Supporting Information

Enhanced plasmon-driven photoelectrocatalytic methanol oxidation on Au decorated α-Fe$_2$O$_3$ nanotube arrays

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Figure contents of Supporting Information

Experimental Section

Sample preparation

The prepration of ZnO NRAs: ZnO NRAs grew on FTO substrate by chemical bath deposition (CBD). ZnO NRAs were grown on a clean fluorine tin oxide (FTO) substrate in a two-electrode system with an 500 mL aqueous solution including 2.98 g $Zn(NO_3)_2$, 0.39 g NH_4Ac and 0.70 g HMT in 90 ℃, the deposition time was 50 min, and deposition current was fixed at -2 mA.[1]

The prepration of ZnO/α-Fe$_2$O$_3$ NTAs: ZnO/α-Fe$_2$O$_3$ NTAs were synthesized by typical "sacrificial template-accelerated hydrolysis" (STAH) approach, which is essential to initiating the ZnO/α-Fe$_2$O$_3$ nanotube formation. The as-synthesized ZnO NRAs were placed into a 100 mL 0.1 M $Fe(NO_3)_3·9H_2O$ aqueous solution and kept at 25 ℃ for 1 h. The ZnO NRAs were partially dissolved in turn accelerates Fe^{3+} hydrolysis. Then the sample was dried and treated at 450 ℃ in air for 5h to ensure sufficient oxidation of Fe_2O_3 obtained ZnO/α-Fe$_2$O$_3$ NTAs.[2]

The prepration of ZnO/α-Fe$_2$O$_3$/Au NTAs: The Au nanoparticles were reduced and then uniformly decorated on sequential ZnO/α-Fe$_2$O$_3$ NTAs. The as-synthesized ZnO/α-Fe$_2$O$_3$ NTAs were immersed into 100mL aqueous solution containing 3 mL $HAuCl_4$, 0.025 g $C_6H_5Na_3O_7·2H_2O$, and 0.02 g $NaBH_4$ for 1 h to load Au particles, then the sample was dried at 25 ℃ in air for 5 h to obtain ZnO/α-Fe$_2$O$_3$/Au NTAs.[3]

Physicochemical Characterizations

The surface morphology and detailed microscopic structure of samples were analyzed using field emission scanning electron microscopy (FESEM, JSM-6701F) and transmission electron microscopy equipped (TEM, JEM2010-HR). The crystal phase of the samples were characterized by powder X-ray diffraction (XRD, Bruker, D8 Advance) with Kα irradiation (λ = 0.15418 nm). The chemical-state analysis of the products was measured with X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha). The UV-vis diffuse reflectance spectra (UV-vis DRS) of the samples were obtained using a UV-vis spectrophotometer (Cary 300). The absorbance of samples was measured by UV-vis spectrophotometer (Shimadzu UVmini-1240).

Photoelectrochemical Measurements

The photoelectrochemical performances of the obtained catalysts were measured by electrochemical workstation (CHI 760D, China Chenhua) in a cubical complete quartz cell with a three-electrode system. The as-prepared photoanodes as the working electrode, Ag/AgCl electrode (saturated KCl solution) and Pt sheet served as the reference electrode and counter electrode, respectively. The light source is adjustable 350W Xe lamp for simulated sunlight, and the monochromators (AnHe, Inc., China) were used with Xe lamp for incident photon to current conversion efficiency (IPCE) measurement.

Formaldehyde detection

First of all, the calibration curve was received by concentration gradients from 0 to 0.5 ppm (Fig. S7), and then the aqueous solution mingled with KOH, 4-Amino-3-hydrazino-5-mercapto-1, 2, 4-triazole (AHMT, which was used as colorant) and KIO_4, stirring fully and then standing 10 minutes for colorating. Methanol were oxidated to formaldehyde in a three-electrode quartz cell (50 mL electrolyte solution contained 95% CH_3OH in 0.10 M NaOH) under full light at 0.80 V vs. Ag/AgCl. To quantify formaldehyde, five aliquots were extracted at the following times of reaction 0, 15, 30, 45 and 60 min. The extracted 0.1 mL electrolyte was mixed with 4.2 mL of 5 M KOH, 0.50% AHMT and 1.5% KIO_4 in H_2O, according to the reported procedure. The UV-vis absorption spectrums of the final mixtures were then measured at 549 nm by UV-vis spectrophotometer.[4,5]

The Faradaic efficiency (FE) was estimated using the following equation:[5]

$$PE = \frac{mol\ of\ detected\ CH_2O}{mol\ of\ CH_2O\ calculated\ from\ the\ bulk\ electrolysis} \times 100$$

It is a potential method for photoelectrochemical formaldehyde synthesis. Under the action of h+, methanol can be oxidate due to the following reaction:[5]

$$CH_3OH + 2h^+ \rightarrow CH_2O + 2H^+$$
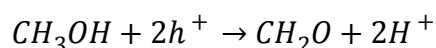
where h^+ represents a photohole on the photoanode. It is a potential route for

photoelectrochemical oxidation of methanol.

Photoelectrochemical testing

The carrier density of the electrodes can be calculated from the following equation:

$$N = \left(2/\varepsilon\varepsilon_0 e_0\right)[d(1/C^2)/dV]^{-1}$$

Where ε denotes the dielectric constant of the semiconductor, ε_0 denotes the permittivity of a vacuum (8.85×10^{-12} Fm^{-1}), e_0 denotes the electronic charge unit (1.60×10^{-19} C), and V denotes the potential applied at the electrode.

The incident photon to current conversion efficiency (IPCE) measurement is further performed to quantify the photoelectric conversion efficiency of photoanodes under various incident light wavelengths according to the following formula:

$$IPCE = 1240J / \lambda J_{light}$$

where J is the measured photocurrent density at the specific wavelength (mA cm^{-2}), λ is the incident light wavelength, and J_{light} is measured irradiance at the specific wavelength (mW cm^{-2}).
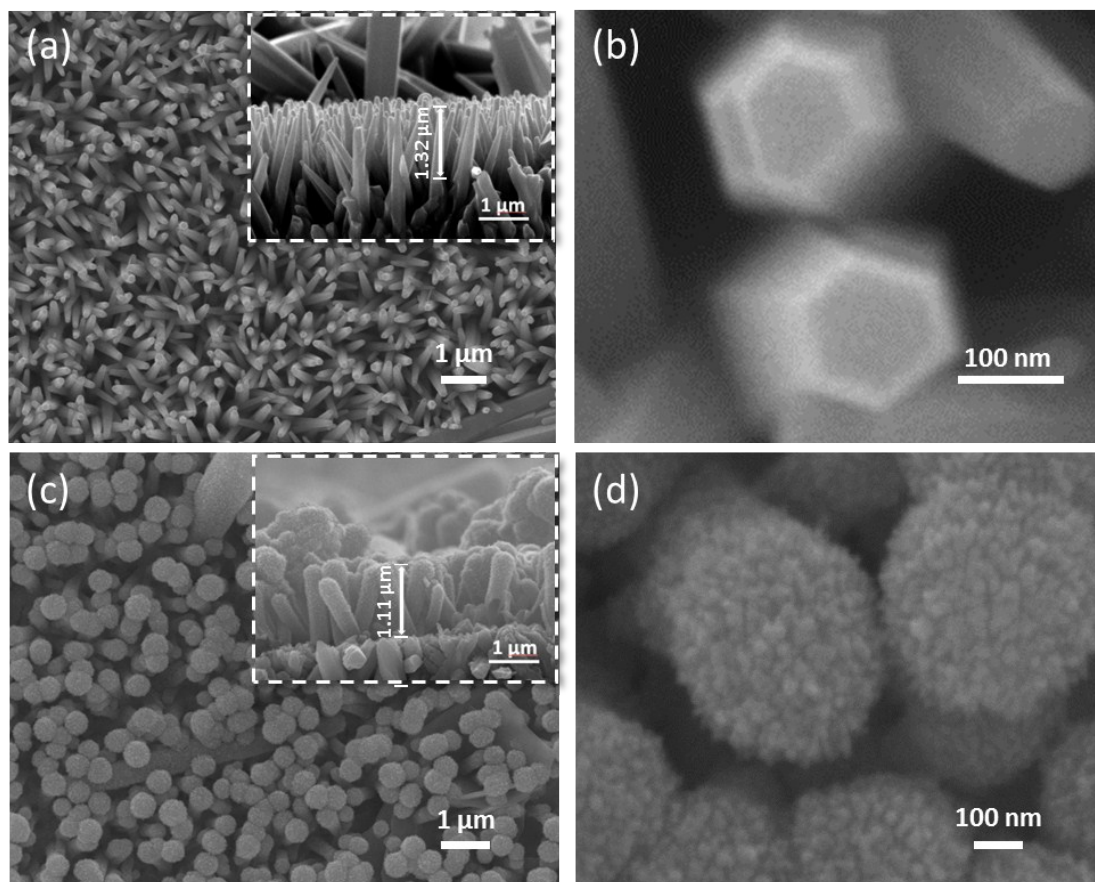
Supplementary Figures

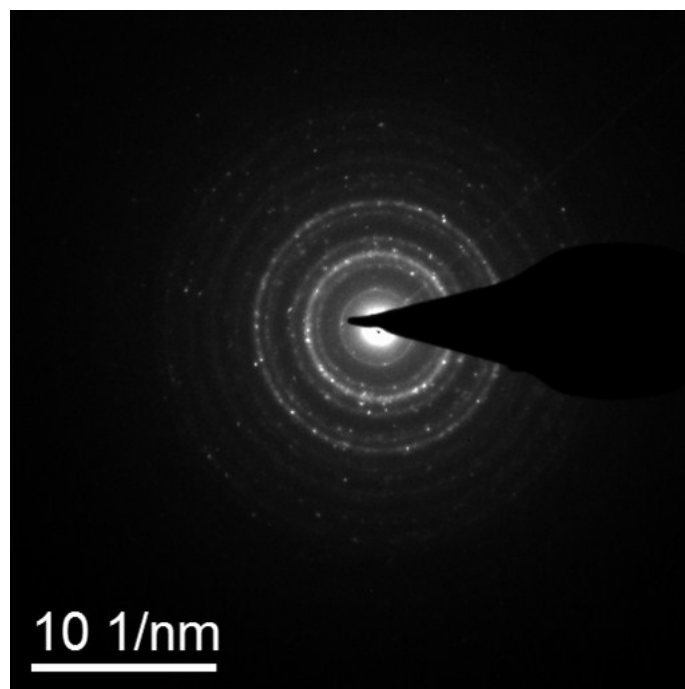

Fig. S1 SEM images of the a), b) ZnO NRAs; c), d) α-Fe$_2$O$_3$/ZnO NTAs.

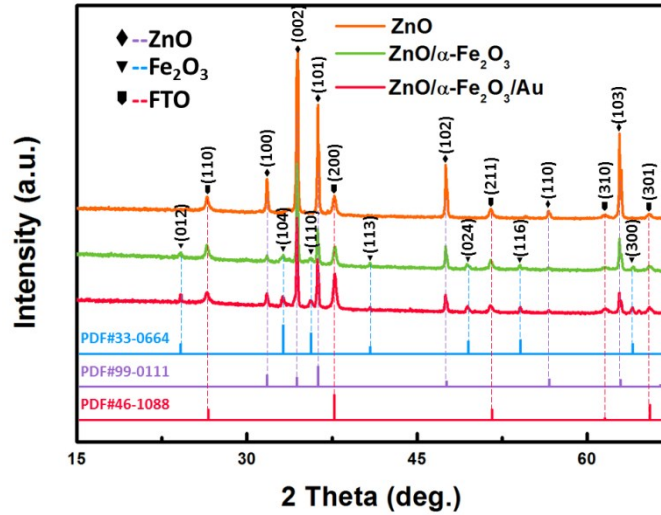**Fig. S2** SAED pattern of ZnO/α-Fe$_2$O$_3$/Au NTAs.

Fig. S3 XRD pattern of ZnO NRAs, ZnO/α-Fe₂O₃ NTAs and ZnO/α-Fe₂O₃/Au NTAs.

Distinct diffraction peaks at 31.77°, 34.42°, 36.25°, 47.54°, 56.59° and 62.85° correspond to (100), (002), (101), (102), (110) and (103) planes of ZnO (JCPDS:99-0111), which indicated that the as-prepared ZnO NRAs has high crystallinity. And the relatively impotent diffraction peaks at 24.14°, 33.15°, 35.61°, 40.85°, 49.48°, 54.09° and 63.99° correspond to (012), (104), (110), (113), (024), (116) and (300) planes of α-Fe₂O₃ (JCPDS:33-0664).

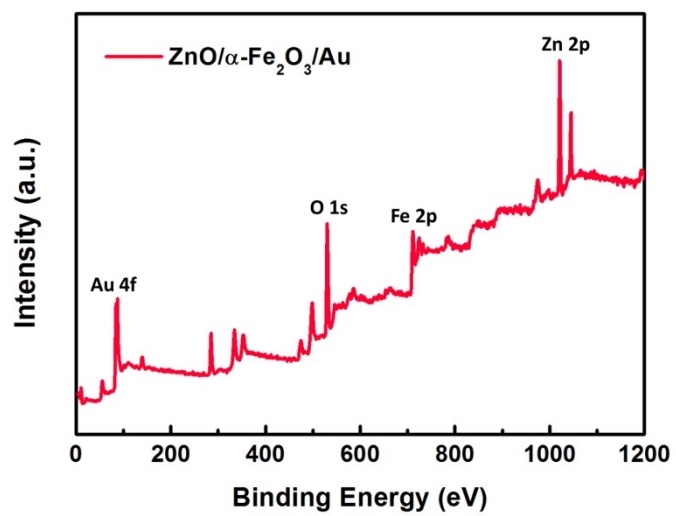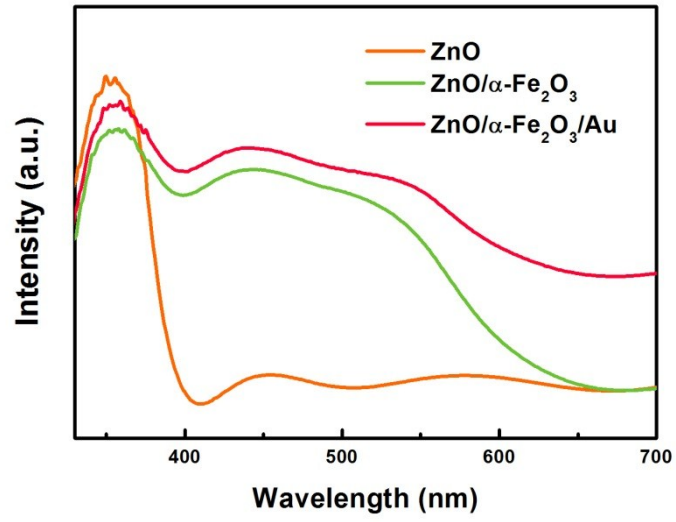**Fig. S4** XPS survey spectrum of ZnO/α-Fe$_2$O$_3$/Au NTAs.

Fig. S5 UV-vis diffuse spectra of ZnO NRAs, α-Fe$_2$O$_3$/ZnO NTAs and Au/α-Fe$_2$O$_3$/ZnO NTAs.
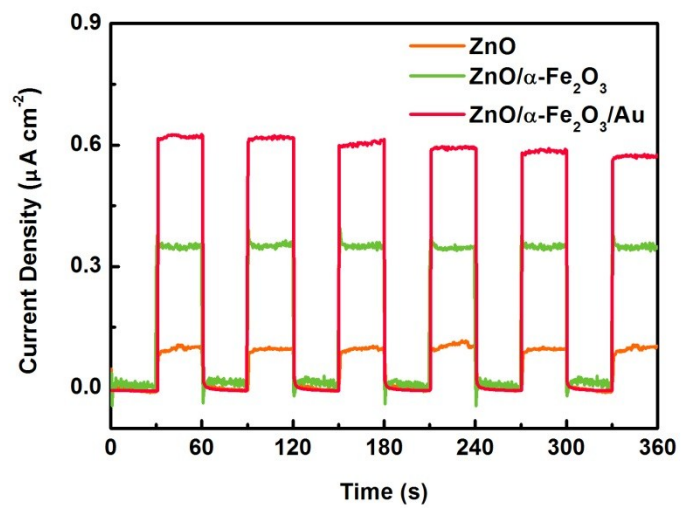
Fig. S6 Transient photocurrents of ZnO, ZnO/α-Fe$_2$O$_3$ and ZnO/α-Fe$_2$O$_3$/Au.
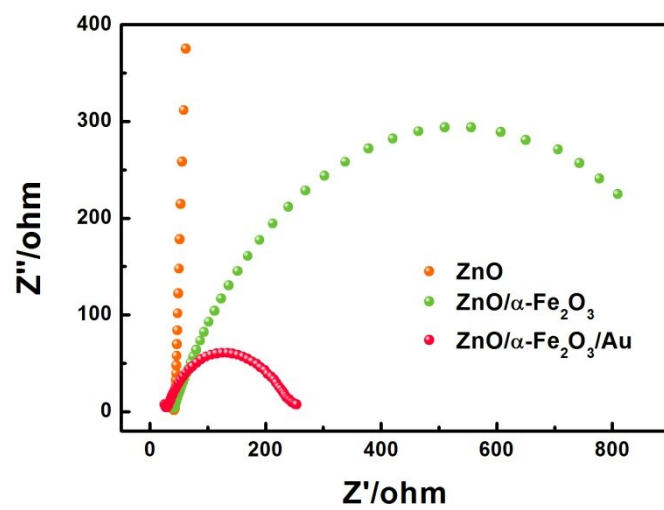
Fig. S7 EIS of ZnO NRAs, ZnO/α-Fe$_2$O$_3$ NTAs and ZnO/α-Fe$_2$O$_3$/Au NTAs.
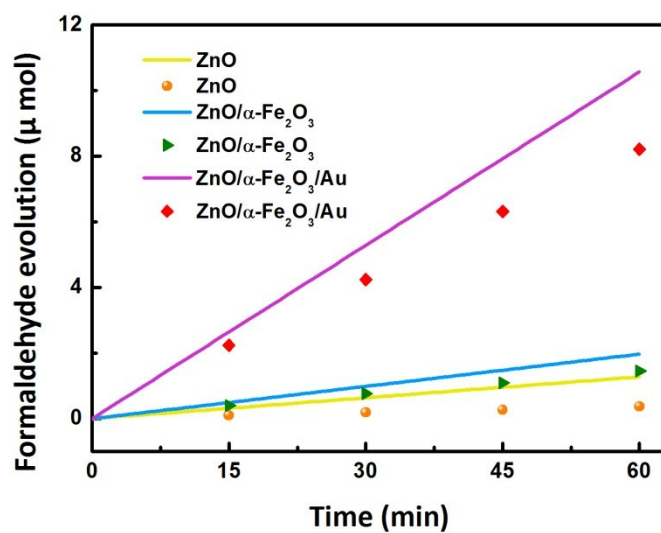
Fig. S8 Formaldehyde evolution calculated from the bulk electrolysis (line) and quantified from the calibration curve (circles) of ZnO NRAs, ZnO/α-Fe$_2$O$_3$ NTAs and ZnO/α-Fe$_2$O$_3$/Au NTAs under full light.

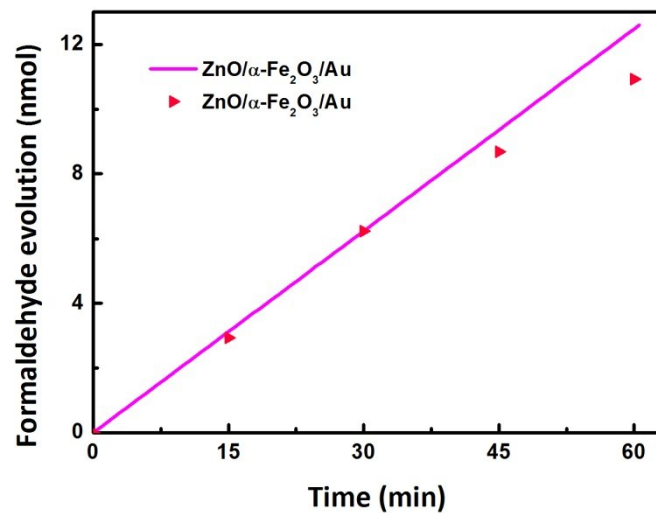**Fig. S9** Formaldehyde evolution calculated from the bulk electrolysis (line) and quantified from the calibration curve (circles) of ZnO/α-Fe$_2$O$_3$/Au NTAs under visible light ($\lambda \geq 420$ nm).

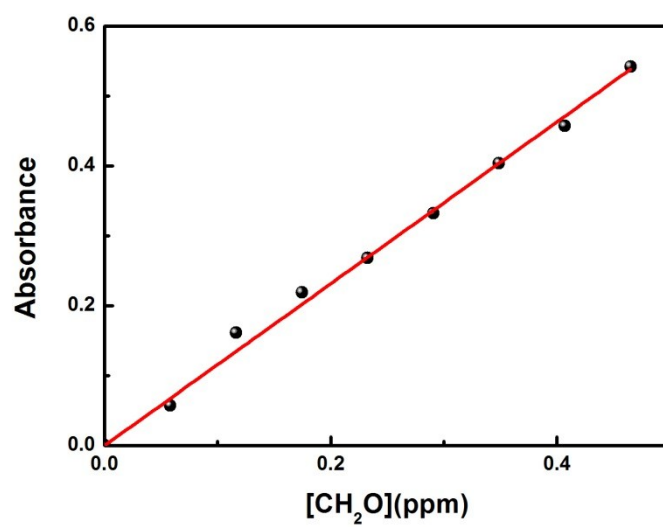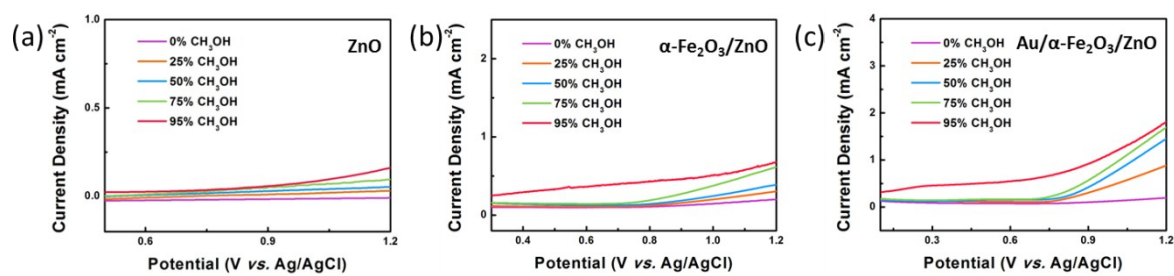**Fig. S10** CH$_2$O calibration curve, prepared follwing the reported procedure.

Fig. S11 Current/potential response of the measured photoanodes under full light. (a) ZnO, (b) ZnO/α-Fe₂O₃ and (c) ZnO/α-Fe₂O₃/Au photoanodes were measured in 0.1 M NaOH aqueous solution (violet) and 25% methanol (orange), 50% methanol (blue), 75% methanol (green) and 95%.

References

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