Electrocatalytic Properties of a Novel β-PbO₂/Halloysite Nanotube Composite Electrode

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ABSTRACT: To improve the efficiency of electrochemical degradation of wastewater, lead dioxide was synthesized by a hydrothermal method with low cost, simple operation, and high conversion rate. β-PbO₂/HNT composites were prepared by a hydrothermal method with Halloysite nanotubes (HNTs) and β-PbO₂. The PbO₂/HNT/ITO electrode was prepared by modifying the β-PbO₂/HNT composite on an indium tin oxide (ITO) conductive glass electrode. The morphology of the material was characterized by scanning electron microscopy and transmission electron microscopy. The electrochemical performance of the electrode was measured by cyclic voltammetry, the galvanostatic charge–discharge method, and the AC impedance method. Electrolysis of typical dye wastewater by electrochemical oxidation was carried out. The effect of electrochemical degradation of wastewater with new electrodes was investigated and the degree of electrodes falling off was compared. The solubility of electrodes was investigated by inductively coupled plasma mass spectrometry lead element analysis of wastewater. The results showed that the β-PbO₂/HNT electrodes were prepared successfully and had good charge–discharge performance and lifetime. The removal rate of electrolytic dye wastewater was 85.86%, and the degradation effect was better than that of pure PbO₂ electrodes. In this work, a new type of β-PbO₂/HNT/ITO electrode has been prepared, which improved the degradation efficiency of wastewater and opened up the prospect of HNT application.

1. INTRODUCTION
The shortage of freshwater resources is a worldwide problem, which seriously restricts the development of social economy.1,2 In addition, pollutants have a serious impact on human health and ecological environment, which has caused widespread concern of governments and society. Water pollution is closely related to people’s daily production and life and is the focus of environmental governance. Dye wastewater is the main type of water pollution. Dye wastewater has the characteristics of high chroma, high content of organic matter, complex components, strong toxicity, and difficult biodegradation.3 As a large textile producing country, China discharges about 1.6 × 10⁸ m³ dye wastewater every year.4 The main dye pollutants include direct dyes, reactive dyes, disperse dyes, sulfide dyes, cationic dyes, and acid dyes. The treatment methods of printing and dyeing wastewater mainly include adsorption, ozone degradation, microbial degradation, electrochemical degradation, and others.5–6 However, the traditional treatment of dye wastewater has been unable to meet the requirements of environmental protection. For example, the adsorption method has simple operation but mainly adsorbs pollutants in wastewater through certain substances, which cannot destroy the structure of dyes, and has low treatment efficiency; although the ozone degradation method has simple treatment process, rapid reaction, and no secondary pollution problem, it has high oxygen consumption for wastewater treatment and high power consumption for ozone production; the microbial process has the advantages of long cycle, large equipment investment, low efficiency, but no harm; the electrochemical method is characterized by simple equipment, easy operation management, and maintenance.7–9 The new efficient methods of dye degradation pursue simple, green, and high efficiency, among which the electrochemical method is a hot research method. The combination of electrochemical and nanomaterial technology makes the wastewater more economical and effective.

Electrochemical oxidation is an efficient method to degrade wastewater, which has the advantages of high efficiency, environmental compatibility, and easy to be applied to automation. In electrochemical oxidation, the electrode material is an important factor to determine the efficiency and economy.10 For the electrochemical oxidation degradation of azo dyes, the performance of activated carbon fiber,11 Pt,12 PbO₂,13 SnO₂,14 RuO₂,15 diamond electrode, and other anode
properties were studied. However, due to the limitation of the electrode surface area, the current efficiency is low, which makes the electrode removal performance not ideal. Therefore, it is necessary to explore a new and efficient electrode for wastewater degradation. Amadelli et al. examined the physicochemical and catalytic properties of lead dioxide electrodeposition and found that the electrode was photoresponsive to light exposure with an approximately 3-fold increase in electrode lifetime. Knysh et al. studied the effect of colloidal titanium dioxide particles on the morphology and structure of lead dioxide coatings and found that the presence of colloidal titanium dioxide particles in the electrolyte resulted in faster formation of lead dioxide. Velichenko et al. studied the preparation and physicochemical properties of PbO2 TiO2 and PbO2-ZrO2 composites by electrodeposition. It was found that the physicochemical properties of the composites were obviously different from that of pure PbO2. PbO2 has good electrical conductivity, corrosion resistance, and chemical stability. PbO2 can also pass through high current and has the advantage of low price. It is not only an ideal metal matrix material but also a widely used electrode material. Meanwhile, PbO2 can also improve the electrochemical properties of functional materials when they are combined together.

Hallowsite nanotubes (HNTs) are a kind of natural nanotube material with a special tubular structure. Compared with traditional carbon nanotubes, HNTs have larger cavity volume, higher biocompatibility, and lower price. At present, HNTs has shown good application prospects in biomedicine, catalysis, environmental protection, and other fields. HNTs not only has excellent material strengthening performance but also has excellent performance in material adsorption, storage, transport, catalysis, electrochemistry, energy storage, and so on.

Among the existing textile dyes, cationic red X-GRL is a dark red powder, which is easily soluble in water. It is a common heterocyclic monoazo cationic dye. Its molecular formula is C18H21BrN6. It has good light resistance, washing fastness, and good lifting power. It is used in varnish, plastic, textile, and other aspects, but it is difficult to degrade cationic red X-GRL by a traditional technology. In this study, using cationic red X-GRL as a pollutant model, β-PbO2/HNT composites were prepared by a hydrothermal synthesis method. The prepared composite materials were applied to the modification of the electrode. The performance of electrode materials was studied by cyclic voltammetry, galvanostatic charge-discharge, electrochemical impedance spectroscopy (EIS), and electrochemical oxidation treatment of wastewater.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of β-PbO2 and β-PbO2/HNTs. Sodium hypochlorite was used to convert lead oxide to lead dioxide in the experiment. Sodium hypochlorite dissolved in water will produce strong oxidative hypochlorite. Lead oxide and hypochlorite react hydrothermally to produce lead dioxide. The reaction for the preparation of lead dioxide is as follows

\[
\begin{align*}
2\text{CH}_3\text{COOH} + \text{PbO} \rightarrow (\text{CH}_3\text{COO})_2\text{Pb} + \text{H}_2\text{O} \\
(\text{CH}_3\text{COO})_2\text{Pb} + 2\text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{Pb(OH)}_2 \\
\text{Pb(OH)}_2 + \text{NaClO} \rightarrow \text{PbO}_2 + \text{NaCl} + \text{H}_2\text{O}
\end{align*}
\]

For powder X-ray diffractometry, the source of radiation was Cu Kα target (\(\lambda = 1.541 \text{ Å}, 20 \leq 2\theta \leq 80^\circ\)). Phase characterization of the prepared samples of β-PbO2 and β-PbO2/HNTs can be found, as shown in Figure 1, the characteristic peaks of β-PbO2 appear, and there are almost no peaks of PbO2; thus, the conversion of PbO2 is close to 100%. Typical diffraction peaks appeared at 2\(\theta\) diffraction angles of 25.40, 32.00, 36.23, and 49.10°, which corresponded to (110), (101), (200), and (211) of the standard β-PbO2 phase and corresponded exactly to the standard card.

Therefore, according to the above information, it can be determined that the sample prepared in this experiment is pure β-PbO2. It can be found in the X-ray diffraction (XRD) patterns of the β-PbO2/HNT composites that, in addition to the characteristic peaks of β-PbO2, the characteristic peaks appeared at the 2\(\theta\) diffraction angles of 38.47 and 45.4° corresponding to (111) and (200) of the standard card; the characteristic peaks appear at the diffraction angles of 20.96 and 26.56°, corresponding to (100) and (011) of the standard card SiO2, so it can be inferred that β-PbO2 and HNTs were successfully combined.

The morphology of the prepared β-PbO2 and β-PbO2/HNT composites was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 2a,b, the insertion of HNTs into β-PbO2 was uniform. The TEM image shows that the particles between 50 and 100 nm were obtained under this condition (Figure 2c,d). The two materials are combined together because of the electrostatic adsorption. The addition of HNTs means that the particles of β-PbO2 are no longer closely connected, have larger pores, and can absorb dyes through the tube holes of HNTs. Compared with the pure β-PbO2 electrode, the contact area with dye wastewater is enlarged, the adsorptivity to dye
wastewater is enhanced, and the charge contacts with dye molecules more efficiently, thus improving the waste reduction performance of the electrode. Scanning results of the composites by connected photoelectron spectroscopy are shown in Figure 3. The composites contain S, Al, Si, O, and C elements. These elements are all elements contained in HNTs, and in addition, PbO2 and HNTs are added at a ratio of 10:1 in the preparation, so the content of Pb element is the highest. Therefore, it is speculated that the composite contains two materials, PbO2 and HNTs, which can be judged by combining their electron microscopy images that the two materials are compounded together.

2.2. Performance Test and Analysis of Electrode Materials. 2.2.1. Cyclic Voltammetric Curve Analysis. The relative surface roughness of the electrode reflects the real surface area of the electrode surface, and its value is the ratio between the real surface area and the geometric surface area of the electrode, which is one of the important parameters to evaluate the electrocatalytic activity of the electrode. Figure 4a shows the cyclic voltamogram of the electrode of the β-PbO2 material. It can be seen from the figure that the curve symmetry is good within the scanning range of 0−1.4 V, but it does not show a better rectangular characteristic, and the electrochemical performance is relatively general. Figure 4b shows the cyclic voltammetry diagram of the composite electrode of β-PbO2/HNTs. From the diagram, it can be seen that the curve symmetry is good in the scanning range of 0−1.4 V and presents rectangular characteristics in the range of 0.3−0.9 V, showing good electrochemical performance. As the scanning speed increases, the peak current of the electrode increases gradually, and the peak potential of the reaction shifts, so the area included in the curve increases accordingly. When 0.1 mol·L−1 of Na2SO4 and 200 mg·L−1 of cationic red X-GRL were used as electrolyte solutions, the cyclic voltammetric curves of both electrodes did not scan the reduction peaks of organic compounds, which indicated that cationic red X-GRL on the electrode surface could not be degraded by electrochemical oxidation directly. Its main reason can be contributed to the high oxygen evolution potential of the lead dioxide electrode, which produces strong oxidative hydroxyl radicals during the electrolysis process to oxidize and degrade the dye. In addition, the curve is symmetrical, which means that the composite electrode material has a stable capacitance process.31

2.2.2. Analysis of a Constant Current Charge−Discharge Curve. Constant current charging and discharging is a common test method used to study the electrical properties of electrodes and capacitors. Through multiple cyclic charge−discharge experiments, the cycle life of capacitors or microcells can also be evaluated, and the reversibility of capacitors and electrochemical reactions can be judged according to the symmetry of charge−discharge curves. Figure 5a shows the constant current cyclic charge−discharge curve of the electrode of the β-PbO2 material. Under a current density of 1 A·g−1, the charge−discharge curve of the electrode of the PbO2 composite material has good symmetry, which indicates that the electrode has good reversibility of chemical reaction. However, the voltage of the electrode suddenly increases during the cyclic charging and discharging process, judging that the electrode material gradually loses its activity, but according to the curve, it can be judged that it has a better cycle life. Figure 5b shows the constant current cyclic charge−discharge curve of the β-PbO2/HNT composite electrode. Under a
current density of 1 A·g⁻¹, the cyclic charge–discharge times of the PbO₂/HNT composite electrode are much greater than that of the pure PbO₂ electrode, and its charge–discharge curve has good symmetry, and the charge–discharge voltage remains stable. In the process of 500 s as a cycle charging, the maximum service life of the electrode is reached when the charging and discharging voltage increases after 20 cycles of charging and discharging, but it still has a longer service life and better charge and discharge performance than that of the β-PbO₂ electrode, which indicates that the addition of HNTs can increase the stability and service life of the electrode material. Therefore, the composite electrodes of β-PbO₂/HNTs have longer life and better charge and discharge performance.

These results suggest that the composite electrodes of β-PbO₂/HNTs have a better development prospect.

The solution resistance and the electrochemical reaction resistance of the poles are very small. The interface contact resistance (Re) of the β-PbO₂ and β-PbO₂/HNT electrodes is 85.86Ω, which is 59.33Ω and 47.96Ω, respectively. The interface contact resistance of β-PbO₂ and β-PbO₂/HNT electrodes is very close, but the difference of charge transfer resistance is large, which indicates that the addition of HNTs can improve the charge transfer ability and speed up the electrochemical reaction.

2.3. Determination of Cation Red X-GRL Concentration by an Ultraviolet–Visible Spectrophotometer. 2.3.1. Drawing of a Standard Curve. Scanning results using an ultraviolet spectrophotometer are shown in Figure 7a. The maximum absorption wavelength is located at 530 nm. Therefore, it can be determined that the absorbance of cationic red X-GRL needs to be measured at 530 nm.

According to the results of the absorbance value of a standard solution determined by an ultraviolet–visible spectrophotometer, the volume of a standard solution added was 10, 20, 30, 40⁻, and 50 mg·L⁻¹, respectively, and the measured absorbance values were 0.171, 0.364, 0.545, 0.713, and 0.911. The standard curve was drawn with the concentration as the abscissa and the absorbance as the longitudinal coordinate. The regression equation is \( A = 0.01818 - 0.00376C \), and the correlation coefficient \( R^2 = 0.9996 \), where \( A \) is the absorbance and \( C \) is the solution concentration. Cationic red X-GRL has a good linear relationship in the range of 0–50 mg·L⁻¹, as shown in Figure 7b.

2.3.2. Determination of Cation Red X-GRL Concentration. Cationic red X-GRL degradation experiments were carried out with different material electrodes. Dye wastewater (3 mL) samples were taken every 30 min, and the absorbance was determined after dilution. The result of concentration calculation by absorbance is shown in Figure 8. It can be seen from the diagram that the degradation effect of the β-PbO₂/HNT material electrodes on cationic red X-GRL is greater than that of the β-PbO₂ electrodes, and the β-PbO₂/HNT material electrodes still have strong activity to continue to degrade cationic red X-GRL after 5 h of operation. The longer the electrolysis time, the smaller the absorbance value measured. According to the formula, \( A = 0.01818C - 0.00376 \), the removal rate of β-PbO₂ is 54.59%, and the removal rate of β-PbO₂/HNTs is 85.86%.

\( R^2 > R^2 \) can be found by kinetic curve fitting, so the reaction is more in accordance with the first-order kinetic reaction. Its kinetic equation is as follows.

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c05651)

Figure 5. Constant current charge–discharge curves of (a) β-PbO₂ and (b) β-PbO₂/HNT electrodes, charge discharge current: 1 A·g⁻¹.

![Figure 6](https://dx.doi.org/10.1021/acsomega.0c05651)

Figure 6. Electrochemical impedance spectra of β-PbO₂ and β-PbO₂/HNT electrodes.

of the composite electrodes of β-PbO₂ and β-PbO₂/HNTs measured at frequencies ranging from 10 mHz to 100 kHz and with amplitudes of 5 mV. Under the open circuit potential, the low-frequency part is almost a straight line, which is about 45° above the x-axis abscissa, representing the pure capacity of the electrode; at the high-frequency part, it can be seen that the diameter of the small semicircle is very small, indicating that the charge migration resistance in the reaction is very small. The solution resistance and the electrochemical reaction resistance of the poles are very small. The interface contact resistance (Re) of the β-PbO₂ and β-PbO₂/HNT electrodes is 1.329 and 1.236 Ω, respectively, from the intersection of the curve and the real axis. The arc radius in the high-frequency region is the charge transfer resistance (Rct), which is 59.33 and 47.96 Ω, respectively. The interface contact resistance of β-PbO₂ and β-PbO₂/HNT electrodes is very close, but the difference of charge transfer resistance is large, which indicates that the addition of HNTs can improve the charge transfer ability and speed up the electrochemical reaction.

2.2.3. AC Impedance Spectrogram Analysis. EIS is one of the powerful tools for studying electrochemical processes at electrodes/interfaces. Figure 6 shows the impedance spectra of the composite electrodes of β-PbO₂ and β-PbO₂/HNT electrodes.
First-order kinetic equation: \[ C = C_0 - k_1 \cdot e^{-k_2 \cdot t} \] \[ \text{(2)} \]

Second-order kinetic equation: \[ C = C_0 - \frac{q_1 \cdot q_2 \cdot t}{1 + q_2 \cdot t} \] \[ \text{(3)} \]

where \( C \) is the concentration, \( t \) is the time, and \( k_1, k_2, \) and \( k_3 \) are the degradation rate constants. \( C_0 \) is the initial concentration of the solution, \( q_1 \) and \( q_2 \) are the theoretical maximum degradation amounts.

As shown in Figure 9, it is found that the shedding degree of the \( \beta \)-PbO\(_2\)/HNT electrodes is much less than that of the \( \beta \)-PbO\(_2\) electrodes, indicating that the addition of HNTs improves the adhesion of the electrodes, thereby increasing the lifetime of the electrodes and reducing the secondary pollution of the water quality caused by the shedding of the electrodes. As shown in Table 1, by inductively coupled plasma mass spectrometry (ICP–MS) analysis of lead elements in dye wastewater, it is found that both \( \beta \)-PbO\(_2\) and \( \beta \)-PbO\(_2\)/HNT electrodes dissolve slightly, but the solubility of \( \beta \)-PbO\(_2\)/HNT electrodes is less than that of \( \beta \)-PbO\(_2\) electrodes. This indicates that the addition of HNTs improves the stability of the electrodes and reduces the secondary pollution of water caused by the dissolution of the electrodes.

2.3.3. Degradation Mechanism Analysis of Cationic Red X-GRL

Generally, the electrochemical oxidation degradation of organic pollutants in wastewater mainly has two mechanisms: direct oxidation and indirect oxidation, in which direct oxidation refers to the direct oxidation of organic pollutants through anode electron transfer on and near the anode surface.
and indirect oxidation refers to the use of inert electrodes, which absorb water molecules in the electrode lattice and electrode surface through inert electrodes with high oxygen evolution potential. The electrooxidation of a large number of organic and inorganic compounds on different electrode materials, including PbO₂, proceeds simultaneously with the evolution of oxygen.36 Amadelli et al. studying the oxidative degradation of phenolic compounds with different electrochemical systems found that strongly oxidizing species, such as hydroxyl radicals, formed during the anodization of water were able to oxidize most organic compounds sequentially. Since inert electrodes do not act directly with pollutants and degrade pollutants by adsorbing groups on the electrode surface, which is one of the most commonly used anodes to destroy organic matter because the rate of oxidation potential of 2.80 V in water, which is greater than the oxidation capacity of conventional oxidants such as oxygen and ozone, and can rapidly oxidize organic compounds, but its existence is very short, generally 10⁻¹⁸ s.38 Panizza and Cerisola believed that lead dioxide has a high peroxide potential and that “inactive” electrodes form oxidizing free radical "OH on the surface of electrodes, which is one of the most commonly used anodes to destroy organic matter because the rate of oxidation has been proved to be higher than other traditional anodes. According to the report in ref 40, by GC–MS detection of intermediate products, it can be deduced that the hydroxyl radical first attacks the azo bond, then the azo bond breaks down, and then escapes or forms nitrate in the form of nitrogen, which causes the decolorization of cationic red X-GRL wastewater. The main degradation pathways are shown in Figure 10.

\[
PbO₂ + H₂O_{ads} \rightarrow PbO₂(\cdot OH_{ads}) + H^+ \tag{4}
\]

In the formula, \(H₂O_{ads}\) represents molecular water adsorbed on the surface of anode adsorption, and \(PbO₂(\cdot OH)_{ads}\) represents hydroxyl radicals adsorbed between lead dioxide lattices on the surface of the anode. Hydroxyl radical is a very strong oxidant, with an oxidation potential of 2.80 V in water, which is greater than the oxidation capacity of conventional oxidants such as oxygen and ozone, and can rapidly oxidize organic compounds, but its existence is very short, generally 10⁻¹⁸ s.38 Panizza and Cerisola believed that lead dioxide has a high peroxide potential and that “inactive” electrodes form oxidizing free radical "OH on the surface of electrodes, which is one of the most commonly used anodes to destroy organic matter because the rate of oxidation has been proved to be higher than other traditional anodes. According to the report in ref 40, by GC–MS detection of intermediate products, it can be deduced that the hydroxyl radical first attacks the azo bond, then the azo bond breaks down, and then escapes or forms nitrate in the form of nitrogen, which causes the decolorization of cationic red X-GRL wastewater. The main degradation pathways are shown in Figure 10.

![Figure 10. Degradation mechanism of cationic red X-GRL.](image-url)

### 3. CONCLUSIONS

\(\beta\)-PbO₂ was successfully prepared by hydrothermal synthesis with low cost, simple operation, and high conversion. Analysis by field emission SEM and TEM shows that the particle size of PbO₂ is between 50 and 100 nm. Combining the EDX spectra, we can see that the two materials were successfully combined together. HNTs are combined with PbO₂ by electrostatic adsorption. The resulting composite increases the contact area between materials and dye wastewater and enhances the adsorbability of dye wastewater, which makes charges more efficiently contact with dye molecules, thus improving the electrodes’ waste reduction performance.

It was found by cyclic voltammetry that there were no redox peaks on \(\beta\)-PbO₂ and \(\beta\)-PbO₂/HNT electrodes, which indicated that cation red X-GRL could not be directly oxidized and degraded on the electrode surface. The constant current charge and discharge analysis showed that the number of cyclic charge and discharge times of the PbO₂/HNT composite electrode was much larger than that of the pure PbO₂ electrode, and the charge discharge voltage was stable relative to the pure PbO₂ electrode. The results show that the PbO₂/HNT composite electrode has longer service life and better charge discharge performance; AC impedance spectra shows that the material of the electrodes exhibits pure double-layer capacitance at open-circuit potential, and the solution resistance and electrochemical reaction resistance of the electrodes are very small. From the point of intersection of curve and real axis, the interface contact resistance between \(\beta\)-PbO₂ and \(\beta\)-PbO₂/HNT electrodes is close, but the difference of charge transfer resistance is large, which indicates that the addition of HNTs can improve the charge transfer ability and speed up the electrochemical reaction.

The results of ultraviolet–visible spectrophotometer analysis show that the degradation effect of the \(\beta\)-PbO₂/HNT electrodes is greater than that of the \(\beta\)-PbO₂ electrodes, and the concentration of cationic red X-GRL decreases with the electrolysis time. The longer the time, the greater the concentration reduction. The degradation rate can reach 85.86% after 5 h of electrolysis. By comparing before and after the operation of the electrodes, it was found that the shedding degree of the \(\beta\)-PbO₂/HNT electrodes was less than that of the \(\beta\)-PbO₂ electrodes, indicating that the addition of HNTs improved the adhesion ability of the electrodes and the lifetime of the electrodes. ICP–MS lead element analysis of dye wastewater shows that the addition of HNTs improves the stability of the electrodes and reduces the secondary pollution caused by the dissolution of the electrodes.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials and Instruments

Experimental materials: Indium tin oxide (ITO) conductive glass (Luoyang Guluo Glass Co., Ltd.), lead oxide (orthorhombic crystal system, Shanghai Aladdin Biochemical Technology Co., Ltd.), ammonium persulfate (AR, Shanghai Aladdin Biochemical Technology Co., Ltd.), sodium hypochlorite (AR, McLean), basic red 46 (also known as cation red X-GRL, McLean), HNTs (Al₂Si₂O₅(OH)₄·nH₂O, Guangzhou Runwo Material Technology Co., Ltd.), and sodium hydroxide (AR, Yonghua Chemical Technology (Jiangsu) Co., Ltd.).

Experimental instruments: a 500 mL autoclave, an electric blast drying oven (Shanghai Hengke Instrument Co., Ltd.), a collecting type constant temperature heating magnetic stirrer.
4.4. Preparation and Performance Test of the New Electrode. ITO conductive glass was placed in a certain amount of acetone, ethanol, and double-distilled water, ultrasonically cleaned for 20 min, then washed with absolute ethanol three to five times, and then dried naturally at room temperature. Then, β-PbO₂/HNTs and epoxy resin were mixed in the ratio of 8:1. An appropriate amount of absolute ethanol was added and evenly dispersed by ultrasound. An appropriate amount of dispersed liquid drops was placed on the electrode surface and dried at 40 °C in the oven. When the loading amount reaches 5 mg cm⁻², the obtained electrode is recorded as the β-PbO₂/HNT/ITO electrode.

The β-PbO₂/HNT/ITO (measuring area: 1 cm × 2 cm) electrode is used as a working electrode, a platinum electrode as an auxiliary electrode, a saturated calomel electrode as a reference electrode, and 0.1 mol L⁻¹ of sodium sulfate as the electrolyte solution to form a three-electrode system. The electrochemical impedance test (EIS) was performed at an electrochemical workstation at an amplitude of 5 mV to determine the performance of the electrode materials. The cyclic voltammetry curve of the anode was recorded at a sweep speed of 1, 5, 10, and 20 mV s⁻¹ in the range of 0 to 1.5 V potential, and the constant current charge–discharge curve of the anode was recorded at a sweep speed of 1 A g⁻¹.

4.5. Performance Test of Typical Dyestuff Electrolysis Waste Reduction. The electrolytic device mainly consists of DC power supply and electrodes. Wastewater with cationic red X-GRL as a pollutant model is electrolyzed and the concentration of cationic red X-GRL is detected by a UV–visible spectrophotometer.

The anode is the β-PbO₂/HNT/ITO electrode, and the cathode is a stainless steel mesh with the same area grid of 1 mm × 1 mm. The current density is 2 mA cm⁻² and pH is 9. The temperature is 25 °C. The concentration of Na₂SO₄ solution is 0.1 mol L⁻¹. The volume of 200 mg L⁻¹ cationic red X-GRL solution is 250 mL. The stirring speed is 200 rpm min⁻¹. During the experiment, the current is kept unchanged and the voltage changes slightly.

The maximum absorption wavelength of cationic red X-GRL was determined by scanning the whole band with an ultraviolet spectrophotometer.

In the process of electrolysis, samples were taken every 30 min, and the absorbance value of wastewater at 530 nm was determined by a UV–visible spectrophotometer.

Drawing of a standard curve: 0.5, 1.0, 1.5, 2.0, and 2.5 mL of cationic red X-GRL solution were added to a 25 mL volumetric flask to make a 2, 4, 6, 8, and 10% (v/v) solution. Water was used as a blank solvent, the absorbance of the solution with a ultraviolet visible spectrophotometer was determined, and the concentration of cationic red X-GRL in the solution by absorbance was calculated as follows

\[ T_i = \frac{C_0 - C}{C_0} \]  

where \( T_i \) is the removal rate, \( C_0 \) is the concentration of cationic red X-GRL water before treatment, and \( C \) is the concentration of treated water (mg L⁻¹).

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