High-Performance Graphene Coating on Titanium Bipolar Plates in Fuel Cells via Cathodic Electrophoretic Deposition

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Abstract: In this article, we proposed a facile method to electrophoretically deposit a highly conductive and corrosion-resistant graphene layer on metal bipolar plates (BPs) while avoiding the oxidation of the metal substrate during the electrophoretic deposition (EPD). p-Phenylenediamine (PPD) was first grafted onto negatively charged graphene oxide (GO) to obtain modified graphene oxide (MGO) while bearing positive charges. Then, MGO dispersed in ethanol was coated on titanium plates via cathodic EPD under a constant voltage, followed by reducing the deposited MGO with H$_2$ at 400°C, gaining a titanium plate coated with reduced MGO (RMGO@Ti). Under the simulated environment of proton exchange membrane fuel cells (PEMFCs), RMGO@Ti presents a corrosion current of $< 10^{-6}$ A·cm$^{-2}$, approximately two orders of magnitude lower than that of bare titanium. Furthermore, the interfacial contact resistance (ICR) of RMGO@Ti is as low as 4 mΩ·cm$^2$, which is about one-thirtieth that of bare titanium. Therefore, RMGO@Ti appears very promising for use as BP in PEMFCs.

Keywords: graphene; titanium; electrophoretic deposition; bipolar plates; fuel cells

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are a clean and highly efficient electrochemical devices that convert chemical energy directly into electrical energy, widely used as mobile, portable, and stationary power sources in a wide field of applications [1–9]. Bipolar plates (BPs) are a multifunctional component in PEMFCs, connecting single cells in a stack, conducting electric current between them, distributing fuel or oxidant to the electrodes, and separating the fuel and oxidant from the neighboring cells [7,10]. Consequently, the material to make BPs should exhibit high corrosion resistance, excellent electrical and thermal conductivity, and gas impermeability [11].

Graphite used to be the material of choice in BP manufacture [12]. While being an excellent corrosion-resistant conductor of electricity and heat, graphite is brittle and has poor manufacturability, which could lead to bulky and expensive PEMFC stacks [13–16]. To take advantages of graphite’s excellent properties while avoiding its drawbacks, various graphite–polymer and carbon–carbon composite BPs have been designed and explored [17–21]. Alavijeh et al. [20] used the bulk molding compound process to synthesize the graphite/nano-copper BP and found that the properties and efficiency of the nanocomposite were improved. Chen et al. [22] found that the graphene film self-assembled on aluminum BPs was highly conductive and corrosion resistant. Sim et al. [23] obtained poly(methyl methacrylate)-derived multilayer graphene coatings on nickel BP. Lopez-Oyama et al. [24] studied two methods of the reduced graphene oxide coatings on 304 L SS substrates. Stoot et al. [25] found the superior non-perfect multilayer graphene coating on stainless steel BPs. Weissbecker et al. [26] discussed the graphene-like coating to stainless steel, which advantageously has sufficient stability and the necessary electrical conductivity. Jiang et al. [19] enhanced the corrosion resistance of 304 stainless steel BP by...
Metallic BP became more attractive in recent years on account of their many desirable physical properties [3,22,27–29], as well as their suitability for mass production with high efficiency. Currently, the most common materials to make metallic BPs are stainless steel, titanium, or aluminum, and the factors that guide the material choice are the corrosion-resistant, specific weight, mechanical strength, and cost of the metal. Unfortunately, none of these metals have satisfied corrosion-resistant in the harsh environment of PEMFCs. While passivated metal would increase interfacial contact resistance (ICR) and thus lower the power output, dissolved metal ions can poison the catalyst and hinder proton transport in PEMFCs [27].

These problems with metallic BP have led researchers to resort to coatings that conduct electricity and have better corrosion resistance. Hao et al. [30] deposited amorphous carbon (a–C) film on 316L stainless steel BPs using the direct current magnetron sputter technique. Cooper et al. [31] investigated a 316L stainless steel BP with bilayered titanium nitride (TiN)-polyaniline (PANI) coating. Khan et al. [32] compared the performance of TiN, chromium nitride (CrN), aluminum nitride titanium (AlTiN), and aluminum chromium nitride (AlCrN) coatings on 304 stainless steel BP. Marzo et al. [33] plated Ni–P and Ni–P–Cr coatings on aluminum alloy BPs by chemical deposition. Zhang et al. [34] coated zirconium carbide (ZrC) on titanium BPs by plasma technology. Gao et al. [35] used carbon/polytetrafluoroethylene (PTFE)/TiN composite coatings to enhance both the corrosion resistance and hydrophobicity of titanium BP. Xu et al. [36] showed that a cyanide zirconium (ZrCN) film can effectively protect titanium alloy BP. Despite the many efforts, coatings well meeting the requirements of metallic BP are still rare and the coating methods employed often suffer from high cost or low efficiency. There is still an urgent need for coating material and coating methods for metallic BP improvement.

In this paper, we propose an approach to coat graphene via electrophoresis for protecting metallic BP, using a titanium plate as an example. The two-dimensional graphene, with its outstanding chemical stability, electron mobility, and thermal conductivity [37], is a satisfied conductive coating material. While the electrophoretic coating method has been widely adopted in the industry because of its high manufacturability and cost-effectiveness. Graphene oxide (GO), the widely available source of graphene, is modified with p-phenylenediamine (PPD) following Hwang et al. [38]. The modified graphene oxide (MGO) bears positive charges and is electrophoretically deposited on the cathode to prevent the possible oxidation of metallic substrate during the deposition. The MGO deposited on titanium plate is finally reduced to graphene, or more precisely to reduced MGO (RMGO), with H₂ at 400 °C to obtain the desired protective coating.

2. Materials and Methods

2.1. Materials and Reagents

Titanium plates (Ta1, 0.08 mm) were bought from Jinbu Titanium Nickel Equipment Manufacturing Co., Baoji, China. Graphite powder (≥99%, 40 µm) was supplied by Xianfeng Nano Co., Nanjing, China. For other materials, see Supporting Materials for details.

2.2. Sample Preparation

GO was obtained from graphite flakes following an improved Hummers method [39]. MGO was prepared according to Ref. [40]. See Supporting Materials for details.

The coating agent was MGO dispersed in ethanol with the MGO concentration of 0.5 mg mL⁻¹. Before each electrophoretic deposition (EPD), the coating agent was ultrasonicated for 2 h to ensure the homogeneous dispersion of MGO and adjusted to pH 2 with acetic acid.

The as-received titanium plate (Ti-Unpretreated) was polished with sandpapers successively, from 300 to 2000 grit, to remove its passivation layer. The polished titanium plate was ultrasonically cleaned in acetone and ethanol in succession, each for 10 min. Finally,
it was immersed in a 20 wt.% oxalic acid solution at 90 °C for 0.5 h to further clear away the passivation layer on the surface of the titanium plate, and then we got a pretreated titanium plate (Ti-pretreated).

The cathodic electrophoretic MGO deposition on titanium plate was achieved employing a DC power cell (UTP1306S, UNI-TREND Technology (China) Co. Ltd., Shenzhen, China) with Ti-Pretreated and a carbon plate, placed 15 mm apart from each other, immersed in the coating agent at room temperature. A constant voltage of 15 V is exerted across the two plates for 1.5 h to obtain MGO-coated titanium plate (MGO@Ti), which was then taken out and dried at 25 °C for one day. Afterward, the dried MGO@Ti sample was heat-treated at 400 °C in H₂ atmosphere for 2 h, leaving a titanium plate coated with reduced MGO (RMGO@Ti). After cooling to room temperature, the samples of RMGO@Ti were stored in a polyethylene bag before being characterized or tested.

For comparison, the samples of GO-coated titanium plate (GO@Ti) were prepared via anodic electrophoresis. The preparation method was similar to the cathodic EPD of MGO described above, except that the coating agent was replaced with GO dispersed in aqueous with the GO concentration of 0.5 mg·mL⁻¹, the polarity of titanium and carbon plate reversed, and the coating time reduced to 0.5 h. To obtain reduced GO on the titanium plate (RGO@Ti), the coated GO was reduced following the same method as in reducing the coated MGO.

2.3. Characterization and Electrochemical Corrosion Tests

The wide-angle X-ray diffraction (XRD) patterns of samples were recorded with a Brook D8-FOCUS X-ray diffractometer (BRUKER AXS, Ltd., Karlsruhe, Germany). Fourier transform infrared spectra (FTIR) of samples were collected on a Nicolet 6700 spectrometer (Thermo Fisher Scientific, MA, USA). X-ray photoelectron spectra (XPS) were recorded on a Thermo Electron PHI-5000 VersaProbe II instrument (Thermo Fisher Scientific, MA, USA). The Raman spectrum was recorded via a Raman spectrometer (LabRAM HR Evolution, HORIBA Trading Co., Ltd., Kyoto, Japan). Scanning electron microscope analysis (SEM, S-4800, Hitachi, Ltd., Tokyo, Japan) was conducted to study the morphologies of the samples. The surface charge carried by MGO in the coating agent was detected via a zeta-potential analyzer (Zetasizer Nano ZS, Malvern, Malvern, England). A contact angle goniometer (JC-2000C1, POWER EACH, Shanghai, China) was conducted to study the surface hydrophilicity.

Electrochemical measurements were carried out with a three-electrode cell connected to the electrochemical workstation (PARSTAT 2273, AMETEK, PA, USA). For the samples to be measured, a platinum plate and a saturated calomel electrode (SCE) served as the working, counter, and reference electrode, respectively. All samples to be tested were made to expose an area of 1 cm² to the electrolyte, with the rest covered by a silicone rubber coating. The electrolyte was a mixture containing 0.5 mol·L⁻¹ H₂SO₄ and 2 ppm hydrofluoric acid with air or H₂ bubbling to emulate the cathodic or anodic environment of PEMFCs. The corrosion current density (I_corr) and corrosion potential (E_corr) were measured by both potentiodynamic and potentiostatic polarization methods. Before polarization tests, the samples to be tested were stable at open circuit potential (OCP) in the electrolyte for 1 h. The potentiodynamic polarization test was performed through potential scanning centered in the OCP at the rate of 1 mV·s⁻¹. During the potentiostatic polarization test, the applied potential was −0.1 V or 0.6 V (vs. SCE) for anodic or cathodic polarization, respectively.

2.4. ICR Measurements

The ICR between the sample and carbon papers (TGPH-060, Toray, Tokyo, Japan) was calculated based on the method presented in our previous papers [10,22]. The schematic diagram of the measuring cell is displayed in Figure S1. The ICR was calculated using Equation (1):
where \( R_1 \) is the sum of the carbon paper bulk resistance \( R_{cp} \) and the contact resistance between the copper electrode and the carbon papers, which is measured by inserting one piece of carbon paper between the measuring electrodes. \( R_2 \) is the total value measured when the sample placed between two pieces of carbon paper is set in between the measuring electrodes. \( A \) is the practical contact area between the sample and carbon paper.

3. Results and Discussion

3.1. Characterization

The FTIR spectra of GO and MGO indicate that PPD has been attached to GO after the modification (Figure 1a). In comparison with the spectrum of GO, three new peaks appear at 1515, 1173, and 819 cm\(^{-1}\) in the spectrum of MGO, respectively. These are corresponding to the absorption of \(-\text{C}–\text{NH}_2\), \(-\text{C}–\text{N}–\), and \(-\text{N}–\text{H}–\) groups in PPD and its linkage with GO [41], indicating that MGO is GO grafted chemically with PPD. This is confirmed by the results of XPS (Figure S3), in which a \(-\text{C}–\text{N}–\) peak at 258.9 eV is identified (Figure S3b), suggesting a chemical linkage between GO and PPD.

Figure 1. (a) FTIR spectra, (b) zeta potential of graphene oxide (GO) and modified graphene oxide (MGO) the full XPS spectra of (c) MGO@Ti, (d) RMGO@Ti.

GO was partially reduced during the modification process. The FTIR spectrum of GO presents four peaks at 1060, 1620, 1730, and 3400 cm\(^{-1}\), which are consistent with the vibrations of \(-\text{C}–\text{O}–\text{C}–, \text{C}–\text{C}, \text{–COOH}, \) and \(-\text{OH} in GO [42]. It was noticed that the peaks of \(-\text{COOH} and \(-\text{C}–\text{O}–\text{C}–, \) at 1730 and 1060 cm\(^{-1}\), respectively, become weak or disappear in the spectrum of MGO, indicating that GO was partially reduced. The partial reduction in GO during the modification was also revealed by XPS (Figures S3 and S4), Raman (Figure S2a), and XRD (Figure S2b). The grafting of PPD to GO would be a direct cause of the reduction [34]. The thermal reduction of GO may also happen during the modification, considering the temperature and time experienced.
The successive H₂ treatment of MGO@Ti at high temperature further reduces its coating, as evidenced by XPS results. Figure 1c,d show that the O1s peak of RMGO@Ti is markedly smaller than that of MGO@Ti, indicating that the O-containing groups of the former are much less than that of the latter. It is noted that the N-containing groups of RMGO@Ti are also less than that of MGO@Ti, for the N1s peak of RMGO@Ti is smaller. C1s spectrum also reveals that the peak of –C–N groups shrink as MGO@Ti is changed to RMGO@Ti (Figure S3c,d). The lessened N-containing groups in RMGO@Ti over MGO@Ti (see Figure S5 and S3) might explain the better corrosion resistance of RMGO@Ti than that of MGO@Ti. It is worth mentioning that RMGO@Ti well satisfies the US Department of Energy (DOE) 2020 target for resistance of BPs [46], i.e., 4 × 10⁻⁶ A·cm⁻², while Ti-Pretreated possesses the corrosion current density (Icorr) of 3.37 × 10⁻⁶ A·cm⁻², and 2.91 × 10⁻⁷ A·cm⁻² separately for Ti-Unpretreated. Therefore, a more corrosion-resistant coating, as evidenced by XPS results. Figure 1c,d show that the O1s peak of RMGO@Ti is markedly smaller than that of MGO@Ti, indicating that the O-containing groups of the former are much less than that of the latter. It is noted that the N-containing groups of RMGO@Ti are also less than that of MGO@Ti, for the N1s peak of RMGO@Ti is smaller. C1s spectrum also reveals that the peak of –C–N groups shrink as MGO@Ti is changed to RMGO@Ti (Figure S3c,d). The lessened N-containing groups in RMGO@Ti over MGO@Ti (see Figure S5 and S3) might explain the better corrosion resistance of RMGO@Ti than that of MGO@Ti.

While GO commonly carries negative charges [37,43,44], the PPD modification transforms GO into positively charged MGO as demonstrated by the zeta potential measurement (Figure 1b). The zeta potential of MGO at pH 2 is above 30 mV, sufficient for the MGO flakes to be mutually repellent [45] and thus stably dispersed in ethanol. The positive charges in the low pH range are presumably due to the protonation of nitrogen-containing groups in MGO [38], i.e., NH₂–MGO → N⁺H₃–MGO. Sufficient positive charges bearing by MGO are important not only for its stable dispersion but also for enabling its cathodic EPD on metal plates. With increasing pH, the zeta potential of MGO decreases (Figure 1b), which is a consequence of the counteraction by its residual carboxyl groups, which tend to dissociate more completely at higher pH.

The microscopic images of different samples are shown in Figure 2. It can be noted that the surface of Ti-Pretreated is very rough (Figure 2a), which should benefit the bonding between the titanium surface and MGO layer. A wrinkled texture, characteristic of GO, is seen on the surface of MGO@Ti (Figure 2b). The reduction in MGO with high-temperature H₂ has hardly changed the surface morphology of the sample, i.e., RMGO@Ti (Figure 2c). This is different from our previous paper, in which the wrinkled GO surface became smooth after H₂ reduction [10]. In the case of MGO, presumably, the grafted PPD hinders the rearrangement of graphene flakes during H₂ treatment. The cross-sectional image of RMGO@Ti, together with the C and Ti profiles along the vertical direction, indicates that the RMGO layer on top of the titanium plate has a thickness of about 2 µm (Figure 2d).

Figure 2. Surface SEM images of (a) Ti-Pretreated; (b) MGO@Ti; (c) RMGO@Ti; and (d) the cross-sectional SEM image of RMGO@Ti, with Ti (red) and C (green) profiles via EDS line scan.
3.2. Electrochemical Corrosion Tests

The potentiodynamic polarization curves for Ti-Unpretreated, Ti-Pretreated, MGO@Ti, and RMGO@Ti samples under the simulated PEMFC environment are shown in Figure 3a,c. The respective corrosion current density ($I_{corr}$) and corrosion potential ($E_{corr}$) of the samples are summed up in Table 1. Ti-Unpretreated shows the $I_{corr}$s of $9.78 \times 10^{-6}$ and $4.95 \times 10^{-6}$ A·cm$^{-2}$, while Ti-Pretreated possesses the $I_{corr}$s of $1.88 \times 10^{-5}$ and $2.91 \times 10^{-5}$ A·cm$^{-2}$. As the well-known anticorrosion property of metal titanium stems from a passivation layer on its surface, the relatively low $I_{corr}$ of Ti-Unpretreated, as compared with Ti-Pretreated, is easily understandable. However, the passivation layer on bare titanium cannot sufficiently resist the corrosion of bare titanium in the PEMFC environment, as evidenced by the $I_{corr}$s (see Tables 1 and 2) of Ti-Unpretreated. Therefore, a more corrosion-resistant coating for titanium is necessary if it is to be used in PEMFC. Graphene is confirmed as suitable for such coating, as both graphene-coated samples MGO@Ti and RMGO@Ti show a markedly lower corrosion current and raised corrosion potential as compared with the bare titanium samples Ti-Unpretreated and Ti-Pretreated (Table 1). In particular, RMGO@Ti presents the lowest $I_{corr}$, $7.55 \times 10^{-7}$ and $7.52 \times 10^{-7}$ A·cm$^{-2}$ separately under the simulated anodic and cathodic PEMFC environment. As a comparison, MGO@Ti exhibits the $I_{corr}$s of $3.37 \times 10^{-6}$ and $1.58 \times 10^{-6}$ A·cm$^{-2}$ under the simulated anodic and cathodic PEMFC environment. The higher graphitization degree and hydrophobicity of RMGO@Ti over MGO@Ti (see Figures S3 and S5) might explain the better corrosion resistance of RMGO@Ti than that of MGO@Ti. It is worth mentioning that RMGO@Ti well satisfies the US Department of Energy (DOE) 2020 target for $I_{corr}$ of BPs [46], i.e., $\leq 10^{-6}$ A·cm$^{-2}$. Regarding corrosion resistance, RMGO@Ti is also among the superior different coated titanium plates published to date which are intended for BP application (as shown in Table S3).

![Figure 3](image_url)

Figure 3. Electrochemical measurements curves for Ti-Unpretreated, Ti-Pretreated, MGO@Ti, and RMGO@Ti under anodic (a,b), and cathodic (c,d) conditions.

The potentiostatic polarization curves of Ti-Unpretreated, Ti-Pretreated, MGO@Ti, and RMGO@Ti samples in the simulated PEMFC environment are shown in Figure 3b,d, while the respective $I_{corr}$ of the samples is summarized in Table 2. RMGO@Ti displays the
$I_{\text{corr}}$s of $2.64 \times 10^{-7}$ and $2.94 \times 10^{-7}$ A·cm$^{-2}$ under the simulated anodic and cathodic PEMFC environment. As expected, the $I_{\text{corr}}$s of RMGO@Ti under potentiostatic and potentiodynamic polarizations are very similar, consistent with the results of graphene-coated metal plates previously reported [10,47]. It is worth mentioning that the $I_{\text{corr}}$s of RMGO@Ti under anodic and cathodic PEMFC environment are not only low enough to meet the US DOE 2020 target [46], but also quite flat during the 5 h tests, showing no tendency of further increase. Moreover, the surface morphology of RMGO@Ti presents no sign of degradation after the 5 h tests (Figure S6). These results indicate that the graphene layer deposited via cathodic electrophoresis can be highly corrosion-resistant and stable.

Table 1. Potentiodynamic $I_{\text{corr}}$ and $E_{\text{corr}}$ of samples in the simulated proton exchange membrane fuel cell (PEMFC) environment.

| Samples          | Anode $I_{\text{corr}}$ (A·cm$^{-2}$) | Anode $E_{\text{corr}}$ (V) | Cathode $I_{\text{corr}}$ (A·cm$^{-2}$) | Cathode $E_{\text{corr}}$ (V) |
|------------------|--------------------------------------|-----------------------------|-----------------------------------------|-------------------------------|
| Ti-Unpretreated  | $9.78 \times 10^{-6}$                | $-0.496$                    | $4.95 \times 10^{-6}$                  | $-0.128$                      |
| Ti-Pretreated    | $1.88 \times 10^{-5}$                | $-0.561$                    | $2.91 \times 10^{-5}$                  | $-0.295$                      |
| MGO@Ti           | $3.37 \times 10^{-6}$                | $-0.333$                    | $1.58 \times 10^{-6}$                  | $0.067$                       |
| RMGO@Ti          | $7.55 \times 10^{-7}$                | $-0.177$                    | $7.52 \times 10^{-7}$                  | $0.019$                       |

Table 2. Potentiostatic $I_{\text{corr}}$ of the samples in the simulated PEMFC environment.

| Samples          | $I_{\text{corr}}$ (A·cm$^{-2}$) |
|------------------|-------------------------------|
|                  | Anode                         | Cathode                        |
| Ti-Unpretreated  | $7.41 \times 10^{-6}$         | $4.30 \times 10^{-6}$         |
| Ti-Pretreated    | $2.03 \times 10^{-5}$         | $1.66 \times 10^{-5}$         |
| MGO@Ti           | $1.22 \times 10^{-6}$         | $2.09 \times 10^{-6}$         |
| RMGO@Ti          | $2.64 \times 10^{-7}$         | $2.94 \times 10^{-7}$         |

3.3. ICR Measurements

The ICR of BPs must be taken care of in addition to corrosion resistance. As ICR adversely affects the power output of PEMFCs and more so with the increased output current [48]. The ICRs of a few titanium-based samples varied with compaction force are shown in Figure 4. It is seen that the ICRs of all the samples tested decrease with increased pressure. The ICR of Ti-Unpretreated decreases from 499.85 mΩ·cm$^2$ at 30 N·cm$^{-2}$ to 173.62 mΩ·cm$^2$ at 180 N·cm$^{-2}$. However, RMGO@Ti stands out for its low ICR ($14.56$ mΩ·cm$^2$ at 30 N·cm$^{-2}$ and 3.98 mΩ·cm$^2$ at 180 N·cm$^{-2}$), which is noticeably lower than the lowermost ICRs of other samples even at a very small compaction force. RMGO@Ti is also among the superior different coated titanium plates published to date concerning ICR (as shown in Table S3). As the bulk resistance of the coating is included in ICR, the very low ICR of RMGO@Ti could be attributed to its sufficient MGO reduction and higher graphitization degree, for it explains the much higher ICR of MGO@Ti and GO@Ti over RMGO@Ti. Another important factor should be that the specific coating strategy, i.e., cathodic electrophoresis, can effectively avoid forming a passivation layer on titanium during graphene deposition, which explains the fact that the ICRs of MGO@Ti and RMGO@Ti are lower than that of GO@Ti and RGO@Ti, respectively. Indeed, the conventional anodic EPD of graphene, as in the case of GO@Ti and RGO@Ti, results in a passivation layer on titanium substrate as evidenced by EDS analysis (Figure S10). Lastly, the ICR of RMGO@Ti about 4 mΩ·cm$^2$ translates into a through-plate resistance (TPR) of approximately 8 mΩ·cm$^2$, as the bulk resistance of metal titanium is orders of magnitude lower and thus neglectable [49]. Therefore, RMGO@Ti meets the US DOE 2020 target of BPs’ areal specific resistance being less than 10 mΩ·cm$^2$ [46].
4. Conclusions

We report the preparation of a graphene-coated titanium plate for high-performance bipolar plates in proton exchange membrane fuel cells with an industrially viable method. Coating graphene oxide on titanium by cathodic electrophoretic deposition while preventing metal oxidation is enabled by a prior modification of graphene oxide precursor with p-phenylenediamine, and then the coating was reduced to graphene by H₂ heat treatment. Morphology characterizations demonstrate that the graphene coating is smooth and dense, and the thickness of it is 2 μm. The resulting graphene-coated titanium plate shows the corrosion current of 10⁻⁷ A·cm⁻² in a simulated proton exchange membrane fuel cells’ environment, and the interfacial contact resistance of 4 mΩ·cm², reaching the US DOE 2020 target for bipolar plates. Therefore, our method to coat graphene on titanium appears very promising for preparing high-performance metal bipolar plates in proton exchange membrane fuel cells.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/coatings11040437/s1, Table S1: Potentiodynamic Icorr and Ecorr of three RMGO@Ti samples, Table S2: Potentiostatic Icorr of three RMGO@Ti samples, Table S3: A summarization of the performance of different coated titanium plates, Table S4: Elements quantitative results, Figure S1: Schematic diagram of the device for ICR, Figure S2: (a) Raman spectra; and (b) XRD spectra of GO and MGO, Figure S3: Cls XPS spectra of (a) GO; (b) MGO; (c) MGO@Ti; and (d) RMGO@Ti, Figure S4: The full XPS spectra of (a) GO; and (b) MGO, Figure S5: The static water contact angles on (a) MGO@Ti; and (b) RMGO@Ti, Figure S6: Surface SEM images of RMGO@Ti after electrochemical measurements, Figure S7: Through-plate resistance (TPR) of Ti-Unpretreated, MGO@Ti, and RMGO@Ti, Figure S8: Surface SEM images of (a,b) RMGO@Ti/pH = 3.0, and (c,d) RMGO@Ti/pH = 4, Figure S9: Electrochemical measurements curves for RMGO@Ti/pH = 2.0, RMGO@Ti/pH = 3.0, RMGO@Ti/pH = 4.0 under anodic (a,b), and cathodic (c,d) conditions, Figure S10: EDS element compositions of Ti-Pretreated, Ti-Anodized/Water, Ti-Anodized/GO.

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