

Research Article

Electrolyte Concentration Effect of a Photoelectrochemical Cell Consisting of TiO_2 Nanotube Anode

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The photoelectrochemical responses of a TiO_2 nanotube anode in ethylene glycol (EG), glycerol, ammonia, ethanol, urea, and Na_2S electrolytes with different concentrations were investigated. The TiO_2 nanotube anode was highly efficient in photoelectrocatalysis in these solutions under UV light illumination. The photocurrent density is obviously affected by the concentration change. Na_2S generated the highest photocurrent density at 0, 1, and 2 V bias voltages, but its concentration does not significantly affect the photocurrent density. Urea shows high open circuit voltage at proper concentration and low photocurrent at different concentrations. Externally applied bias voltage is also an important factor that changes the photoelectrochemical reaction process. In view of the open circuit voltage, EG, ammonia, and ethanol fuel cells show the trend that the open circuit voltage (OCV) increases with the increase of the concentration of the solutions. Glycerol has the highest OCV compared with others, and it decreases with the increase in the concentration because of the high viscosity. The OCV of the urea and Na_2S solutions did not show obvious concentration effect.

1. Introduction

Titanium dioxide (TiO_2) has been widely studied because it has good photovoltaic property. Photoelectrochemical cell (PEC) is a device that could degrade pollutants, splitting water by utilizing photon energy while electric energy is generated. Clean energy generation by environmentally friendly method is a very important issue. Hydrogen is used in fuel cells, but nature gas is still a main source for hydrogen production. It contains contaminative byproducts. Only a few part of hydrogen is produced by water splitting in the world [1]. Pollutant degradation is another very important application of PEC. TiO_2 nanostructured anode has the high potential for clean energy production and hazardous material degradation. Many hazardous organic materials can be converted into clean substances by TiO_2 anode PEC, which include methylene blue [2, 3], glucose [4],

organic compounds [5, 6], waste water [7], dye pollutant [8], and even CO_2 [9] of the greenhouse gas.

By using various electrolytes, different levels of open circuit voltage, current density, filling factor can be reached [10–12]. The bias potential and concentration of electrolytes can also influence the performance of a PEC cell. Normally, the additionally applied external bias voltage can further enhance the PEC reaction process because the conduction band edge of anode material cannot lie above the energy level. Quan et al. [13] selected 0.0, 0.2, 0.4, and 0.6 V bias and 0, 0.005 M, and 0.01 M Na_2SO_4 electrolyte used in PEC and study on the effect. Normally, the higher bias and concentration enhanced the PEC process. But not all of the high concentration can benefit the fuel cell. There is a watershed for concentration effect on PEC. When the concentration reached a level, performance of PEC will be stabilized [14]. Some papers mentioned the concentration

effect on the performance of PEC, but the concentration range is all within a small range from 0.001 M to 0.5 M [4, 15, 16]. Such a small range concentration has limitation. A wide range (0 to 100% or saturated) of concentration would allow us to know this effect better. Milczarek et al. [17] studied the concentration effect of sulfuric acid within the range from 0.5 to 5 M. No significant effect due to the change in the sulfuric acid concentration was found. Most of people would like to choose 1 M H_2SO_4 as an optimal concentration for PEC. The iodine concentration effect was studied by Hao et al. [18]. When the iodine concentration increased from 0.025 to 0.1 M, OCV and photocurrent density decreased, while the fill factor increased. The best concentration of electrolyte can enhance the performance of PEC. But different solution shows different concentration effect.

In this paper, we selected three main types of solutions including alcohols, polyols, and some pollutant materials. Different with others' research, the concentration range is broader, which is from 0 to saturated. The purpose of this study is to find the best concentration for each solution and compare the different processes of these electrolytes in PEC.

2. Experimental

2.1. Chemicals. All chemicals were used as received without further purification. Ti foil (99.9% purity, 0.127 mm), ethanol (99% purity), ethylene glycol (99% purity), glycerol (99% purity), urea (99.9% purity), $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (98% purity), NH_4OH (30% wt. NH_3), H_3PO_4 (85% wt in water), and NaF (98% purity) were purchased from Alfa Aesar.

2.2. TiO_2 Nanotube Fabrication. Electrochemical anodization method was applied to synthesize self-organized TiO_2 nanotube by using titanium foil (3 mm \times 40 mm). Before electrochemical anodization, the titanium foil was cleaned using acetone, ethanol, and distilled water, and dried in air stream. TiO_2 nanotube was fabricated in 1 M H_3PO_4 and 0.2 M NaF solutions where the Ti foil was used as anode and a platinum wire was used as cathode. The voltage and time for anodizing Ti are 20 V and 19 hours. The nanotube was cleaned by using distilled water and the samples were dried in air. Anodization was performed at 25°C. The TiO_2 nanotube was annealed in the air at 450°C for 4 hours to convert the amorphous structure of TiO_2 into anatase crystalline structure.

2.3. Fuel Concentration. We used ethanol, and ethylene glycol, glycerol, urea, Na_2S , ammonia as the fuels. The concentrations of ethylene glycol, glycerol, and NH_4OH were from 0 to 100% wt. The concentrations of urea were from 0 to 108 g/mL water (saturated), and those of Na_2S were from 0 to 20 g/mL water (saturated) at 25°C.

2.4. Photoelectrocatalytic Response. A photoelectrochemical fuel cell was made using the TiO_2 NTs anode, Pt wire cathode. Ethanol, ethylene glycol, glycerol, urea, Na_2S , and ammonia were used as the fuels, and the ultraviolet lamp was the UVL-21 (365 nm UV, 4 W, 0.16 Amps) with the illumination

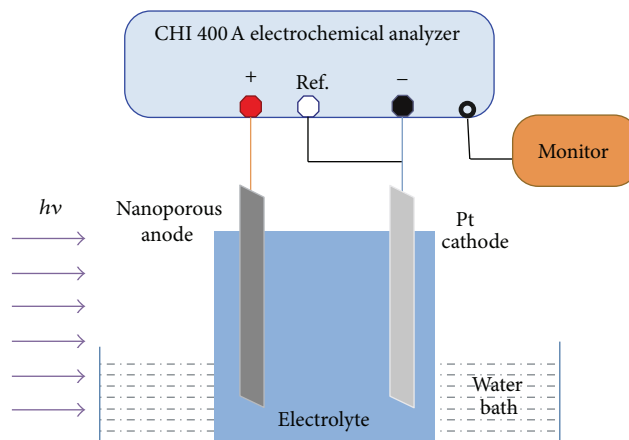


FIGURE 1: Schematic diagram of the PEC system.

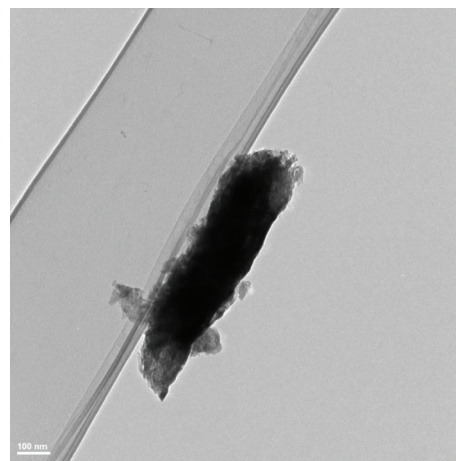


FIGURE 2: TEM image of a TiO_2 nanotube.

intensity of 40 mW/cm^2 . The water bath is used to keep the temperature as constant. A CHI 400A electrochemical workstation was used to measure the open circuit voltage and current density of the fuel cell and supply the bias potential (Figure 1).

3. Results and Discussion

3.1. TEM Image Analysis. TiO_2 nanotube specimen was examined by transmission electron microscopy (TEM) using the JEOL 2100F TEM. Figure 2 is the TEM image of a typical TiO_2 nanotube. The TiO_2 nanotube was scraped off from the Ti substrate before examination on the TEM. The length of nanotube is 770 nm and the diameter is 200 nm.

3.2. Photocurrent Density. For testing the open circuit voltage, we used the two-electrode method (Figure 1). Compared with the method using the Ag/AgCl reference, the two electrode approach is more stable because there is no unwanted chemical reaction during testing. In order to study fuel concentration effect on the PEC process, we selected five solutions which contained three major substances, alcohols,

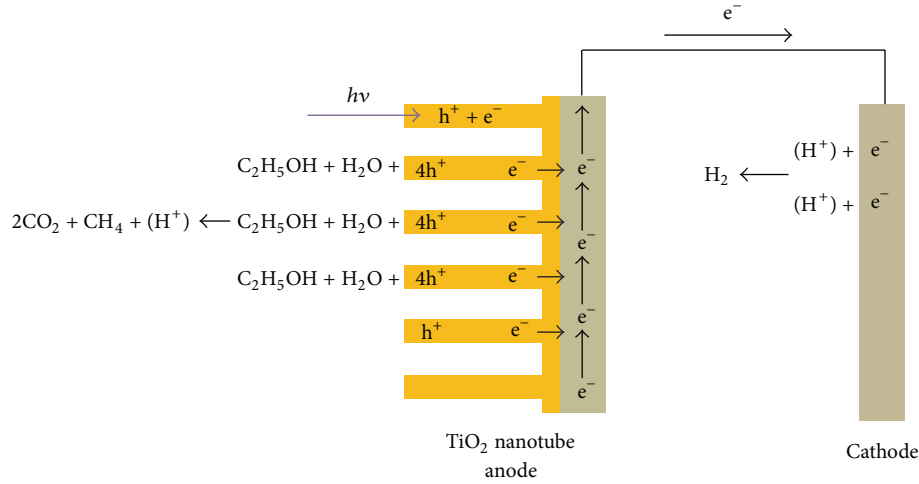


FIGURE 3: Mechanism of PEC using ethanol as the fuel.

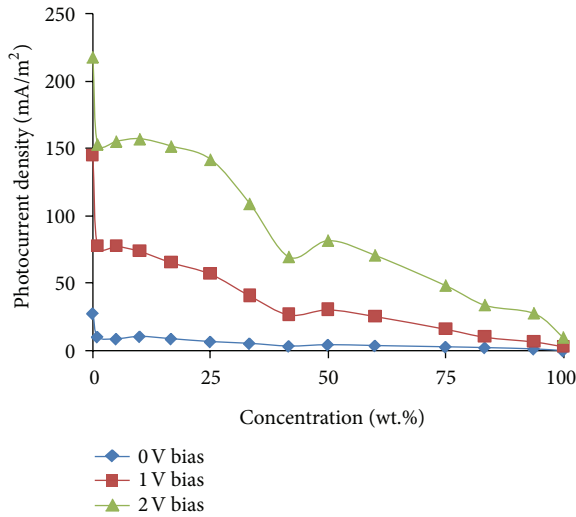


FIGURE 4: Photocurrent density versus concentration of ethanol at different bias potentials.

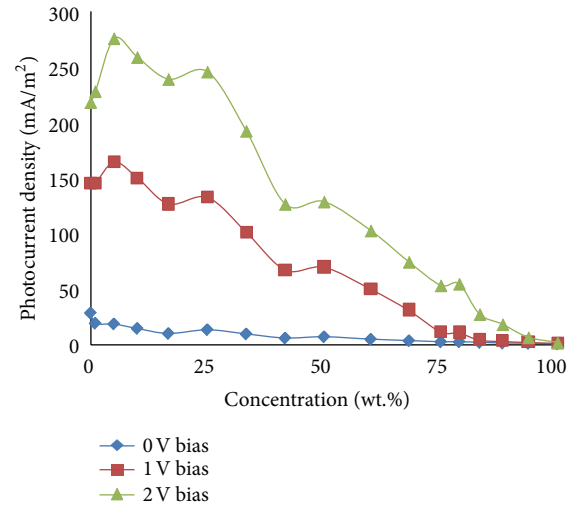
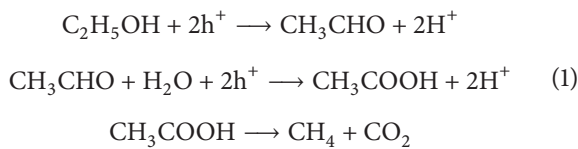
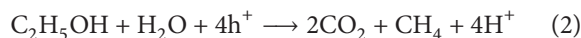


FIGURE 5: Photocurrent density versus concentration of ethylene glycol at different bias potentials.

polyols, and pollutant materials. These materials show different PEC properties. For different fuels, the reaction mechanisms are different [19]. Ethanol is an alcohol substance, and the reaction mechanisms are as follows (also shown in Figure 3):



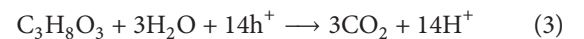
The total reaction is



At the anode, TiO₂ is excited under light energy to form holes and electrons on the surface. Holes will react with the fuels

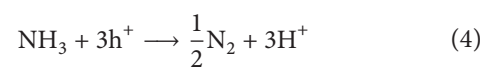
such as ethanol (Figure 3), and water and the reactions can generate CO₂, CH₄ and H⁺. H⁺ flows to cathode through the electrolyte. The higher transfer rate of H⁺ and e⁻ will result in higher current density. The external bias can increase the potential energy of system and the flow rate of electrons and H⁺. So the reaction rate increases with the bias potential level.

For the polyols substance such as glycerol, the reaction is



For same amount of molecules, glycerol generates more CO₂ and H⁺ than ethanol does.

For the ammonia, the chemical reaction at photo anode is as follows:



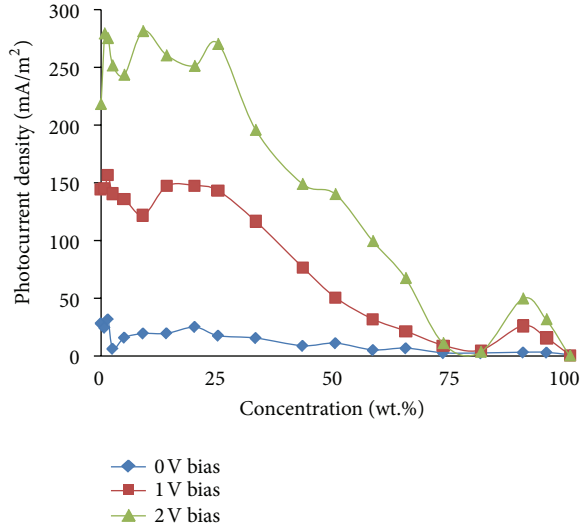


FIGURE 6: Photocurrent density versus concentration of glycerol at different bias potentials.

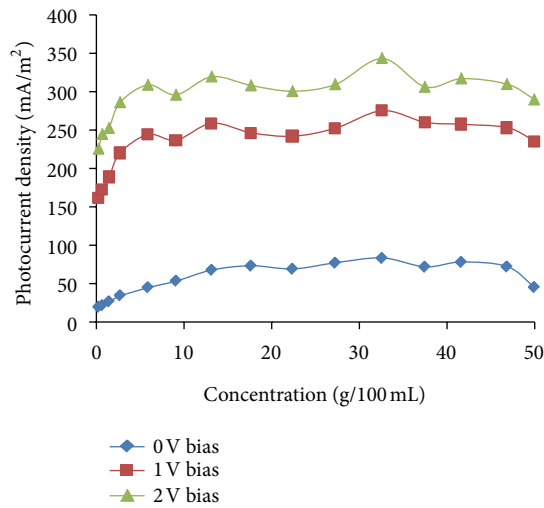
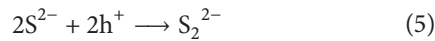


FIGURE 7: Photocurrent density versus concentration of urea solution at different bias potentials.

The Na_2S oxidative process is following the reaction



where h^+ is the hole formed on TiO_2 .

Bias potential draws the induced electrons to the counter electrode. The higher value of the bias, the higher the driver force of the system. A larger photocurrent density should be obtained. We have the same conclusion from the experimental studies as verified by the results from Figure 4 to Figure 9; the highest photocurrent is obtained at 2 V bias and the lowest is obtained at 0 V bias.

The positive and negative ion transfer velocities (v_+ and v_-) increase with the electric field intensity E : $v_+ = \mu_+ E$ and

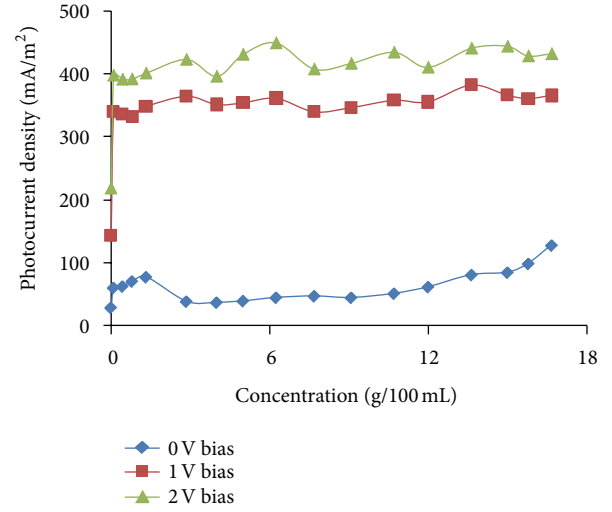


FIGURE 8: Photocurrent density versus concentration of Na_2S at different bias potentials.

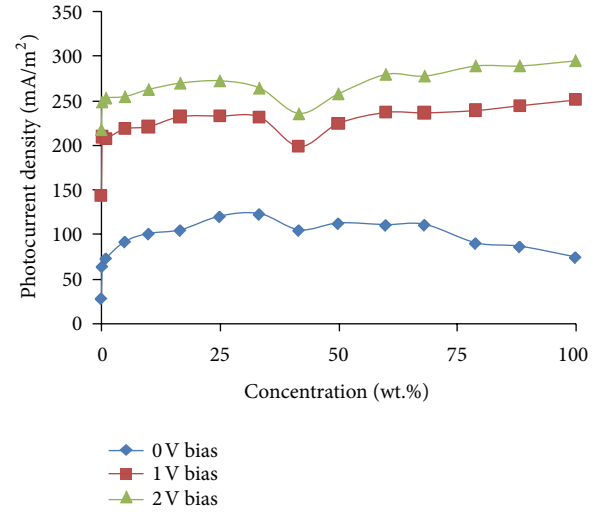


FIGURE 9: Photocurrent density versus concentration of NH_4OH at different bias potentials.

$v_- = \mu_- E$ is the ion transfer rate. A high bias voltage can supply a high value of E . The conductivity of the solution is

$$\sigma = ne(\mu_+ + \mu_-), \quad (6)$$

where σ is the conductivity, n is the ion concentration, and e is the absolute value of electronic charge.

Current density increases with the increase in the ion concentration and mobility. But the mobility of ions increases with decreasing in the solution viscosity. Since glycerol (Figure 4) is a high viscosity substance, with the increase in concentration of glycerol, the high viscosity will impede the ion transfer process.

The alcohols, polyols fuels have the similar performance (Figures 4–7). But the glucose has an opposite trend [4]. The glucose and alcohols are similar organic materials which cannot conduct electrons. But why they show different

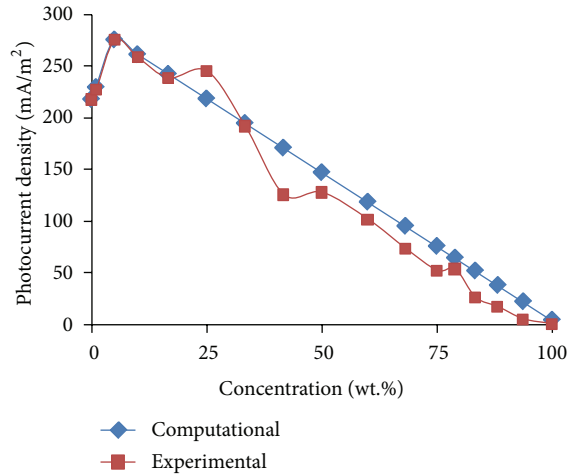


FIGURE 10: Computing results versus experimental data (I versus c) in ethylene glycol at 2 V.

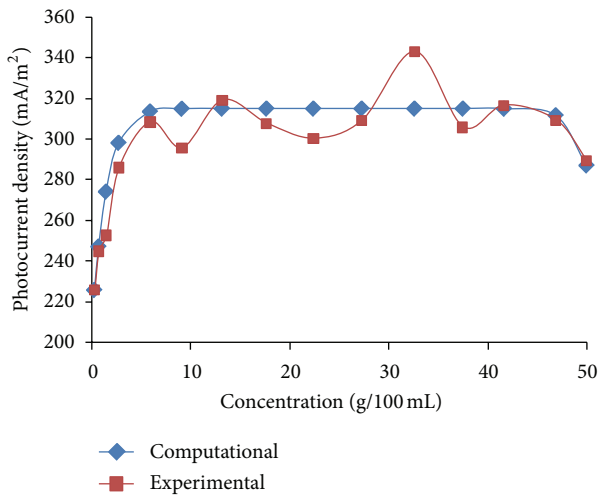


FIGURE 11: Computing results versus experimental data (I versus c) in urea at 2 V.

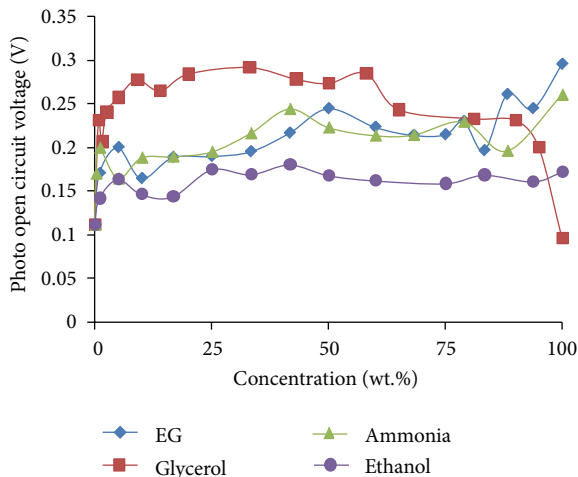


FIGURE 12: Photovoltage versus concentration of ethylene glycol, glycerol, and ammonia.

properties? The reason is due to the fact that the glucose concentration range is small. They only picked the range from 0 to 6 mM/L. If they select the range from 0 to saturated, the result may be changed. Alcohols and polyols are organic substances and the polarity of them is weak. The pure alcohols do not have conductivity. With the water content increase, the water is ionized and the electron conductivity is improved. The photocurrent density of ethanol is the lowest. Compared with ethylene glycol and glycerol, the value of photocurrent density by using ethanol fuel is about 50% lower than that of others. Viscosity is another important factor affecting the microscale diffusion. Current is the density of ions in motion. It is very similar with a concentration flux of mass; that is, Fick's law is satisfied as follows:

$$J(x, t) = c(x, t) v(x, t), \quad (7)$$

where J is the current density, c the concentration, and v the ion transfer rate.

Some solutions with high concentrations have low ion transfer rates, such as alcohols, polyols solutions. These substances are needed to be in electrolyte solutions. The pure alcohols and polyols are not ideal as fuels for PEC. If the concentration increases, the attractive force between the ions will constrain the ion transfer. The micromass transfer and diffusion of alcohol and polyol molecules limit the reactions on the surface of TiO_2 nanotubes. There is a diffusion layer between the TiO_2 nanotube surface and electrolyte. With the concentration being increased, the ionization of alcohols and polyols is decreased. The transfer rate in the diffusion layer is low and causes the photocurrent density to be low. Figure 4 shows I versus c curves of ethanol with different bias. The highest photocurrent is at 1 wt.% which is even lower than the case of pure water as the fuel. The photocurrent density of ethylene glycol is higher than that of pure water (Figure 5). The maximum photocurrent is obtained at 5% wt. of ethylene glycol. The glycerol shows different I versus c characteristic from ethanol and ethylene glycol. The photocurrent density of glycerol is constant and high t 0–25 wt%. When the concentration exceeds 25%, the photocurrent decreases sharply.

Urea, Na_2S , and ammonia are electrolytes that contain larger amounts of free ions. The conductivity of urea, Na_2S , and ammonia is higher than that of alcohols and polyols. In the experiments, the concentration of urea, Na_2S , and ammonia is selected from zero to saturation levels. The current density almost has no change with the concentration variations (Figures 7–9).

Different solutions showed different photocurrent densities. Na_2S solution has the highest photocurrent density which is about 100, 300, or 450 mA/m^2 at 0, 1, or 2 V bias. Generally, ionized solutions have higher photocurrent density than alcohols and polyols. Ethanol has the lowest photocurrent density which is about 10, 75, or 150 mA/m^2 at 0, 1, or 2 V bias. This photocurrent density generated by ethanol is even lower than pure water. The trends of I versus c curves of Na_2S and ammonia are dissimilar to others. The photocurrent almost showed no change with the increase of the concentration (Figures 8 and 9). The ions mobility is

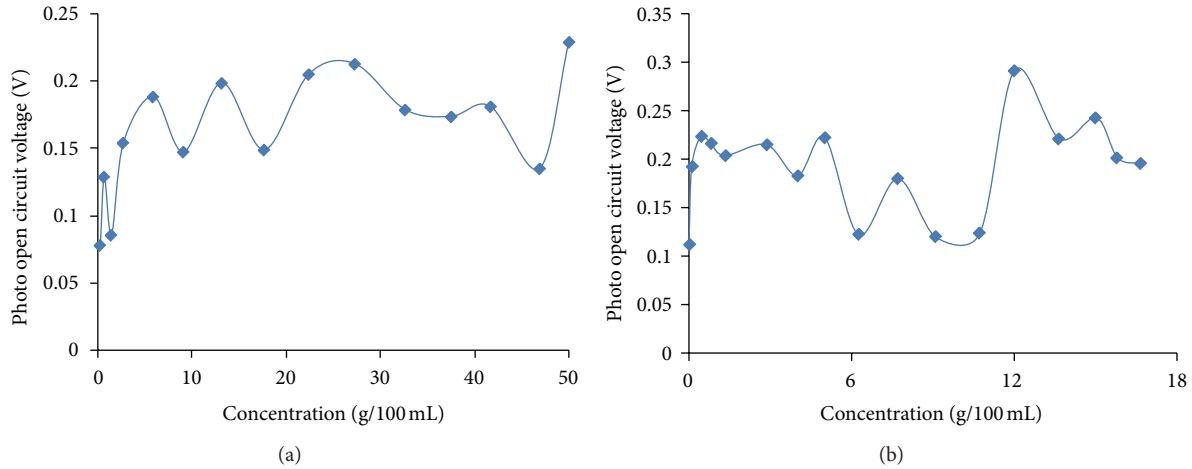


FIGURE 13: (a) Photo voltage versus concentration of urea. (b) Photo voltage versus concentration of Na_2S .

already high, and the high concentration cannot improve it further in Na_2S and ammonia solutions.

3.3. Kinetics Study of Influences on Photocurrent Responding. Figures 4–6 show the photocurrent density obtained from different electrolytes and at various bias potential levels using alcohols, polyols as fuels. The photocurrent density decreases with the concentration increasing. Computer simulation reveals that the I versus c curve of ethylene glycol fits.

$$I = -R_1 \times c + R_2, \quad (8)$$

where R_1 and R_2 are constants and c is the concentration. For ethylene glycol at 2 V bias (Figure 10), the process can be divided into two parts (0–5 wt.% and 5–100 wt.%). For 0–5 wt.%, the R_1 , R_2 are -11.5 and 218.25 . For 5–100% wt., the values of R_1 , R_2 are 2.85 and 290 , respectively. R_1 and R_2 are related to the bias. With the increase of the bias, the values of R_1 and R_2 increased. Higher values of R_1 and R_2 also measure present higher kinetic energies of these systems.

The I versus c curve of urea is not linear (Figure 7). We found that the I versus c curve follows

$$I = -P_1 \times (c - 25)^{16} + P_2, \quad (9)$$

where P_1 and P_2 are two parameters. For urea at 2 V bias (Figure 11), the process may be divided into two parts (0–32.61 g/mL and 32.61–50 g/mL). For concentration of 0–32.61 g/mL, P_1 , P_2 are $4.5E - 21$ and 315 , respectively. For concentration of 32.61–50 g/mL, P_1 , P_2 are $1.2E - 21$ and 315 , respectively. P_1 determined the shape of the plot and P_2 is related to the maximum value of the photocurrent density. We can use these equations to find any concentration versus photocurrent of urea electrolyte.

The behavior of Na_2S and ammonia can simply be expressed by

$$I = Q, \quad (10)$$

where Q is a constant. There is no obvious concentration effect on the photocurrent density for these solutions.

3.4. Photo Voltage. For the open circuit voltage (OCV) test, we also used the two-electrode method. The trend of OCV is that with the increase in concentration of solution, the OCV is increased except for glycerol solution (Figure 12). Glycerol is a high viscosity solution with low ion mobility. When the concentration of glycerol reaches 90%, the OCV is shapely decreased. So, 90% glycerol is a maximum concentration to obtain a reasonable OCV from the system. Glycerol has the maximum photovoltage compared with others and ethanol always has the minimum photo voltage (Figure 12). EG, glycerol, ammonia, and ethanol show a constant voltage with the increase in concentration. But the photo voltage of urea and Na_2S show more fluctuations than others (Figure 13). There are larger concentration effects for urea and Na_2S solutions than for EG, glycerol, ammonia, and ethanol.

4. Conclusions

The kinetics and mechanism of TiO_2 nanotube photoelectrochemical cells with different concentrations of ethanol, EG, glycerol, ammonia, urea, and Na_2S were studied. These solutions can be divided into alcohols, polyols, and electrolyte pollutants three major types. The TiO_2 nanotube anode was highly efficient in photoelectrocatalysis in these solutions under UV light illumination. The concentration effect on kinetic of the PEC with alcohols and polyols is obvious. With the concentration being increased, the photocurrent density was decreased. The reason for this is that the viscosity and mobility of solutions changed at different concentrations. For the concentration effect on electrolyte pollutant materials such as urea, Na_2S , and ammonia, urea has large photocurrent density at middle range (5–45 g/100 mL) and has low photocurrent at low or high concentration regime. Na_2S showed the maximum photocurrent density at 0, 1, 2 V bias compared with others, and the concentration of Na_2S does not affect the value of photocurrent density. External bias voltage is another significant factor affecting the PEC. Obviously, the high bias leads to a large photocurrent. The photocurrent increasing rate was decreased with the increase

in the bias potential. The relationship of I versus c can be defined by $I = -R_1 \times c + R_2$ for alcohols, polyols, and $I = -P_1 \times (c - 25)^{16} + P_2$ for urea by selecting different constant R_1 , R_2 , P_1 , and P_2 . Since the behavior of Na_2S and ammonia shows a horizontal line, it can be expressed as $I = Q$.

In view of the open circuit voltage, EG, ammonia, and ethanol show OCV increasing with the increase of the solution concentration. Glycerol has the maximum OCV and it decreased at the high concentration because of the high viscosity. Urea and Na_2S solutions did not show obviously concentration effect.

Acknowledgments

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