



Article

Preparation and Characterization of a Dual-Layer Coating with Synergistic Ionic Selectivity and Photocathodic Protection Property

Chuyuan Cui ¹ , Yongsheng An ², Xiangpeng Wang ³ and Ping Qiu ^{1,*} ¹ College of New Energy and Materials, China University of Petroleum (Beijing), Beijing 102249, China; cuichuyuan2022@163.com² College of Safety and Ocean Engineering, China University of Petroleum (Beijing), Beijing 102249, China; an_yongsheng@126.com³ Carbon Neutrality Research Institute, Shandong Institute of Petroleum and Chemical Technology, Dongying 257061, China; wangxiangpeng1989@163.com

* Correspondence: qiuping@cup.edu.cn

Abstract

Inspired by the mechanism of ion exchange resins, this study is a first-report in constructing a dual-layer photocathodic protective coating with ionic selectivity to enhance corrosion resistance property. The microstructure, composition, and ion selectivity of the coating are characterized by scanning electron microscopy, Raman spectroscopy, infrared spectroscopy, and membrane potential. It shows that the outer g-C₃N₄/TiO₂ cation-selective layer plays a role in preventing corrosive Cl[−] ions passing through the coating; the inner g-C₃N₄-TiO₂-CTAB anion-selective layer could prevent Fe²⁺ ions from diffusing through the coating. Furthermore, the coated carbon steel sample demonstrates a minimum OCP (open circuit potential) value of −770 mV (vs. SCE) under illumination in 3.5% NaCl media. Interestingly, the OCP remains around −720 mV (vs. SCE) even after light deprivation. The synergistic effect between ion selectivity and photocathodic protection is described, in detail, in the following.

Keywords: photocathodic protection; bipolar coating; ion selectivity; carbon steel



Academic Editor: Philippe Refait

Received: 6 September 2025

Revised: 11 October 2025

Accepted: 12 November 2025

Published: 17 November 2025

Citation: Cui, C.; An, Y.; Wang, X.; Qiu, P. Preparation and Characterization of a Dual-Layer Coating with Synergistic Ionic Selectivity and Photocathodic Protection Property. *Corros. Mater. Degrad.* **2025**, *6*, 60. <https://doi.org/10.3390/cmd6040060>

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1. Introduction

The development of offshore oil and gas resources has actively driven the application of steel marine contexts. Exposed steel surfaces undergo severe corrosion under marine atmospheric conditions [1–10]. The photochemical cathodic protection methodology possesses considerable application potential in the realm of anti-corrosion. However, as the coating lacks the ability to act as an ion barrier, corrosive anions will gradually penetrate the coating and reach the substrate, resulting in substrate corrosion and coating failure. Hence, it is of paramount importance to develop a kind of corrosion resistant coating that effectively impedes ion migration.

TiO₂ nanomaterials have undergone extensive research as photocatalytic materials in the past few decades. TiO₂ nanomaterials are extensively employed in fields such as solar cells and environmental protection, owing to their exceptional electronic and optical characteristics, electrochemical corrosion resistance, non-toxicity, remarkable stability, low cost, and abundant accessibility [11–15]. However, its wide band gap (3.2 eV) restricts light absorption of ultraviolet wavelengths (~5% of solar spectrum), severely limiting solar energy utilization efficiency.

g-C₃N₄ is a typical non-metallic semiconductor, which has stable chemical properties, a narrow band gap (2.7 eV), can respond to visible light, is low cost and easy to prepare, and has gradually attracted attention in the field of photocathodic protection. However, its application in the field of photocathodic protection is limited due to its few active sites, low electron mobility, and insufficient hole oxidation capacity.

Therefore, in order to improve the photocathodic protection performance of TiO₂ and g-C₃N₄ for metals, it is a good strategy to combine TiO₂ and g-C₃N₄. Zhang et al. [16] used the hydrothermal method to prepare g-C₃N₄/graphene/TiO₂ ternary composite material, which formed an internal electric field to facilitate electron transport from the photoelectrode to metallic substrates, thus enhancing the photochemical corrosion protection of 304 stainless steel. Guan et al. [17] prepared a g-C₃N₄ co-decorated rutile TiO₂ nanorods composite film by a three-step chemical vapor deposition method, achieving 4.5 times higher in photocurrent density compared to unmodified TiO₂ film. Under white light irradiation, the corrosion potential is reduced by 680 mV, and the protection effect of the photoelectrode is significantly enhanced. However, in practical applications, the coating generally faces the problem that the electrolyte will gradually enter the metal matrix from the defects in the coating preparation process, resulting in metal corrosion. By adding anti-corrosive fillers to the coating, although the corrosion can be delayed to a certain extent, it cannot fundamentally solve the problem.

Therefore, in order to solve the above problems, we propose a collaborative application of photocathodic protection and ion barrier. Firstly, g-C₃N₄ and TiO₂ were combined to prepare cation-selective g-C₃N₄-TiO₂ composite filler. Using CTAB (Cetyltrimethylammonium bromide) as a cationic surfactant, g-C₃N₄-TiO₂ and CTAB were further combined to prepare the anion-selective composite filler g-C₃N₄-TiO₂-CTAB. The bipolar coating on carbon steel was prepared by epoxy resin. The microstructure and ion selectivity of the composite coatings were characterized, and their photocathodic protection performance on carbon steel was evaluated. Additionally, the corresponding protection mechanism was analyzed.

2. Experimental Section

2.1. Materials Preparation

The composition of Q235 carbon steel used in this experiment was as follows: Carbon (C): 0.12–0.22%; Manganese (Mn): 0.30–0.70% Silicon (Si): 0.17–0.37% Phosphorus (P): 0.045–0.045% Sulfur (S): 0.03–0.050%, Iron (Fe): balance. Carbon steel specification: 10 mm × 10 mm × 5 mm, prepared into electrodes for subsequent use.

All the chemical reagents in this experiment were of analytical grade from Aladdin Biochemical Technology Co., LTD., Shanghai, China and used without further processing. Ultrasonic cleaner used was KQ3200DB, from Huruiming Instrument Co., Ltd., Guangzhou, China. TG16-WS benchtop high-speed centrifuge was from Xiangyi Experimental Instrument Development Co., Ltd., Hunan, China.

TiO₂ was prepared via the sol-gel method: 30 mL tetrabutyl titanate was dissolved in 30 mL of anhydrous ethanol and the solution was added to the excessively deionized water in the agitated state, once the solution was stabilized. The reaction products were filtered and dried in an oven at 105 °C [18] and subsequently pre-treated at 250 °C for 2 h to obtain TiO₂ powder.

Synthesis of g-C₃N₄: The urea was annealed in a tube furnace at 550 °C for 4 h under a N₂ atmosphere, and the resulting yellow product was washed with distilled water and ethanol, followed by drying at 80 °C [19].

Preparation of g-C₃N₄-TiO₂ composites: A certain amount of g-C₃N₄ and TiO₂ were dispersed in deionized water by mild ultrasound, respectively. The TiO₂ dispersion was

dropped into the $g\text{-C}_3\text{N}_4$ dispersion. The mixture underwent additional ultrasonic treatment for 20 min and then filtered. The collected solid was dried at 60°C and further calcined at 450°C . Finally, a yellow product was collected.

Preparation of $g\text{-C}_3\text{N}_4\text{-TiO}_2\text{-CTAB}$ composite material: $g\text{-C}_3\text{N}_4\text{-TiO}_2$ powder was dispersed in ethanol and subjected to ultrasonic treatment for 30 min to form A suspension. CTAB was dissolved in anhydrous ethanol and ultrasonically treated for 30 min to obtain solution B. Solution A and B were mixed and stirred at 60°C for 4 h followed by centrifuging and collecting the precipitate. Then, the mixture was cleaned and precipitated with deionized water three times. The precipitate was put into an oven and dried at 80°C for 24 h. The collected substance was recorded as $g\text{-C}_3\text{N}_4\text{-TiO}_2\text{-CTAB}$.

Preparation of bipolar coatings: The polished carbon steel electrode was ultrasonic treated in ethanol for 30 min for subsequent use. The $g\text{-C}_3\text{N}_4\text{-TiO}_2$ powder was added to the epoxy resin according to the appropriate proportion. The diluent was dispersed evenly to obtain the cation-selective filler A. Repeating the above steps, a certain amount of $g\text{-C}_3\text{N}_4\text{-TiO}_2\text{-CTAB}$ powder was mixed with resin to obtain anion-selective filler B. Then, filler B was applied evenly on the carbon steel electrode. Before the first layer was fully cured, filler A was loaded on its top. The control sample was coated with the same film thickness of fillers A or B to prepare the coating with only cationic or anionic selectivity. In addition, the thickness of a double layer was approximately $300 \pm 20\ \mu\text{m}$. The specific preparation process of the above samples is shown in Figure 1.

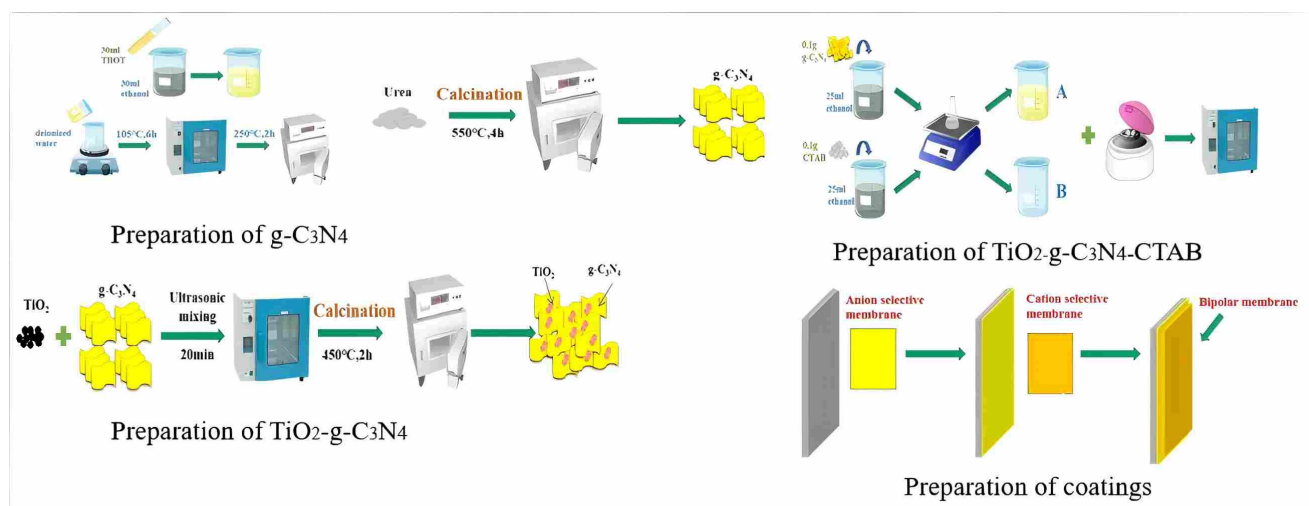


Figure 1. Schematic illustration of the representative coating preparation procedure.

2.2. Surface and Chemical Characterization

The morphology of the composite coating was characterized by scanning electron microscopy (SEM, SU8010, HITACHIA, Tokyo, Japan). Raman spectrometer (Renishaw inVia, 514 nm laser, Renishaw, Germany) and $50\times$ Lwd objective lens (Olympus, Japan) were used to record Raman spectra and analyze the corresponding chemical components. The Raman spectral resolution was $1\text{--}2\ \text{cm}^{-1}$. The structural changes before and after modification were characterized by Fourier infrared spectroscopy (Nicolet 470 spectrometer, Nicolet, Green Bay, WI, USA) with KBr compression method. The spectral scanning accuracy was $4\ \text{cm}^2$, and the scanning range was $4000\text{--}900\ \text{cm}^{-1}$. In the membrane potential test, KCl solution (C1) with a fixed concentration of $0.01\ \text{mol}\cdot\text{L}^{-1}$ was shown on the left. On the right side were KCl solutions (C2) of $0.0001\ \text{mol}\cdot\text{L}^{-1}$, $0.001\ \text{mol}\cdot\text{L}^{-1}$, $0.01\ \text{mol}\cdot\text{L}^{-1}$, $0.1\ \text{mol}\cdot\text{L}^{-1}$ and $1\ \text{mol}\cdot\text{L}^{-1}$ [20–22], respectively. During the test, both the reference electrode and the auxiliary electrode were Ag/AgCl electrode.

2.3. Photoelectrochemical Properties Characterization

Measurements were made at the Zahner IM6eX station (Zahner, Germany) using a three-electrode quartz battery in 3.5% NaCl solution. The prepared photoanode was used as the working anode. The electrode, Pt wire and SCE (saturated calomel electrode) were used as the opposite electrode and reference electrode, respectively. Timing amperage tests were performed under intermittent and constant lighting. A xenon lamp ($100 \text{ mW} \cdot \text{cm}^{-2}$) was used to simulate the illumination of sunlight.

3. Results and Discussion

Figure 2a shows the Raman spectra of $\text{g-C}_3\text{N}_4\text{-TiO}_2$ before and after surface modification by CTAB [23]. Compared with $\text{g-C}_3\text{N}_4\text{-TiO}_2$, the spectral peaks observed at 2850 cm^{-1} and 2921 cm^{-1} after CTAB composite were attributed to C–H ($-\text{CH}_2-$ and $-\text{CH}_3$) of CTAB, which proved that CTAB was successfully compounded. Figure 2b shows the FTIR spectra of $\text{g-C}_3\text{N}_4\text{-TiO}_2\text{-CTAB}$. The vibration peak of Ti–O–Ti bond appeared in the range of $400\text{--}600 \text{ cm}^{-1}$. The spectral peak in the range of $1200\text{--}1650 \text{ cm}^{-1}$ could be considered as the C–N bond in $\text{g-C}_3\text{N}_4$. The spectral peak in the range of $3400\text{--}3450 \text{ cm}^{-1}$ was the vibration peak of surface adsorbed water. All of the above can prove that $\text{g-C}_3\text{N}_4$ had successfully combined with CTAB and TiO_2 .

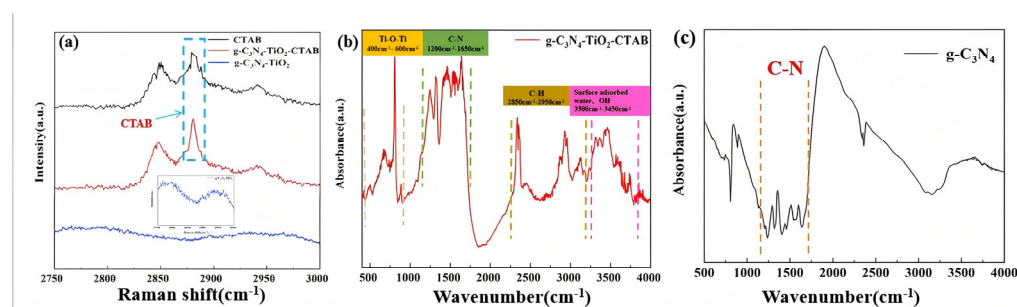


Figure 2. Raman spectra of $\text{g-C}_3\text{N}_4\text{-TiO}_2$ prior to and after the surface modification of CTAB (a), FTIR spectra of $\text{g-C}_3\text{N}_4\text{-TiO}_2\text{-CTAB}$ (b), and FTIR spectra of $\text{g-C}_3\text{N}_4$ (c).

The TiO_2 before and after modification is characterized via SEM to observe the variations in microscopic morphology. Figure 3a,b,e,f represents the surface morphologies of TiO_2 and $\text{g-C}_3\text{N}_4$. It can be discerned that TiO_2 was distributed on the surface in a granular manner and relatively uniformly, while $\text{g-C}_3\text{N}_4$ exhibited a lamellar structure. Figure 3c,g are the surface morphologies of $\text{g-C}_3\text{N}_4$ compounded with TiO_2 . It can be observed that TiO_2 particles were evenly dispersed on the layer structure of $\text{g-C}_3\text{N}_4$. Figure 3d,h are the surface morphologies of $\text{g-C}_3\text{N}_4\text{-TiO}_2$ modified by adding CTAB. It can also be noticed that the particles are evenly distributed on the $\text{g-C}_3\text{N}_4$ lamellar structure, and the addition of CTAB increases the lamellar spacing and the dispersion of $\text{g-C}_3\text{N}_4$.

In order to investigate the ion selectivity of the modified filler coating, a membrane potential test of the coating was carried out. When the concentration on the right side was higher than that on the left side, under the influence of the concentration gradient, the anions in the solution on the right side would spontaneously migrate to the left side where the ion concentration was lower. When the system was stabilized, if the measured membrane potential was positive, it indicated that there were too many Cl^- ions on the left side and too many K^+ ions on the right side, indicating both that the migration of K^+ ions was inhibited and that the membrane had anion selectivity. If the measured membrane potential was negative, it indicated that there was an excess of K^+ ions on the left and Cl^- ions on the right, indicating that the migration of Cl^- ions was inhibited and that the membrane had cation selectivity. As can be seen from Figure 4, as the concentration

of the electrolytic cell on the right increased, the film potential of the CTAB-modified $g\text{-C}_3\text{N}_4\text{-TiO}_2$ coating was positive and slightly increased, while the film potential of the $g\text{-C}_3\text{N}_4\text{-TiO}_2$ coating was negative and gradually became more negative with the increase in concentration. The results show that the prepared CTAB-modified $g\text{-C}_3\text{N}_4\text{-TiO}_2$ coating had anion selectivity, and the $g\text{-C}_3\text{N}_4\text{-TiO}_2$ coating had cation selectivity. At the same time, the slope of the membrane potential can also indicate the strength of ion selectivity. It can be seen from the figure that the $g\text{-C}_3\text{N}_4\text{-TiO}_2$ coating had strong cation selectivity, while the CTAB-modified $g\text{-C}_3\text{N}_4\text{-TiO}_2$ coating had weak anion selectivity.

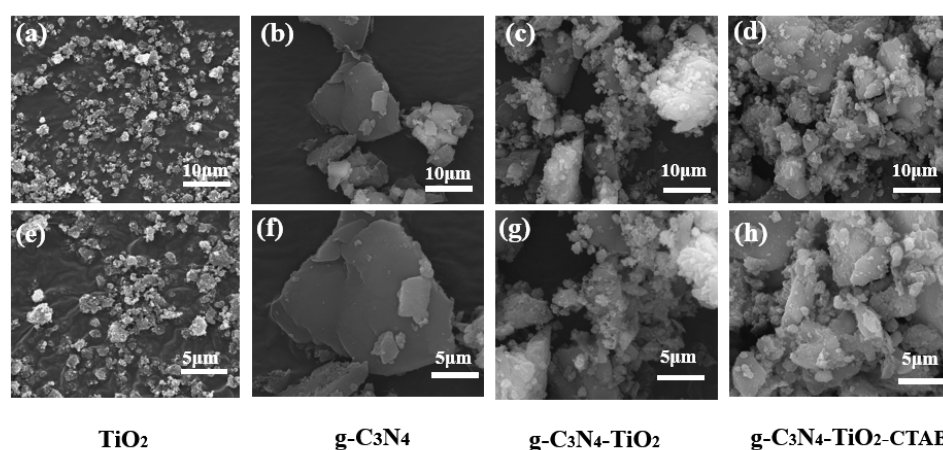


Figure 3. The SEM images of unmodified TiO_2 (a,e), $g\text{-C}_3\text{N}_4$ (b,f), $g\text{-C}_3\text{N}_4\text{-TiO}_2$ (c,g), and $g\text{-C}_3\text{N}_4\text{-TiO}_2$ modified by the addition of CTAB (d,h).

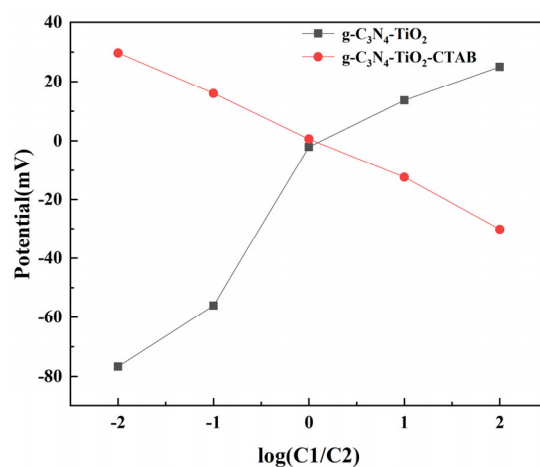


Figure 4. Membrane potential diagram of modified fillers.

In order to explore the photocathodic protection effect of the nanocomposite coupled with carbon steel, the alterations of open circuit potential (OCP) and photocurrent density under intermittent light for a duration of 5 min with light on and 5 min with light off were recorded. The test results are presented in Figure 5a. It was observed that the potential promptly exhibited a considerable negative shift under illumination. The potential of the photoanode with anionic selectivity dropped to -680 mV (vs. SCE), the potential of the photoelectrode with cation selectivity descended to -550 mV (vs. SCE), and the potential of the carbon steel coupled with the bipolar photoanode reduced to -770 mV (vs. SCE). Since the corrosion potential of uncoupled carbon steel was -430 mV (vs. SCE), the potential decline indicated that all these photoanodes could offer cathodic protection to the carbon steel. A bipolar photoanode provided greater protection. In similar studies, this photoelectric process was described as follows: photogenerated electrons and holes can be

promptly generated under light. The photogenerated electrons were then transferred to the carbon steel substrate so that the carbon steel underwent a negative potential shift [24].

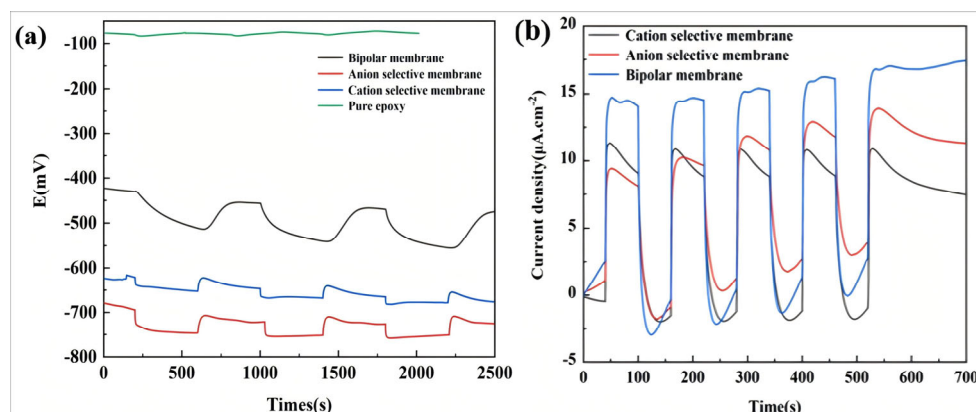


Figure 5. OCP variations (a), chronoamperometry (b) of bipolar filler, cation-selective filler, and anion-selective filler is coated on the carbon steel electrode.

The variation in photocurrent density was utilized to examine the transport characteristics of photogenerated electrons. Figure 5b exhibited the photocurrent density curve of the fabricated nanocomposite coupled with carbon steel under intermittent light for a duration of 30 s with light on and 30 s with light off. The spikes witnessed during the initial light phase were attributed to the separation of photogenerated electrons and holes in the space-charged layer of the nanocomposite. The photogenerated electrons subsequently moved to the conduction band of the nanocomposite and then transferred to the matrix. Concurrently, the holes migrated towards the interface between the electrode and the electrolyte, where they were reduced to produce oxygen or recombine with electrons in the surface state. Furthermore, a certain amount of recombination of the electrons and holes also took place in the prepared composites, which correspondingly reduced the photocurrent density. When the production and recombination rate reached a dynamic balance, a stable photocurrent density could be obtained. Once the light was removed, the electrons and holes recombined rapidly, leading to a rapid decrease in photocurrent density.

Figure 6 displays the test results of the AC impedance spectrum in 3.5 wt% NaCl solution after the carbon steel electrode was coated with composite fillers and bipolar fillers of diverse ion selectivity. The test conditions of the AC impedance spectrum were ultraviolet illumination. It is evident from the Bode diagram in Figure 6b that all the composite coatings manifested constant state of time. At the same time, it can be perceived from the Nyquist diagram in Figure 6a that the arc radius of the bulk reactance of the bipolar coating was the smallest, indicating that the electron transfer speed was faster. Figure 6c is the fitted equivalent circuit of the AC impedance spectra of different fillers, where R_s represents solution resistance, R_1 and CPE_1 represent film resistance and film capacitance, and R_2 and CPE_2 represent charge transfer resistance and double layer capacitance. Table 1 is the result of fitting the data obtained from the AC impedance spectrum test by employing the fitting equivalent circuit and ZSimpWin 3.3 software. The fitted R_2 values reflect the cathode reaction properties of the prepared nanocomposites. Generally speaking, the smaller the R_2 value, the better the photocathodic protection performance [25]. Coatings with anionic selectivity had R_2 values of $994.2 \Omega\cdot\text{cm}^2$, coatings with cationic ion selectivity had R_2 values of $2752 \Omega\cdot\text{cm}^2$, and bipolar coatings had R_2 values of $337.4 \Omega\cdot\text{cm}^2$. It was discovered that the interfacial reaction resistance was approximately eight times lower than that of a single selective coating. For R_1 values, the order of their magnitudes was the same as that for R_2 values. Therefore, the photocathodic protection performance of the bipolar coating was the best.

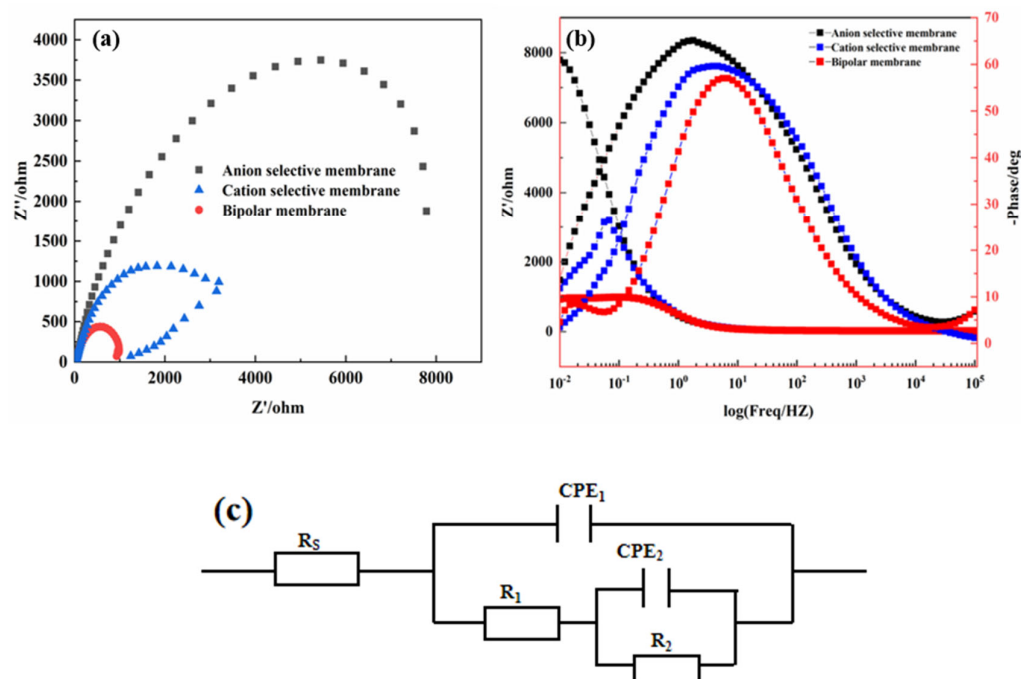


Figure 6. Nyquist (a), Bode (b) of composite and bipolar fillers with different ion selectivity are coated on the carbon steel electrode, and the corresponding equivalent circuit model used to fit the impedance data (c).

Table 1. Derivative parameters obtained by fitting the impedance data.

Conditions	R_s ($\Omega \cdot \text{cm}^2$)	CPE_1		R_1 ($\Omega \cdot \text{cm}^2$)	CPE_2		R_2 ($\Omega \cdot \text{cm}^2$)
		$Y_{01} \times 10^{-4}$ ($\Omega^{-1} \cdot \text{S}^n \cdot \text{cm}^{-2}$)	n_1		$Y_{02} \times 10^{-4}$ ($\Omega^{-1} \cdot \text{S}^n \cdot \text{cm}^{-2}$)	n_2	
Anion selective coating	17.52	1.48	0.75	33.07	9.79	0.76	994.2
Cation selective coating	15.84	1.46	0.79	151.3	7.99	0.83	2752
Bipolar coating	23.06	1.13	0.83	30.28	1.23	0.86	337.4

In order to delve into the time-delay photocathodic protection performance of the fabricated bipolar composite coating, the OCP coupling between the prepared bipolar composite coating and carbon steel was recorded under one hour of illumination and one hour of darkness. As presented in Figure 7, after one hour of testing in the dark state, the OCP negatively shifted to -730 mV (vs. SCE) and the OCP was still lower than the self-corrosion potential of carbon steel, signifying that carbon steel remained in a cathodic polarization state in the dark. This may have resulted from the “electron aggregation” effect, by which photogenerated electrons are slowly released under dark conditions [26], thus offering protection to the carbon steel in the dark.

As shown in Figure 8, the designed structure not only prevented corrosive anions from entering the surface of the metal substrate, but it also inhibited the diffusion of Fe^{2+} inherent in carbon steel, preventing its combination with OH^- to form the initial corrosion product $\text{Fe}(\text{OH})_3$, thereby slowing down the occurrence of the corrosion process. Meanwhile, the designed structure underwent a series of photocatalytic reactions when exposed to light. When the obtained $\text{g-C}_3\text{N}_4\text{-TiO}_2$ layered structure was irradiated by visible light, the photoelectrons of $\text{g-C}_3\text{N}_4$ may have transferred from the conduction band (CB) of $\text{g-C}_3\text{N}_4$ to the CB of TiO_2 . This could have effectively reduced the recombination rate of photogenerated electron-hole pairs. Furthermore, electrons in TiO_2 CB could easily have been transferred to the valence band (VB) of $\text{g-C}_3\text{N}_4$, thereby promoting the transfer of carriers between the two materials [27]. Therefore, the bipolar coating prepared in

this study had the advantages of ion barrier effect, high coating stability, and effective separation of electron-hole pairs. This can provide better protection for metals.

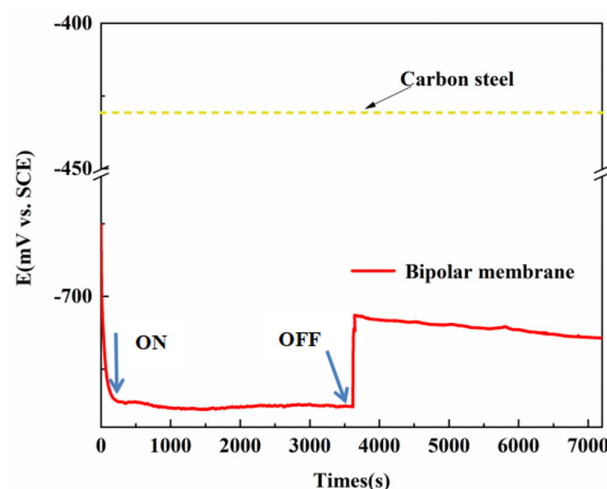


Figure 7. OCP stability of bipolar composite coatings.

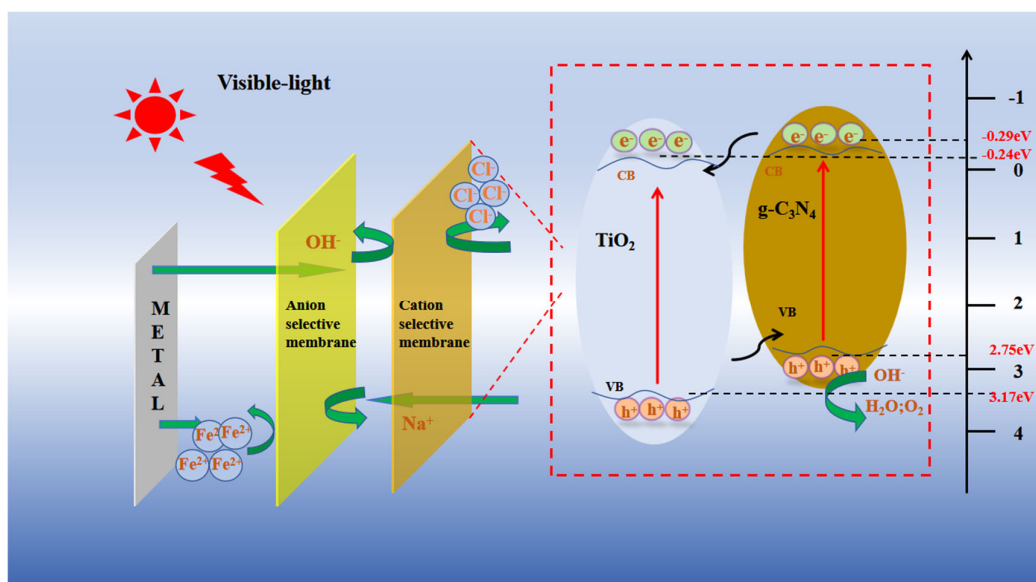


Figure 8. Mechanism of photocathodic protection of bipolar coatings on carbon steel.

4. Conclusions

This study reported a dual-layer coating with ionic selectivity and photocathodic protection property. The outer g-C₃N₄/TiO₂ cation-selective layer combined with the inner g-C₃N₄-TiO₂-CTAB anion-selective layer and prohibited immigration of both Cl[−] ions and Fe²⁺ ions. Particularly, this coating presented photoactive and electron aggregation behaviors, which OCP reached −770 mV (vs. SCE) under illumination and retained around −720 mV (vs. SCE) in the dark. Therefore, this study supplied a strategy for the development of a long-term corrosion resistant coating.

Author Contributions: Methodology, X.W.; software, X.W.; formal analysis, C.C.; investigation, Y.A.; data curation, C.C.; writing—original draft preparation, C.C.; writing—review and editing, C.C.; visualization, Y.A.; supervision, P.Q.; project administration, P.Q.; funding acquisition, P.Q. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Science and Technology Major Project, Deep Earth probe and Mineral Resources Exploration–National Science and Technology Major Project [Grant No. 2025ZD1010104] and Carbon Neutrality Research Institute Fund [Grant No. CNIF 20240109].

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Acknowledgments: The author wishes to thank all the Ph.D. students, postdoctoral fellows, and industrial collaborators who have contributed to our studies. Special thanks go to Christofer Leygraf, who have inspired us on corrosion studies.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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