.* Reviews of Geophysics, 2017. 55(3): p. 636-674.

[2] Zhao, X., L. Du, B. You, and Y. Sun, *Integrated design for electrocatalytic carbon dioxide reduction.* Catalysis Science & Technology, 2020. 10(9): p. 2711-2720.