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Enhanced Hydrogen Production from Ethanol Photoreforming by Site-Specific Deposition of Au on Cu₂O/TiO₂ p-n Junction

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Abstract: Hydrogen production by photoreforming of biomass-derived ethanol is a renewable way of obtaining clean fuel. We developed a site-specific deposition strategy to construct supported Au catalysts by rationally constructing Ti³⁺ defects in TiO₂ nanorods and Cu₂O-TiO₂ p-n junction across the interface of two components. The Au nanoparticles (~2.5 nm) were selectively anchored onto either TiO₂ nanorods (Au@TiO₂/Cu₂O) or Cu₂O nanocubes (Au@Cu₂O/TiO₂) or both TiO₂ and Cu₂O (Au@TiO₂/Cu₂O@Au) with the same Au loading. The electronic structure of supported Au species was changed by forming Au@TiO₂ interface due to the adjacent Ti³⁺ defects and the associated oxygen vacancies while unchanged in Au@Cu₂O/TiO₂ catalyst. The p-n junction of TiO₂/Cu₂O promoted charge separation and transfer across the junction. During ethanol photoreforming, Au@TiO₂/Cu₂O catalyst possessing both the Au@TiO₂ interface and the p-n junction showed the highest H₂ production rate of 8548 μmol g_{cat}⁻¹ h⁻¹ under simulated solar light, apparently superior to both Au@TiO₂ and Au@Cu₂O/TiO₂ catalyst. The acetaldehyde was produced in liquid phase at an almost stoichiometric rate, and C–C cleavage of ethanol molecules to form CH₄ or CO₂ was greatly inhibited. Extensive spectroscopic results support the claim that Au adjacent to surface Ti³⁺ defects could be active sites for H₂ production and p-n junction of TiO₂/Cu₂O facilitates photo-generated charge transfer and further dehydrogenation of ethanol to acetaldehyde during the photoreforming.

Keywords: ethanol reforming; hydrogen production; Au catalyst; Ti³⁺ defect; site-specific deposition

1. Introduction

Hydrogen is extensively used in various industrial processes, e.g., in the petrochemical industry, metallurgy, fine chemical engineering, etc. [1]. Hydrogen, as a clean and renewable fuel, has aroused tremendous attention from both academic and industrial perspectives in the past decades because its energy-extraction process produces only water as a byproduct and emits no greenhouse gases, e.g., CO₂ or any pollutants [2,3]. At present, industrial production of hydrogen depends predominantly on steam reforming of CH₄, an energy-consuming process accompanied by CO₂ emissions. Therefore, it is highly desirable to develop efficient, economical and energy-neutral processes for sustainable H₂ production.

Ethanol could be produced in a sustainable way from huge-amount, low-grade biomass, e.g., lignocelluloses and agriculture waste besides from the conventional petrochemical route [4].

In addition, over several tens of million tons biomass-derived ethanol (bio-ethanol) is produced per year. Therefore, ethanol reforming provides an alternative and promising means of H_2 production from abundant and low-value biomass resources [5,6]. Photoreforming could be one of the most promising potential reforming ways because H_2 production is activated on catalysts by sunlight and is achieved conveniently at room temperature and ambient pressure [7–10]. Another advantage of ethanol photoreforming is that hydrogen in the gas phase and acetaldehyde in the liquid phase can be formed at a stoichiometric rate without CO_2 emission. Acetaldehyde can be used directly in many situations, or can be further converted into other chemicals. Exploiting high-efficiency catalysts is of great importance for achieving high activity in ethanol photoreforming under mild conditions.

Metal-supported TiO_2 photocatalysts have been extensively studied in alcohol photoreforming. Au-supported TiO_2 catalysts have been tuned with respect to metal particle size, annealing conditions in different gas atmospheres, and the phase structure of TiO_2 (anatase and rutile) [11]. The AuPd alloy was further studied for adjusting the electronic structure of metal component, resulting in enhanced activity in this reaction [12]. The films of metal/ TiO_2 supported on glass were tested under UV light irradiation of ethanol/water mixtures, revealing that Pt was slightly more active than Au under those conditions [13]. It is recognized that the longitudinal SPR mode of Au is the main channel for transferring the hot electrons from Au to TiO_2 [14]. The selective deposition of TiO_2 or other electron acceptors at the tip of Au nanorods (NRs) or at the edge of Au nanodisks (NDs) results in highly active plasmonic photocatalysts [15]. Yang and co-workers studied the gold nanodisks and TiO_2 nanophases sandwich between zeolite nanosheets for hydrogen production by plasmonic photocatalytic reforming of methanol [16]. It has been reported that anatase TiO_2 is more active than the rutile one, and the higher surface availability of the former for Au is beneficial to H_2 production from ethanol under UV light irradiation. However, the significant amounts of other gaseous products (mostly CO, CO_2 and CH_4) were also released, probably by further photo-induced decomposition of ethanol [17].

It is highly desirable to explore alternative strategies of catalyst design for enhancing hydrogen production from bio-ethanol photoreforming and simultaneously inhibiting C–C cleavage of ethanol. Herein, we propose a strategy for constructing both p–n junctions between two kinds of semiconducting oxides and Au@ TiO_2 interface by site-specific Au deposition for enhancing hydrogen production from ethanol reforming. The results indicate that the interaction of Au and the adjacent Ti^{3+} defects on Au@ TiO_2 / Cu_2O catalyst affects the electronic structure of Au. In addition, the p–n junction between Cu_2O and TiO_2 facilitates the charge separation and transfer across the interface. The simultaneous construction of the p–n junction and the metal/oxide interface on the supported catalyst results in a record-level H_2 production rate of $8548 \mu mol g_{cat}^{-1} h^{-1}$ under simulated solar light and excellent recycling stability. Accompanied by hydrogen production, acetaldehyde at a stoichiometric rate is solely produced in the liquid phase, indicative of efficient inhibition of C–C cleavage during ethanol reforming.

2. Results and Discussion

The procedure for catalyst preparation is shown in Scheme 1. The experimental details are stated in Section 3 Materials and Methods.

High-resolution transmission-electron microscope (HRTEM) photographs are shown in Figure 1. Cu_2O nanocubes with an average size of ~40 nm were grown on TiO_2 nanorods with a lateral size of 80–120 nm. The close contact between them can be clearly observed and the lattice d-spacing of 0.243 nm and 0.31 nm is assigned to the plane (103) of anatase phase TiO_2 [18] and (110) of cubic phase Cu_2O [19], respectively (Figure 1a). The junction can be formed between two oxides having intimate contact [20]. The Au nanoparticles are site-specific deposited on either TiO_2 or Cu_2O or both, showing the same average size of 2.5 nm and high dispersion (Figure 1b–d). The Au loading is determined to be 0.85 wt% in the three catalysts Au@ Cu_2O / TiO_2 , Au@ TiO_2 / Cu_2O and Au@ TiO_2 / Cu_2O @Au by ICP analyses. The lattice distance of 0.235 nm corresponds to the plane (111) of cubic phase Au [21]. The Au nanoparticles display a well-defined spherical morphology and high crystallinity (Figure 1b–d).

The size and loading of Au nanoparticles change a little, whatever Au is deposited on any support. EDS elemental mappings show the homogeneous distribution of Ti and O in the nanorods and Cu and O in the nanocubes (Figure 1)

Scheme 1. The procedure for catalyst preparation by site-specific deposition of Au on the support.

Figure 1. HRTEM images and EDS mapping of (a) $\text{Cu}_2\text{O}/\text{TiO}_2$ (b) $\text{Au@Cu}_2\text{O}/\text{TiO}_2$, (c) $\text{Au@TiO}_2/\text{Cu}_2\text{O}$, (d) $\text{Au@TiO}_2/\text{Cu}_2\text{O@Au}$, with histogram of Au NPs size distribution of each sample (100 particles are counted).

X-ray diffraction patterns of the samples indicate that TiO_2 exist in the form of anatase phase (JCPDS No. 21-1272). The second phase in the samples with p-n junction can be indexed to cubic Cu_2O (Figure S1). The diffraction related to Au phase is not observed in the Au-supported samples because of the low loading of Au (~ 0.85 wt%) and/or high dispersion of small-sized Au particles (~ 2.5 nm) on the surface of the support. X-ray photoelectron spectra (XPS) were used to analyze the chemical

valence and electronic structure of each element. Two peaks were fitted at binding energy (B.E.) of 457.9 and 458.3 eV in the Ti 2p_{3/2} region of Cu₂O/TiO₂ and Au-supported catalysts, corresponding to Ti³⁺ and Ti⁴⁺ species, respectively (Figure 2A) [22–24]. The B.E. values hardly shift among these samples. However, the peak area ratio of Ti³⁺ to Ti⁴⁺ is lower when Au is deposited on TiO₂ i.e., Au@TiO₂/Cu₂O and Au@TiO₂/Cu₂O@Au (0.96 and 1.03), compared to that of Au-free TiO₂/Cu₂O and Au deposition on Cu₂O i.e., Au@Cu₂O/TiO₂ (1.17 and 1.11) (Table 1). This indicates that the site-specific deposition of Au differs at defect-rich TiO₂ and Cu₂O, leading to a variation to Ti³⁺ content when Au is deposited to TiO₂. In our previous studies, the ratio of Ti³⁺:Ti⁴⁺ increased as the amount of NaBH₄ increased. When the ratio reaches around 1, even when increasing the amount of NaBH₄, the ratio will not increase any more, which suggests that it is approaching saturation of Ti³⁺:Ti⁴⁺ ratio [25].

Figure 2. XPS spectra of (A) Ti 2p, (B) O 1s: (a) Cu₂O/TiO₂, (b) Au@TiO₂/Cu₂O, (c) Au@TiO₂/Cu₂O@Au, (d) Au@Cu₂O/TiO₂, and (C) Au 4f core level spectra: (a) Au@TiO₂/Cu₂O, (b) Au@TiO₂/Cu₂O@Au, (c) Au@Cu₂O/TiO₂.

Table 1. Ti 2p XPS analyses of the samples.

Sample	B.E. in 2p _{3/2} (eV)		B.E. in 2p _{1/2} (eV)		Ti ³⁺ /Ti ⁴⁺ Ratio ¹
	Ti ³⁺	Ti ⁴⁺	Ti ³⁺	Ti ⁴⁺	
TiO ₂ /Cu ₂ O	457.9	458.3	463.4	464.3	1.17/1
Au@TiO ₂ /Cu ₂ O	457.9	458.3	463.3	464.2	0.96/1
Au@TiO ₂ /Cu ₂ O@Au	457.9	458.3	463.4	464.3	1.03/1
Au@Cu ₂ O/TiO ₂	457.8	458.2	463.4	464.2	1.11/1

¹ The value refers to the ratio of the respective integral peak area.

The O 1s spectra were deconvoluted to three peaks at 530.0 eV, 532.0 eV and 533.5 eV (Table 2), respectively, which are assigned to lattice oxygen (O_L), adsorbed oxygen adjacent to surface oxygen vacancy (O_V) and surface chemisorbed or dissociated oxygen species (O_C) (Figure 2B) [25]. The B.E. values of each oxygen species shift little among different samples. Nevertheless, the O_V/O_L ratio associated with the peak area is decreased when Au is deposited on Au@TiO₂/Cu₂O and Au@TiO₂/Cu₂O@Au (0.71 and 0.74) compared with that of TiO₂/Cu₂O (0.86). The O_V/O_L ratio in Au@Cu₂O/TiO₂ (0.81) is close to that of TiO₂/Cu₂O (0.86). This tendency is consistent with that of the Ti³⁺/Ti⁴⁺ ratio. The amount of oxygen vacancy (O_V) decreases with the decreasing Ti³⁺ content because the Ti³⁺ defects are closely associated with O_V in defect-rich TiO₂ support [26].

Table 2. O 1s XPS analyses of the samples.

Sample	B.E. (eV)			O _V /O _L Ratio ¹
	O _L	O _V	O _C	
TiO ₂ /Cu ₂ O	530.0	532.0	533.5	0.86
Au@TiO ₂ /Cu ₂ O	530.0	532.0	533.5	0.71
Au@TiO ₂ /Cu ₂ O@Au	530.0	532.0	533.5	0.74
Au@Cu ₂ O/TiO ₂	530.0	532.0	533.5	0.81

¹ The value refers to the ratio of the respective integral peak area.

Au 4f spectra of each Au-supported catalyst were shown and compared in Figure 2C. The main Au 4f peaks are located at 87.8 eV (4f_{5/2}) and 84.0 eV (4f_{7/2}). The fitted peak appears at B.E. of 84.0 eV in the Au 4f_{7/2} region of Au@Cu₂O/TiO₂, which is assigned to Au⁰ species [27]. In contrast, when Au is deposited on both TiO₂ and Cu₂O, the B.E. shifts to a lower value of 83.7 eV, with a negative shift of 0.3 eV (Table 3). The negative shift of B.E. hints at the increased electron density of Au⁰ species on Au@TiO₂/Cu₂O@Au compared to that on Au@Cu₂O/TiO₂. The B.E. continually shifts to a lower value of 83.4 eV when Au is only deposited on TiO₂. The more negative shift (−0.6 eV) indicates higher electron density of Au because of strong metal-support interaction (SMSI) between Au nanoparticles and defect-rich TiO₂ in Au@TiO₂/Cu₂O [28,29]. The negatively charged Au adjacent to Ti³⁺ sites associated with oxygen vacancies could be active sites for ethanol reforming [25]. The higher electron density of Au on Au@TiO₂/Cu₂O facilitates proton reduction to hydrogen during ethanol photoreforming.

Table 3. Au 4f XPS analyses of the samples.

Sample	B.E.(eV)	ΔB.E.(eV) ¹
Au@TiO ₂ /Cu ₂ O	83.4	−0.6
Au@TiO ₂ /Cu ₂ O@Au	83.7	−0.3
Au@Cu ₂ O/TiO ₂	84.0	−

¹ The value refers to the shift compared to that of Au@Cu₂O/TiO₂.

XPS spectra were carried out to determine the chemical states of Cu species in the catalysts. Figure 3A shows the Cu 2p core level spectra. The binding energies at 932.1 eV and 951.9 eV, respectively, in Cu 2p_{3/2} and Cu 2p_{1/2} region were assigned to Cu⁺ species [30]. The binding energies hardly shift among these catalysts. There is no shake-up satellite peak in the Cu 2p spectra. The absence of the satellite peak excludes the existence of Cu²⁺ species [31,32]. However, the Cu⁺ and Cu⁰ species cannot be distinguished in Cu XPS spectra because the binding energies assigned to Cu⁺ and Cu⁰ are very close to each other. The difference in binding energies is merely around 0.1–0.2 eV [33,34]. Consequently, Cu LMM Auger spectra were analyzed to distinguish between Cu⁰ and Cu⁺ species (Figure 3B). The spectra were fitted to two peaks at 917.0 eV and 919.0 eV, respectively, which is assigned to Cu⁺ and Cu⁰ species [35]. The Cu⁺ is the dominating species on the basis of Auger spectra. The coexistence of Cu⁺ and Cu⁰ species in Cu₂O nanocubes or nanoparticles is also observed in the previous literatures [36]. There is no shift in the kinetic energies regardless of Au deposition on either Cu₂O or TiO₂. This is an indication that the chemical states of Cu₂O changes little in these catalysts.

Figure 3. (A) Cu 2p core level spectra: (a) $\text{Cu}_2\text{O}/\text{TiO}_2$, (b) $\text{Au@TiO}_2/\text{Cu}_2\text{O}$, (c) $\text{Au@Cu}_2\text{O}/\text{TiO}_2$, (d) $\text{Au@TiO}_2/\text{Cu}_2\text{O@Au}$, and (B) Cu LMM Auger spectra: (a) $\text{Cu}_2\text{O}/\text{TiO}_2$, (b) $\text{Au@TiO}_2/\text{Cu}_2\text{O}$, (c) $\text{Au@Cu}_2\text{O}/\text{TiO}_2$, (d) $\text{Au@TiO}_2/\text{Cu}_2\text{O@Au}$.

The electron paramagnetic resonance (EPR) spectra are shown in Figure 4A. An intense EPR signal appears at a g value of 2.003 for $\text{Cu}_2\text{O}/\text{TiO}_2$. This signal is usually assigned to surface O-species, formed via the interaction of dioxygen and Ti^{3+} defects in TiO_2 [24,37–39]. The EPR signal appears at the same g value for $\text{Au@Cu}_2\text{O}/\text{TiO}_2$, $\text{Au@TiO}_2/\text{Cu}_2\text{O@Au}$ and $\text{Au@TiO}_2/\text{Cu}_2\text{O}$. The intensity of the signal in Au-supported catalysts is lower than that in un-supported $\text{Cu}_2\text{O}/\text{TiO}_2$. The intensity of O-related EPR signal ($g = 2.003$) could be associated with the $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio in TiO_2 . The lower signal intensity in Au-supported catalysts indicates the smaller $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio. The $\text{Au@TiO}_2/\text{Cu}_2\text{O}$ has the smallest $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio of 0.96 among these samples, showing the lowest signal intensity of g value. This is consistent with the results presented in XPS Ti 2p analyses (Table 1).

The digital photos of the catalysts display that all are in black color (Figure 4B). The UV-Vis absorption spectra were compared in Figure 4C. Compared to the spectrum of TiO_2 , the $\text{Cu}_2\text{O}/\text{TiO}_2$ junction shows stronger absorption in the visible light region besides in the UV regime. The Au-supported catalysts possess more intensive absorption throughout the visible light wavelength. The absorption band (~ 560 nm) associated with Au surface plasmon resonance (SPR) is not clearly observed within the UV-vis absorption spectra of Au-supported catalysts because of the intense visible absorption of $\text{Cu}_2\text{O}/\text{TiO}_2$ itself [40]. The fluorescence emission spectra of TiO_2 and $\text{Cu}_2\text{O}/\text{TiO}_2$ showed a broad band peaked at 423 nm under the excitation of 350 nm (Figure 4D). The latter has lower emission intensity, indicating that the carrier recombination is inhibited due to the existence of $\text{Cu}_2\text{O}/\text{TiO}_2$ junction. After Au is deposited on either TiO_2 or Cu_2O , the emission intensity of supported catalysts further decreases. It indicates that forming the interface of Au and semiconducting oxides facilitates the separation of photogenerated electrons and photogenerated holes by charge transfer across the metal-oxide interface [22,41].

Figure 4. The EPR spectra (A) and digital photos (B) of $\text{Cu}_2\text{O}/\text{TiO}_2$, $\text{Au@Cu}_2\text{O}/\text{TiO}_2$, $\text{Au@TiO}_2/\text{Cu}_2\text{O}$, and $\text{Au@TiO}_2/\text{Cu}_2\text{O@Au}$; UV-Vis absorption spectra (C) and Fluorescence emission spectra (D) of TiO_2 , $\text{Cu}_2\text{O}/\text{TiO}_2$, $\text{Au@Cu}_2\text{O}/\text{TiO}_2$, $\text{Au@TiO}_2/\text{Cu}_2\text{O@Au}$, and $\text{Au@TiO}_2/\text{Cu}_2\text{O}$. The excitation wavelength is 350 nm.

The photocurrent tests were carried out to evaluate the charge separation within the catalysts. The photocurrent–time traces of photoelectrodes were obtained in the photoelectrochemical cell at a bias of 1.23 V vs. RHE under chopped AM 1.5G light illumination (Figure 5). The Au loading on $\text{Cu}_2\text{O}/\text{TiO}_2$ enhances the photocurrent compared to $\text{Cu}_2\text{O}/\text{TiO}_2$ itself, which indicates the improved charge separation across the metal/oxide interface. The Au@TiO_2 electrode shows a higher photocurrent than $\text{Au@Cu}_2\text{O}/\text{TiO}_2$. The interface of Au and TiO_2 is more favorable to charge separation than that of Au and Cu_2O due to the lower conduction band potential of TiO_2 than that of Cu_2O [42]. In addition, the existence of Ti^{3+} defects associated with adjacent oxygen vacancies intensifies the interaction of Au and TiO_2 [25]. The $\text{Au@TiO}_2/\text{Cu}_2\text{O}$ electrode exhibits the highest photocurrent among all electrodes, 2.5 times higher than Au@TiO_2 . This hints at the contribution of $\text{TiO}_2/\text{Cu}_2\text{O}$ p-n junction combined with the interface of Au and TiO_2 to charge separation and transfer. The photocurrent of $\text{Au@TiO}_2/\text{Cu}_2\text{O}$ is also higher than $\text{Au@TiO}_2/\text{Cu}_2\text{O@Au}$. This is an indication that the site-specific deposition of Au on TiO_2 leads to charge separation more efficiently under light illumination than the random deposition of Au on both TiO_2 and Cu_2O .

Figure 5. Photocurrent-time traces of photoelectrodes at a bias of 1.23 V vs. RHE under chopped AM 1.5G illumination ($100 \text{ mW}\cdot\text{cm}^{-2}$), back illumination. Solution: 0.1 M phosphate buffer (pH 7).

The photoreforming of ethanol was achieved using pure ethanol in an Ar atmosphere (1.4 bar) under simulated solar irradiation. The H_2 production rate is contrasted on each catalyst (Figure 6A). The rate of H_2 production reaches $6932 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ on $\text{Au@Cu}_2\text{O/TiO}_2$, 8.35 times higher than that on $\text{Cu}_2\text{O/TiO}_2$ ($830 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$, Table 4). It is apparent that proton reduction is greatly accelerated on the Au-supported catalyst for H_2 production. Additionally, the charge separation is improved by loading Au on the semiconductor, evidenced by photocurrent measurements (Figure 5). The Au@TiO_2 catalyst exhibits higher activity ($7143 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$) towards H_2 production than $\text{Au@Cu}_2\text{O/TiO}_2$. This suggests that constructing the interface of Au and TiO_2 is more favorable than that of Au and Cu_2O , which could direct the structural design of catalysts for ethanol photoreforming. The rate of H_2 production on $\text{Au@TiO}_2/\text{Cu}_2\text{O}$ ($8548 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$) is apparently higher than that on either Au@TiO_2 ($7143 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$) or $\text{Au@TiO}_2/\text{Cu}_2\text{O@Au}$ ($7348 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$). Table S4 compares the H_2 yield rates reported for TiO_2 -supported noble-metal catalysts with the result in this work. The p-n junction between TiO_2 and Cu_2O contributes the enhanced H_2 production. However, the selective deposition of Au on defect-rich TiO_2 is essential for higher activity because the $\text{Au-O}_v\text{-Ti}^{3+}$ sites are more active in ethanol photoreforming [25]. The quantity of $\text{Au-O}_v\text{-Ti}^{3+}$ sites is relatively less in randomly deposited $\text{Au@TiO}_2/\text{Cu}_2\text{O@Au}$ than in site-specifically deposited $\text{Au@TiO}_2/\text{Cu}_2\text{O}$. As a consequence, the latter shows higher activity than the former. In addition, the lower H_2 production rate of $\text{Au@Cu}_2\text{O/TiO}_2$ may be due to the alloying of Au-Cu, leading to a smaller number of active sites on gold according to the previous report [43].

Table 4. H_2 production via photoreforming of ethanol on the catalysts under simulated solar light.

Catalysts	Production Rate ($\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$) ¹					
	Gas Phase				Liquid Phase	
	H_2	CH_4	CO	CO_2	CH_3CHO	CH_3COOH
$\text{Au@TiO}_2/\text{Cu}_2\text{O}$	8548	5	-	3	8806	-
$\text{Au@Cu}_2\text{O/TiO}_2$	6932	12	3	9	7239	-
$\text{Au@TiO}_2/\text{Cu}_2\text{O@Au}$	7348	13	-	7	7561	-
Au@TiO_2	7143	7	-	7	7356	-
$\text{Cu}_2\text{O/TiO}_2$	830	-	-	-	1020	-
TiO_2	136	-	-	-	273	-

¹ Suspension of the photocatalyst (1 g/L) in ethanol under stirring were irradiated with simulated solar light (100 mW cm^{-2}) at Ar atmosphere (1.4 bar) at 25 °C for 6 h.

Figure 6. (A) H₂ and acetaldehyde production rate via the photoreforming of ethanol under simulated solar light (AM 1.5G). (B) The cycle tests of Au@TiO₂/Cu₂O for photocatalytic hydrogen evolution. Conditions: suspension of the photocatalyst (1 g/L) in ethanol under stirring were irradiated with simulated solar light at Ar atmosphere (1.4 bar) for 6 h.

The products except H₂ in the gas phase, e.g., CH₄, CO, CO₂, are below 0.3% on all catalysts (Table 4), which clearly indicates the efficient inhibition of C–C cleavage during the photoreforming. Also, high-purity H₂ can be produced on these catalysts. For instance, the purity of H₂ is beyond 99.9% on Au@TiO₂/Cu₂O catalyst. Acetaldehyde is the only detectable product in the liquid phase, evidenced by GC-MS analysis (Figure S2). The high selectivity of acetaldehyde is due to the absence of O₂ activation to peroxide intermediates and hydroxyl species on the surface of Au NPs under Ar ambient [43,44]. In addition, acetaldehyde is produced in almost stoichiometric yield with H₂, which is consistent with the reforming pathway of ethanol via a redox process [11]. The photo-generated holes in the valence band of semiconductor oxidize ethanol to acetaldehyde and the electrons on the active sites adjacent to Au reduce protons to H₂ during the process.

The optimal Au@TiO₂/Cu₂O catalyst was recycled five times and the H₂ yield was hardly decreased (Figure 6B). The structural stability of catalysts was further evidenced by HRTEM and Ti 2p, O 1s, Au 4f XPS and Cu LMM Auger analyses. The size of Au particles remains 2.5 nm, the same as that before the reactions (Figure S3). In addition, the Au loading after reaction is not changed by ICP measurement (0.84 wt%). The Ti³⁺/Ti⁴⁺ ratio and O_V/O_L ratio in the catalyst have no change before and after reactions (Figure S4, Tables S1 and S2). The peak in the Au 4f region appears at 83.5 eV and has little shift compared to that before reactions (Figure S4, Table S3). Additionally, the peaks in Cu 2p XPS and Cu LMM Auger spectra keep unchanged after photoreforming (Figure S5). These findings verify that the catalyst is structurally stable and keeps activity after repeated use.

The in situ FTIR spectra of ethanol adsorption on the catalysts were first collected in the dark after adsorption of ethanol for 40 min, and then recorded every hour during photoreforming. The spectra of the three supported catalysts showed intensive absorption bands at 1000–1200 cm^{−1}, 1200–1500 cm^{−1}, 2700–3100 cm^{−1}, and 3600–3800 cm^{−1}, which are respectively assigned to the vibrations of ν(C–O), δ(CH_x), ν(CH_x), and ν(O–H) of ethanol (Figure 7) [45].

Figure 7. In situ FTIR spectra of ethanol adsorption on the catalysts during the photoreforming: (A) Au@Cu₂O/TiO₂, (B) Au@TiO₂/Cu₂O, (C) Au@TiO₂/Cu₂O@Au.

The band at 1755 cm^{−1} gradually increases with the extension of irradiation time, which corresponds to the vibration related with acetaldehyde molecule [46]. This is consistent with the increased acetaldehyde production in liquid phase with the reaction. The band shifts little

among the three catalysts. The band at around 2350 cm^{-1} , assigned to the vibration of CO_2 [47], does not appear in the FTIR spectra. This verifies that the C–C cleavage of ethanol is greatly inhibited on the three Au-supported catalysts during the photoreforming. Consequently, the dehydrogenation of ethanol to acetaldehyde is the dominating step, accompanied with high-purity H_2 production on these catalysts.

The energy levels of semiconductors play a critical role in the activity and selectivity of ethanol photoreforming. In a catalyst with a p–n junction, the charge separation and transfer are strongly dependent on the relationships of energy levels [48]. The flat band potentials (E_{fb}) of the TiO_2 nanorods and Cu_2O nanocubes were determined by electrochemical Mott–Schottky measurements at varied frequencies and room temperature. The Mott–Schottky plots of TiO_2 exhibit positive slopes, indicative of their characteristic of n-type semiconductor (Figure 8A). The E_{fb} values are estimated by extrapolating the linear portion of the plots measured at varied frequencies to the intercept of x-axis. It is generally considered that the bottom of the conduction band (CB) in n-type semiconductors is approximately equal to its flat band potential. [49,50] Consequently, the conduction band of TiO_2 nanorod is -0.63 V vs. Ag/AgCl . This potential was converted to -0.02 V vs. RHE according to the following formula [51].

$$E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + 0.197 + 0.059\text{pH}, \quad (1)$$

The bandgap of TiO_2 nanorod was estimated to be 2.76 eV using the Kubelka–Munk equation, i.e., $F(R) = (1 - R)^2/2R$, where R is the reflectance (Figure S6). This value is smaller than that reported for bulk anatase TiO_2 of $\sim 3.2\text{ eV}$ [52]. It is documented that the Ti^{3+} defect-rich anatase TiO_2 exhibits narrower bandgap owing to the involvement of defect energy levels [53]. The valence band TiO_2 nanorod is calculated to be 2.74 eV from the bandgap and the conduction band level.

The Mott–Schottky plots of Cu_2O show negative slope, an indication of p-type semiconductor (Figure 8B). The flat band potential of 0.65 V vs. Ag/AgCl was converted to 1.26 V vs. RHE according to Formula (1). It is usually considered that the bottom of valence band (VB) in p-type semiconductors was 0.30 V more positive than the flat band potential [54,55]. The valence band level of Cu_2O is 1.56 V vs. RHE. Based on the bandgap of Cu_2O (2.2 eV) [56,57], the conduction band (CB) level of Cu_2O is estimated to be -0.64 V .

Figure 8. Mott–Schottky plots of (A) TiO_2 nanorods and (B) Cu_2O nanocubes measured at varied frequencies and room temperature. Solution: 0.1 M phosphate buffer ($\text{pH } 7$).

Based on the findings above, we proposed possible charge transfer pathways on the $\text{Au@TiO}_2/\text{Cu}_2\text{O}$ catalyst during ethanol photoreforming. The p–n junction is formed when p-type Cu_2O and n-type TiO_2 come into contact with each other (Scheme 2). The photo-generated holes are transferred from the valence band of TiO_2 to that of Cu_2O owing to the more positive valence band level of TiO_2 .

The electrons generated on Cu_2O under visible light irradiation are transferred to the conduction band of TiO_2 . In addition, the hot electrons of Au under visible light irradiation are transferred to the conduction band of TiO_2 due to the SPR effect of Au. The strong interaction between Au and defect-rich TiO_2 enhances the hot electron transfer from Au to the interface of Au/ TiO_2 . As a consequence, the interface of Au and TiO_2 is rich in the electrons, leading to high electron density on the Au-Ov- Ti^{3+} interfacial sites. The proton reduction is promoted on the electron-rich interfacial sites, resulting in higher H_2 production rate than the $\text{Au@Cu}_2\text{O}/\text{TiO}_2$ catalyst without the interfacial sites. Consequently, the dual effects of Au-Ov- Ti^{3+} active sites and p-n junction endow $\text{Au@TiO}_2/\text{Cu}_2\text{O}$ catalyst with higher activity towards ethanol photoreforming by the site-specific deposition of Au on defect-rich TiO_2 nanorods.

Scheme 2. Diagram of energy levels and charge transfer on $\text{Au@TiO}_2/\text{Cu}_2\text{O}$ catalyst.

3. Materials and Methods

3.1. Materials

$\text{C}_2\text{H}_5\text{OH}$ (anhydrous ethanol), CH_3OH (methanol), CuSO_4 (anhydrous copper sulfate), PVP (polyvinyl pyrrolidone), TBOT (tetrabutyl titanate), HNO_3 (nitric acid), NaBH_4 (sodium borohydride), AA (ascorbic acid), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, EDTA (Ethylenediamine) were obtained from Shanghai Aladdin Biochemical Technology Co. Ltd. (Beijing, China). H_2 (99.9%), N_2 (99.9%) and Ar (99.9%) were supplied by Beijing Haipu Gas Co. Ltd. (Beijing, China). All reagents were of analytical grade and used as received. Deionized water was used throughout the experiments.

3.2. Synthesis of Defect-Rich TiO_2 Nanorods

The defect-rich TiO_2 nanorods were synthesized by a NaBH_4 reduction method according to a previous literature [22]. In a typical procedure, the mixture ($\text{TiO}_2/\text{NaBH}_4 = 2:1$ molar ratio) was continuously stirred for 30 min and treated at 350°C for 1 h in a flow of N_2 . The sample was washed with diluted HCl solution and water thoroughly. The sample was named as TiO_2 .

3.3. Synthesis of Cu_2O Nanocubes

The Cu_2O nanocubes were prepared by a chemical precipitation method, modified from a literature's one [58]. In a typical run, 155 mg of CuSO_4 and 400 mg of PVP were dissolved in 160 mL of deionized water to obtain a light blue solution. The pH was adjusted to 10 by dropwise addition of NaOH (1 M). An amount of 176 mg of ascorbic acid (AA) was dispersed in the solution to reduce Cu^{2+} to Cu_2O . The suspension was stirred for 20 min. Subsequently, the suspension was centrifuged and washed thoroughly with deionized water and ethanol to remove PVP. The product was collected after

the color of solution changed from light blue to brownish yellow. The solid product was finally dried under vacuum at 60 °C.

3.4. Synthesis of $\text{Cu}_2\text{O}/\text{TiO}_2$

2 g of TiO_2 nanorod sample was added into the CuSO_4 and PVP solution, and the pH of the solution was adjusted to 10 with an aqueous solution of NaOH (1 M). Subsequently, AA was added to the solution and stirred for 20 min. The solid product was collected by centrifugation and washed with ethanol and water. The product was finally dried under vacuum at 60 °C.

3.5. Synthesis of Au@TiO_2 and $\text{Au@TiO}_2/\text{Cu}_2\text{O}$

2 g of TiO_2 nanorod sample was dispersed in 200 mL of H_2O containing 2 mL of HAuCl_4 solution (0.051 M). The pH of suspension was adjusted to 10 with an aqueous solution of NaOH (1 M). 10 mL of methanol was added and stirred for 3 h. The Au@TiO_2 sample was obtained by a photo-reduction method under UV irradiation. After the photo-reduction, the precipitation was centrifuged, washed with water thoroughly to neutral and dried in vacuum at 60 °C. The Au@TiO_2 product was suspended in 160 mL of aqueous solution containing 155 mg of CuSO_4 and 400 mg of PVP. The pH was adjusted to 10 with an aqueous solution of NaOH (1 M). 176 mg of AA was added and stirred for 20 min. The solid product was collected by centrifugation and washed with by ethanol and water and finally dried under vacuum at 60 °C. The product was denoted as $\text{Au@TiO}_2/\text{Cu}_2\text{O}$.

3.6. Synthesis of $\text{Au@Cu}_2\text{O}/\text{TiO}_2$

The as-synthesized Cu_2O and PVP was suspended in 100 mL of H_2O . 2 mL of HAuCl_4 solution (0.051 M) was added and the pH of suspension was adjusted to 10 with an aqueous solution of NaOH (1 M). 10 mL of methanol was added and stirred for 3 h. The $\text{Au@Cu}_2\text{O}$ sample was obtained by a photo-reduction method under visible light irradiation. The as-synthesized TiO_2 nanorod was suspended in the solution and stirred for 1 h. The solid product was collected by centrifugation and washed with by ethanol and water and finally dried under vacuum at 60 °C. The product was denoted as $\text{Au@Cu}_2\text{O}/\text{TiO}_2$.

3.7. Synthesis of $\text{Au@TiO}_2/\text{Cu}_2\text{O@Au}$

2 g $\text{Cu}_2\text{O}/\text{TiO}_2$ sample was suspended in 200 mL of H_2O containing 2 mL of HAuCl_4 solution (0.051 M). The pH of suspension was adjusted to 10 with an aqueous solution of NaOH (1 M). 10 mL of methanol was added and stirred for 3 h. The $\text{Au@TiO}_2/\text{Cu}_2\text{O@Au}$ sample was obtained by a photo-reduction method under UV-visible light irradiation. The solid product was collected by centrifugation and washed with ethanol and water and finally dried under vacuum at 60 °C.

3.8. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were obtained by a Shimadzu XRD-6000 diffractometer using graphite-filtered $\text{CuK}\alpha$ radiation (40 kV, 30 mA, $\lambda = 0.15418$ nm) in a 2theta range of 10–70°.

Transmission electron microscopy (TEM) measurements were carried out on a JEOL JEM-3010 high-resolution transmission electron microscope.

Elemental analysis was performed on a Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectrometer (ICP-AES).

The XPS spectra were recorded on a Thermo VG ESCALAB MK II X-ray photoelectron spectrometer at a pressure of 2×10^{-9} Pa using $\text{Al K}\alpha$ X-ray as the excitation source (1486.6 eV). The positions of all binding energies were calibrated using the C1s line at 284.6 eV.

UV-visible diffuse reflectance spectra were performed on a Shimadzu UV-3000 spectrometer equipped with an integrating sphere attachment with BaSO_4 (10 mg) as reference.

Photoluminescence (PL) emission spectra were recorded by a Hitachi F-7000 spectrofluorometer using laser excitation at a wavelength of 350 nm.

Electron paramagnetic resonance (EPR) measurements were performed on a Bruker E500 spectrometer with a 9.53 GHz X-band. The sample mass was 50 mg. The spectra were recorded in the magnet field range of 318–328 mT.

The liquid phase products were determined by GC-MS measurements using a Thermo Fisher ISQ Trace1300 and the sample volume was 1 μ L.

Electrochemical impedance spectroscopy (EIS) was performed on an electrochemical workstation at an open-circuit voltage of 0.3 V vs. RHE under illumination with 10 mV amplitude of perturbation and a frequency between 1.0 kHz, 1.5 kHz and 2.0 kHz. Mott-Schottky plots were measured at room temperature in the dark.

In situ Fourier Transform Infrared Spectroscopy (FTIR) was conducted in an in situ reaction cell on a Bruker Tensor II spectrometer installed with MCT narrow-band detector. The sample was pretreated in a flow of high-purity N_2 at 100 $^{\circ}$ C for 1 h. After an initial scan as the background spectrum, ethanol was induced into the cell through a flow of N_2 for 30 min. After flowing N_2 to remove the residual ethanol vapor, the FTIR spectra were collected in the range of 4000–950 cm^{-1} at room temperature.

3.9. Photoreforming of Ethanol

In a typical run, 25 mg of catalyst was added to 25 mL of ethanol and ultrasonically dispersed for 15 min. The suspension was transferred into a high-pressure stainless steel reactor (volume: 50 mL) equipped with a sapphire crystal window. A flow of Ar was purged into the reactor for 30 min and the reactor was evacuated. The Ar was re-purged and the pressure in the reactor was maintained at 1.4 bar. The suspension was irradiated by a 300 W Xenon lamp equipped with an AM 1.5G filter (100 $mW \cdot cm^{-2}$) under magnetic stirring for 6 h. After the reaction, the catalyst was removed from the solution by filtration. The gaseous products were detected by an online gas chromatograph (GC-2014C, Shimadzu, Japan) equipped with a high-sensitivity thermal conductivity detector (TCD) and Ar was used as the carrier gas. The liquid products were analyzed by a gas chromatograph (GC-2014C, Shimadzu) equipped with a flame ionization detector (FID). The reaction rate of H_2 followed the formula below:

$$\text{Reaction rate of production} = \frac{n_{\text{production}} (\mu\text{mol})}{m_{\text{cat.}} (\text{g}) \times \text{time} (\text{h})} \quad (2)$$

3.10. Recycled Use

The catalyst was separated from the solution after the reaction, washed with deionized water, and finally dried under vacuum at 60 $^{\circ}$ C for 6 h. The dried catalyst was reused in a next catalysis run under the same reaction conditions.

4. Conclusions

The TiO_2/Cu_2O -supported Au catalysts were delicately constructed by the site-specific deposition of Au on either defect-rich TiO_2 nanorods or Cu_2O nanocubes. The selective anchoring of Au nanoparticles on TiO_2 nanorods combined with the p-n junction of TiO_2/Cu_2O leads to the highest activity towards ethanol photoreforming. The H_2 production rate reaches a record level of 8548 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ under simulated solar light. The acetaldehyde in liquid phase was generated at an almost stoichiometric rate, which indicates the effective inhibition of C–C cleavage of ethanol to CH_4 or CO_2 . Extensive spectroscopic studies verified that Au species adjacent to Ti^{3+} defects and the associated oxygen vacancies on TiO_2 nanorods activate the proton reduction to H_2 . The p-n junction between TiO_2 and Cu_2O facilitates charge separation and transfer owing to the matching of energy levels, which accelerates photo-generated hole transfer and the dehydrogenation of ethanol to acetaldehyde on the junction. This site-specific deposition strategy could be applicable in the enhancement in

other biomass hydrogen production by rationally designing the delicate structure of catalysts and maximizing the catalytic capability.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/5/539/s1>, Figure S1: XRD patterns; Figure S2: GC-MS spectra; Figure S3: HRTEM photographs; Figure S4: Ti 2p, O 1s and Au 4f XPS spectra; Figure S5: Cu 2p XPS and Cu LMM Auger spectra; Figure S6: Bandgap estimation; Table S1: Ti 2p XPS analyses; Table S2: O 1s XPS analyses; Table S3: Au 4f XPS analyses; Table S4: Comparisons of photocatalysts for ethanol photoreforming.

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