Electronic Supplementary Information (ESI)

Near-Infrared-Activated $NaYF_4$: Yb^{3+}, Er^{3+}/Au/CdS for H_2 Production via Photoreforming of Bio-Ethanol: Plasmonic Au as Light Nanoantenna, Energy Relay, Electron Sink and Co-catalyst

Wenhui Feng,[a] Lulu Zhang,[a] Yan Zhang,[a] Yu Yang,[a] Zhibin Fang,[a] Bo Wang,[a] Shiying Zhang,[b] and Ping Liu*[a]

[a] *Research Institute of Photocatalysis, State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou 350002, P. R. China.*

[b] *Hunan Provincial Collaborative Innovation Center for Environment and Energy Photocatalysis, Changsha University, Changsha 410022, P. R. China.*

**Corresponding author, Fax: +86-591-8377-9239; Tel:+86-591-8377-9239; E-mail: liuping@fzu.edu.cn.*

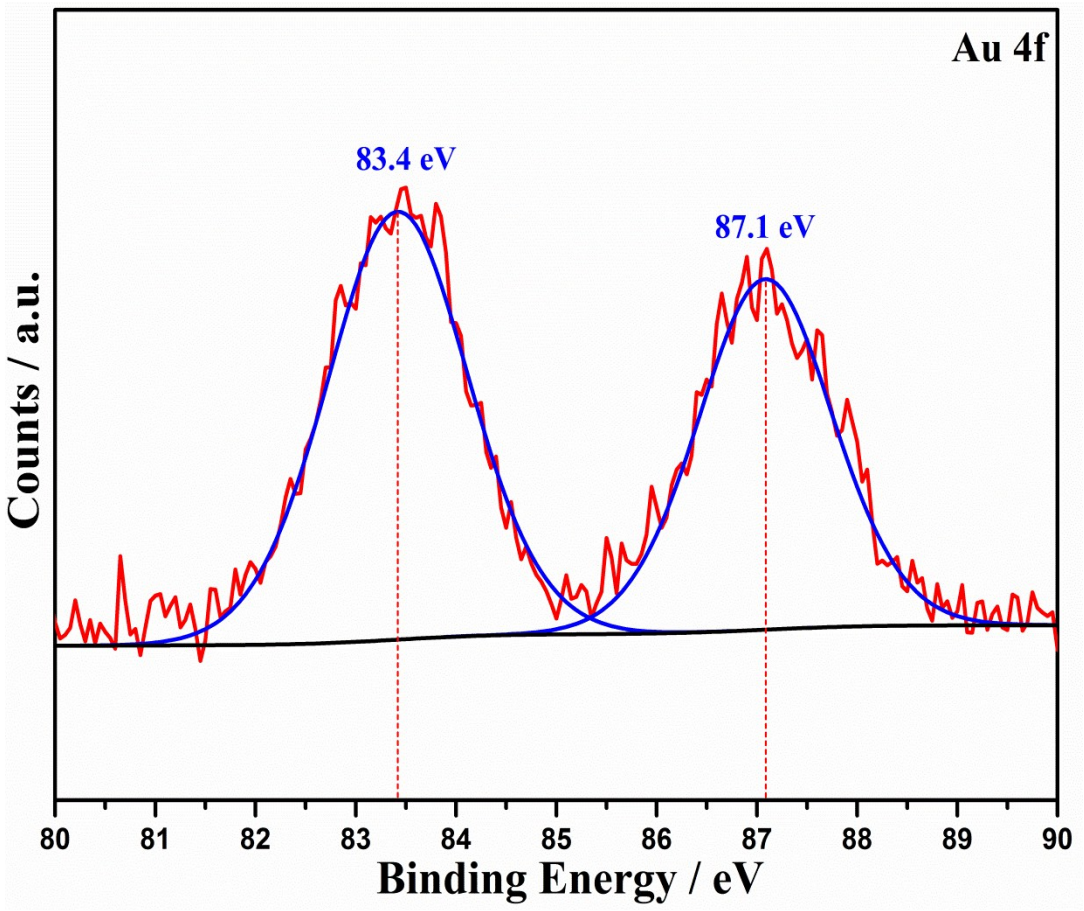

Fig. S1 XPS spectra of Au 4f for NYF/Au/CdS composite.

Synthesis of Au colloids:

Au colloids with an average diameter of 15 nm were prepared by the conventional sodium citrate reduction method. Typically, an aqueous solution of HAuCl4 (100 mL, 0.25 mM) was heated to boiling, followed by the rapid addition of tri-sodium citrate solution (200 μL, 0.5 M). The resulting solution was kept boiling for about 15 min, producing a stable, deep-red dispersion of Au nanoparticles with an average diameter of about 15 nm. The citrate-protected Au colloids (Au-Cit) suspension was then cooled to room temperature for later use.

Synthesis of Au/CdS:

0.05 mmol $Cd(NO_3)_2 \cdot 4H_2O$ was mixed with an aqueous solution of *L*-cysteine (2.5 mL, 0.04 M) and stirred for 30 min. Then, a given amount of Au-Cit colloids (20 mL, 0.25 mM) was dropped into the resulting

mixture and stirred for 1 hr. After that, 60 mL absolute ethyl alcohol was added into the obtained suspension, and continue to stir for a further 5 min. The resulting suspension subsequently was transferred into a 100 mL Teflon-lined autoclave and heated at 160 °C for 12 hr. After cooling to room temperature, the as-prepared Au/CdS was collected by centrifugation, washing with DI water and absolute ethanol several times and drying at 60 °C in vacuum.

Table S1. Gas Product yields for photocatalytic bio-ethanol reforming on various samples.[a]

	Dark				λ>700nm			AM 1.5G		
Gas Products	H_2 (μmol •g^{-1}•h^{-1})	CO (μmol •g^{-1}•h^{-1})	CH_4 (μmol •g^{-1}•h^{-1})	CO_2 (μmol •g^{-1}•h^{-1})	CO (μmol •g^{-1}•h^{-1})	CH_4 (μmol •g^{-1}•h^{-1})	CO_2 (μmol •g^{-1}•h^{-1})	CO (μmol •g^{-1}•h^{-1})	CH_4 (μmol •g^{-1}•h^{-1})	CO_2 (μmol •g^{-1}•h^{-1})
No Cat.	-	0.14	-	0.77	0.15	-	0.72	0.16	-	0.80
NYF	-	0.14	-	0.68	0.14	-	0.99	0.33	-	1.91
NYF/Au	-	0.17	-	0.87	0.18	0.09	1.19	0.78	0.68	3.95
NYF/CdS	-	0.16	-	0.82	0.17	-	0.78	0.59	1.33	14.91
NYF/Au/CdS	-	0.16	-	0.90	0.10	0.04	1.96	0.54	1.00	39.92
NYF-Au/CdS-M	-	0.18	-	0.84	0.17	0.10	1.35	0.80	1.52	21.64

[a] Stirred suspensions of the photocatalyst (15 mg) in the simulated bio-ethanol solution were irradiated with different light under atmosphere of Ar gas (~1 bar) at 25 °C; hyphens represent the data below detection limits.

Table S2. Liquid Product yields for photocatalytic bio-ethanol reforming on various samples.

	Dark		λ>700nm		AM 1.5G	
Liquid Products	CH_3CHO(μmol •g^{-1}•h^{-1})	Acetal (μmol• g^{-1}•h^{-1})	CH_3CHO(μmol •g^{-1}•h^{-1})	Acetal (μmol• g^{-1}•h^{-1})	CH_3CHO(μmol •g^{-1}•h^{-1})	Acetal (μmol• g^{-1}•h^{-1})
No Cat.	-	-	-	-	-	-
NYF/Au@CdS	-	-	-	-	-	166.27

[a] Stirred suspensions of the photocatalyst (15 mg) in the simulated bio-ethanol solution were irradiated with different light under atmosphere of Ar gas (~1 bar) at 25 °C; hyphens figures lower than the corresponding detection limits.