

Photoelectrochemical Oxidation

Photoelectrochemical Catalysis toward Selective Anaerobic Oxidation of Alcohols

Ruikang Zhang, Mingfei Shao,* Zhenhua Li, Fanyu Ning, Min Wei,* David G. Evans, and Xue Duan^[a]

Abstract: Selective oxidation of alcohols to aldehydes plays an important role in perfumery, pharmaceuticals, and agrochemicals industry. Different from traditional catalysis or photocatalytic process, here we report an effective photoelectrochemical (PEC) approach for selective anaerobic oxidation of alcohols accompanied with H₂ production by means of solar energy. By using TiO₂ nanowires modified with graphitic carbon layer as photoanode, benzyl alcohol (BA) has been oxidized to benzaldehyde with high efficiency and selectivity (>99%) in aqueous media at room temperature, superior to individual electrocatalytic or photocatalytic processes. Moreover, this PEC synthesis method can be effectively extended to the oxidation of several other aryl alcohols to their corresponding aldehydes under mild conditions. The electron spin resonance (ESR) results indicate the formation of intermediate active oxygen (O₂^{•-}) on the photoanode, which further reacts with alcohols to produce final aldehyde compounds.

The development of green and sustainable pathways for the transformation of organic compounds into fine chemicals has gained considerable interest in the past decades.^[1–5] Free radicals are known to be highly reactive chemical species, which makes it possible to overcome the large energy barriers and break the inert organic bonds (e.g., C–H, C=C) in synthetic chemistry. Traditionally, free radicals are generated by thermal homolytic bond cleavage, which requires significant amount of energy.^[6,7] Recently, photo-induced electron-hole pairs have emerged as one of the most promising approaches for photo-conversion technologies by utilizing solar energy in the environment and energy fields. For instance, photocatalytic reactions based on semiconductors are widely investigated in water splitting,^[8–11] environmental remediation,^[12–15] and CO₂ transformation to fuel.^[16–18] Remarkably, although a few exam-

ples have been successively developed (e.g., selective photocatalytic oxidation of toluene or aromatic alcohols),^[19–26] photocatalysis-based organic synthesis demonstrates a large potential for green synthesis. However, all these photocatalytic transformations require certain rigorous conditions (e.g., external O₂ import, organic solvent, as well as relatively high temperature and pressure) due to the sluggish reaction kinetics and limited efficiency. Therefore, the development of facile synthesis routes for the transformation of organic substrates remains a big challenge in organic synthesis and green chemistry.

Photoelectrochemical (PEC) water splitting has been envisioned as a promising route for harvesting the energy of sunlight and storing it in the form of chemical bonds (H₂ and O₂).^[27–30] A PEC cell is based on a semiconductor/liquid junction: charge carriers (electrons and holes) generated in the semiconductor upon light excitation transfer to the junction interface by the electric field, in which they can drive a redox reaction, such as the oxidation/reduction of water to O₂/H₂. From the viewpoint of photocatalytic organic synthesis, if the PEC-generated highly active oxygen or hydrogen species directly participates in the chemical oxidation or reduction reaction, a promising strategy based on PEC water-splitting/organic-synthesis coupling can be achieved. The following advantages are expected in this new reaction system: firstly, PEC facilitates the charge separation owing to the introduction of a bias, giving rise to high catalytic efficiency; secondly, highly-active oxygen or hydrogen species originating from PEC water splitting serves as clean and cost-effective oxidant or reducing agent, without the consumption of noxious organic counterparts. In addition, this PEC water-splitting/organic-synthesis coupling process may occur at normal pressure and temperature in aqueous media, so as to achieve a green synthesis pathway.

The transformation of alcohols to corresponding aldehydes in liquid-phase oxidation has been well-developed previously by using various catalysts, including noble metal catalysts (e.g., Pd, Au)^[31–34] and non-precious-metal catalysts.^[35,36] Differently, here we report photoelectrochemical oxidation of alcohols in the photoanode with H₂ generated in the cathode, which couples PEC water splitting with selective oxidation reaction of organic molecules. To achieve this PEC transformation process, a sophisticated photoanode was fabricated by depositing electron capture layer (graphitic carbon) on the surface of TiO₂ nanowires (NWs) array. The resulting TiO₂/C photoanode exhibits a high activity for the oxidation of benzyl alcohol (BA), giving a reaction rate of 0.048 mmol h⁻¹ (≈ 16.4 times larger

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than that of pristine photocatalytic process) and a selectivity of > 99% for benzaldehyde. A further introduction of the hole-trapping agent Co_3O_4 (denoted as $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ photoanode) demonstrates a high performance toward PEC water splitting other than BA oxidation. The electron spin resonance (ESR) results indicate the graphited carbon layer enhances the formation of intermediate active oxygen ($\text{O}_2^{\cdot-}$), which participates in the selective oxidation of alcohols. However, the Co_3O_4 as an efficient oxygen evolution reaction (OER) catalyst only accelerates the production of molecular oxygen. In addition, this PEC synthesis method is also successfully demonstrated in the oxidation of several other aryl alcohols to corresponding aldehydes with high efficiency and selectivity under mild conditions (room temperature, aqueous media).

The preparation procedure of TiO_2 , TiO_2/C and $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ NWs on fluorine-doped tin oxide (FTO) is illustrated in Figure 1A (see details in the Experimental Section). The TiO_2 NWs were firstly grown on a FTO substrate via a reported hydrothermal method,^[37] with an average diameter of ~ 200 nm (Figure 1B and C). XRD pattern shows two sharp diffraction peaks located at 36.1° and 62.8° , corresponding to the (101) and (002) reflection of rutile TiO_2 phase (Figure S1 in the Supporting Information). Subsequently, TiO_2/C NWs array was prepared by coating polypyrrole (PPy) using a photo-assisted deposition followed by a calcination process in N_2 atmosphere. A carbon layer is observed on the surface of TiO_2 NWs with enhanced roughness (Figure 1D and E). In Figure S2, Raman spectra show vibrational modes of rutile TiO_2 at 240, 445, and 608 cm^{-1} , which can be assigned to the second order effect (SOE), E_g and A_{1g} , respectively.^[38] For the Raman spectra of TiO_2/C NWs, two bands located at ≈ 1359 (D band) and $\approx 1586\text{ cm}^{-1}$ (G band) demonstrate the presence of graphited carbon. Finally, Co_3O_4 nanoparticles (3–5 nm in diameter) were in situ deposited onto TiO_2/C to obtain $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ NWs (Figure 1F and G). The TEM image displays the (400) plane of Co_3O_4 phase embedded in the (111) plane of rutile TiO_2 (Figure S3).

The PEC measurements were performed using the studied sample as photoanode in a neutral medium (0.5 M Na_2SO_4 aqueous solution), and the PEC setup is shown in Figure S4 in the Supporting Information. A full spectrum generated by a 150 W Xe lamp was used as the illumination source, from which UV light region is available for TiO_2 -based photoanode. As shown in Figure 2A, pristine TiO_2 NWs display a relatively low photoresponse over the whole potential window, with a photocurrent density of 0.94 mA cm^{-2} at 0.6 V vs. SCE. In contrast, an enhanced photocurrent density (1.41 mA cm^{-2}) is observed for the TiO_2/C NWs. In addition, the coating carbon layer can be tuned from approximately 2 to 10 nm (Figure S5) according to the deposition time of PPy precursor. It is found that a moderate thickness of carbon layer (≈ 5 nm) on the surface of semiconductor gives the best PEC performance (Figure S6). For the $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ NWs, the photocurrent density

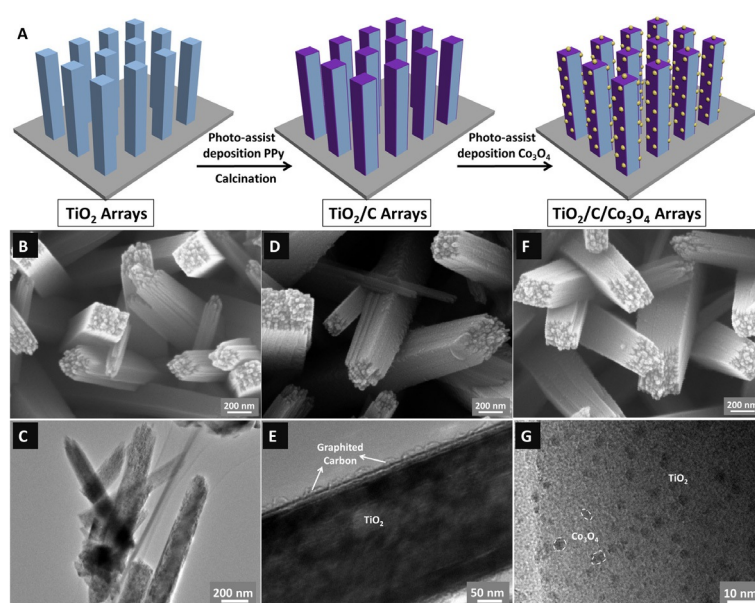


Figure 1. (A) Schematic illustration for the fabrication of TiO_2 , TiO_2/C and $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ NWs; SEM images of (B) TiO_2 , (D) TiO_2/C , (F) $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ NWs, respectively; TEM images of (C) TiO_2 , (E) TiO_2/C , and (G) $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ NWs, respectively.

further increases to 1.77 mA cm^{-2} at 0.6 V vs. SCE. Moreover, the photoconversion efficiency, a key issue in the practical application, was calculated based on the current–voltage (J - V) curve as a function of applied voltage (Figure 2B). The $\text{TiO}_2/\text{C}/$

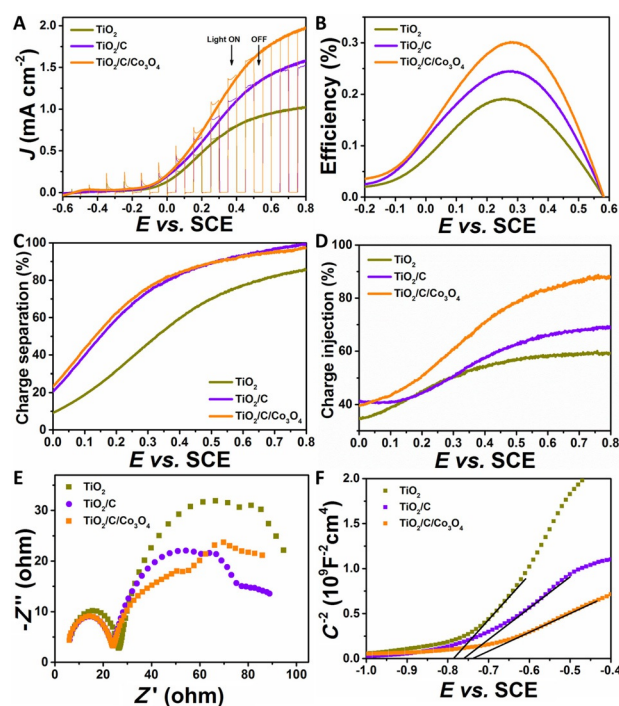


Figure 2. (A) Current–voltage curves, (B) photoconversion efficiency as a function of applied voltage, (C) charge separation efficiency and (D) charge injection efficiency vs. potential curves, (E) EIS curves measured at 0 V vs. SCE under illumination, (F) Mott–Schottky plots for the TiO_2 , TiO_2/C , and $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ NWs, respectively.

Co₃O₄ photoanode shows a maximum photoconversion efficiency of 0.31 % at 0.28 V, which is significantly larger than that of TiO₂/C (0.25 %) and pristine TiO₂ (0.19 %) at the same applied potential. The results above demonstrate that the incorporation of carbon and Co₃O₄ largely improves the PEC water splitting performance of pristine TiO₂ photoanode.

Notably, an intense absorption in visible light region (400–800 nm) is observed in TiO₂/C and TiO₂/C/Co₃O₄ NWs due to the presence of carbon (Figure S7 in the Supporting Information). As TiO₂ in this system serves as photocatalyst to generate electron-hole pairs, the enhanced visible light absorption does not represent an extended light response range for PEC water splitting. To gain a deep insight into the function of each component in TiO₂/C/Co₃O₄ NWs, the charge separation efficiency and surface charge injection efficiency are used to identify charge separation property and surface reaction kinetics (see details in the experimental section and Figure S8).^[39–41] A largely enhanced charge separation efficiency is observed both in TiO₂/C and TiO₂/C/Co₃O₄ NWs (93.2 and 92.3 % at 0.6 V vs. SCE, respectively), in comparison with TiO₂ NWs (77.2 %), which indicates that the charge separation efficiency of photogenerated electron-hole pairs is significantly improved via the incorporation of carbon (Figure 2C). For the charge injection efficiency, a slight increase is found for TiO₂/C NWs (65.8 % at 0.6 V vs. SCE) whereas a giant improvement (83.6 % at 0.6 V vs. SCE) is obtained for TiO₂/C/Co₃O₄ NWs (Figure 2D), implying that Co₃O₄ acts as a highly-efficient electrocatalyst toward water oxidation.

Electrochemical impedance spectroscopy (EIS) studies further provide information about the charge transport behavior in these photoanodes.^[42,43] As shown in Figure 2F, the first arc (high frequency) diameter of TiO₂/C and TiO₂/C/Co₃O₄ NWs decreases relative to TiO₂ NWs, indicating the introduced carbon can enhance the charge separation. The ternary TiO₂/C/Co₃O₄ NWs display the smallest water oxidation resistance in low frequency region (corresponding to the second arc) among these three samples, suggesting the fastest charge transport to the electrolyte. These results are consistent with the discussions on the charge separation and charge injection properties (Figure 2C and D). The charge carrier density of photoanodes was calculated according to the Mott–Schottky plots (Figure 2F; see experimental sections for details).^[44,45] The TiO₂/C/Co₃O₄ photoanode gives the largest charge carrier density ($1.95 \times 10^{18} \text{ cm}^{-3}$) compared with TiO₂/C ($1.06 \times 10^{18} \text{ cm}^{-3}$) and pristine TiO₂ ($8.31 \times 10^{17} \text{ cm}^{-3}$). This demonstrates that the charge recombination is significantly suppressed on the surface of composite photoanode, which facilitates the PEC performance.

The PEC catalytic performance of the as-synthesized three photoanodes were further evaluated by the selective oxidation of benzyl alcohol (BA) to benzaldehyde, which is an important chemical intermediate in cosmetics, perfumery, food, and pharmaceutical industry.^[46,47] After the addition of BA into the Na₂SO₄ electrolyte, all these three photoanodes deliver an significantly enhanced photocurrent, implying the oxidation of BA on the surface of photoanode without O₂ import (Figure 3A and Figures S9 and S10 in the Supporting Information). Benzaldehyde is the main product, as identified by GC-MS. To

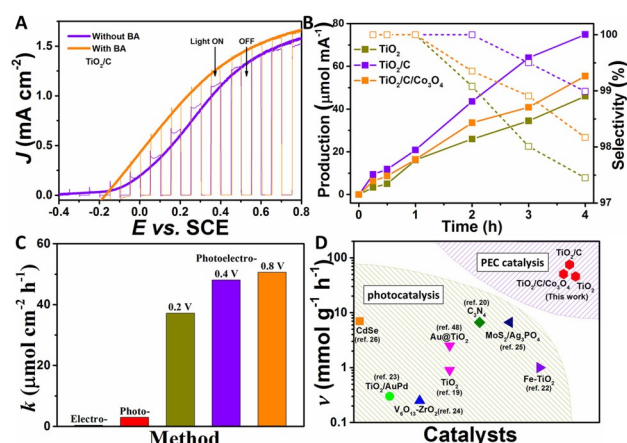


Figure 3. (A) Current-voltage curves over TiO₂/C photoanode with or without BA; (B) benzaldehyde production and corresponding selectivity vs. reaction time for the PEC oxidation of BA over TiO₂, TiO₂/C, and TiO₂/C/Co₃O₄ photoanode, respectively; (C) reaction rate of BA oxidation by using photocatalysis, electrocatalysis and PEC catalysis, respectively; (D) comparison of reaction rate between PEC catalysis in this work and photocatalysis reported previously.

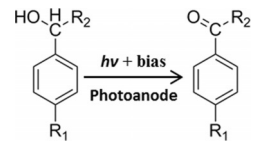
evaluate the catalytic activity, the reaction rate was normalized by the current. Figure 3B displays the benzaldehyde yield and corresponding selectivity versus reaction time for the oxidation of BA over these photoanodes. It is observed that TiO₂ shows the lowest oxidation activity ($46.0 \mu\text{mol mA}^{-1}$ at 4 h) and selectivity (97.5 % at 4 h). TiO₂/C photoanode displays an enhanced catalytic activity ($74.8 \mu\text{mol mA}^{-1}$ at 4 h) and selectivity (99 %), which suggests that the graphitic carbon (as electron capture agent) facilitates the oxidation of BA to benzaldehyde. However, with further incorporation of Co₃O₄, the benzaldehyde production decreases to $55.4 \mu\text{mol mA}^{-1}$ at 4 h for TiO₂/C/Co₃O₄ photoanode, accompanied with a slight decrease of selectivity (98.1 %). Notably, the selectivity shows a little decrease with the detection of benzoic acid after 2 h, due to the further oxidation of benzaldehyde to benzoic acid with an accumulated concentration of benzaldehyde. The inconsistent results of PEC water splitting and BA oxidation indicate two different transformation pathways for these two PEC processes. It is reasonable to conclude that the interface property of photoanode, derived from the modification of carbon and Co₃O₄, plays a key role in the BA oxidation.

The photoelectrochemical process is a combination of photocatalysis and electrocatalysis. To further understand the PEC catalytic process, different operation formulations were employed by using TiO₂/C photoanode (Figure 3C). The oxidation reaction of BA was explored by bubbling sufficient O₂ via individual electrochemical catalysis route (with bias but without light). It was found that BA does not undergo oxidation at all under this condition. On the other hand, when the reaction was carried out in unitary photocatalytic process (with light but without bias), a rather low production of benzaldehyde was obtained ($2.95 \mu\text{mol cm}^{-2} \text{ h}^{-1}$). In contrast, a highly efficient and selective oxidation of BA can only be triggered by the PEC process (light + bias). As a result, the reaction rate enhances from 37.2 to $50.6 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ along with the increase of ap-

plied voltage. Moreover, the simultaneous production of H_2 demonstrates that an H_2O molecule is involved in the redox reaction and serves as the source of active-oxygen species. The oxidation of BA to benzaldehyde by various photocatalysts has been reported, but with a low reaction rate (normally below $10 \text{ mmol g}^{-1} \text{ h}^{-1}$) and rigorous conditions (e.g., external O_2 import, organic solvent, high temperature and pressure).^[19–26,48] The PEC catalysis in this work yields an order of magnitude enhancement in reaction rate ($\approx 76 \text{ mmol g}^{-1} \text{ h}^{-1}$) under mild reaction conditions (room temperature, aqueous media), in comparison with photocatalysis process (Figure 3D).

We further studied the PEC oxidation of other three aryl alcohols over the TiO_2/C photoanode, and the production and selectivity toward corresponding aldehyde are listed in Table 1.

Table 1. PEC oxidation of several typical aryl alcohols over the TiO_2/C photoanode

Substrates		
	Production ^[a] [mmol]	Aldehyde Selectivity ^[a] [%]
benzyl alcohol	0.144	100
4-methylbenzyl alcohol	0.180	100
4-fluorobenzyl alcohol	0.161	100
1-phenyl-1-propanol	0.045	100

[a] $t = 1 \text{ h}$

It is found that a selectivity of 100% for aldehyde is achieved in 1 h for all these alcohol substrates, with a aldehyde production ranging in $0.045\text{--}0.180 \text{ mmol h}^{-1}$, demonstrating that the PEC oxidation of these aryl alcohols occurs successfully by using the TiO_2/C photoanode. In addition, the different production rate of aldehydes can be ascribed to the reactivity of hydroxyl group influenced by the surrounding spatial effect and electronic effect. Steric hindrance would impose a main effect on the oxidation of 1-phenyl-1-propanol and result in a low reaction rate.

A basic point of view in the PEC anaerobic oxidation of alcohols can be identified through the results of BA oxidation process. It is found that no conversion of benzaldehyde occurs for pristine electrocatalysis route bubbled with efficient O_2 , which indicates that molecular O_2 without activation cannot directly participate in the benzaldehyde oxidation reaction in the aqueous medium. For the photocatalysis route, benzaldehyde undergoes a sluggish oxidation with a low reaction rate. It has been reported that the radical dioxygen species ($\text{O}_2^{\cdot-}$) coming from the combination of O_2 molecule with photoinduced electron of semiconductors serves as the original oxidant in photocatalytic organic synthesis.^[20,21,25] However, the photocatalytic efficiency is normally restrained by the limited active radical species as a result of the facile electron-hole recombination. The results above indicate that a highly active oxygen species

originating from PEC water splitting plays a critical role in the oxidation reaction of BA. Figure 4A shows the electron spin resonance (ESR) spectra of these three photoanodes with dimethyl pyridine *N*-oxide (DMPO) as a spin-trapping reagent. A clear ESR signal attributed to $\text{O}_2^{\cdot-}$ is observed over $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ upon UV light irradiation, which is stronger than the

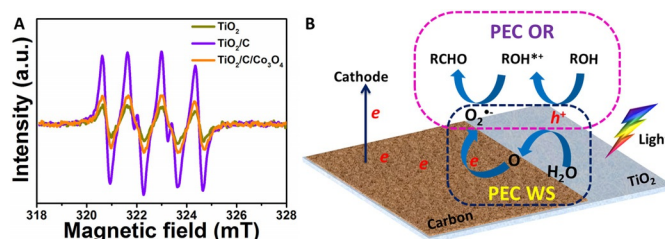


Figure 4. (A) DMPO spin-trapping ESR spectra recorded for $\text{DMPO-O}_2^{\cdot-}$ over TiO_2 , TiO_2/C , and $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ sample, respectively. Conditions: $[\text{DMPO}] = 0.10 \text{ M}$, $m_{\text{cat}} = 2 \text{ mg}$, $V_{\text{solvent}} = 0.5 \text{ mL}$, ambient temperature; (B) schematic illustration for the PEC WS-OR coupling process.

pristine TiO_2 . Remarkably, TiO_2/C photoanode gives the highest intensity of $\text{O}_2^{\cdot-}$ signal. This suggests that carbon accelerates the generation of $\text{O}_2^{\cdot-}$ species, whereas Co_3O_4 hinders the effect of carbon. The order of generated $\text{O}_2^{\cdot-}$ intensity is consistent with the catalytic activity of BA oxidation over TiO_2 , $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$, and TiO_2/C , respectively.

Based on the previous results and discussions on photocatalytic and electrocatalytic process, the process of PEC water splitting and anaerobic oxidation of alcohols can be proposed (Figure 4B). The electron-hole pairs are firstly generated in TiO_2 under illumination. Then electrons tend to transfer from TiO_2 to carbon and holes are captured by Co_3O_4 for the oxidation of water to produce oxygen. The opposite transmission of electron and hole enhances the charge separation efficiency. Consequently, the ternary $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ photoanode exhibits the best catalytic performance toward water splitting with a high charge separation and charge injection efficiency by means of the synergetic effect of carbon and Co_3O_4 . In the case of TiO_2/C photoanode, the PEC water-splitting/oxidation-reaction coupling (defined as PEC WS-OR) occurs in the absence of Co_3O_4 electrocatalyst toward water oxidation: the intermediate active oxygen species generated from water oxidation is reduced to superoxide radicals ($\text{O}_2^{\cdot-}$) by active electrons (denoted as PEC WS process); the holes at the valence band of TiO_2 oxidize the organic substrates (aryl alcohols) to carbocations ($\text{ROH}^{\cdot+}$),^[19–21,23,24] which further react with $\text{O}_2^{\cdot-}$ to produce the final aldehyde compounds (denoted as PEC OR process). The introduction of carbon maximizes the separation efficiency of photogenerated carriers and exhibits electron storage and transfer ability, which enhances the formation of $\text{O}_2^{\cdot-}$ and thereby achieves a largely improved reaction rate for the BA oxidation. However, in the ternary $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ system, Co_3O_4 as an efficient oxygen evolution reaction (OER) electrocatalyst only accelerates the water splitting process and the production of oxygen, which blocks the occurrence of BA oxidation reaction. As a result, $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ photoanode shows superior PEC water splitting behavior (PEC WS) while TiO_2/C ex-

hibits satisfactory catalytic performance toward PEC water splitting-oxidation reaction coupling (PEC WS-OR).

In summary, a green organic synthesis route based on the PEC WS-OR coupling was firstly demonstrated in this work. By means of the TiO_2/C NWs photoanode, several aryl alcohol reactants are successfully oxidized into their corresponding aldehydes with a high selectivity (>99%) under mild conditions (without O_2 import, in aqueous media, and at room temperature). A comparison study revealed that the hole trapping agent Co_3O_4 only facilitates the water oxidation but shows a negative effect on the alcohols oxidation. Further efforts will be focused on the exploration of new PEC processes (such as PEC water splitting-reduction reaction coupling) and in-depth understanding on the reaction mechanism involved in this PEC catalysis. We believe the work described herein would find applications in the transformation of organic compounds into fine chemicals, offering a new avenue for benign and clean chemical synthesis.

Experimental Section

Preparation of TiO_2 , TiO_2/C , $\text{TiO}_2/\text{C}/\text{Co}_3\text{O}_4$ Arrays

A previously reported hydrothermal method was used to prepare the TiO_2 arrays on FTO substrate.^[31] Polypyrrole (PPy) was coated on TiO_2 arrays via a photo-assisted electrodeposition method. The polymerization was carried out in a three-electrode system, with the TiO_2 substrate as working electrode, saturated calomel electrode (SCE) as reference electrode, and Pt wire as counter electrode, in aqueous electrolyte containing 0.15 M pyrrole and 0.001 M NaClO_4 . A potential of 0.2 V vs. SCE with light illumination at a power density of 120 mW cm^{-2} was carried out during the potentiostatic deposition. TiO_2/C arrays were obtained following by a calcination process at 400°C for 2 h in N_2 atmosphere. Photo-assisted electrodeposition of Co_3O_4 onto TiO_2/C arrays was performed with the similar process of coating PPy. The potentiostatic deposition was carried out at a potential of 0.4 V vs. SCE with light illumination at a power density of 120 mW cm^{-2} in 0.005 M cobalt nitrate solution.

Photoelectrochemical measurements

All the PEC measurements were operated on an electrochemical workstation (CHI 660e, CH Instruments Inc., Shanghai) at room temperature in a neutral medium aqueous solution (0.5 M Na_2SO_4) with a three-electrode optical cell. A full spectrum generated by a 150 W Xe lamp with an average power density of 120 mW cm^{-2} on the operated photoanode was used as the illumination source. The current-voltage curves were measured by cyclic voltammetry (CV) or linear-sweep voltammetry (LSV) at a scan rate of 10 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was evaluated by applying an AC voltage at 0.4 V with frequency ranging from 0.1 to 100 kHz under illumination. Mott-Schottky plots were carried out at DC potential range from -1.0 to -0.4 V at a frequency of 1 kHz under illumination.

Photoelectrochemical oxidation measurements

In a typical reaction, 1 mL benzyl alcohol was added to the PEC three-electrode cell. The benzyl alcohol suspension (with Na_2SO_4 electrolyte) was formed in anode cell under magnetic stirring.

Benzyl alcohol oxidation was carried out just as the PEC water splitting measurement. Stirring and measurements were stopped according to the reaction time and the organic production can be separated from Na_2SO_4 electrolyte by gravity in a few minutes. The clear supernatant reaction mixture (0.2 mL) was removed periodically from reactor. The production was mixed with mesitylene (0.2 mL, external standard) for GC analysis. Samples were analyzed off-line by using GC (Shimadzu GC-2014C equipped with a flame ionization detector). A known standard was used to identify the products. Each group of data was tested for more than three times until a standard deviation was less than 5%. The other aryl alcohols were analyzed with the similar route.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alcohols • oxidization • green synthesis • photoelectrochemical water splitting • TiO_2 nanowire arrays

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