

Article

Highly Efficient CuInSe₂ Sensitized TiO₂ Nanotube Films for Photocathodic Protection of 316 Stainless Steel

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Abstract: CuInSe₂ nanoparticles were successfully deposited on the surface of TiO₂ nanotube arrays (NTAs) by a solvothermal method for the photocathodic protection (PCP) of metals. Compared with TiO₂ NTAs, the CuInSe₂/TiO₂ composites exhibited stronger visible light absorption and higher photoelectric conversion efficiency. After 316 Stainless Steel (SS) was coupled with CuInSe₂/TiO₂, the potential of 316 SS could drop to −0.90 V. The photocurrent density of CuInSe₂/TiO₂ connected to 316 SS reached 140 μA cm^{−2}, which was four times that of TiO₂ NTAs. The composites exhibited a protective effect in the dark state for more than 8 h after 4 h of visible light illumination. The above could be attributed to increased visible light absorption, the extended lifetime of photogenerated electrons, and generation of oxygen vacancies.

Keywords: TiO₂ NTAs; CuInSe₂; photocathodic protection; 316 SS; EIS



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1. Introduction

316 SS is widely used for industrial applications because of its good corrosion resistance and excellent mechanical properties. Nevertheless, stainless steel (SS) is prone to pitting corrosion in Cl[−]-rich solution [1–3]. Metal corrosion is extremely harmful, causing huge economic losses and even safety accidents every year [4,5]. Many anti-corrosion methods, including corrosion inhibitors [6], anticorrosion coatings [7] and cathodic protection [8], have been developed to inhibit the corrosion of steel. Photocathodic protection (PCP) is a new type of green anti-corrosion technology. Its principle is that when the semiconductor is irradiated by light which possesses higher energy than the band gap (E_g) of the semiconductor, electrons are excited from the valence band (VB) to the conduction band (CB); then, the photogenerated electrons are transferred from the semiconductor to the connected metal to reduce the potential of the metal surface, thereby inhibiting the metal corrosion. Compared with traditional cathodic protection techniques, PCP technology neither consumes energy nor releases metal ions into the environment [9–11]. Therefore, the development of PCP systems to protect metal against substrates is a promising approach for many industrial applications.

TiO₂ has attracted great interest as a photoanode material for PCP application due to its stable physical and chemical properties, lack of toxicity, excellent photoelectric properties and low cost [12–14]. Unfortunately, some inherent defects of TiO₂ limit its application. First of all, TiO₂ is unable to utilize most sunlight (less than 5% of solar energy) due to its wide E_g [15]. Secondly, the photogenerated carriers in TiO₂ are easy to recombine, which greatly reduces its photoelectric conversion efficiency [16], making it unable to protect metals in dark environments. Therefore, it is necessary to modify the TiO₂, for example, through doping, with metal elements (W [17], Fe [18], Ni [19], etc.) or non-metal elements (N [20], B [21], etc.), and co-sensitizing with narrow gap semiconductors (MoS₂ [22], Co(OH)₂ [23], FeS₂ [24], etc.).

Ternary semiconductors have aroused great attention because of their adjustable E_g and electronic energy level, controllable composition and internal structure [25]. Polymetallic sulfides/selenides have good electrochemical properties due to the synergistic effect of two metal atoms [26,27]. At present, AgInS_2 and AgInSe_2 have been used to modify TiO_2 and have achieved good PCP effects [28,29]. In addition, selenides have faster heterogeneous electron transfer rates than sulfides because the electronegativity of Se is lower than S [30]. CuInSe_2 is regarded as a promising photovoltaic material due to its adjustable band gap, high optical stability and excellent photoelectric conversion efficiency. Therefore, the sensitization of CuInSe_2 may improve the composites' efficiency of utilization of sunlight [31]. More importantly, the CB potential (E_{CB}) of CuInSe_2 was more negative than that of TiO_2 , so it is possible to construct a $\text{CuInSe}_2/\text{TiO}_2$ heterojunction, which can facilitate the efficient transfer of electrons from CuInSe_2 to TiO_2 [32]. Therefore, CuInSe_2 may be an ideal semiconductor material for modifying TiO_2 . According to previous reports, some researchers have constructed $\text{CuInSe}_2/\text{TiO}_2$ nanostructures for photocatalytic degradation of organic pollutants [33] and solar cell applications [34]. However, there are no reports on the PCP performance of $\text{CuInSe}_2/\text{TiO}_2$ for metals.

In this paper, $\text{CuInSe}_2/\text{TiO}_2$ composites were synthesized by anodic oxidation and solvothermal methods. The morphologies, crystal structures, composition and light absorption properties of the composite materials were studied. The PCP performances of photoanodes were studied by electrochemical test methods. Through density functional theory (DFT) calculations, the electronic structure changes of composites were calculated. The PCP mechanism of $\text{CuInSe}_2/\text{TiO}_2$ on 316 SS was studied.

2. Materials and Methods

2.1. Chemicals and Reagents

The Ti foils ($40 \text{ mm} \times 10 \text{ mm} \times 0.1 \text{ mm}$; 99.9% purity) were purchased from Shanghai Gao Dewei Co., Shanghai, China, and 316 SS was purchased from Shanghai Baosteel Co., Shanghai, China with the following ingredients (wt%): C 0.08%, Si 0.90%, P 0.045%, S 0.029%, Mn 1.80%, Ni 14.00%, Cr 17% and balanced Fe. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99.0%), $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (99.9%), Se powder (99.0%), $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (98%), NaOH (99%) and NaCl (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Fabrication of $\text{CuInSe}_2/\text{TiO}_2$ Photoelectrodes

Figure 1a illustrates the process for preparation of $\text{CuInSe}_2/\text{TiO}_2$ nanotube array (NTA) photoanodes. TiO_2 NTAs were synthesized on a Ti foil by electrochemical anodization. The Ti foil was first chemically buffed in a mixed solution of 2.5 mL H_2O , 0.45 g NH_4F , 6.0 mL H_2O_2 and 6.0 mL HNO_3 , and then cleaned with first deionized water (DI water) and then absolute ethanol. The cleaned Ti foil and the Pt plate were used as the anode and cathode, respectively. The Ti foil was immersed in the electrolyte solution (0.36 g NH_4F , 4.0 mL H_2O , 60 mL ethylene glycol) for anodic oxidation at 30 V for 30 min, and then rinsed with, respectively, DI water and ethanol. The oxidized Ti foil was placed in a muffle furnace at 450°C for 2 h, and then TiO_2 NTAs were obtained.

CuInSe_2 nanoparticles were synthesized on the TiO_2 by a solvothermal method. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1, 0.2, 0.3 mmol), $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (0.1, 0.2, 0.3 mmol) and Se powder (0.2, 0.4, 0.6 mmol) were mixed with 60 mL methanol and magnetically stirred for 20 min. The mixed solution and the as-fabricated TiO_2 were immersed in a Teflon-lined autoclave and sintered at 200°C for 12 h. Finally, $\text{CuInSe}_2/\text{TiO}_2$ composites were obtained. The synthesized photoanodes were marked, respectively, as $\text{CuInSe}_2/\text{TiO}_2$ -A, $\text{CuInSe}_2/\text{TiO}_2$ -B and $\text{CuInSe}_2/\text{TiO}_2$ -C.

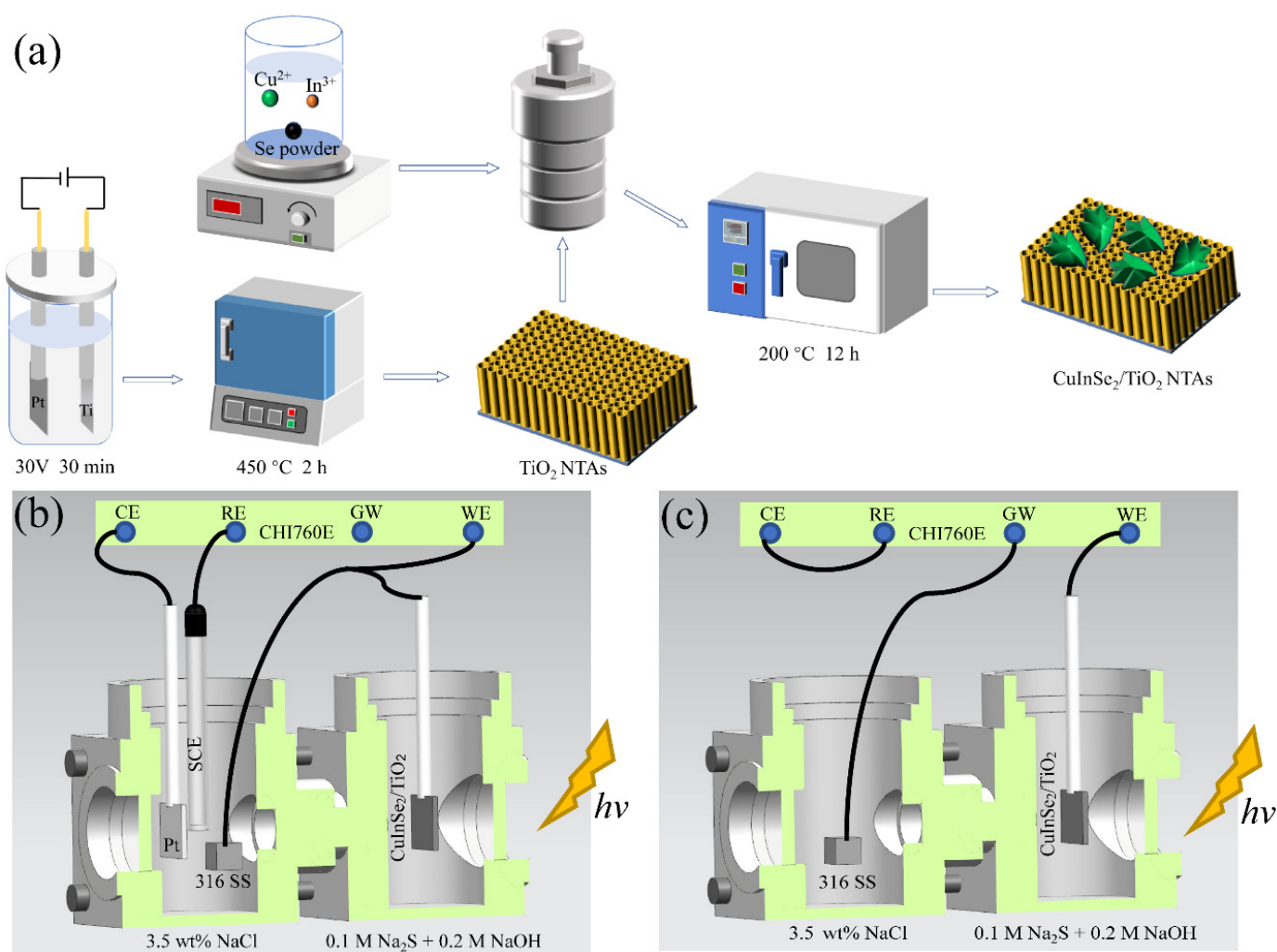


Figure 1. Schematic illustration of (a) the synthesis process for the CuInSe₂/TiO₂ NTAs. Test devices for measuring (b) OCP, Tafel and EIS, and (c) photocurrent densities.

2.3. Characterization

The morphologies of the photoelectrodes were observed using a scanning electron microscope (SEM, Hitachi SU8220, Tokyo, Japan) with Quantax75 energy-dispersive X-ray spectroscopy (EDS, Hitachi SU8220, Tokyo, Japan). The crystal structures of the photoelectrodes were obtained using X-ray diffraction (XRD, D8-advance, Bruker AXS Co., Karlsruhe, Germany) the Cu K α radiation. The chemical components and element chemical states were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, Waltham, MA, USA, Al-K α radiation, 1486.6 eV). The optical properties of the photoelectrode were tested using a UV-Vis diffuse reflectance spectrophotometer (DRS, Hitachi UH4150, Tokyo, Japan). Photoluminescence (PL, Ex: 320 nm) spectra were measured using an FLS980 series fluorescence spectrum scanner. Surface morphologies of 316 SS electrodes were obtained by a metallographic microscope (Axiocam 105 color, Oberkochen, Germany).

2.4. Photoelectrochemical Measurements

All measurements were carried out on an electrochemical workstation (CHI 760E, Chenhua Instrument Co., Ltd., Shanghai, China). The test device was composed of a corrosion cell (3.5 wt% NaCl) and a photoanode cell (0.1 M Na₂S + 0.2 M NaOH). The two cells were connected by Nafion film. The 316 SS electrode (1 cm $\times$ 1 cm $\times$ 1 cm) was encapsulated in epoxy resin with an exposed area of 1 cm². A 300 W xenon lamp (PLS-SXE 300C, Beijing Perfectlight Technology Co., Ltd., Beijing, China) with a 420 nm cut-off filter

was used as a visible light source to illuminate the photoanode material vertically. The open circuit potentials (OCP), Tafel curves and electrochemical impedance spectroscopy (EIS) were recorded by the two-cell system (Figure 1b). The corrosion potential (E_{corr}) and corrosion current density (J_{corr}) were recorded by Tafel curves which were measured at a scanning rate of $0.5 \text{ mV} \cdot \text{s}^{-1}$ from -250 to 250 mV vs. OCP. The EIS data were obtained in the frequency range of 10^5 – 10^{-2} Hz with OCP as the initial potential and the amplitude of AC signal was 5 mV . The Mott–Schottky (M–S) curves were recorded from -1.0 V to 0.5 V with a frequency and an amplitude of 1000 Hz and 10 mV , respectively. The I–V and M–S tests were both carried out in $0.1 \text{ M Na}_2\text{SO}_4$ solution. The 316 SS in the corrosion cell and the photoanodes in the photoanode cell were connected by wires to the working electrode (WE). The saturated calomel electrode (SCE) and Pt plate were set as reference electrode (RE) and counter electrode (CE), respectively. The setup used to measure the photocurrent densities is shown in Figure 1c; CE and RE were connected with wires, 316 SS and photoanodes were connected to ground wire and WE, respectively.

3. Results and Discussion

3.1. Morphology and Chemical Compositions

The morphologies of TiO_2 and $\text{CuInSe}_2/\text{TiO}_2$ -B were studied by SEM. Figure 2a,b shows that the average inner diameter and tube length of TiO_2 nanotubes were about 40 and 1600 nm , respectively. The ordered structure of TiO_2 NTAs can promote the separation and transport of e^-/h^+ pairs [35]. As shown in Figure 2c,d, CuInSe_2 nanoparticles were successfully loaded on the TiO_2 surface. It is evident that the deposition of the CuInSe_2 nanoparticles had no effect on the morphology of the nanotubes. The elemental mapping results of $\text{CuInSe}_2/\text{TiO}_2$ -B show that the composite material is composed of Ti, O, Cu, In and Se elements. It further indicates that CuInSe_2 nanoparticles were formed uniformly on the surface of the nanotubes in the composite by the simple solvothermal method.

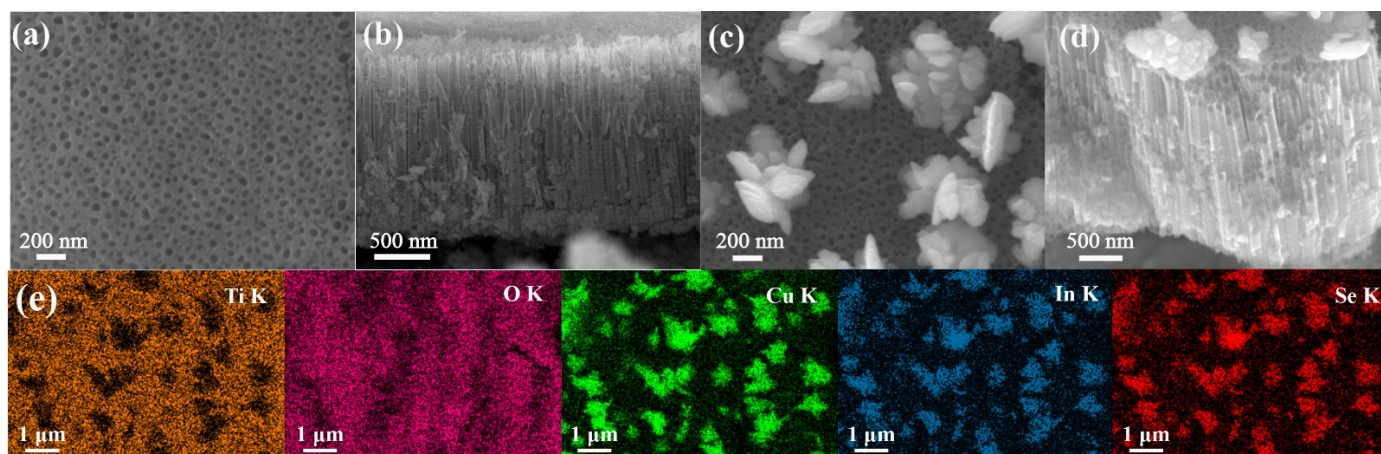


Figure 2. (a) SEM Top-view and (b) cross-section of the TiO_2 NTAs, (c) SEM top-view, (d) cross-section view of the $\text{CuInSe}_2/\text{TiO}_2$ -B NTAs, and (e) EDS elemental mapping of the $\text{CuInSe}_2/\text{TiO}_2$ -B NTAs.

XRD spectra were used to determine the crystal structural information of the synthesized photoanodes. Figure 3 shows the XRD patterns of TiO_2 and $\text{CuInSe}_2/\text{TiO}_2$ -B. For TiO_2 , the XRD peaks at 25.3° , 49.5° and 53.9° corresponded to (101), (200) and (105) planes of anatase TiO_2 (JCPDS No. 21-1272), respectively. The other peaks of TiO_2 were derived from the Ti substrate. For $\text{CuInSe}_2/\text{TiO}_2$ -B photoanode, the XRD peaks at 27.3° , 28.3° , 43.9° and 44.2° corresponded to (112), (103), (105) and (301) crystal planes of tetragonal chalcopyrite CuInSe_2 . No diffraction peak of the impurity phase was detected by XRD. Combined with the results of SEM and XRD, the $\text{CuInSe}_2/\text{TiO}_2$ photoanode materials with high purity were successfully prepared by anodic oxidation and solvothermal methods.

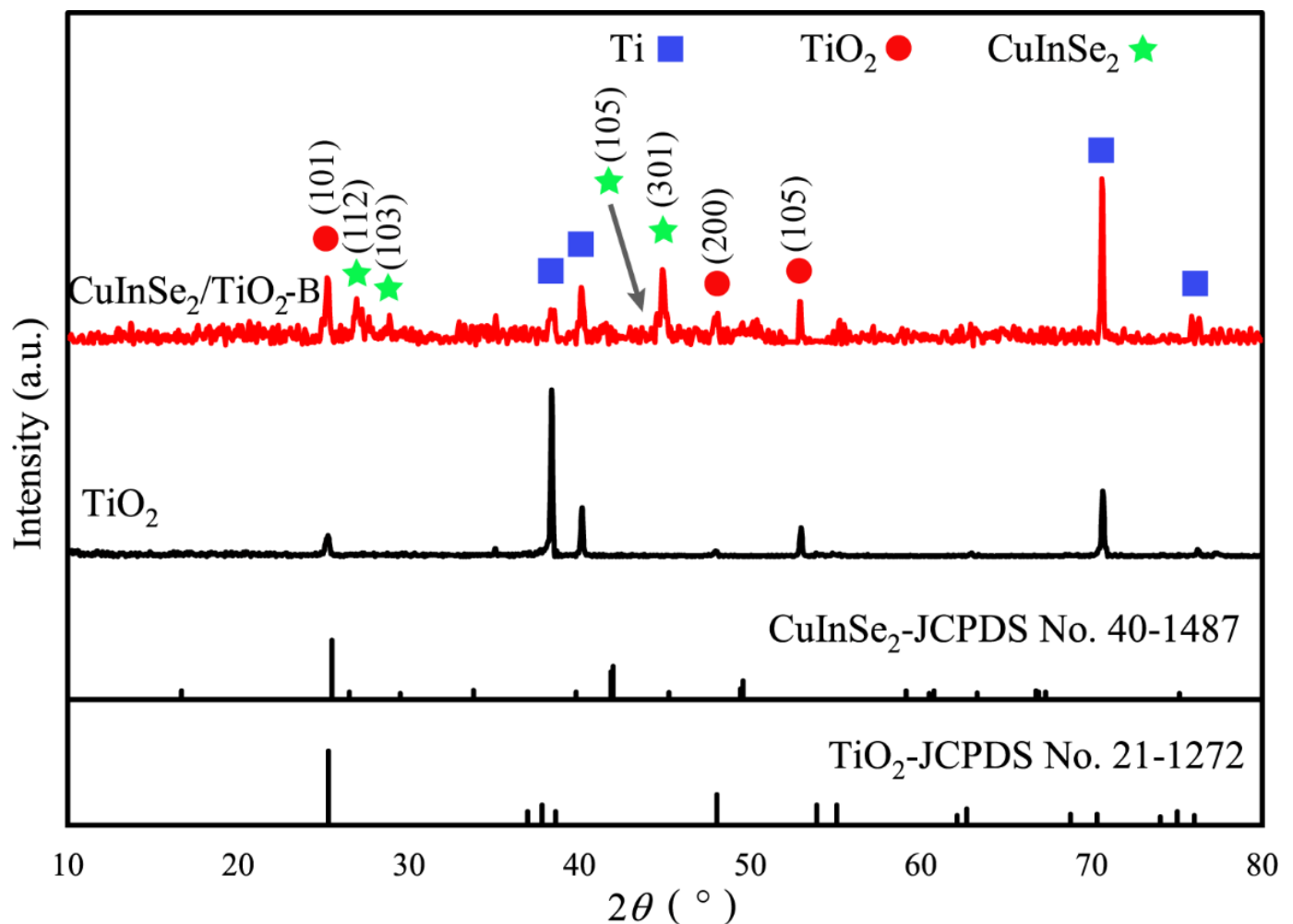


Figure 3. XRD patterns of TiO_2 and $\text{CuInSe}_2/\text{TiO}_2\text{-B}$.

The elemental chemical state of $\text{CuInSe}_2/\text{TiO}_2\text{-B}$ was determined by XPS spectra. Figure 4a shows that the dominant elements of the composite material were Se, In, Ti, O, and Cu, in addition to C element. This result is consistent with the EDS mapping results. The peaks at 458.6 and 464.3 eV were in agreement with $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$, respectively, indicating that Ti exists in the form of Ti^{4+} , which is derived from TiO_2 [36] (Figure 4b). Figure 4c shows the peaks of 529.8 and 531.3 eV that were attributed to the lattice oxygen (O_L) and adsorbed oxygen (O_A) [37], respectively. The presence of O_A indicates that oxygen vacancies were generated on the surface of the synthesized sample. Oxygen vacancy can facilitate electron transfer to the material surface, thus reducing the recombination of photogenerated carriers [38]. The binding energies of $\text{In } 3d_{5/2}$ and $3d_{3/2}$ located at 444.5 and 452.4 eV, respectively (Figure 4d), corresponded to the binding energies of In^{3+} from CuInSe_2 [39]. As shown in Figure 4e, the peak at 54.2 eV was indexed to $\text{Se } 3d_{5/2}$, indicating the presence of Se^{2-} in the composite, and no selenium oxide was formed [40]. Two main peaks with the binding energy peaks at 932.7 and 952.5 eV in Figure 4f were attributed to $\text{Cu } 2p_{3/2}$ and $\text{Cu } 2p_{1/2}$, respectively. The difference between the two binding energy peaks is 19.8 eV confirming Cu^{2+} was reduced to Cu^+ during the process of reaction [41]. The above analysis further demonstrated the successful synthesis of $\text{CuInSe}_2/\text{TiO}_2$ photoanode composites.

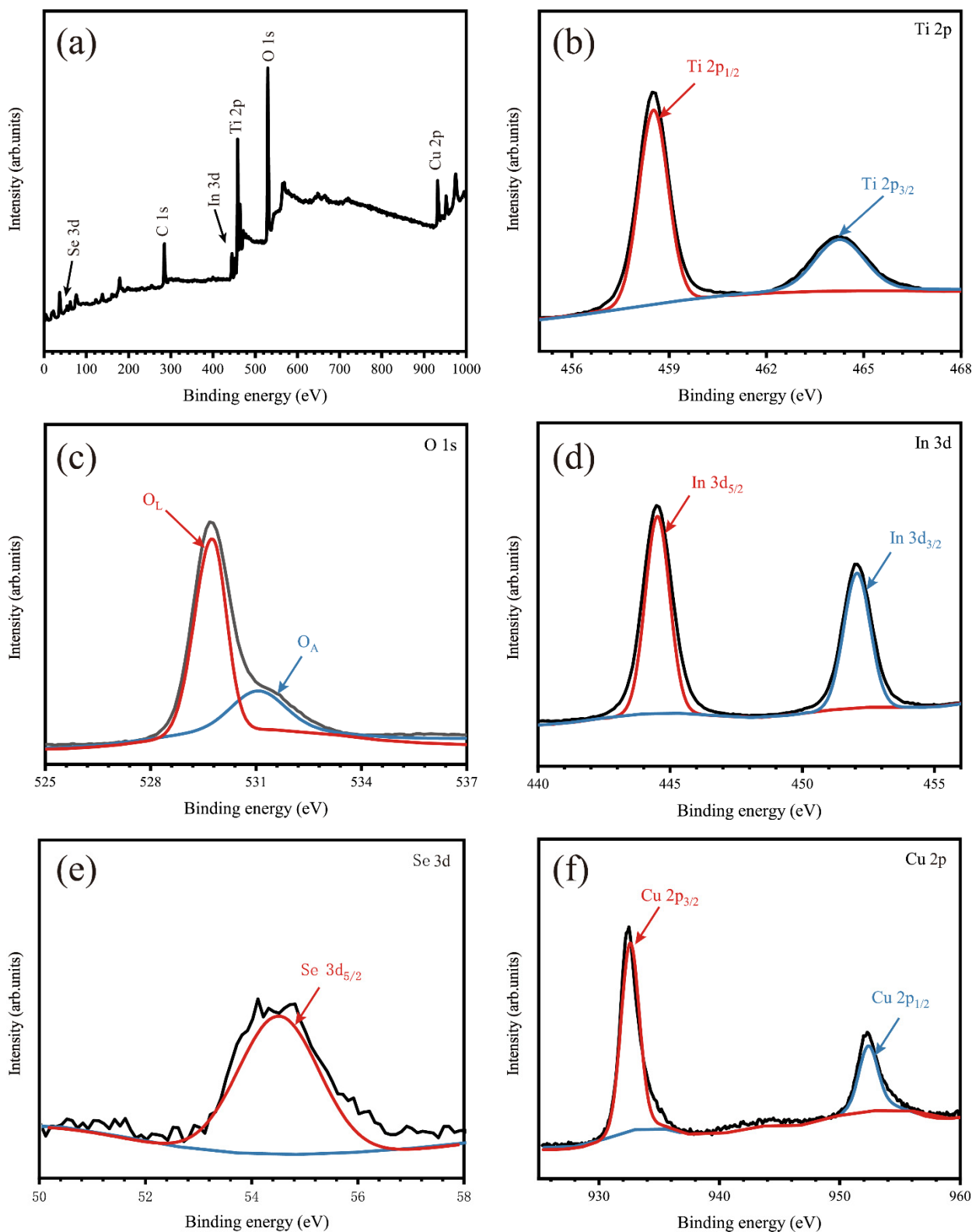


Figure 4. (a) The total XPS survey spectrum; high-resolution spectra of (b) Ti 2p, (c) O 1s, (d) In 3d, (e) Se 3d and (f) Cu 2p of CuInSe₂/TiO₂-B NTAs.

3.2. Optical Properties Analysis

The light absorption performances of pure TiO₂ and CuInSe₂/TiO₂-B were studied by UV-vis DRS. Figure 5a shows that pure TiO₂ can only absorb UV light with a wavelength

less than 370 nm. In addition, the light absorption of TiO₂ in the range of 400–800 nm may be due to light scattering caused by cracks in TiO₂ [42]. The absorption edge was red-shifted to 520 nm after depositing CuInSe₂ on the TiO₂. This indicates that the sensitization of CuInSe₂ nanoparticles improved the visible light absorption capacity of TiO₂ NTAs.

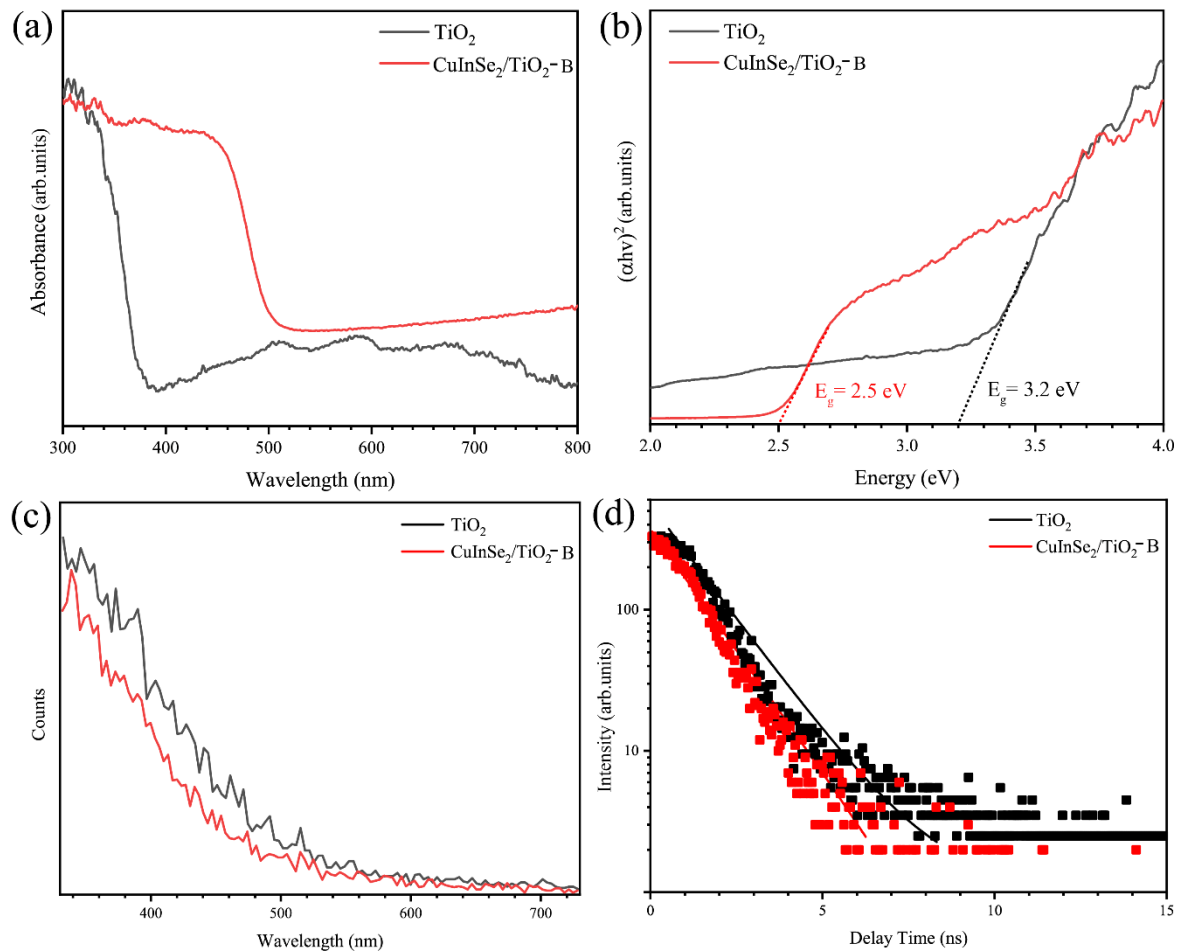


Figure 5. (a) UV-vis DRS, (b) Tauc plots, (c) PL spectra and (d) time-resolved PL spectra of the prepared TiO₂ and CuInSe₂/TiO₂-B.

The E_g of the photoanode materials can be calculated by the formula [43]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

where α , h , ν , and A stand for absorption coefficient, Planck's constant, optical frequency, and characteristic constant, respectively. Figure 5b shows that the E_g of TiO₂ and CuInSe₂/TiO₂ NTA composites were 3.2 and 2.5 eV, respectively.

The recombination rates of photogenerated carriers of CuInSe₂/TiO₂ and TiO₂ NTAs were analyzed by PL spectra. Figure 5c shows that the peak intensity of TiO₂ was larger than that of CuInSe₂/TiO₂, suggesting the photogenerated carrier recombination rate of CuInSe₂/TiO₂ decreases. The lifetime of the photogenerated carriers was evaluated by time-resolved PL spectra (Figure 5d), which were used to characterize the lifetime of photogenerated carriers. The attenuation curve was fitted by the formula:

$$R(t) = B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)} \quad (2)$$

The emission-decay time-constant values associated with τ_1 , τ_2 , B_1 and B_2 can be calculated by the formula:

$$R(t) = (B_1\tau_1^2 + B_2\tau_2^2) / (B_1\tau_1 + B_2\tau_2) \quad (3)$$

Table 1 displays the fitting and calculation results from Figure 5d. The mean electron lifetimes of TiO₂ and CuInSe₂/TiO₂ were 1.26 and 1.32 ns, respectively. This indicated that the formation of the CuInSe₂/TiO₂ heterojunction inhibited the recombination of e[−]/h⁺ pairs, thus enhancing the performance of PCP.

Table 1. Fitting results from Figure 5d.

Samples	τ_1	B_1	τ_2	B_2	t
TiO ₂	1.26	202.54	1.26	245.59	1.26
CuInSe ₂ /TiO ₂	1.32	308.75	1.32	362.61	1.32

3.3. PCP Performance and Stability Evaluation

The PCP performances were evaluated by comparing the values of the photocurrent densities of 316 SS connected to different photoelectrode materials. As shown in Figure 6a, the photocurrent densities of all the photoanodes were almost zero before illumination, indicating that the photoanodes offered no protective effect for 316 SS in the dark state. When the light source was turned on, the photocurrent response of the composite material was considerably improved compared to TiO₂. The composite materials prepared with different precursor concentrations also showed different photocurrent densities, and the CuInSe₂/TiO₂-B connected to 316 SS exhibited the largest photocurrent density (140 $\mu\text{A cm}^{-2}$).

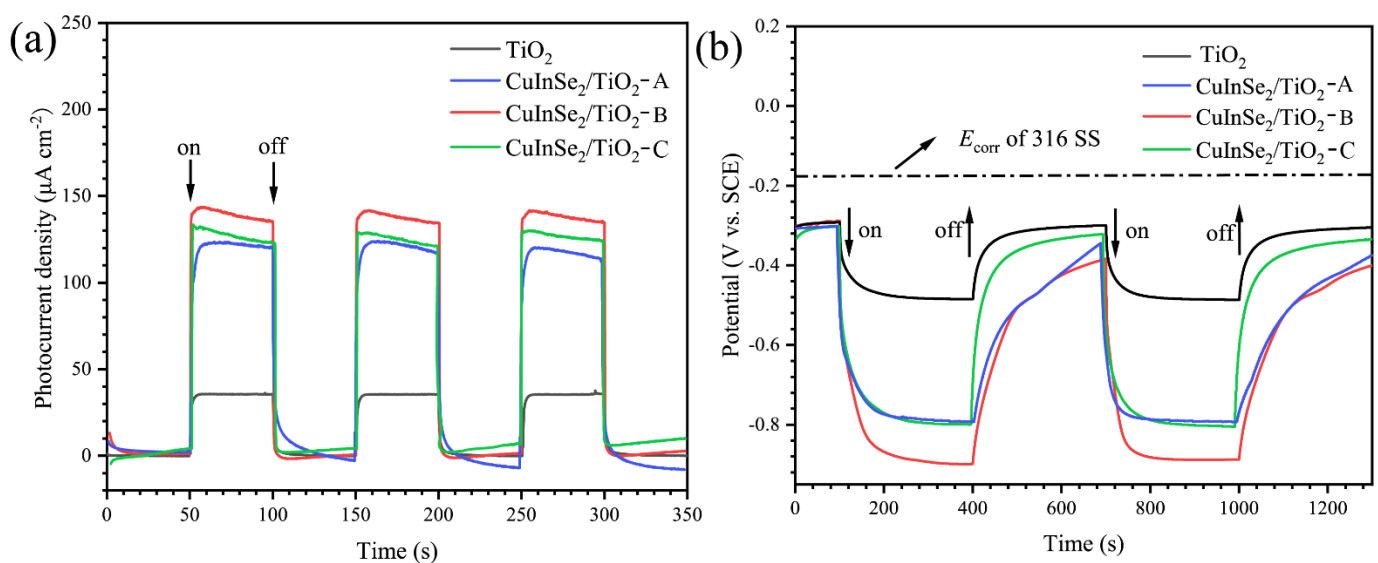


Figure 6. (a) I–t curves and (b) OCP–t curves between the different materials and 316 SS.

The potential change of the metal coupled with the photoelectrode is also a critical parameter for evaluating the properties of PCP. The more the potential drops, the better the performance of PCP [44]. In order to further study the PCP properties of photoelectrode materials, the OCP change curves of 316 SS connected with different photoelectrode materials were tested. As demonstrated in Figure 6b, the potential of 316 SS in 3.5 wt% NaCl was −0.19 V (vs. SCE). When the light source was turned on, the potentials of 316 SS connected with TiO₂ and CuInSe₂/TiO₂ NTAs both shifted negatively and then tended to be stable. The potential drops of TiO₂ under visible light irradiation was 0.29 V. For CuInSe₂/TiO₂ composites, the CuInSe₂/TiO₂-B showed the largest drop (0.71 V), which was consistent with the results of the photocurrent densities. With the increase in precursor concentration, the protective effect of the composite on 316 SS first increased and then decreased, which

may be due to the excess of CuInSe₂ blocking the pores of the TiO₂ NTA and hindering the absorption of visible light. The potentials of the composite were still lower than those of 316 SS after the light source was closed, suggesting that the composite can also protect 316 SS for a period of time in the dark state.

Figure 7a shows the Tafel curves of 316 SS, 316 SS coupled with TiO₂ and CuInSe₂/TiO₂-B NTAs in light and dark states. The fitting data of the Tafel curves are shown in Table 2. In the absence of light, the E_{corr} of 316 SS connected with TiO₂ and CuInSe₂/TiO₂-B negatively shifted to -0.44 and -0.47 V (vs. SCE), respectively, which may be because of the galvanic effect [20]. Under visible light irradiation, the negative shift of the E_{corr} of 316 SS coupled with CuInSe₂/TiO₂-B was larger than that of TiO₂, indicating that CuInSe₂/TiO₂-B has a better protection effect. In addition, the J_{corr} of 316 SS connected with CuInSe₂/TiO₂-B was significantly increased compared to TiO₂, which may be due to the increased electrochemical reaction rate at the interface caused by the polarization of photogenerated electrons [8].

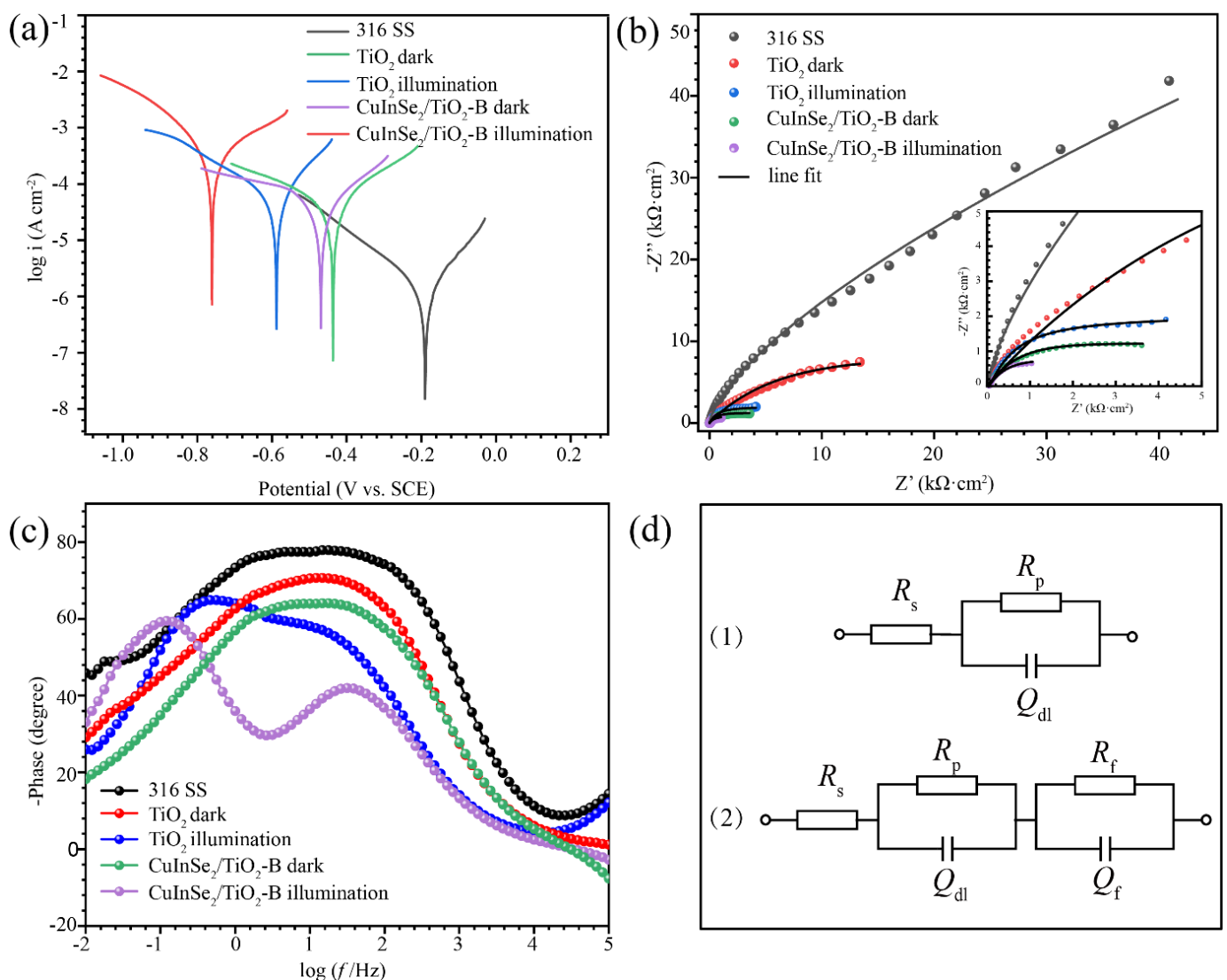


Figure 7. (a) Tafel curves, (b) Nyquist plots, and (c) Bode-phase curves of pure 316 SS and 316 SS coupled with different photoanodes under intermittent visible light; (d) the equivalent circuit for fitting the impedance data.

The interfacial properties of CuInSe₂/TiO₂-B were investigated by EIS. Figure 7b,c displays the Nyquist plots and Bode-phase curves of pure 316 SS and 316 SS connected with different photoanodes under intermittent visible light. The impedance arc radius of 316 SS connected with CuInSe₂/TiO₂-B was smaller than that of TiO₂ under light, which may be because more electrons were transferred from CuInSe₂/TiO₂-B to 316 SS, thus facilitating the electrochemical reaction rate of the interface [45]. In addition, the resistance arc radius of CuInSe₂/TiO₂-B NTAs coupled with 316 SS in the dark state was still smaller than that of 316 SS, indicating that CuInSe₂/TiO₂-B can also protect 316 SS in the dark state. Figure 7d shows the fitted equivalent circuit models from EIS data, where R_s represent solution resistance, R_p and Q_{dl} represent polarization resistance and double-electric-layer capacitance, respectively, and R_f and Q_f represent surface-film resistance and capacitance, respectively. The equivalent circuit model of bare 316 SS can be described as $R_s(R_p Q_{dl})$. The equivalent circuit of the 316 SS coupled with different photoanode materials can be fitted as $R_s(R_p Q_{dl})(R_f Q_f)$. Table 3 shows the electrochemical parameters fitted from the equivalent circuits. The values of R_p can reflect the difficulty of corrosion [46–48]. The smaller value of R_p means more electrons were transferred to 316 SS. The R_p value of 316 SS was significantly reduced after 316 SS was connected to CuInSe₂/TiO₂-B under visible light, indicating that CuInSe₂/TiO₂-B had a higher separation efficiency of photoinduced carriers than TiO₂.

Table 2. Electrochemical parameters obtained by Figure 7a.

Samples	E_{corr} (V vs. SCE)	J_{corr} ($\mu A\ cm^{-2}$)
316 SS	−0.19	1.58
TiO ₂ dark	−0.44	5.22
CuInSe ₂ /TiO ₂ -B dark	−0.47	5.31
TiO ₂ illumination	−0.59	32.31
CuInSe ₂ /TiO ₂ -B illumination	−0.76	76.26

Table 3. Electrochemical impedance parameters of the as-prepared photoanodes obtained from Figure 7b.

Samples	R_s ($\Omega \cdot cm^2$)	Q_f		R_f ($\Omega \cdot cm^2$)	Q_{dl}		R_p ($\Omega \cdot cm^2$)
		Y_{01} ($S'' \cdot \Omega^{-1} cm^{-2}$)	n_1		Y_{02} ($S'' \cdot \Omega^{-1} cm^{-2}$)	n_2	
316	5.559	–	–	–	2.186×10^{-5}	0.9232	1.001×10^5
TiO ₂ ^a	7.558	4.984×10^{-4}	1.00	22.190	3.232×10^{-4}	0.7796	4.357×10^4
CuInSe ₂ /TiO ₂ -B ^a	4.869	1.912×10^{-3}	0.8027	1.948×10^3	6.390×10^{-4}	0.8369	2.840×10^4
TiO ₂ ^b	3.567	2.879×10^{-7}	0.99	3.636	6.784×10^{-4}	0.7243	3.783×10^3
CuInSe ₂ /TiO ₂ -B ^b	6.677	3.167×10^{-3}	0.8916	1.616×10^3	9.438×10^{-4}	0.7958	20.990

^a Dark. ^b Visible light illumination.

Figure 8a shows the photoinduced I–V curves of CuInSe₂/TiO₂-B and TiO₂ with visible light turned on and off. The photocurrent densities of the CuInSe₂/TiO₂-B NTA photoelectrode were higher than those of TiO₂. This indicates that the heterojunction structure formed between CuInSe₂ and TiO₂ can increase the transfer rate of photoelectrons and promote the separation of photogenerated carriers.

Figure 8b–d displays the M–S plots of different photoanodes. The three curves all show a positive slope, suggesting that prepared photoanodes have the characteristics of an n-type semiconductor. The flat band potential (E_{fb}) of a semiconductor can be estimated using $C^{-2} = 0$ in the M–S curve [49]. Figure 8b–d shows that the E_{fb} of TiO₂, CuInSe₂ and CuInSe₂/TiO₂-B were −0.20, −0.68 and −0.41 V (vs. SCE), respectively. Obviously, the E_{fb} of CuInSe₂/TiO₂-B was more negative than that of TiO₂, indicating that the modification of CuInSe₂ can promote charge transfer in TiO₂ NTAs [50]. The slope of M–S plot is negatively correlated with the charge density [51]. The slope of the CuInSe₂/TiO₂-B curve was more negative than that of TiO₂, demonstrating that CuInSe₂/TiO₂-B had a higher free carrier density and superior photoelectrochemical performance than TiO₂.

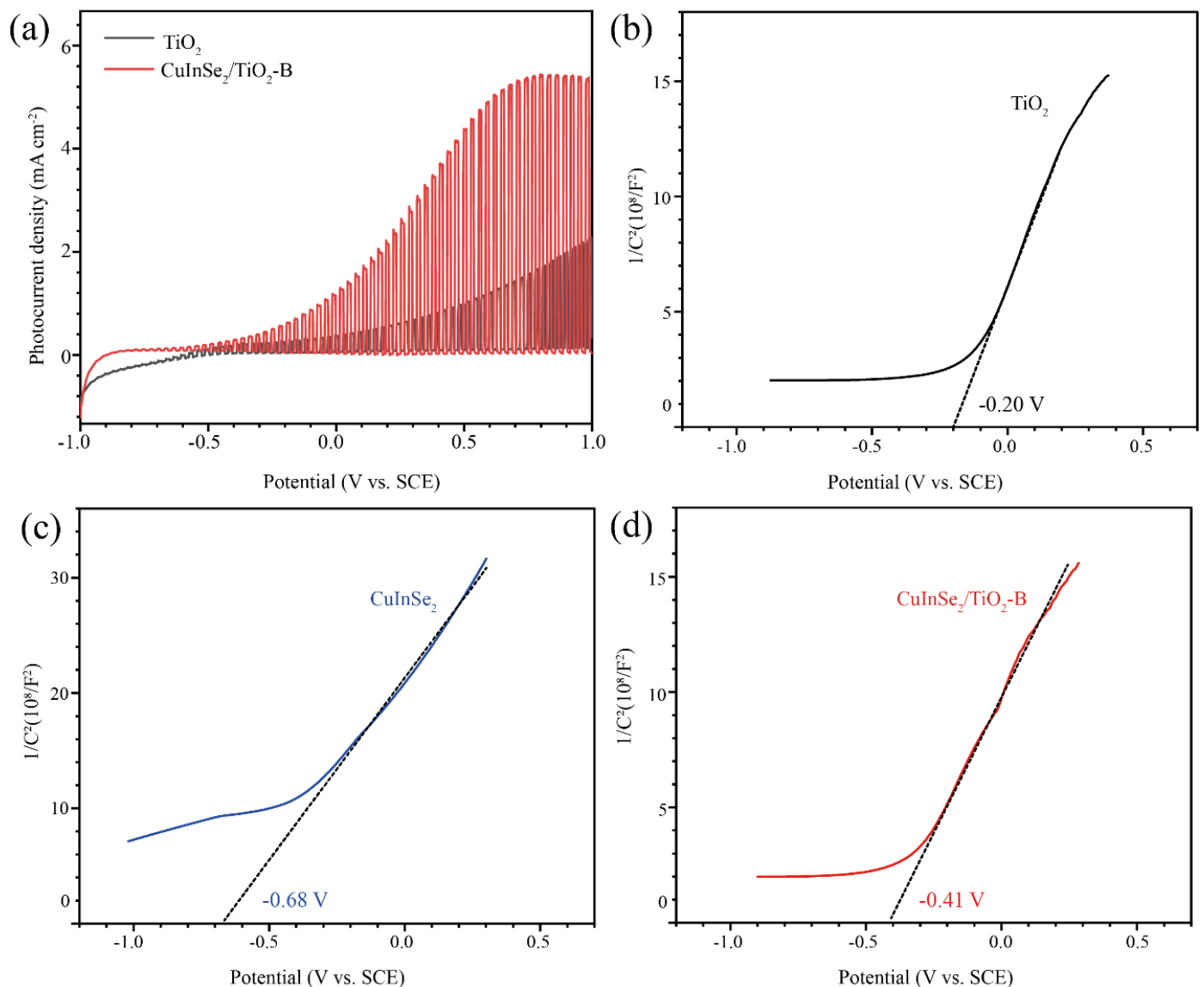


Figure 8. (a) I–V curves of the prepared TiO₂ and CuInSe₂/TiO₂-B; (b–d) M–S plots of TiO₂, CuInSe₂ and CuInSe₂/TiO₂-B.

The stability of the photoanodes is important for their PCP applications. Therefore, a long-term OCP test was performed. As shown in Figure 9a, after the CuInSe₂/TiO₂-B was illuminated for 4 h, the potential of 316 SS coupled with CuInSe₂/TiO₂-B can be stabilized at −0.82 V. The potentials were still lower than the self-corrosion potential of 316 SS for more than 8 h in the dark state. This may be due to the extended lifetime of photogenerated electrons and the generation of oxygen vacancies. Figure 9b shows the XRD spectra of CuInSe₂/TiO₂-B before and after long-term OCP measurements. The XRD results showed that the crystal structure of the photoanode did not change after long-term testing. It indicated that CuInSe₂/TiO₂ composite had superior stability. The surface of the 316 SS before and after the experiment was characterized by metallographic microscopy. According to Figure 9c,e, the surface of 316 SS protected by CuInSe₂/TiO₂-B was consistent with that before the experiment, while several pitting holes appeared on the surface of the unprotected 316 SS. These demonstrated the protective performance of CuInSe₂/TiO₂ for 316 SS.

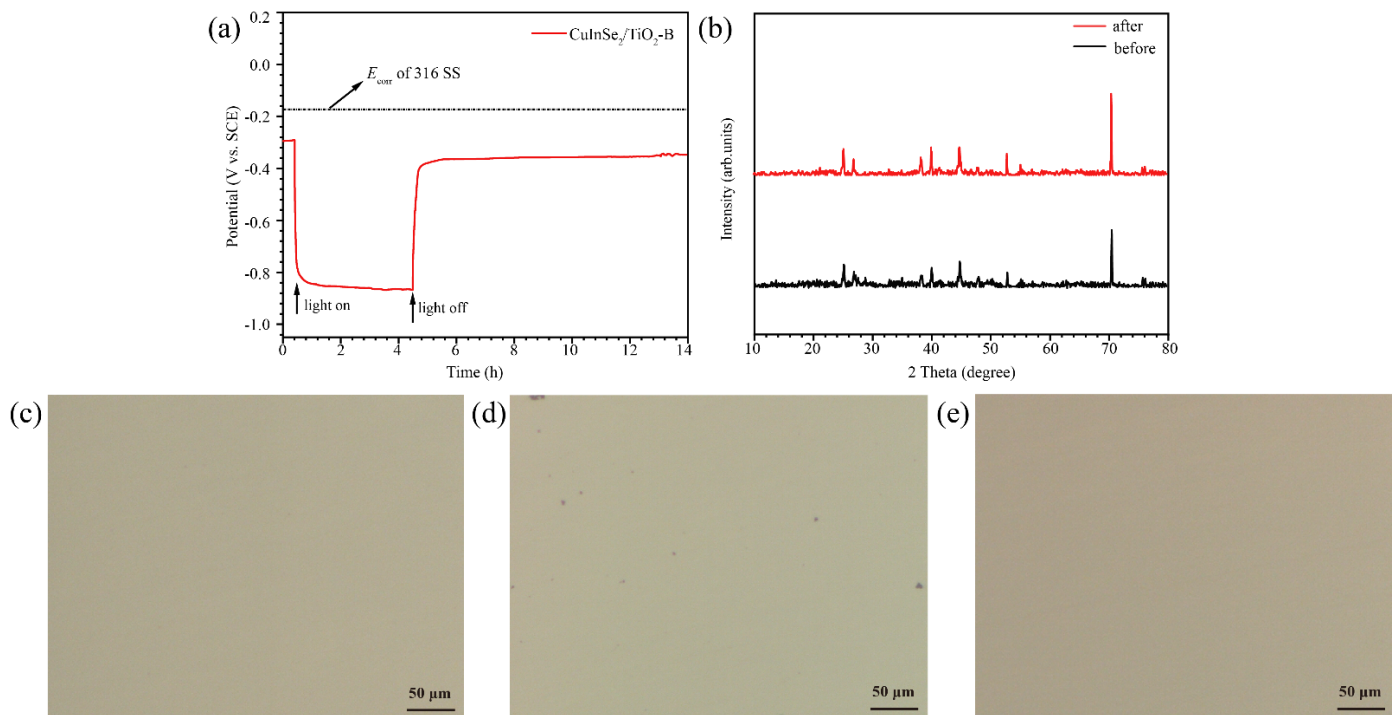


Figure 9. (a) Long-term OCP change of 316 SS connected to the CuInSe₂/TiO₂-B photoanode under on and off visible light illumination; (b) XRD images of CuInSe₂/TiO₂-B before and after long-term OCP measurements; the optical images of the 316 SS (c) before the experiment, (d) unprotected and (e) protected by CuInSe₂/TiO₂-B for 14 h.

3.4. DFT Analysis and PCP Mechanism

The total electronic density of states (TDOS) and partial electronic density of states (PDOS) of the prepared CuInSe₂/TiO₂ NTAs and pure TiO₂ NTAs were calculated using first-principles density functional theory (calculation methods were provided in the Supplementary Materials). In pure TiO₂, the maximum value of valence band (VBM) is provided by the electrons of O 2p state electrons, and the minimum value of conduction band (CBM) is provided by the electrons of Ti 3d state electrons (Figure 10a). The E_g can be estimated by the difference between VBM and CBM. The calculated E_g (2.0 eV) of TiO₂ is smaller than the DRS result (3.2 eV), which is due to the generalized gradient approximation (GGA) theory underestimating the Hubbard interaction [52]. In CuInSe₂, the primary contribution of VBM is of Cu 3d electrons (Figure 10b), and CBM is mainly provided by Se 4p electrons. When CuInSe₂ was deposited on the surface of TiO₂ NTAs, the 3d electrons of Cu were hybridized with the 3d electrons of Ti and the 2p electrons of O at VB, which further improved the mobility of the photogenerated carriers. Compared with TiO₂, after the formation of the CuInSe₂/TiO₂ heterostructure, the CBM of TiO₂ shifted negatively, and the E_g decreased significantly, indicating the enhanced visible light absorption of the CuInSe₂/TiO₂ heterostructures. The DFT calculation results are consistent with the DRS results.

The possible mechanism for the improved protection of CuInSe₂/TiO₂ photoanodes was analyzed (Figure 11). The E_{fb} of TiO₂ and CuInSe₂ obtained from the M–S curves were −0.20 and −0.68 V (vs. SCE), respectively, which are equal to 0.04 and −0.44 V vs. NHE, pH = 7, respectively. The E_{CB} of an n-type semiconductor is 0.2 eV more negative than E_{fb} [30], so the E_{CB} of TiO₂ and CuInSe₂ were −0.16 and −0.64 eV, respectively. The E_{VB} of TiO₂ and CuInSe₂ were 3.04 and 1.13 eV, respectively, obtained from the empirical formula $E_{VB} = E_g + E_{CB}$. Under visible light irradiation, photoelectrons migrated from the CB of CuInSe₂ to the CB of TiO₂, because the E_{CB} of CuInSe₂ is more negative than that of TiO₂, and then to the surface of 316 SS. As a result, the potentials of 316 SS were lower than

the self-corrosion potential, thereby inhibiting the anodic oxidation reaction of 316 SS. In addition, the photogenerated holes in the VB of TiO_2 were transferred to the VB of CuInSe_2 and consumed by reaction with the hole scavenger, thereby reducing the recombination of e^-/h^+ pairs.

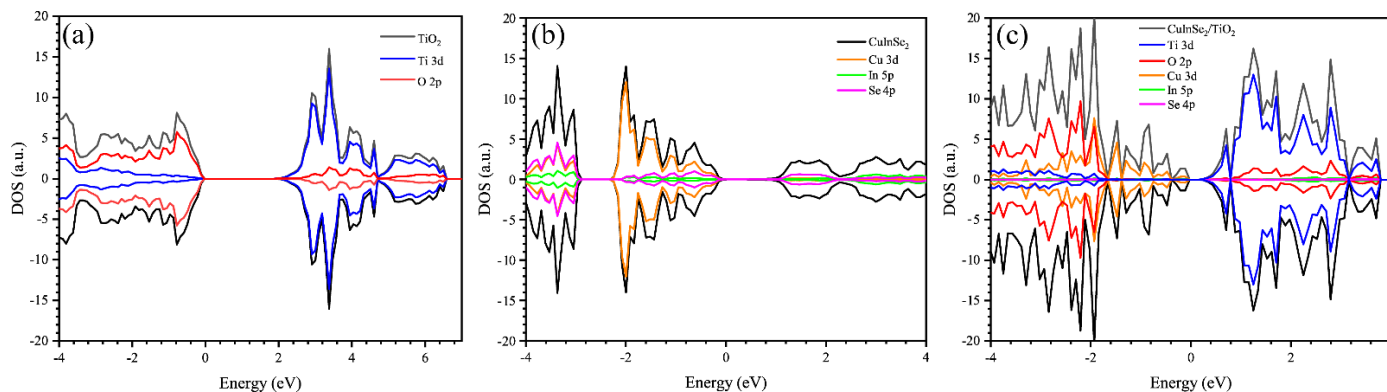


Figure 10. The calculated TDOS and PDOS for (a) TiO_2 , (b) CuInSe_2 and (c) $\text{CuInSe}_2/\text{TiO}_2$.

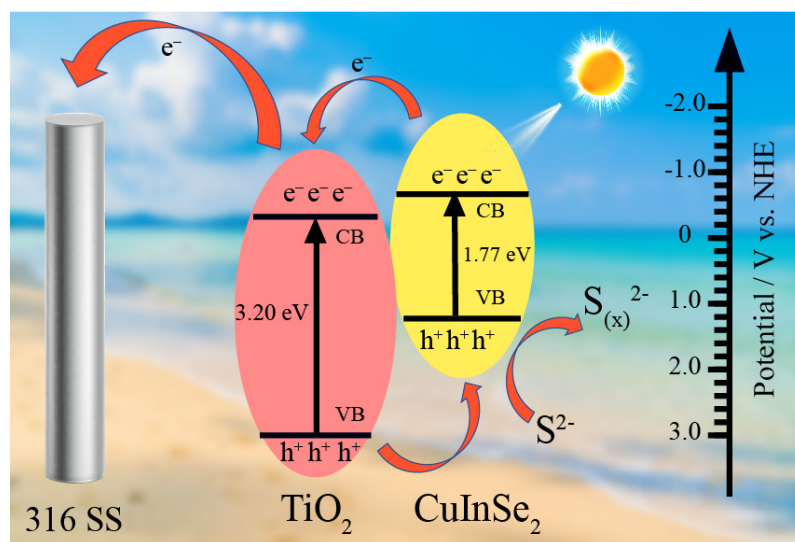


Figure 11. Possible electron-transfer mechanism of the $\text{CuInSe}_2/\text{TiO}_2$.

4. Conclusions

In this study, novel $\text{CuInSe}_2/\text{TiO}_2$ NTA photoanodes were successfully fabricated by electrochemical anodic oxidation and a solvothermal method. A highly efficient heterojunction was formed between tetragonal chalcopyrite CuInSe_2 and anatase TiO_2 . The sensitization of CuInSe_2 improved the absorption capacity of the composites to visible light, inhibited the recombination of electron-hole pairs and improved the electron transfer ability. The $\text{CuInSe}_2/\text{TiO}_2$ -B NTA photoanode exhibited the best PCP performance. The photocurrent density of the composite connected to 316 SS could reach $140 \mu\text{A cm}^{-2}$ under visible light, and the potential drops to -0.90 V , which is much lower than the self-corrosion potential of 316 SS (-0.19 V). In addition, the protection effect can still be maintained for more than 8 h after 4 h of visible light irradiation. The optical images of the protected 316 SS fully demonstrated the excellent protection capability of $\text{CuInSe}_2/\text{TiO}_2$ NTAs. Therefore, $\text{CuInSe}_2/\text{TiO}_2$ NTAs show great potential application in the field of PCP.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings12101448/s1>. Supplementary Materials: Computational methods.

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