Interfacial Analysis of Anatase TiO$_2$ in KOH Solution by Molecular Dynamics Simulations and Photoelectrochemical Experiments

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ABSTRACT: Hydrogen can be produced by photoelectrochemical (PEC) water splitting using a KOH solution as an electrolyte and TiO$_2$ as a photoanode. In this work, we fabricated anatase TiO$_2$ nanoring/nanotube arrays and TiO$_2$ nanotube arrays using an anodic oxidation method, confirmed by field-emission scanning electron microscopy (FESEM) and X-ray diffractometry (XRD), and then conducted the photoelectrochemical experiments with 1 M KOH and Na$_2$SO$_4$ solutions. The bias voltage, small impedance, negative flat-band potential, large capacitance, and depletion layer width in the anatase TiO$_2$–KOH system were observed, leading to the stable and large photocurrent density. To understand the effects of KOH on the interface properties of TiO$_2$–H$_2$O, the electric double layers of anatase TiO$_2$(001), (100), (101)/KOH interfaces were further investigated by calculating the ion–surface interaction with molecular dynamics simulations. It is noted that the number density of potassium ions has the same trend as that of oxygen atoms due to the layering effect in liquids and the strongest ionic hydration of K$^+$ on anatase (101) is observed by analyzing the radial distribution function and coordination number. In addition, the electrostatic characteristics along the TiO$_2$/KOH interfaces were analyzed based on the Grahame double layer model. The potential drops in the outer Helmholtz layer of anatase (001), (100), and (101) surfaces are 1.08, 0.26, and 0.51 V, respectively. Compared with TiO$_2$–H$_2$O systems, the larger potential drops in the TiO$_2$–KOH system explain the phenomenon that KOH solute contributes substantially to a chemical bias in PEC reactions. At the same time, we estimated the depletion layer widths of anatase TiO$_2$(001), (100), and (101) surfaces as 37.48, 173.25, and 64.49 Å, respectively, which are of similar magnitude to the experimental results. Anatase TiO$_2$(100) with the widest depletion layer is suggested in photocatalysis. These works provide a clear understanding of interfacial behavior of KOH on anatase TiO$_2$ from a microscale, which can be used to explain the promotion effect of the KOH electrolyte and guide the design of TiO$_2$ nanocrystals in the PEC system.

1. INTRODUCTION

TiO$_2$ is regarded as one of the popular photoanode materials for solar water splitting into hydrogen and oxygen. Apart from the experimental studies, there are a few theoretical research works that shed light on the electronic structures, thermodynamics of protonation and deprotonation, photocatalytic mechanism, and electron transfer in the process. Moreover, more attention has been paid to the electrode/electrolyte interface. The semiconductor surfaces acquire charge in solution, and then, the charge is balanced by oppositely charged counterions, forming an electric double layer (EDL). Foissy and his colleagues determined the charge density of the double layer at the TiO$_2$–electrolyte interface using complementary techniques, assuming that the double layer is represented by a series of capacitors. Sumita et al. found that water molecules around the interface between TiO$_2$ and bulk water can be described by a two-layer model, which well accounts for the experimental results. Liu et al. reported density functional theory simulations of liquid water on rutile (110) that show that the aqueous film is layered, with slow-moving molecules in the contact layer and fast-moving molecules in the second layer. Futera and English investigated static/structural and dynamic properties of anatase (101) and rutile (110) interfaces with liquid bulk water. A layered, well-organized structure of water in the interface region was clearly observed within 6.5 Å.

Within these contexts, several theoretical continuum models against the solution side of the interface about potential distribution have been developed. In the early time, a parallel plate capacitor model was proposed by Helmholtz. Then, the Gouy–Chapman model, Stern model, and Grahame double layer model were developed by taking electrostatic interaction, particle size, and ion-specific adsorption into account, respectively. In 2004, Predota et al. studied the adsorption
of Rb⁺, Na⁺, Sr²⁺, Zn²⁺, and Ca²⁺ on the rutile (110) surface and found that part of ions formed a diffuse Gouy–Chapman layer. In 2006, Köppen and Langef15 simulated the interface of the rutile (100) surface with the NaCl solution, which confirmed that the Stern model is a rigid compact layer of the adsorbed counterions on the charged TiO₂ surface and a diffused Gouy–Chapman layer. Furthermore, the measurement of the rutile (110)–NbOH solution interface proved that the counterions are not a single layer in the adsorptive state but a diffusion layer.16 In 2007, Ishimatsu et al.17 studied the surface charge densities of the LiCl solution at different concentrations within the framework of the Stern–Grau model.

KOH is commonly used as an electrolyte in the photoelectrochemical (PEC) water splitting system.18,19 Cachet and similar result that TiO₂ nanotubes show notable photocatalytic activity at low concentrations of KOH.23 It is observed that the interfaces of anatase (001), (100), and (101) in 1 M KOH solution have been studied using classical molecular dynamics to simulate the dynamic process of K⁺ and OH⁻ in the {K + (H₂O)}₂TiO₂(110) systems and draw the conclusion that potassium adatoms can facilitate the dissociation of water, forming (OH)⁻ in units with very low mobility on the TiO₂(110) substrate. On the other hand, the structural and dynamic properties of water have significantly changed with the addition of hydroxide, preferring the OH⁻(H₂O)₄ structure at low concentrations of KOH.25 It is observed that the research works about TiO₂ with the KOH electrolyte are mainly carried out through experiments. Herein, we use classical molecular dynamics to simulate the dynamic process of K⁺ and OH⁻ on the TiO₂ surface, which is more conducive to further understand the interfacial behavior from a microscopic scale. In addition, the electric double layer of KOH and the depletion layer of TiO₂ have received much less attention from a molecular simulation point of view. Care must be taken since this can be used to understand the enhanced photoelectrochemical performance in alkaline solution than neutral solution.

From the three main polymorphs of titania occurring naturally (rutile, anatase, and brookite), anatase is the most active one and used abundantly. In our previous work,24,25 the interfaces of anatase (001), (100), and (101) with pure water and anatase (001) with the KOH solution were studied using classical molecular dynamics calculations. Based on these works, the structure and electrostatic characteristics of anatase (001), (100), and (101) in 1 M KOH solution have been discussed in this paper. Toward the TiO₂–H₂O system, the Gouy–Chapman model was suitable for analyzing the interface energy at the solution side, while the Grahame model should be used for the TiO₂–KOH system due to the charged interface in the alkaline medium.25,26 Then, the depletion layer width was calculated. Before that, we prepared one-dimensional TiO₂ nanoring/nanotube (RT) arrays and TiO₂ nanotube (NT) arrays on Ti foils via an anodization process and their photocurrent, capacitance, impedance, flat-band potential, interfacial donor density, and depletion layer width were compared with those of 1 M KOH and Na₂SO₄ as electrolytes to study the role of KOH in photocatalytic water splitting. This investigation, obtained by molecular dynamics simulations and PEC experiments of the strong interactions between TiO₂ and KOH, can provide suggestive messages for the design of reactive photocatalytic TiO₂ nanocrystals.

## 2. COMPUTATIONAL METHODS

The three-dimensional models of anatase (001), (100), (101)–KOH were prepared and are described in Table 1.

| phase (surface) | x, y, z (Å) | molecular number |
|----------------|------------|-----------------|
| anatase (001)  | 22.66, 22.66, 199.56 | (TiO₂)₂(H₂O)₂(KOH)₆₀ |
| anatase (100)  | 18.88, 37.94, 152.60 | (TiO₂)₃(H₂O)₂(KOH)₆₀ |
| anatase (101)  | 27.21, 22.66, 177.75 | (TiO₂)₃(H₂O)₂(KOH)₆₀ |

Bulk anatase TiO₂ has lattice vectors a₀ = b₀ = 3.776 Å, c₀ = 9.486 Å and symmetry group I4₁/amd, which is tetragonal. All surfaces were constructed by cleaving the anatase TiO₂ supercell. For the diluted KOH solution, the initial configuration was generated from an equilibrated configuration of 60 K⁺, 60 OH⁻, and 2400 H₂O molecules. Water is assumed to be adequately represented by the SPC model, which assigns partial charges to oxygen, qO = −0.82e, and hydrogen, qH = +0.41e (e being the elementary charge).27 The OH⁻ ion was created by removing one hydrogen atom from an H₂O molecule. The z dimensions of the supercells were chosen to accommodate 2400 H₂O molecules of bulk density 1 g/cm³, and the lengths were long enough (>50 Å) to remove the effect of TiO₂ on the bulk solution. The vacuum thicknesses against all slabs were set as 20 Å to eliminate the interaction between the periodically replicated cells.

The classical molecular dynamics simulations were performed in the canonical ensemble (NVT) at 298 K in conjunction with a Nose–Hoover thermostat. Based on our previous confirmations, it is regarded that the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field can well describe the configurations of the TiO₂–H₂O system, in which the system energy can be written as eq 1

\[
E_{\text{total}} = E_b + E_\theta + E_\sigma + E_d + E_{bd} + E_{h\theta} + E_{b\theta} + E_{h\theta} + E_{\theta\theta},
\]

\[+ E_{\theta\theta\sigma} + E_{\text{elc}} + E_{\text{ LJ}} \]

The potential functions are divided into valence terms, including the diagonal and off-diagonal cross-coupling terms and the nonbond interaction terms. The valence terms include \(E_b\), \(E_\theta\), and \(E_d\) for bond, angle, torsion, and out-of-plane angle coordinates, respectively, and \(E_{bd}\), \(E_{h\theta}\), \(E_{b\theta}\), and \(E_{\theta\theta}\) for cross-coupling terms between internal coordinates. \(E_{\text{elc}}\) is a Coulombic function for an electrostatic interaction, and \(E_{\text{ LJ}}\) is an LJ-9-6 function of the van der Waals.

To verify that the established KOH model and applied force field are rational, molecular dynamics simulation of the KOH solution was conducted with a time step of 1 fs and a simulation time of 500 ps. Figure 1 displays the radial distribution functions (RDFs) of K⁺–H₂O and K⁺–O⁻ in the KOH solution. The peak position of \(g_{\text{K⁺–H₂O}}(r)\) is about 2.82 Å, which is in the range of the standard value (2.65–2.92 Å).28 The effective ionic radius is the difference between the first peak position of the radial distribution function of ion-oxygen and the effective radius of H₂O. The effective radius of H₂O is 1.38 Å. The first peak position of \(g_{\text{K⁺–O⁻}}(r)\), shown in Figure 1b, is 2.53 Å. Thus, the effective ionic radius of K⁺ was calculated as 1.15 Å, which is close to the Pauling radius of 1.33 Å.29 In addition, the first minimum of \(g_{\text{K⁺–O⁻}}(r)\) is shallow and the principal maximum shows a distinct shoulder that
delineates a second population of H₂O molecules beyond the inner-most water molecules, explained in ref 3. Above all, it is regarded that the COMPASS force field can well describe the TiO₂−KOH system with the established KOH model. The Ewald summation methods were used for long-range electrostatic interactions with a cutoff distance of 18.5 Å. The total simulation time was 2.4 ns with a 1.2 fs time step. All molecular dynamics simulations were based on the periodic boundary in two dimensions. The structural optimization of TiO₂−KOH systems with the energy-minimum structures and random initial velocities were determined by a steepest descent method and a conjugate gradient method. In the process, the lowest trilayers of TiO₂ were kept frozen, while the rest of the atoms were allowed to relax their atomic positions fully. Afterward, the dynamical properties were statistically analyzed on the basis of the trajectories built from configurations separated by 0.6 ps and collected during the equilibration time. All calculations presented in this work were performed using the Forcite program package in Materials Studio 7.0.

3. RESULTS AND DISCUSSION

3.1. Role of the KOH Electolyte in PEC Water Splitting. 3.1.1. Surface Morphologies, Crystalline Phases, and Optical Properties of RT and NT Electrodes. Figure 2a shows the images of the as-synthesized TiO₂ nanoring/nanotube arrays (left) and TiO₂ nanotube arrays (right). The hierarchical structure RT consists of a ring-shaped top and a tubular bottom. The nanotubes with an average diameter of 30 nm are randomly distributed inside every nanoring with a diameter of 100 nm. NT has a highly ordered one-dimensional nanotube structure whose tube diameter is approximately 80 nm. During the preparation, calcination at 450 °C can crystallize the film on Ti foil. X-ray diffractometry (XRD) patterns of RT and NT confirm the existence of anatase TiO₂ (JCPDS 21-1272) and titanium (JCPDS 44-1294). To obtain the optical properties of the resulting samples, the UV−vis diffusion reflectance spectra were measured and are shown in Figure 2b. The major absorption region of them at wavelengths lower than 380 nm is ascribed to the intrinsic band gap absorption of TiO₂. The absorption intensity of NT is almost higher than that of RT in the whole scope. Additionally, it is notable that RT presents oscillating peaks with a certain frequency and amplitude in the visible light region due to its special structure.

3.1.2. Photocurrent Densities of RT and NT Electrodes in KOH and Na₂SO₄ Solutions. Figure 3 depicts the photocurrent
density–time curves (I–t) of RT and NT electrodes under AM 1.5 illumination (100 mW/cm²) in 1 M KOH and Na₂SO₄ aqueous solutions. At 0 V vs Ag/AgCl, the photocurrent densities of RT-KOH, RT-Na₂SO₄, NT-KOH, and NT-Na₂SO₄ are 0.42, 0.24, 0.21, and 0.12 mA/cm², respectively. Whether in KOH or Na₂SO₄, the RT electrode exhibits larger photocurrent density. The photocurrent densities corresponding to the KOH solution are almost 2 times those of Na₂SO₄.

In 1 M Na₂SO₄ electrolyte with 1 V vs Ag/AgCl, the photocurrent densities of RT and NT are 0.40 and 0.22 mA/cm², respectively, which are in accordance with the results of KOH. Also, the I–t curves with applied bias at the moment of “light on” get smoother and steadier. Therefore, K⁺ and OH⁻ ions not only provide bias voltage for the photoelectrochemical reaction but also stabilize the reaction on the TiO₂ electrode at the same time.

3.1.3. Electrochemical Impedance. Figure 4 shows the Nyquist plots of imaginary impedance versus real impedance recorded at $10^{-1}$–$10^4$ Hz. Generally, a smaller radius corresponds to a lower charge-transfer resistance. An equivalent circuit (inset of Figure 4) is used to fit the data, wherein $R_s$ serves as the solution resistance, CPE is the constant-phase element, and $R_{ct}$ represents the charge-transfer resistance. The photoelectrochemical impedance spectroscopy (EIS)-fitted parameters extracted from Nyquist plots of RT-KOH, RT-Na₂SO₄, NT-KOH, and NT-Na₂SO₄ are shown in Table 2. The $R_s$ of RT-KOH (NT-KOH) is smaller than that of RT-Na₂SO₄ (NT-Na₂SO₄), yielding faster charge transfer. Furthermore, the small arc radii of RT and NT in KOH correspond to the low $R_{ct}$ values, indicating the fast charge transport at the TiO₂/KOH interface.

### Table 2. EIS-Fitted Parameters from Nyquist Plots of RT-KOH, RT-Na₂SO₄, NT-KOH, and NT-Na₂SO₄ Photoanodes

| sample            | $R_s$ (Ω/cm²) | $R_{ct}$ (Ω/cm²) | CPE (F/cm²) |
|-------------------|---------------|------------------|-------------|
| RT-KOH            | 5.093         | 1366             | 4.572 x 10⁻⁴|
| RT-Na₂SO₄         | 10.1          | 3431             | 7.027 x 10⁻⁵|
| NT-KOH            | 15.07         | 2050             | 1.251 x 10⁻⁴|
| NT-Na₂SO₄         | 221.7         | 7349             | 1.237 x 10⁻⁴|

3.1.4. Flat-Band Potential, Interfacial Donor Density, and Depletion Layer Width. The flat-band potential, $U_{fb}$, is the potential that is imposed over the electrode/electrolyte interface to make the energy band flat, which has an important effect on the interfacial electron transfer. Here, Mott–Schottky (MS) plots were used to probe the flat-band potential at 3000 Hz, as shown in Figure 5. In the plots, the flat-band potential approximately equals the voltage obtained at the intersection of the tangents of the Mott–Schottky curves with the horizontal potential axis. In KOH, the flat-band potentials of RT and NT are −0.58 and −0.66 V, respectively; in Na₂SO₄, the flat-band potentials of RT and NT are −0.50 and −0.57 V, respectively. The samples in KOH exhibit more negative flat-band potentials, indicating lower energy barriers for interfacial electron transfer.

In the case of an n-type semiconductor, the electrons are depleted in the depletion layer of TiO₂. Its width is inversely proportional to the reverse square of the carrier concentration, which is calculated as

$$d_{SC} = \sqrt{\frac{2\varepsilon_0\varepsilon_r(U - U_{fb})}{en_D}}$$

(2)
respectively. Applying the slope \( k \) of the linear fits of \( \text{RT-KOH}, \text{RT-Na}_2\text{SO}_4, \text{NT-KOH}, \) and \( \text{NT-Na}_2\text{SO}_4 \) were calculated as 1.31, 10\(^{10}\), 8.8, and 32.11 Å for \( \text{RT-Na}_2\text{SO}_4 \). The wider depletion layer of \( \text{RT-KOH}, \text{RT-Na}_2\text{SO}_4, \text{NT-KOH}, \) and \( \text{NT-Na}_2\text{SO}_4 \) are 1.29, 10\(^{10}\), 1.92, and 3.37 Å, respectively. All of them are larger than 2.82 Å, shown in Figure 1a, due to the electrostatic force between \( \text{K}^+ / \text{OH}^- \) ions and \( \text{TiO}_2 \). The smallest value of the (101) surface means that the distance of \( \text{K}^+ - \text{H}_2\text{O} \) is the shortest, i.e., potassium ionic hydration on the (101) surface is the strongest, followed by that on (001) and (100). In addition, the high and pointed peak of the RDF diagram of anatase (101) indicates that the arrangement of water molecules around potassium atoms is relatively regular. The ionic hydration in the solution not only affects the ions’ short-range structure but also changes the diffusivity.\(^{29} \) If the ionic hydration is strong, the diffusion of ions is limited due to the inhibition of surrounding water molecules. Thus, the diffusion coefficient of \( \text{K}^+ \) ions on the anatase (101) surface is the smallest. There are two peaks at about 6.5 Å, which originate from the two hydrogen atoms of \( \text{H}_2\text{O} \) molecules, which are corresponding to the smaller peaks in Figure 1a. The radial distribution functions of \( \text{K}^+ - \text{O}_w \) on anatase \( \text{TiO}_2 \) (001), (100), and (101) surfaces are shown in Figure 6b. The first peaks are located at 3.06, 3.11, and 3.10 Å, respectively. They are slightly higher than the internuclear distances of \( \text{K}^+ - \text{O}_w \) (2.79 ± 0.08 Å),\(^{26} \) caused by the difference of potential function and force field applied in simulations.

### 3.2.2. Coordination Number of \( \text{K}^+ \)

The coordination number, \( n_i(r) \), defined as the number of ions that are close to a contrary sign ion, was calculated by integrating the radial distribution function, \( g_{ij}(r) \), as shown in eq 4

\[
g_{ij}(r) = \frac{2}{\varepsilon_0 \varepsilon_{RI} D} \left( \frac{U - U_{FB} - kT}{e} \right)
\]

where \( C_{SC} \) is the capacitance of the depletion layer and \( k \) and \( T \) represent the Boltzmann constant \((1.38 \times 10^{-23} \text{ J/K})\) and temperature, respectively. At room temperature, the value of \( kT/e \) is negligible. As shown in Figure 5, the slopes \( k \) for \( \text{RT-KOH}, \text{RT-Na}_2\text{SO}_4, \) \( \text{NT-KOH}, \) and \( \text{NT-Na}_2\text{SO}_4 \) are 1.29 × 10\(^{10}\), 8.8 × 10\(^8\), 5.26 × 10\(^9\), and 3.35 × 10\(^9\) \text{F}^2\cdot\text{cm}^{-2}\cdot\text{V}^{-1}\), respectively. Applying the slope \( k = (2/(\varepsilon_0 \varepsilon_{RI} D)) \), the interfacial donor densities of \( \text{RT-KOH}, \text{RT-Na}_2\text{SO}_4, \) \( \text{NT-KOH}, \) and \( \text{NT-Na}_2\text{SO}_4 \) were calculated as 1.31 × 10\(^{20}\), 1.92 × 10\(^{21}\), 3.21 × 10\(^{19}\), and 5.04 × 10\(^{20}\) \text{cm}^{-3}\), respectively. Once \( N_D \) is known, the depletion layer widths were estimated as 63.47 Å for \( \text{RT-KOH}, 15.42 \) Å for \( \text{RT-Na}_2\text{SO}_4, \) 136.96 Å for \( \text{NT-KOH}, \) and 32.11 Å for \( \text{NT-Na}_2\text{SO}_4 \). The wider depletion layer of anatase \( \text{TiO}_2 \) in KOH results in the longer lifetime of the charge carriers and bigger capacitance in the depletion layer, causing greater photocatalytic activity. It is notable that the photoelectric properties of the systems with different electrolytes are codetermined by the light absorption and interfacial properties in the electrolyte-electrode region. Therefore, the depletion layer widths of RT and NT have a different order from that of their photocurrent densities (Figure 3). To deeply analyze the effect of the interaction between KOH and \( \text{TiO}_2 \) on the photocatalytic reaction, we further completed the molecular dynamics simulations of anatase (001), (100), (101)–KOH systems from a microscale.

#### 3.2. State of \( \text{K}^+ \) on the Anatase (001), (100), and (101) Surfaces

### 3.2.1. Ionic Hydration and Ionic Radius

The radial distribution functions (RDFs) of \( \text{K}^+ - \text{H}_2\text{O}, \) shown in Figure 6a, exhibit a similar tendency for anatase (001), (100), and (101) surfaces, and their first peaks are located at 3.39, 3.42, and 3.37 Å, respectively. All of them are larger than 2.82 Å, shown in Figure 1a, due to the electrostatic force between \( \text{K}^+ / \text{OH}^- \) ions and \( \text{TiO}_2 \). The smallest value of the (101) surface means that the distance of \( \text{K}^+ - \text{H}_2\text{O} \) is the shortest, i.e., potassium ionic hydration on the (101) surface is the strongest, followed by that on (001) and (100). In addition, the high and pointed peak of the RDF diagram of anatase (101) indicates that the arrangement of water molecules around potassium atoms is relatively regular. The ionic hydration in the solution not only affects the ions’ short-range structure but also changes the diffusivity.\(^{29} \) If the ionic hydration is strong, the diffusion of ions is limited due to the inhibition of surrounding water molecules. Thus, the diffusion coefficient of \( \text{K}^+ \) ions on the anatase (101) surface is the smallest. There are two peaks at about 6.5 Å, which originate from the two hydrogen atoms of \( \text{H}_2\text{O} \) molecules, which are corresponding to the smaller peaks in Figure 1a. The radial distribution functions of \( \text{K}^+ - \text{O}_w \) on anatase \( \text{TiO}_2 \) (001), (100), and (101) surfaces are shown in Figure 6b. The first peaks are located at 3.06, 3.11, and 3.10 Å, respectively. They are slightly higher than the internuclear distances of \( \text{K}^+ - \text{O}_w \) (2.79 ± 0.08 Å),\(^{26} \) caused by the difference of potential function and force field applied in simulations.

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\[
g_{ij}(r) = \frac{2}{\varepsilon_0 \varepsilon_{RI} D} \left( \frac{U - U_{FB} - kT}{e} \right)
\]
\[ n_j(r) = 4\pi \rho \int_0^r r^2 g_j(r) \, dr \]  

(4)

where \( i \) and \( j \) represent different particles and \( \rho \) is the number density of \( j \) in the bulk. The formula gives the relationship between the distance and the coordination numbers of \( i \) and \( j \).

The coordination numbers of K⁺ on anatase TiO₂(001), (100), and (101) surfaces in the first coordination layer are calculated according to the first peak position in Figure 6a and displayed in Figure 7, which are 0.85, 0.80, and 0.94, respectively. The largest coordination number of K⁺ on the anatase (101) surface means more water molecules around K⁺ ions, and the result is consistent with the above analysis on ionic hydration (Figure 6a).

3.2.3. Adsorption Sites of K⁺. Understanding the structure and thermodynamics of K⁺ is crucial in dissecting its role in interface properties. Figure 8 shows the snapshots of the computational KOH solution on anatase (001), (100), and (101) surfaces at 1500 ps. As seen from the vertical view, we can get the structure of the three surfaces. The anatase (001) surface has a flat plane connected by alternating rows of undercoordinated fivefold-coordinated titanium atoms Ti₅c and twofold-coordinated O₂c atoms. O₂c atoms and threefold-coordinated O₃c atoms are presented on the anatase (100) surface. Moreover, O₃c atoms with fully coordinated Ti₆c atoms, which lie at the bottom of the grooves along the \( x \)-direction, are exposed. The anatase (101) surface exhibits a zigzag-like structure formed by O₃c bonded to Ti₆c and O₂c bonded to Ti₅c.

The chemical adsorption structures of K⁺ are sensitive to the oxygen atoms at TiO₂ surfaces. For example, Calzado et al. demonstrated that the most stabilized status of K⁺ on the rutile TiO₂(110) surface is bound to two bridge oxygen atoms. There are three adsorption sites of K⁺ on the anatase (001) surface. Most of the potassium ions are adsorbed between two bridging oxygen atoms (A1), forming two bonds. A few are adsorbed directly on bridging oxygen atom or around it (A2/A3). Two types of adsorbed K⁺ can be recognized on the anatase (100) facet. One is between three-coordinated oxygen atoms and the bridging oxygen atom at the top of the grooves (A1) with four bonds. The other (A2) is closer to one bridging oxygen atom, forming three bonds with two surrounding bridging oxygen atoms. Three adsorption types of K⁺ are recognized on the anatase (101) facet. First is the K⁺ interacting with two bridging oxygen atoms (A1) by two bonds. The second is K⁺ absorbed on terminal oxygen atoms (A2) bonding with another bridging oxygen atom. The last one is directly adsorbed on bridging oxygen atoms (A3). These adsorption sites of K⁺ are similar to those of the other cations. At pH 8, Zn²⁺ is found to adsorb at two different sites, i.e., monodentate above the bridging O site and bidentate between two neighboring terminal O sites. Rb⁺, Na⁺, Sr²⁺, and Ca²⁺ occupy the tetradentate site and come into contact with two terminal and two bridging oxygen atoms. With a comprehensive picture of the interface between aqueous solutions and anatase TiO₂ surface, cations are bonded directly to surface oxygen atoms, while the specific binding geometry and reaction stoichiometry are dependent on the ionic radius and external conditions.

3.2.4. Number Density of Oxygen Atoms and Potassium and Hydroxyl Ions. The number density distributions of oxygen atoms (O₂) and potassium/hydroxyl ions (K⁺/OH⁻) are shown in Figure 9. Predota et al. confirmed that the structural and dynamic properties at the interfaces recovered within about 15 Å from the surface. Therefore, the results in the range of 0–16 Å are displayed. The first peaks of oxygen atoms on anatase (001), (100), and (101) surfaces are about 2.35, 2.70, and 1.76 Å, respectively. With the increase in distance, the number densities gradually converge to 30 nm⁻³ in the bulk region.

The dynamics of the potassium ions are strongly dominated by the layered structure of water and the oxygen atoms at TiO₂ surfaces. Thus, the number densities of K⁺ have the same trends with oxygen atoms, ascribing to the layering effect. The first peaks of K⁺ on anatase TiO₂(001), (100), and (101) surfaces are located at about 2.27, 1.28, and 1.76 Å, respectively. In the bulk region, the number densities of K⁺...
tend to be zero because the cations are mostly located at the surface, which is also observed in the literature. During K+ and H2O coadsorption, a potassium hydroxide film grows, inducing a reduction of the work function, which was recorded by Irkha. However, OH− does not form a surface characteristic adsorption layer shown in the inset. It is explained that TiO2 is an n-type semiconductor and the surface states are available for electron trapping, causing a negatively charged surface. Accordingly, K+ cations are mostly found in the interface location, while OH− ions are asymmetrically distributed in the bulk, controlled by repulsive force.

### 3.3. Electrostatic Properties of Anatase TiO2/KOH Interfaces

#### 3.3.1. Charge and Electric Field Distributions

Given that the water molecules and potassium and hydroxyl ions are redistributed in the dynamics process, the charge repartition has happened. The electron density at the anatase TiO2 surface was reversibly tuned by alkali-based adsorbates, affecting the charge-transfer processes and chemical reactions induced by the K 4s electrons. Here, the profiles of charge distribution σ(z) across the molecule layer are calculated according to hydrogen, oxygen, and potassium atomic densities and illustrated in Figure 10a. The charge distribution profiles exhibit pronounced oscillation in the near-surface and then gradually decay to 0 e/Å3 at 6 Å away from the interfaces.

The electric field, E(z), in the direction perpendicular to the surface is usually calculated by using the following Poisson equation

\[
E(z) = \frac{1}{\varepsilon_0} \int_{z_{\text{bulk}}}^{z} \sigma(c) \, dc
\]

The integration was done numerically from the middle of the bulk water region (z_{bulk}) to the TiO2 surface with the boundary condition \( E(z_{\text{bulk}}) = 0 \).

In Figure 10b, the electric fields near anatase (001), (100), and (101) surfaces change from −0.35 to 1 V/Å. The order of the maximum electric field intensity is 0.92 V/Å for (001), 0.78 V/Å for (101), and 0.60 V/Å for (100). As for the second peak, the values for (001) and (101) are obviously larger than that for (100) surface (0 V/m). The extraordinary strong field
is an indicator of strong adsorption on the TiO$_2$ surface and large charge changes occurring in this region.

3.3.2. Electrostatic Potential Drop and Grahame Double Layer Model of TiO$_2$/KOH Interfaces. The electrostatic potential distribution of the semiconductor/electrolyte interface is essential for understanding the photoelectric behavior of the semiconductor electrodes and electrolytes. Therefore, we further calculated the electrostatic potential, $\psi(z)$, by eq 6

$$\psi(z) = -\int_{z_{d_{sr}}}^{z} E(z) \, dz$$

(6)

**Figure 11** shows the electrostatic potential distribution of KOH solutions on anatase (001), (100), and (101) surfaces.

![Figure 11](image)

**Figure 11.** Electrostatic potential distribution ($\psi(z)$) of KOH solutions on anatase TiO$_2$(001), (100), and (101) surfaces and the Grahame model. IHL (OHL) represents the inter (outer) Helmholtz layer. $d$ and $V_s$ are the width and potential drop of the outer Helmholtz layer, respectively.

With the increase in distance, the potential on anatase (101) reaches a stable value at 6.5 Å, which is quite consistent with the results calculated by reactive force fields in ref 12. Thus, the structures and methods in the simulation are proved to be reasonable once again. Well, an interesting phenomenon is that the potential on the anatase (001) surface decreases continuously until it reaches 0 V, while the potential on anatase (100) first decreases and then rebounds to 0 V. Similar great variations of surface potential can be found in ref 41.

For the TiO$_2$–H$_2$O system, the Gouy–Chapman model is used to satisfy the electronic double layer and the ions controlled by the electrostatic attraction and heat movement are distributed around surfaces by the Boltzmann formula. Here, the specific adsorption of K$^+$ has greatly changed the potential distribution in the interface region, thus affecting the rate of chemical reaction on the TiO$_2$ surface. To make a reasonable analysis, a new interpretation of these results was proposed. Taking ref 42 as a reference, the simulation results are captured with the Grahame model by dividing the interface region into three zones (Figure 11): the inner Helmholtz layer (IHL) in which the K$^+$ ions population is dependent on the TiO$_2$ surface and almost no OH$^-$ ions in there, the outer Helmholtz layer (OHL) that hosts a population of K$^+$ plus a handful of OH$^-$ whose population is described by a Langmuir adsorption model, and the diffuse layer where the ion distribution is well described using the Poisson–Boltzmann theory. From Figure 11, the potential drops, $V_{fi}$ in the Helmholtz layer of anatase TiO$_2$(001), (100), and (101) are 1.08, 0.26, and 0.51 V, respectively, corresponding to the Helmholtz layer widths of 3.63, 4.04, and 2.95 Å. Compared with that of the pure water system (0.14 V of anatase (001)–H$_2$O, 0.28 V of anatase (100)–H$_2$O, and 0.62 V of anatase (101)–H$_2$O), the larger potential drop can explain the phenomenon that KOH solute contributes substantially to a chemical bias in experiments (Figure 3).

3.3.3. Calculation of the Depletion Layer Width. With the potential drop in the Helmholtz layer, the depletion layer width, $d_{SC}$ is calculated as follows

$$d_{SC} = \frac{2V_s \epsilon_r d}{V_{ff} \epsilon_{KOH}}$$

(7)

where $\epsilon_{KOH}$ and $\epsilon_r$ are the relative dielectric constants of the KOH solution and anatase TiO$_2$ (83.6), respectively, and $V_s$ is the surface potential barrier of anatase TiO$_2$ (0.2 V).

Because the H$_2$O molecules adsorbed on the TiO$_2$ surface cannot be easily rotated, $\epsilon_{H_2O}$ was set as 25. Further considering the addition of K$^+$ and OH$^-$, the relative dielectric constant $\epsilon_{KOH}$ was set as 3. Finally, the surface depletion layer widths of anatase (001), (100), and (101) surfaces were estimated as 37.48, 173.25, and 64.49 Å, respectively, and they are of similar magnitude to the experimental results, i.e., tens of Å. The surface depletion layer width order of magnitude is (100) $>$ (101) $>$ (001). By examining the trapping energies and trapping sites of simulated photogenerated holes and electrons based on density functional theory, Ma et al. present that the order of the relative photooxidation and photoreduction activities of anatase TiO$_2$ is (100) $>$ (101) $>$ (001). Thus, KOH has improved the reactivity of all three surfaces without changing their relative relation. It also reminds us that anatase (100) should be increased in the KOH solution for improving the efficiency of PEC water splitting.

4. CONCLUSIONS

In this work, TiO$_2$ nanoring/nanotube arrays and TiO$_2$ nanotube arrays were prepared and the subsequent PEC experiments were conducted. It is indicated that the KOH electrolyte provides 1 V bias voltage for the chemical reaction as opposed to Na$_2$SO$_4$ and K$^+$ and OH$^-$ ions can stabilize the photoelectrochemical reaction on TiO$_2$ electrodes at the same time. In addition, more negative flat-band potential, larger depletion layer width, and larger capacitance indicate a lower energy barrier for interfacial electron transfer and a greater photocatalytic activity in KOH. To better understand the effect of KOH on the interface properties, molecular dynamics simulations were conducted to investigate the dynamic structures and properties of 1 M KOH solution on anatase TiO$_2$(001), (100), and (101) surfaces. K$^+$ ions prefer to adsorb onto the TiO$_2$ surface and bond to O$_2$C. Therefore, the dynamics of the potassium ions are strongly dominated by the layered structure of water and the oxygen atoms on TiO$_2$ surfaces. The coordination numbers of K$^+$ on TiO$_2$(001), (100), and (101) surfaces are 0.85, 0.80, and 0.94, respectively, and the largest value of (101) surface means more water molecules accessing to its m molecules. The adsorption model, and the di
The charge distribution in the three interface regions quickly decays to the bulk value beyond 6 Å from the TiO₂ surface. The electric fields of anatase (001), (100), and (101) change from ~0.35 to 1 V/Å near the surface, and anatase (001) has the strongest electric field, followed by (101) and (100). The potential of anatase (101) quickly converges to 0 V, while that of anatase (001) keeps decreasing until it reaches 0 V and that of anatase (100) first decreases and then rebounds to 0 V. The significant differences are attributed to the specific adsorption of K⁺ on TiO₂ surfaces, while OH⁻ asymmetrically distribute in bulk controlled by repulsive force. Corresponding to the Grahame double layer model, the resulting depletion layer widths of anatase (001), (100), and (101) surfaces were calculated as 37.48, 173.25, and 64.49 Å, respectively. It is suggested that anatase (100) has the largest activity in the KOH solution, followed by (101) and (001).

All of the above results clearly illustrate the improvement in our quantitative understanding of the molecular-scale structure of K⁺ and electrostatic characteristics at TiO₂/KOH interfaces, in combination with the continuum-based Grahame model of the electric double layer. Considering that the dielectric properties of TiO₂ are affected by surface conditions such as defects and impurity doping, more amendments are needed in future research.

5. EXPERIMENTAL SECTION

5.1. Materials. Ti foils (0.25 mm thick, 99.5% purity) were supplied by Alfa-Aesar. Aluminum oxide (Al₂O₃) was purchased from Gaona Powder Company (Shanghai, China). Ethanol (C₂H₅OH), acetone (CH₃COCH₃), ethylene glycol (EG), ammonium fluoride (NH₄F), phosphate acid (H₃PO₄), sodium fluoride (NaF), potassium hydroxide (KOH), and sodium sulfate (Na₂SO₄) were purchased from Beijing Chemical Works. All solutions were prepared without further purification using deionized water.

5.2. Preparation of TiO₂ Nanoring/Nanotube (RT) Arrays and TiO₂ Nanotube (NT) Arrays. First, Ti foils were cut into pieces of 20 mm × 30 mm and then sonicated sequentially in acetone, ethanol, and high-purity deionized water, followed by drying in air. RT was prepared by a two-step anodization method in ethylene glycol solution with NH₄F (0.25 wt %) and water (2 vol %) in a conventional two-electrode configuration with Ti foil as the anode and Pt mesh (20 mm × 30 mm) as the cathode. In first-step anodization, the Ti foil was anodized at 60 V for 60 min and then the as-grown nanotube layer was ultrasonically removed in deionized water. After drying at 50 °C, the pretreated Ti foil was used as the anode again for second-step anodization with 20 V for 60 min. A vertically aligned NT electrode was prepared by one-step anodic oxidation in an aqueous solution of 0.5 M H₃PO₄ and 0.14 M NaF with consecutive ultrasonication (Kunshan Ultrasonic Instrument Co., Ltd., KQ-100DE). DC voltage of 20 V was supplied at room temperature for 60 min. After anodization, the two samples were thoroughly washed with deionized water immediately to remove the absorbed ions and annealed in air at 450 °C for 4 h at a heating rate of 2 °C/min. Finally, the samples were connected to copper wires using silver conductive paste and dried overnight. Both the substrates and the wires were then covered with an insulating epoxy resin, leaving only the desired surface area exposed.

5.3. Characterizations. The morphologies of TiO₂ arrays were characterized by a field-emission scanning electron microscope (FESEM; Hitachi, Japan, S4800). The crystal phases of the samples were determined using an X-ray diffractometer (XRD; D8 Advance Bruker/AXS) with Co (30 mA) radiation. The optical absorption spectra were obtained by employing a Fiber Spectral Instrument (AVANTES, Netherlands) with compressed BaSO₄ powder as a reflectance standard.

5.4. Photoelectrochemical Measurements. The PEC performances were measured in the three-electrode system with TiO₂, a Ag/AgCl electrode, and a Pt mesh as the working, reference, and counter electrodes, respectively. A single-compartment quartz cell filled with 1 M KOH or Na₂SO₄ electrolyte was used as the reactor. The samples were illuminated by a solar simulator (91160, Newport) equipped with an AM 1.5 filter, and the intensity was calibrated to 100 mW/cm². The photocurrent density–time (I–t), electrochemical impedance spectroscopy (EIS) and Mott–Schottky (MS) data were collected at an electrochemical workstation (AUTOLAB PGSTAT302N).

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the National Natural Science Foundation of China (Grant No. 51776009) for financial support.

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