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⁻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\textsubscript{2} production from abundant and low-value biomass resources [5,6]. Photoform ing could be one of the most promising potential reforming ways because H\textsubscript{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\textsubscript{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\textsubscript{2} photocatalysts have been extensively studied in alcohol photoreforming. Au-supported TiO\textsubscript{2} catalysts have been tuned with respect to metal particle size, annealing conditions in different gas atmospheres, and the phase structure of TiO\textsubscript{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\textsubscript{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\textsubscript{2} [14]. The selective deposition of TiO\textsubscript{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\textsubscript{2} nanophases sandwich between zeolite nanosheets for hydrogen production by plasmonic photocatalytic reforming of methanol [16]. It has been reported that anatase TiO\textsubscript{2} is more active than the rutile one, and the higher surface availability of the former for Au is beneficial to H\textsubscript{2} production from ethanol under UV light irradiation. However, the significant amounts of other gaseous products (mostly CO, CO\textsubscript{2} and CH\textsubscript{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\textsubscript{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\textsuperscript{3+} defects on Au@TiO\textsubscript{2}/Cu\textsubscript{2}O catalyst affects the electronic structure of Au. In addition, the p-n junction between Cu\textsubscript{2}O and TiO\textsubscript{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\textsubscript{2} production rate of 8548 \textmu mol g\textsuperscript{-1} h\textsuperscript{-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\textsubscript{2}O nanocubes with an average size of ~40 nm were grown on TiO\textsubscript{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\textsubscript{2} [18] and (110) of cubic phase Cu\textsubscript{2}O [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\textsubscript{2} or Cu\textsubscript{2}O 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\textsubscript{2}O/TiO\textsubscript{2}, Au@TiO\textsubscript{2}/Cu\textsubscript{2}O and Au@TiO\textsubscript{2}/Cu\textsubscript{2}O@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) Cu2O/TiO2 (b) Au@Cu2O/TiO2, (c) Au@TiO2/Cu2O, (d) Au@TiO2/Cu2O@Au, with histogram of Au NPs size distribution of each sample (100 particles are counted).

X-ray diffraction patterns of the samples indicate that TiO2 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 Cu2O (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 CuO/TiO_2 and Au-supported catalysts, corresponding to Ti^{3+} and Ti^{4+} species, respectively (Figure 2A) [22–24]. The B.E. values hardly shift among these samples. However, the peak area ratio of Ti^{3+} to Ti^{4+} is lower when Au is deposited on TiO_2 i.e., Au@TiO_2/CuO and Au@TiO_2/CuO@Au (0.96 and 1.03), compared to that of Au-free TiO_2/CuO and Au deposition on CuO i.e., Au@CuO/TiO_2 (1.17 and 1.11) (Table 1). This indicates that the site-specific deposition of Au differs at defect-rich TiO_2 and CuO, leading to a variation to Ti^{3+} content when Au is deposited to TiO_2. In our previous studies, the ratio of Ti^{3+}:Ti^{4+} increased as the amount of NaBH_4 increased. When the ratio reaches around 1, even when increasing the amount of NaBH_4, the ratio will not increase any more, which suggests that it is approaching saturation of Ti^{3+}:Ti^{4+} ratio [25].

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@TiO_2/CuO and Au@TiO_2/CuO@Au (0.71 and 0.74) compared with that of TiO_2/CuO (0.86). The O_V/O_L ratio in Au@CuO/TiO_2 (0.81) is close to that of TiO_2/CuO (0.86). This tendency is consistent with that of the Ti^{3+}/Ti^{4+} ratio. The amount of oxygen vacancy (O_V) decreases with the decreasing Ti^{3+} content because the Ti^{3+} defects are closely associated with O_V in defect-rich TiO_2 support [26].

![Figure 2. XPS spectra of (A) Ti 2p, (B) O 1s: (a) CuO/TiO_2, (b) Au@TiO_2/CuO, (c) Au@TiO_2/CuO@Au, (d) Au@CuO/TiO_2, and (C) Au 4f core level spectra: (a) Au@TiO_2/CuO, (b) Au@TiO_2/CuO@Au, (c) Au@CuO/TiO_2.](image)

| Sample                     | B.E. in 2p_{3/2}(eV) | B.E. in 2p_{1/2}(eV) | \(\text{Ti}^{3+}/\text{Ti}^{4+}\) Ratio \(^1\) |
|----------------------------|----------------------|----------------------|------------------------------------------|
| TiO_2/CuO                  | 457.9                | 458.3                | 463.4                                   |
| Au@TiO_2/CuO              | 457.9                | 458.3                | 463.4                                   |
| Au@TiO_2/CuO@Au           | 457.9                | 458.3                | 463.4                                   |
| Au@CuO/TiO_2              | 457.8                | 458.2                | 463.4                                   |

\(^1\) The value refers to the ratio of the respective integral peak area.

![Table 1. Ti 2p XPS analyses of the samples.](image)
Table 2. O 1s XPS analyses of the samples.

| Sample                        | B.E. (eV) | O_L | O_V | O_C | O_V/O_L Ratio |
|-------------------------------|-----------|-----|-----|-----|---------------|
| TiO_2/CuO                   | 530.0     | 532.0 | 533.5 |     | 0.86           |
| Au@TiO_2/CuO_O             | 530.0     | 532.0 | 533.5 |     | 0.71           |
| Au@TiO_2/CuO_Au@Au         | 530.0     | 532.0 | 533.5 |     | 0.74           |
| Au@CuO/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@CuO/TiO_2, which is assigned to Au⁰ species [27]. In contrast, when Au is deposited on both TiO_2 and CuO, 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@TiO_2/CuO@Au compared to that on Au@CuO/TiO_2. The B.E. continually shifts to a lower value of 83.4 eV when Au is only deposited on TiO_2. 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 TiO_2 in Au@TiO_2/CuO [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@TiO_2/CuO facilitates proton reduction to hydrogen during ethanol photoreforming.

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

| Sample                     | B.E.(eV) | △B.E.(eV) 1 |
|----------------------------|----------|-------------|
| Au@TiO_2/CuO              | 83.4     | −0.6        |
| Au@TiO_2/CuO@Au           | 83.7     | −0.3        |
| Au@CuO/TiO_2              | 84.0     | −           |

1 The value refers to the shift compared to that of Au@CuO/TiO_2.

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 CuO 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 CuO or TiO_2. This is an indication that the chemical states of CuO changes little in these catalysts.
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 Cu2O/TiO2 itself [40]. The fluorescence emission spectra of TiO2 and Cu2O/TiO2 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 Cu2O/TiO2 junction. After Au is deposited on either TiO2 or Cu2O, 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].

The electron paramagnetic resonance (EPR) spectra are shown in Figure 4A. An intense EPR signal appears at a g value of 2.003 for Cu2O/TiO2. This signal is usually assigned to surface O-species, formed via the interaction of dioxygen and Ti3+/4+ defects in TiO2 [24,37–39]. The EPR signal appears at the same g value for Au@Cu2O/TiO2, Au@TiO2/Cu2O@Au and Au@TiO2/Cu2O. The intensity of the signal in Au-supported catalysts is lower than that in un-supported Cu2O/TiO2. The intensity of O-related EPR signal (g = 2.003) could be associated with the Ti3+/4+ ratio in TiO2. The lower signal intensity in Au-supported catalysts indicates the smaller Ti3+/4+ ratio. The Au@TiO2/Cu2O has the smallest Ti3+/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 TiO2, the Cu2O/TiO2 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 Cu2O/TiO2 itself [40]. The fluorescence emission spectra of TiO2 and Cu2O/TiO2 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 Cu2O/TiO2 junction. After Au is deposited on either TiO2 or Cu2O, 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].
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Figure 4. The EPR spectra (A) and digital photos (B) of Cu₂O/TiO₂, Au@Cu₂O/TiO₂, Au@TiO₂/Cu₂O@Au, and Au@TiO₂/Cu₂O; UV-Vis absorption spectra (C) and Fluorescence emission spectra (D) of TiO₂, Cu₂O/TiO₂, Au@Cu₂O/TiO₂, Au@TiO₂/Cu₂O@Au, and Au@TiO₂/Cu₂O. 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 Cu₂O/TiO₂ enhances the photocurrent compared to Cu₂O/TiO₂ itself, which indicates the improved charge separation across the metal/oxide interface. The Au@TiO₂ electrode shows a higher photocurrent than Au@Cu₂O/TiO₂. The interface of Au and TiO₂ is more favorable to charge separation than that of Au and Cu₂O due to the lower conduction band potential of TiO₂ than that of Cu₂O [42]. In addition, the existence of Ti³⁺ defects associated with adjacent oxygen vacancies intensifies the interaction of Au and TiO₂ [25]. The Au@TiO₂/Cu₂O electrode exhibits the highest photocurrent among all electrodes, 2.5 times higher than Au@TiO₂. This hints at the contribution of TiO₂/Cu₂O p-n junction combined with the interface of Au and TiO₂ to charge separation and transfer. The photocurrent of Au@TiO₂/Cu₂O is also higher than Au@TiO₂/Cu₂O/Au. This is an indication that the site-specific deposition of Au on TiO₂ leads to charge separation more efficiently under light illumination than the random deposition of Au on both TiO₂ and Cu₂O.
The photoreforming of ethanol was achieved using pure ethanol in an Ar atmosphere (1.4 bar) under simulated solar irradiation. The H₂ production rate is contrasted on each catalyst (Figure 6A). The rate of H₂ production reaches 6932 μmol g⁻¹ h⁻¹ on Au@Cu₂O/TiO₂, 8.35 times higher than that on Cu₂O/TiO₂ (830 μmol g⁻¹ h⁻¹, Table 4). It is apparent that proton reduction is greatly accelerated on the Au-supported catalyst for H₂ production. Additionally, the charge separation is improved by loading Au on the semiconductor, evidenced by photocurrent measurements (Figure 5). The Au@TiO₂ catalyst exhibits higher activity (7143 μmol g⁻¹ h⁻¹) towards H₂ production than Au@Cu₂O/TiO₂. This suggests that constructing the interface of Au and TiO₂ is more favorable than that of Au and Cu₂O, which could direct the structural design of catalysts for ethanol photoreforming. The rate of H₂ production on Au@TiO₂/Cu₂O (8548 μmol g⁻¹ h⁻¹) is apparently higher than that on either Au@TiO₂ (7143 μmol g⁻¹ h⁻¹) or Au@TiO₂/Cu₂O@Au (7348 μmol g⁻¹ h⁻¹). Table S4 compares the H₂ yield rates reported for TiO₂-supported noble-metal catalysts with the result in this work. The p-n junction between TiO₂ and Cu₂O contributes the enhanced H₂ production. However, the selective deposition of Au on defect-rich TiO₂ is essential for higher activity because the Au-O₅-Ti³⁺ sites are more active in ethanol photoreforming [25]. The quantity of Au-O₅-Ti³⁺ sites is relatively less in randomly deposited Au@TiO₂/Cu₂O@Au than in site-specifically deposited Au@TiO₂/Cu₂O. As a consequence, the latter shows higher activity than the former. In addition, the lower H₂ production rate of Au@Cu₂O/TiO₂ 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. H₂ production via photoreforming of ethanol on the catalysts under simulated solar light.

| Catalysts               | Production Rate (μmol g⁻¹ h⁻¹) | Gas Phase | Liquid Phase |
|-------------------------|---------------------------------|-----------|--------------|
|                         | H₂ | CH₄ | CO | CO₂ | CH₃CHO | CH₃COOH |
| Au@TiO₂/Cu₂O            | 8548 | 5 | - | 3 | 8806 | - |
| Au@Cu₂O/TiO₂            | 6932 | 12 | 3 | 9 | 7239 | - |
| Au@TiO₂/Cu₂O@Au         | 7348 | 13 | - | 7 | 7561 | - |
| Au@TiO₂                 | 7143 | 7 | - | 7 | 7356 | - |
| Cu₂O/TiO₂               | 830 | - | - | - | 1020 | - |
| TiO₂                    | 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.
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 OV/OI 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 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 OV/OI 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(CH2), ν(CH3), 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@Cu$_2$O/TiO$_2$, (B) Au@TiO$_2$/Cu$_2$O, (C) Au@TiO$_2$/Cu$_2$O@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\(_2\)O 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].

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059pH, \tag{1}
\]

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 \(-3.2\) 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\(_2\)O 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\(_2\)O is 1.56 V vs. RHE. Based on the bandgap of Cu\(_2\)O (2.2 eV) [56,57], the conduction band (CB) level of Cu\(_2\)O is estimated to be \(-0.64\) V.

![Figure 8. Mott-Schottky plots of (A) TiO\(_2\) nanorods and (B) Cu\(_2\)O nanocubes measured at varied frequencies and room temperature. Solution: 0.1 M phosphate buffer (pH 7).](image)

Based on the findings above, we proposed possible charge transfer pathways on the Au@TiO\(_2\)/Cu\(_2\)O catalyst during ethanol photoreforming. The p-n junction is formed when p-type Cu\(_2\)O 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\(_2\)O owing to the more positive valence band level of TiO\(_2\).
The electrons generated on Cu$_2$O 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 Au@Cu$_2$O/TiO$_2$ catalyst without the interfacial sites. Consequently, the dual effects of Au-O$_{v}$-Ti$^{3+}$ active sites and p-n junction endow Au@TiO$_2$/Cu$_2$O catalyst with higher activity towards ethanol photoreforming by the site-specific deposition of Au on defect-rich TiO$_2$ nanorods.

![Diagram of energy levels and charge transfer on Au@TiO$_2$/Cu$_2$O catalyst.](image)

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

3. Materials and Methods

3.1. Materials

C$_2$H$_5$OH (anhydrous ethanol), CH$_3$OH (methanol), CuSO$_4$ (anhydrous copper sulfate), PVP (polyvinyl pyrrolidone), TBOT (tetrabutyltitanate), HNO$_3$ (nitric acid), NaBH$_4$ (sodium borohydride), AA (ascorbic acid), HAuCl$_4$·3H$_2$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 (TiO$_2$/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$_2$O Nanocubes

The Cu$_2$O 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$_2$O. 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 Cu$_2$O/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 Au@TiO$_2$/Cu$_2$O

2 g of TiO$_2$ nanorod sample was dispersed in 200 mL of H$_2$O 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 ethanol and water and finally dried under vacuum at 60 °C. The product was denoted as Au@TiO$_2$/Cu$_2$O.

3.6. Synthesis of Au@Cu$_2$O/TiO$_2$

The as-synthesized Cu$_2$O and PVP was suspended in 100 mL of H$_2$O. 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 Au@Cu$_2$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 ethanol and water and finally dried under vacuum at 60 °C. The product was denoted as Au@Cu$_2$O/TiO$_2$.

3.7. Synthesis of Au@TiO$_2$/Cu$_2$O@Au

2 g Cu$_2$O/TiO$_2$ sample was suspended in 200 mL of H$_2$O 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$_2$/Cu$_2$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 CuKα radiation (40 kV, 30 mA, λ = 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 Al Kα 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 µL.

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\textsubscript{2} at 100 °C for 1 h. After an initial scan as the background spectrum, ethanol was induced into the cell through a flow of N\textsubscript{2} for 30 min. After flowing N\textsubscript{2} to remove the residual ethanol vapor, the FTIR spectra were collected in the range of 4000–950 cm\textsuperscript{-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·cm\textsuperscript{-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\textsubscript{2} followed the formula below:

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

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 °C for 6 h. The dried catalyst was reused in a next catalysis run under the same reaction conditions.

4. Conclusions

The TiO\textsubscript{2}/Cu\textsubscript{2}O-supported Au catalysts were delicately constructed by the site-specific deposition of Au on either defect-rich TiO\textsubscript{2} nanorods or Cu\textsubscript{2}O nanocubes. The selective anchoring of Au nanoparticles on TiO\textsubscript{2} nanorods combined with the p-n junction of TiO\textsubscript{2}/Cu\textsubscript{2}O leads to the highest activity towards ethanol photoreforming. The H\textsubscript{2} production rate reaches a record level of 8548 µmol g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-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\textsubscript{4} or CO\textsubscript{2}. Extensive spectroscopic studies verified that Au species adjacent to Ti\textsuperscript{3+} defects and the associated oxygen vacancies on TiO\textsubscript{2} nanorods activate the proton reduction to H\textsubscript{2}. The p-n junction between TiO\textsubscript{2} and Cu\textsubscript{2}O 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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