



## Research Paper

# Simultaneous photoelectrocatalytic aromatic organic pollutants oxidation for hydrogen production promotion with a self-biasing photoelectrochemical cell



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## ABSTRACT

The degradation of pollutants with the simultaneous promotion of hydrogen production is an attractive and promising solution for the current environmental and energy problem, but few studies have been performed concerning the trends and mechanism of this process. Two classes of typical pollutants, phenols and alkylbenzenes, are treated using a self-biasing photoelectrochemical (PEC) cell to reveal the intrinsic relationships between the redox properties of the pollutants and hydrogen production. The results show that the TOC removal rates of these pollutants range from 63.5% to 93.6%. The highest hydrogen production efficiency ( $\eta_{H_2}$ ), which is the ratio of experimental and theoretical hydrogen production amounts, reaches 81.5%. The degradation rate constant ( $k$ ) decreases as the experimental photoelectrocatalytic oxidation potential ( $E_{PEC}$ ) increases. This trend can be explained by the degradation pathway deduced from the detection of intermediate products using LC-MS and the associated reaction energetics from theoretical calculations. Neither the degradation rate constant ( $k$ ) nor the TOC removal amounts ( $\Delta TOC$ ) determines the hydrogen production. The  $\eta_{H_2}$  value positively depends on the average oxidation current efficiency (ACE), which is the ratio of experimental to theoretical TOC removal amounts. This study reveals a significant theory for the use of wastewater for hydrogen production.

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## 1. Introduction

Environmental quality and the energy shortage have become two major issues faced by modern society [1–3]. Due to the rapid development of industrialization, the consumption of fossil fuels has increased in recent decades. Because of its high energy capacity and lack of secondary pollution, hydrogen is a promising green and sustainable energy carrier for replacing fossil fuels in the future [4–7].

The production of hydrogen via water splitting is considered a promising and environmental method and has attracted increasing interest [8–11]. In recent years, many researchers have studied this process. [12–16] However, the reaction Gibbs free energy ( $\Delta_r G$ ) of 1 mol  $H_2$  produced by water splitting equals  $+237 \text{ kJ mol}^{-1}$ , and this reaction must be driven by an external energy source. In addition, the water splitting reaction, which consists of an oxygen evolution

reaction (OER) and a hydrogen evolution reaction (HER), is limited by its high thermodynamic potential, which is at least 1.23 V [17–22]. Because the standard potential of HER is 0 V, the OER must have a high external bias to occur. The hydrogen production from water splitting in the cathode area is limited by the oxidation reaction in the anode area. Despite extensive research efforts, the current efficiency of producing hydrogen directly from water is still very low. Accordingly, hydrogen production from water splitting requires further study to promote its practical applications.

To overcome these disadvantages and to achieve the goal of producing hydrogen, many studies have been performed to decrease the anodic oxidation potential for promoting hydrogen production [23,24]. The primary method involves adding sacrificial reagents to replace the anode reaction. From a thermodynamic perspective, the oxidation of most organic compounds requires a smaller external bias than that required for water oxidation [25]. In past decades, the oxidation of biomass and its derivatives, such as glucose, glycerol, ethanol and methane, from biological substrates to promote the hydrogen production has been widely studied. [26–28] However, to convert biomass and its derivatives into hydrogen,

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various complicated processes that require harsh conditions or operations are required, leading to high costs and a relatively low efficiency.

It has been found that the organic pollutants in wastewater that contain a high level of chemical energy are excellent electron donors and are available to promote hydrogen production. Thus, the simultaneous degradation of pollutants and hydrogen production has been researched. This approach also resolves the issues regarding environmental pollution [29]. However, the traditional system for hydrogen production from organic pollutants requires an external bias, thus requiring an additional energy input. Therefore, new and efficient methods for simultaneous pollutant degradation and the promotion of hydrogen production are urgently sought. In the last several years, an increasing number of studies has focused on photoelectrochemical energy conversion from solar light to hydrogen [30–33].

To overcome the mentioned shortcomings and to achieve the goal of producing hydrogen, a promising method may be via a self-biasing photoelectrochemical (PEC) cell for the simultaneous degradation of organic pollutants and the promotion of hydrogen production. This system is composed of an n-type semiconductor photoanode with a p-type semiconductor photocathode with different Fermi levels [34–37]. In this system, under light illumination, both of the photoelectrodes can generate electron-hole pairs. When the Fermi level of the photoanode is more negative than that of the photocathode, a self-bias is generated by the Fermi level difference between the photoanode and photocathode, thus providing the driving force. Then, the electrons on the photoanode are transferred through the external circuit to combine with the holes on the photocathode. The holes are separated at the photoanode, and the electrons are separated at the photocathode. Thus, there is a cooperative synergistic effect between the two photoelectrodes (Scheme 1).

The highlight of our previous study was the influence of the Fermi level of the electrode on the self-biasing PEC cell [38]. Compared with traditional wastewater treatment in which the main purpose is pollutant degradation, this system for simultaneous pollutant degradation and the promotion of hydrogen production has great development potential [39].

As previously mentioned, hydrogen production in the cathode area is limited by the pollutant oxidation in the anode area. Thus, the aim of this work is to study how the oxidation of different pollutants can promote hydrogen production. To investigate the influence of the pollutants, two classes of aromatic organic pollutants (phenols (-OH) and alkylbenzenes (-CH<sub>3</sub>)) are selected for this research, including the compounds phenol, hydroquinone, phloroglucinol, toluene, p-xylene, and mesitylene. The molecular structures of these compounds are shown in Table S1. The oxidation of different classes of pollutants leads to different levels

of hydrogen production due to the different redox properties. Specifically, the hydrogen production is limited by the transfer of electrons or the average oxidation current efficiency during the pollutant oxidation process. In this study, TiO<sub>2</sub> nanorods and carbon-coated Cu<sub>2</sub>O nanowires were chosen as the photoanode and photocathode, respectively, because of their excellent performance in our previous research [38]. This work provides clear theoretical guidance for the simultaneous oxidation of aromatic organic pollutants and the promotion of hydrogen production via a self-biasing PEC cell.

## 2. Experiment section

### 2.1. Reagents

Phenol (AR, ≥99%), mesitylene (AR, 97%), titanium butoxide (AR, 99.0%), p-xylene (GC, ≥99.0%) and NaOH (AR, 96.0%) were purchased from Aladdin Reagents Co. Ltd (Shanghai, China). Hydroquinone (AR, ≥99.5%), phloroglucinol (AR, ≥99.0%), toluene (AR, ≥99.5%) and HCl (AR, 36.0%–38.0%) were purchased from Sinopharm Chemical Reagents Co. Ltd (Shanghai, China). The Cu mesh (100 mesh, 0.11-mm wire diameter) was purchased from Alfa Aesar (Shanghai, China).

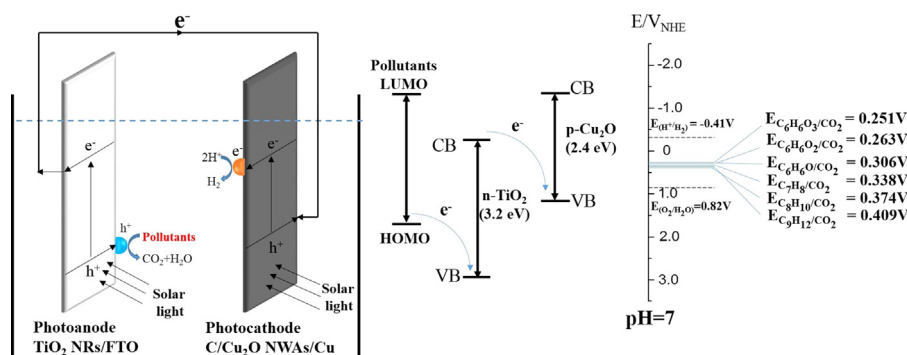
### 2.2. Electrode preparation

TiO<sub>2</sub> NRs/FTO. First, titanium butoxide (0.35 mL) was added to a HCl aqueous solution (6 mol L<sup>-1</sup>, 15 mL), and the mixture was stirred continuously for 30 min at normal atmospheric temperature. Then, the solution was transferred to a Teflon-lined stainless steel autoclave, and an F-doped tin oxide (FTO) sample was placed face down into the autoclave as the conductive surface. The autoclave was placed and well-sealed in an oven at 150 °C for 4 h. The oven temperature changed at a rate of 5 °C min<sup>-1</sup> until the autoclave reached the appropriate temperature. The TiO<sub>2</sub> NRs/FTO was rinsed several times with deionized water and dried in air [38].

C/Cu<sub>2</sub>O NWAs/Cu mesh. A sample of Cu mesh was anodized in a NaOH solution (3 mol L<sup>-1</sup>) for 20 min at 25 °C under 10 mA cm<sup>-2</sup> to generate Cu(OH)<sub>2</sub> NWAs/Cu. Then, the Cu mesh was immersed into a glucose solution (3 mg mL<sup>-1</sup>) for glucose coating. Subsequently, the Cu(OH)<sub>2</sub> NWAs/Cu mesh with the glucose coating was annealed at 550 °C under a N<sub>2</sub> atmosphere for 4 h with heating and cooling rates of 5 °C min<sup>-1</sup> [38].

### 2.3. Photoelectrochemical measurements

A three-electrode configuration whose working electrode, counter electrode and reference electrode were the samples, platinum foil and Ag/AgCl<sub>2</sub>, respectively, was used to characterize



**Scheme 1.** The electron transfer from the pollutants to the electrodes of the self-biasing simultaneous photoelectrochemical system and oxidation potential of pollutants.

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