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Photoelectrocatalytic degradation of organic pollutants in wastewater using titania nanotube arrays: a proof-of-concept study

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ABSTRACT

This study explored the application of highly ordered TiO_2 nanotube arrays in photoelectrocatalytic degradation of organic pollutants. In this proof-of-concept study, model compounds such as ethylene glycol and oxalic acid were used as organics representing pollutants in wastewater. The primary objective of the research was to demonstrate the unique photoelectrocatalytic activity of TiO_2 nanotube arrays in degrading organic compounds with an added benefit of hydrogen production that takes place in a same unit of operation. The TiO_2 nanotube arrays with controllable properties were synthesized by anodization approach. The TiO_2 nanotube arrays possess excellent separation and transport properties for photo-generated electron/hole pair and hence exhibit enhanced photocurrent response and photocatalytic properties for organic compound degradation and hydrogen production. Factors affecting degradation performance were investigated. Results have shown that the pH of electrolyte solution, the chemical property of electrolyte, initial concentration of model pollutants, the redox property of the pollutants, and bias potential were all interrelated that affect the photoelectrocatalytic performance of TiO_2 nanotube arrays. For example, when 0.1 M KOH was used as electrolyte in the presence of 0.5 M ethylene glycol solution, the highest current density of 0.04 mA/cm^2 was achieved at bias potential of 0.45 V.

Keywords: TiO_2 nanotube arrays; Photoelectrocatalytic; Hydrogen generation; Organic degradation; Photocurrent density

1. Introduction

The photo-generated electrons on the conduction band of a photoelectrocatalyst play an important role in photocatalytic process for hydrogen production. However, the photo-generated electrons and holes over TiO_2 nanomaterials exhibit extremely quick recombination rate. The addition of electronic sacrificial agent in the solution can irreversibly capture photo-generated holes, therefore effectively reducing the probability of recombination. The presence of sacrificial agent can not only improve the separation efficiency of electrons and holes but also increase the number of electrons in the conduction band that ultimately facilitates the hydrogen generation reaction. Sodium carbonate is an electronic sacrificial agent, which can improve the efficiency of photocatalytic hydrogen generation enabling the formation

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of hydrogen and oxygen at stoichiometric ratio. Many studies suggest that, as an electronic sacrificial agent, sodium carbonate is beneficial to hydrogen generation efficiency for many semiconductor type of photocatalysts. This is largely because CO_3^{2-} can irreversibly capture photo-generated holes leading to significant increase in the number of photogenerated electrons [1–2].

Organic compounds such as alcohols, organic acids, aldehyde, EDTA or CN^- can serve as electron donors to capture photo-generated holes in the valence band of a photoelectrocatalyst. Some of these organic compounds are pollutants present in wastewater. Photoelectrocatalytic conversion of these organic compounds can degrade the pollutants and simultaneously produce hydrogen in a single unit of operation [3], achieving both environmental and economic benefits. When an organic pollutant is employed as an electronic sacrificial agent, an optimal concentration level exists, exceeding which the photon absorption efficiency for TiO_2 decreases. On the other hand, the use of higher concentration of sacrificial agent can cause competing absorption over photoelectrocatalyst, severely inhibiting the performance of hydrogen generation. Liu et al. [4] studied the effect of initial concentration of *n*-propanol on the performance of photocatalytic hydrogen generation. The results revealed that hydrogen generation rate is positively associated with the increase of initial concentration of *n*-propyl alcohol, indicating that the amount of hydrogen generated is directly related to the concentration of *n*-propanol adsorbed on the photocatalyst [4]. The effect of pH of *n*-propanol solution on the photocatalytic hydrogen generation was investigated and it was found that maximum amount of hydrogen was obtained at pH = 5 [5,6]. In addition, strongly acidic solution inhibited hydrogen generation. Meanwhile, the amount of photocatalytic generated hydrogen was lower in alkaline or neutral solutions. However, when pH of solution was greater or equal to 7, the amount of photocatalytically generated hydrogen was steady [6]. This indicates that the performance of wastewater degradation strongly depends on the pH and the type of organic compounds present in wastewater.

The concentration of NaCl electrolyte showed strong impact on oxidative degradation of rhodamine B (RhB) using TiO_2 as an electrocatalyst [7–9]. This is largely because the addition of NaCl electrolyte increases electrical conductivity of the reaction system, facilitating photoelectrocatalytic reaction kinetics. At appropriate NaCl concentration, H_2O_2 is produced at cathode, and in the meantime, strong oxidizing agent Cl_2 is produced at anode which is quickly converted into electron acceptor HClO to participate in oxidation reaction. The degradation performance is enhanced significantly because of the synergy between photoelectrocatalytic degradation and chemical oxidation. However, when NaCl concentration is too high, the consumption of hydroxyl group •OH increases, inhibiting photoelectrocatalytic reaction. Meanwhile, higher NaCl concentration results in an increase of ionic strength in the solution restricting the thickness of the double electric layer on TiO_2 surface and promoting the condensation of TiO_2, which obviously decreases the performance in degradation reaction [10,11]. Thus, the concentration of electrolyte solution is critical in photoelectrocatalytic degradation of organic compounds and hydrogen production.

The efficiency of hydrogen production is affected by the pH of electrolyte. In the presence of water (pH = 7), high electrolysis voltage is required due to poor conductivity and electrical resistance. In order to reduce the resistance of electrolyte, alkaline ions such as Ba^{2+} and K^+, and anions such as Cl^- and OH^- can be added. In addition, studies showed that the band structure of semiconductor type of photocatalyst will change in the presence of electrolytes at different pH values [9]. In alkaline solution, with the increase of pH in electrolyte the open circuit voltage of a single-cell system increases, therefore the rate of photoelectrocatalytic hydrogen production is increased significantly under constant bias potential. It has been reported that semiconductor type of photocatalysts can effectively degrade organic pollutants and simultaneously produce hydrogen. However, hydrogen production is mainly caused by the bias potential which has exceeded the decomposition voltage of water. Energy savings can be achieved if degradation reaction and hydrogen production can be operated at bias potential lower than water decomposition voltage.

The concentration of electrolyte solution can directly affect the conductivity of solution, which will influence the efficiency of separating photo-generated electrons and holes, and ultimately affect the photoelectrocatalytic reaction. Habibi et al. [12] studied photoelectrocatalytic degradation of rhodamine B and found that when sodium sulfate concentration was lower than 0.5 g/L, the decolorization rate of the dye rose with increase in the concentration of sodium sulfate solution. When the concentration of sodium sulfate solution was higher than 1.0 g/L, the decolorization rate declined with the increase of sodium sulfate concentration. This is because the sodium sulfate can not only increase the conductivity of the electrolyte and enhance the transmission of photo-generated electrons, but also react with hydroxyl free radical (•OH) to form low activity SO_4^-• radical, causing the decrease in photoelectrocatalytic efficiency [13–16]. The reaction mechanism is illustrated in Eq. (1):

$$SO_4^{2-} + \bullet OH \rightarrow SO_4^{-}\bullet + OH^- \qquad (1)$$

In the photoelectrocatalytic system, the potentiostat voltage has an important influence on photoelectrocatalytic reaction. Many studies showed that, in the presence of bias voltage without light illumination or under light illumination without bias voltage, the concentration of organic pollutants changed slightly with time [17–19]. This finding indicates that it is critical to produce photo-generated electrons and holes using light energy source that exceeds band gap energy, and in the meantime, apply bias voltage to effectively separate photo-generated electrons and holes. For different photoelectrocatalytic reaction systems, the optimal bias voltages are different. For example, the optimal bias voltage for the degradation of acid scarlet 3R (reference electrode) is 660 mV [11,14,20–22], whereas the optimal bias voltages for degradation of diethyl phthalate and nitrophenol are 700 mV and 1.0 V, respectively [23–25]. Li et al. [5] adopted the photoelectrocatalytic approach for the degradation of rhodamine B and found that when bias voltage was in the range of 0–0.5 V, the photocurrent increased and the degradation efficiency improved significantly. In order to further improve the efficiency of photoelectrocatalytic degradation of organic pollutants and hydrogen production, the influence of reaction variables including electrolyte conductivity, the pH of the electrolyte, the concentration of pollutants, the chemical property of pollutants, and bias voltage, on the photocurrent were investigated using titania nanotube arrays (TNAs) as a catalyst.

2. Materials and methods

2.1. Experimental apparatus and materials

Photoelectrocatalytic experiments were carried out in an Electrochemical Workstation (CHI660D, Shanghai). Xenon lamp was used as a light source. TNAs electrode was characterized by scanning electron microscope (SEM). Titanium sheet (99.99% purity) and platinum electrode (99.99% purity) were used in the experiments. The reagents used in the experiments were supplied by Tianjin Concord Reagent Company (Tianjin, China). All electrolyte solutions were prepared using deionized water.

2.2. Preparation of TNAs electrode

TNAs electrode was prepared by anodic oxidation method via electrochemical process. The titanium plate was first polished with sand paper followed by washing in acetone, ethanol and deionized water in an ultrasonicated bath at 6°C. After cleaning, the titanium plates were installed as anode and cathode in the electrochemical workstation. The electrolyte consisted of 0.5 wt% NH_4F, 2.0 vol% H_2O and 98 vol% ethylene glycol. The anodic oxidation was carried out at 60 V for 6 h. The TNAs electrode thus fabricated was washed in ethanol and deionized water repeatedly followed by drying in air and calcining at 450°C for 3 h. XRD analysis showed that anatase phase was the major crystal structure of TiO_2 nanotube arrays.

2.3. Experimental device

TNAs electrode with dimension of 2.5 cm × 2.5 cm × 0.25 mm was used as a photoanode. Platinum wire was used as a cathode. The reference electrode used was a saturated calomel electrode (SCE). The degradation and hydrogen production experiments were carried out in the electrochemical workstation. The reactions that take place on anode and cathode are illustrated in Eqs. (2)–(9).

On the anode:

$$2hv + TiO_2 \rightarrow TiO_2 + 2e^- + 2h^+ \tag{2}$$

$$h^+ + H_2O(l) \rightarrow 1/2O_2(g) + 2H^+ \tag{3}$$

$$e^- + O_2 \rightarrow O_2\bullet \tag{4}$$

$$h^+ + H_2O \rightarrow OH\bullet + H^+ \tag{5}$$

$$h^+ + O^- \rightarrow OH\bullet \tag{6}$$

On the cathode:

$$2H^+ + 2e^- \rightarrow H_2(l) \tag{7}$$

Overall reactions:

$$h^+ \text{ and } O_2\bullet- \text{ or } OH\bullet + \text{pollutants} \rightarrow \text{degradation products} \tag{8}$$

$$hv + H_2O(l) \rightarrow 1/2O_2(g) + H_2(g) \tag{9}$$

where h represents Planck's constant, v is the frequency of light source, and h^+ represents the light hole.

2.4. Experimental methods

Photoelectrocatalytic system for wastewater treatment and hydrogen generation comprised of TNAs photoanode, photocathode, substrates, light source, electrolyte and a quartz reactor. The photocathode and photoanode were installed in the substrate electrolyte solution containing 0.1 M Na_2SO_4. Ultraviolent light source was generated from filtered xenon lamp (XQ150 supplied by Sichuan Spectrum Photoelectric Co., Chengdu, China). The filter was D = 3 cm, $\lambda > 425$ nm, supplied by Shanghai Jin Lunmuda optronics Co., Shanghai, China). The light source with the illumination intensity of 60 mW/cm^2 was placed at a distance of 20 cm from the photoanode. During the photocatalytic reaction, organic compounds were oxidized on the photoanode, and in the meantime electrons produced were transferred through the external circuit to the cathode where hydrogen was produced. Bias voltage was supplied from electrochemical workstation. The photocurrent curves of photoelectrocatalytic system were measured and recorded by the electrochemical workstation. The photoelectrocatalytic activities of TNAs were estimated in accordance with the photocurrent density, the oxidation degradation of pollutants and hydrogen generation.

The microstructural features of the TNAs were characterized using a field emission scanning electron microscope (FESEM, 1530VP). The crystalline structure of the TNAs was determined by an X-ray diffractometer (AXS-8 Advance, Bruker, Karlsruhe, Germany). The composition of TNAs was analyzed by X-ray photoelectron spectroscopy (XPS; Kratos Axis Ultra DLD, Al Kα radiation). The photoelectrochemical measurements of TNAs photoanode were performed in a conventional three-electrode electrochemical workstation. TNAs electrode having effective photoactive area of 6.0 cm^2 was employed as the working electrode, and an SCE and a platinum wire electrode served as the reference and counter electrode, respectively. The electrochemical potentials measured were all referred to the SCE unless otherwise stated.

3. Results and discussion

3.1. Characterization of TNAs

The morphology and structure of TNAs were characterized by means of SEM. As shown in Fig. 1, the nanopore length, inner diameter, wall thickness, roughness factor and aspect ratio of TNAs are 25.9 μm, 125.1 nm, 10.2 nm, 175, and 178, respectively.

The X-ray diffraction patterns of TNA and Ti metal sheet are shown in Fig. 2. The TNAs fabricated by anodic oxidation displays a pure anatase phase at (101) crystal face. Average TiO_2 grain size of at (101) crystal face can be calculated by

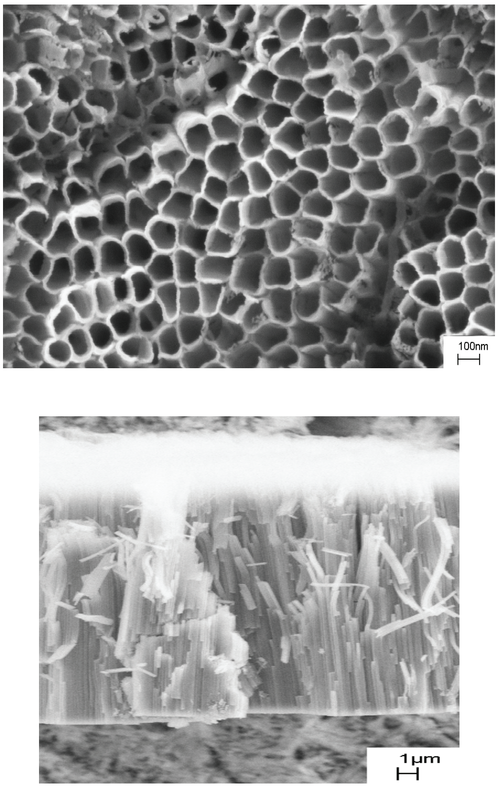

Fig. 1. Morphology and structure of TNAs characterized by SEM.

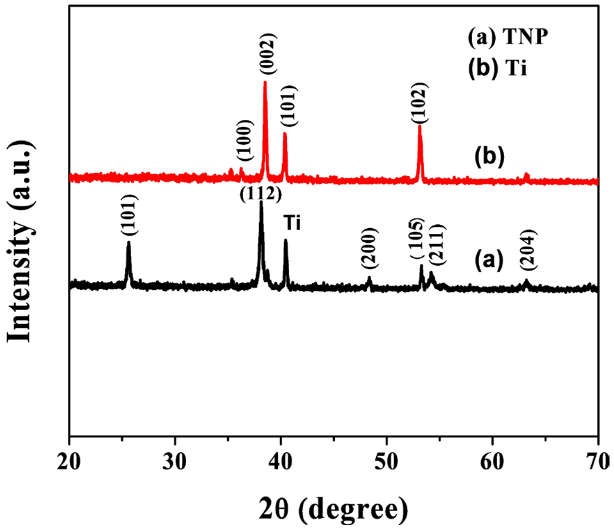

Fig. 2. X-ray diffraction patterns of TNAs and Ti.

using the Debye–Scherrer equation. The grain size of (101) crystal face for TNAs fabricated by anodic oxidation is 42.98 nm. The composition of the TNAs microstructure was determined by XPS.

Fig. 3 illustrates the XPS spectrum of the as-annealed TNAs. The XPS characterization results indicate that the main elements on electrode were titanium and oxygen. Trace amounts of carbon and nitrogen elements were found on the TNAs electrode owing to the residuals from ethylene glycol and NH_4F which were adsorbed on the surface.

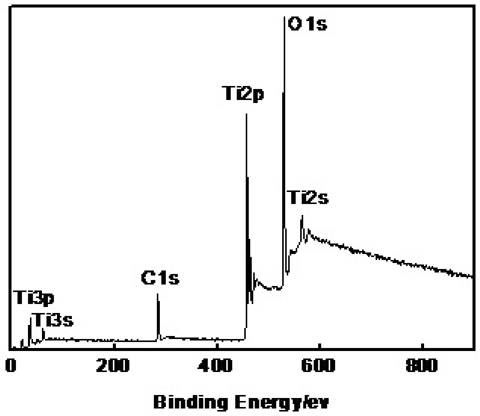

Fig. 3. Characterization of TNAs by XPS.

3.2. Influence of electrolyte on the photoelectrocatalytic performance

The chemical property and composition of electrolyte have strong impacts on the photoelectrocatalytic process. All TNAs presented in this study were prepared under oxidation voltage of 60 V and oxidation time of 6 h, and their photoelectrocatalytic performance was measured under 0.45 bias voltage. As shown in Fig. 4, when 0.5 M ethylene glycol (EG) is used as a model compound representing an organic pollutant in wastewater, the highest current density is obtained using 0.1 M KOH solution as electrolyte. When 0.1 M KOH electrolyte solution is replaced by 0.1 M Na_2SO_4 solution, current density drops from about 0.04 to 0.025 mA/cm^2. A slight decrease in current density is observed when 0.1 M Na_2SO_4 is replaced by 0.1 M Na_2CO_3. The results indicate that in strong alkaline, the photocurrent density generated from degradation of EG depends on the strength and activity of alkaline cations (K^+, Na^+) and anions (OH^-, SO_4^{2-}, CO_3^{2-}). Obviously, alkaline electrolytes provide more hydroxyl ions, therefore more hydroxyl radicals, which facilitate degradation and increase photocurrent intensity. The cation plays a minimal role.

3.3. Impact of electrolyte pH on photoelectrocatalytic performance

In the first set of experiments, 0.1 M Na_2SO_4 solution was used as electrolyte without adding EG. The experiments were conducted under three different pH of 2, 6.8, and 10. The second set of experiments was conducted under the same conditions except the presence of EG. Fig. 5 illustrates the effect of pH on photocurrent density in degradation of EG. In the absence of EG, the photocurrent density measured are 0.0083, 0.013, 0.01 mA/cm^2, respectively. Photocurrent densities are almost doubled in the presence of EG for all three different pH solutions. In both sets of experiments, the highest photocurrent density was obtained at pH = 6.8.

In photoelectrocatalytic degradation of EG, the pH of electrolyte exhibits multiple effects on the process performance. First of all, the pH of an electrolyte affects the charge property of organic pollutant (EG) as well as the charge property of TiO_2 photocatalyst, which will directly impact adsorption and desorption behavior of TiO_2 photocatalyst. Second, the pH of electrolyte can affect the band edge position and

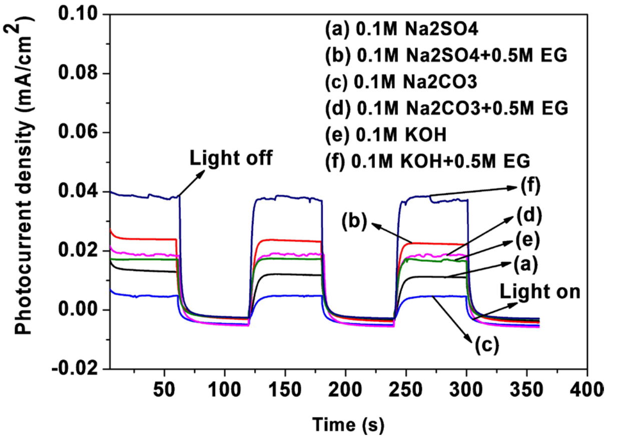

Fig. 4. Photocurrent density of TNAs in different electrolyte solution.

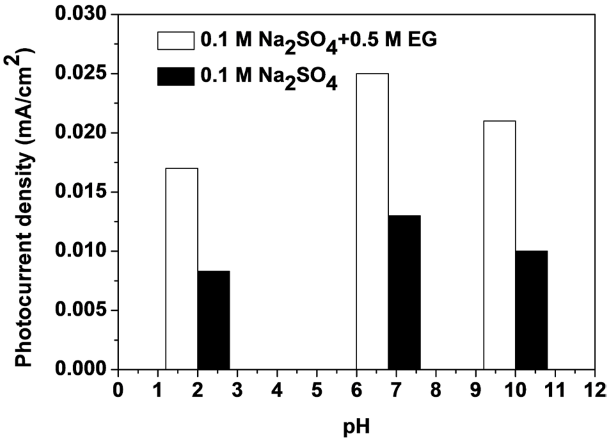

Fig. 5. Photocurrent density of TNAs in different pH electrolyte solutions.

the flat band potential of TiO_2, thus influencing the oxidation and reduction ability of photo-generated electrons and holes. In addition, the pH of electrolyte can affect the concentration of hydroxyl ions (OH^-), which is crucial to the generation of the hydroxyl free radicals (OH•) during the photoelectrocatalytic oxidation reaction [26,27]. As a result, Na_2SO_4 electrolyte containing EG was more conductive and effective in photoelectrocatalytic degradation of organic pollutants.

3.4. Impact of pollutant concentration on photoelectrocatalytic performance

The experiments were carried out in 0.1 Na_2SO_4 electrolyte solution at pH = 6.8 and bias potential of 0.45 V. Fig. 6 shows a positive relationship between initial EG concentration and photocurrent density. At EG concentration of 0.0, 0.1, 0.25, and 0.5 M, the corresponding photocurrent densities are 0.013, 0.013, 0.021, and 0.024 mA/cm², respectively. Magnifying the initial concentration of EG can increase the number of EG molecules adsorbed on the surface of TiO_2 photocatalyst, which favors the capturing of photo-generated holes and transferring more photo-generated electrons to the counter electrode. As a result, increasing the concentration of EG makes the electrolyte solution more conducive, favoring photoelectrocatalytic degradation of pollutants and hydrogen generation.

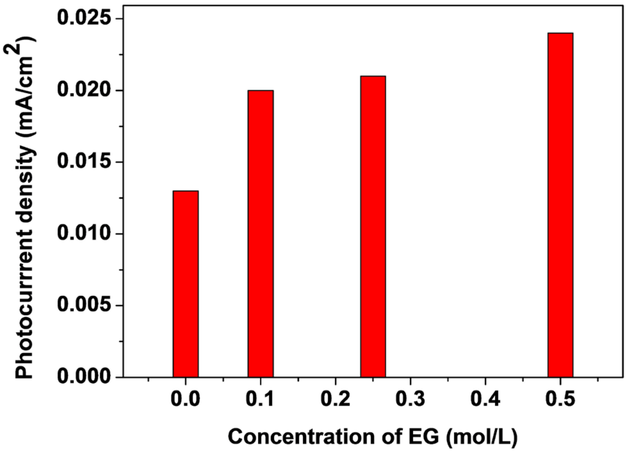

Fig. 6. Photocurrent density of TNAs under different concentration of ethylene glycol (pH = 6.8).

3.5. Impact of bias potential on photoelectrocatalytic performance

The impact of bias potential on photocurrent density was studied using 0.1 M Na_2SO_4 electrolyte solution at pH value of 6.8. The bias potential was varied between 0.45 and 0.9 V. As shown in Fig. 7, in the absence of EG, if bias potential is doubled, photocurrent density only drops slightly from 0.013 to 0.012 mA/cm². In contrast, when EG is added to the electrolyte, photocurrent density decreases from 0.024 to 0.015 mA/cm² due to photoelectrocatalytic degradation of EG. Bias voltage negatively affects photoelectrocatalytic degradation of EG.

3.6. Impact of pollutants' chemical property on photoelectrocatalytic performance

EG and oxalic acid were used as model compounds for the study. In the experiments, 0.1 M Na_2SO_4 was used as electrolyte solution. The experiments were carried out under three different bias potential of 0.0, 0.45, and 0.9 V. As shown in Fig. 8, in the presence of either EG or oxalic acid, photocurrent density is positively related to the increase of applied bias potential. When bias voltage is not applied, the photocurrent density of EG containing solution is slightly higher than that of oxalic acid containing solution. Compared with oxalic acid, the molecular size of EG is smaller. As a result, the surface of TNAs photoanode can adsorb more EG molecules capable of transferring more electrons, therefore producing stronger photocurrent. This explains why without externally applied bias potential, TNAs exhibit stronger photocatalytic effect on EG. With the increase of applied bias potential, the photocurrent density in oxalic acid containing solution is greater than that of EG. This is largely because the redox potential of oxalic acid is lower than EG, meaning that oxalic acid molecule is more easily oxidized by photo-generated holes. Thus, when bias potential is applied, photoelectrocatalytic effect become more significant in oxalic acid containing solution.

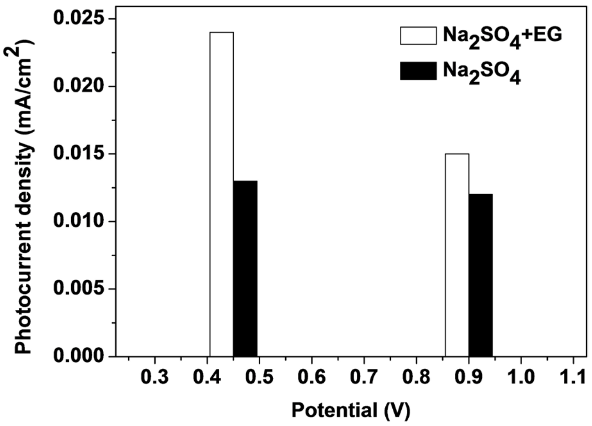

Fig. 7. Photocurrent density of TNAs under different bias potential (pH = 6.8).

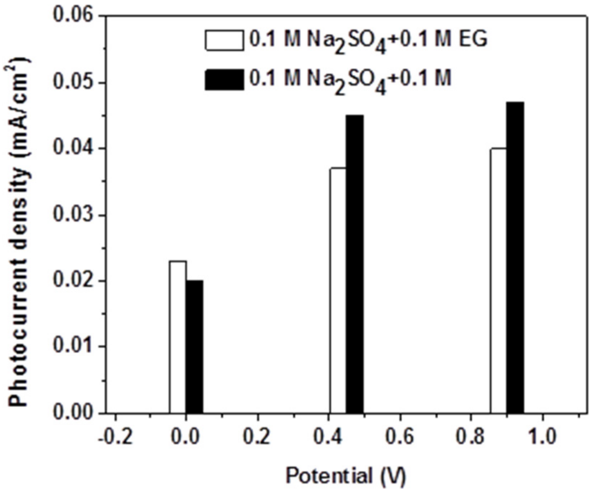

Fig. 8. Photocurrent density of TNAs under different pollutants.

The bias potential was 0.45 V. The production of H_2 was measured in homemade quartz reactor that was connected with a gas chromatograph (GC 2010plus, Shimadzu, Japan). As shown in Fig. 9, when the concentrations of methyl orange were 5, 10, 15, 20, 25 mg/L, the H_2 evolution rates were 18.31, 32.42, 44.71, 57.90, and 69.13 μmol cm^{-2} h^{-1}, respectively. Meanwhile, the photocurrent density values were 0.22, 0.71, 1.11, 1.48, and 1.78 mA cm^{-2}. At the same time, the degradation efficiency of methyl orange as model organic matter was 81.31%, 85.75%, 88.81%, 91.36%, and 93.12%, correspondingly. These results confirm that the increase in methyl orange concentration can capture more photo-generated holes, which facilitates the outstanding enhancement of the photocurrent density, H_2 evolution rates and the degradation efficiency of methyl orange as refractory organic pollutant. The photocurrent supplies electrons at the cathode for hydrogen generation.

4. Conclusions

The TNAs photoelectrode reported in this study comprises of highly ordered nanotube structure on which photo-generated electrons can rapidly be formed and effectively transmitted. TNAs possess excellent separation and transport properties of photo-generated electron/hole pair and hence exhibit enhanced photocurrent response and photochemical properties for water splitting and organic compound degradation. The TNAs photoelectrode can be utilized for wastewater treatment and simultaneous hydrogen production, enabling two processes to take place in a single unit operation. The performance of photoelectrocatalytic degradation depends on a number of interrelated reaction variables including pH of electrolyte solution, the chemical property of electrolyte, initial concentration of model pollutants, the redox property of the pollutants, and bias potential. The photocurrent was positively related to hydrogen generation rate. System approach is necessary to achieve optimal performance. Our research demonstrates that energy savings can be achieved if degradation reaction and hydrogen production can be operated at bias potential lower than water decomposition voltage. Therefore, photoelectrocatalytic wastewater treatment and hydrogen production based on TNAs photoanode have both economic and environmental potentials.

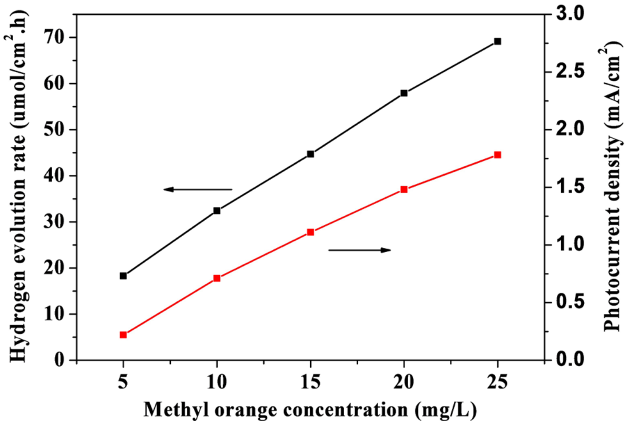

Fig. 9. Relation plot of methyl solution (5, 10, 15, 20, 25 mg/L) with 0.1 M Na_2SO_4 electrolyte between hydrogen evolution rate and photocurrent density in the photoelectrocatalytic system.

Acknowledgments

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