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Effects of Rare Earth Doping on Structural and Electrocatalytic Properties of Nanostructured TiO₂ Nanotubes/SnO₂-Sb Electrode for Electrochemical Treatment of Industrial Wastewater

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Abstract: The solvothermal synthesis technique was employed to successfully fabricate a series of rare earth doped SnO₂-Sb electrodes on the TNTs array substrate, serving as anode material for electrocatalytic degradation of phenol. The electrode doped with rare earth elements demonstrated superior electrocatalytic activity and stability in comparison to the undoped electrode. The influence of adding rare earth elements (i.e., Gd and Nd) into the precursor solution on the structural and property of TNTs/SnO₂-Sb electrodes was studied in detail. The results obtained from SEM and XRD indicated that, compared to TNTs/SnO₂-Sb-Nd, TNTs/SnO₂-Sb-Gd exhibited a finer grain size due to the smaller ionic radius of the Gd element. This facilitated its incorporation into the SnO₂ lattice interior and inhibited grain growth, resulting in a significant decrease in particle size for exposing more active sites. The influence mechanism of rare earth doping on electrochemical activity was investigated through XPS, EPR, LSV, EIS and Hydroxyl radicals (•OH) generation tests. The results demonstrated that the enhanced electrocatalytic activity can be attributed to an increased generation of oxygen vacancies on the electrode surface, which act as active sites for enhancing the adsorption of oxygen species and promoting •OH generation.

Keywords: TNTs/SnO₂-Sb; rare earth; oxygen vacancy; electrocatalytic oxidation



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1. Introduction

The discharge of industrial wastewater has witnessed a significant surge due to the continuous expansion and development of its industrial production scale. Moreover, the composition of this wastewater is becoming increasingly complex, with a growing proportion of toxic and recalcitrant organic matter [1–5]. The simultaneous increase in requirements for pollutant control and the tightening of environmental protection standards pose a challenge to achieving a standard discharge of industrial wastewater. Electrocatalytic oxidation technology, as one of the advanced oxidation technologies, generates hydroxyl radicals or other highly oxidizing radicals and groups to effectively attack organic matter in the water, resulting in its complete decomposition into water and carbon dioxide [6–8]. The characteristics of this technology, including a more thorough decomposition of organic matter, superior efficiency, easy operation and robust environmental compatibility, have garnered significant attention in the field of water treatment [9–11].

The crux of electrocatalytic oxidation technology lies in the meticulous selection and preparation of electrode materials. Considering that the apparent morphology and composition of electrode catalytic coatings are pivotal factors influencing their electrocatalytic properties, a comprehensive investigation into the intricate relationship between the electrode material structure and electrocatalytic performance holds significant theoretical significance and practical potential for developing highly efficient electrocatalytic electrodes, as well as degrading and transforming toxic pollutants.

Ti/SnO₂-Sb electrodes have garnered significant attention for their exceptional oxygen evolution potential and robust electrocatalytic performance [12]. The current focus of research is to intensify efforts in improving the catalytic activity and stability of these electrodes.

The solvothermal method is employed to prepare a nano-scale SnO₂ electrocatalytic anode on a titanium substrate. In comparison to the traditional impregnation method used for non-nano SnO₂ coating electrode preparation, a significant improvement is observed in terms of the cracking phenomenon on the surface of the coating [13]. A highly active SnO₂-Sb layer, based on a Ti substrate, was fabricated using a sol-gel spin coating method. The electrocatalytic performance of the electrode was systematically evaluated to determine the optimal number of active layers. The results demonstrated that with 8 layers, the electrode exhibited a rough and uniform coating, resulting in enhanced electrocatalytic ability for landfill leachate treatment [14].

In addition to the preparation method, there is also a growing focus on the selection of substrate materials for electrode fabrication, particularly regarding the chemical modification of titanium substrates [15]. The vertically aligned arrays of three-dimensional TiO₂ nanotubes (TNTs) on a Ti substrate, which function as micro-structured tubular supports for the active SnO₂ layer, have garnered significant attention in recent years due to their numerous advantages for coating deposition. The densely packed TiO₂ clusters offer an increased surface area and enhanced contact points, thereby promoting the reinforcement of SnO₂-Sb coatings. In comparison to the electrode lacking a TiO₂-NT interlayer, the TiO₂-NTs/SnO₂-Sb electrode exhibits significantly improved catalytic activity and stability [16,17]. The incorporation of the SnO₂-Sb layer, utilizing the enhanced nanotube array (ENTA), was observed to significantly augment both the oxygen evolution potential and active radical generation of the electrode. Furthermore, a substantial improvement in the conversion service lifetime was achieved compared to the conventional one without ENTA [18]. The anode material for the degradation of Acid Red 73 was prepared by screen-printing tin oxide antimony onto Nb-TiO₂ nanotubes, which exhibited a higher oxygen evolution potential and wettability compared to the conventional anode without Nb-TiO₂ nanotubes, resulting in a 2.1 times longer lifetime [19]. The incorporation of tin dioxide with TiO₂ nanotubes also enhanced the photocatalytic activity of this material, wherein SnO₂ could enhance the photoelectrocatalytic (PEC) performance of TiO₂-NTAs for dye wastewater treatment [20].

In addition, the incorporation of exogenous substances into the catalytic coating can effectively enhance the electrocatalytic activity and service life of these electrodes. Hu et al. [21] utilized the sol-gel method to fabricate Ni-TNTs/SnO₂-Sb electrodes, which exhibited a surface layer with uniform and dense nanoparticles. Remarkably, their electrode displayed an increased oxygen evolution potential (OEP) of 2.3 V and an extended lifetime of 653 h. In comparison to the undoped Ti/SnO₂-Sb electrode, significant enhancements were observed in terms of current efficiency and energy consumption reduction. The TiO₂-NTs/SnO₂-Sb electrode doped with Fe and Ce was prepared via pulse electrodeposition. The doped electrode exhibited a service life that was 2.2 times longer than that of its undoped counterpart, which could be attributed to the presence of smaller crystallite particles and the reduced formation of cracks [22]. A microporous film of CNFs/SnO₂-Sb was prepared for the electrocatalytic oxidative degradation of tetracycline. Due to the incorporation of SnO₂-Sb nanoparticles, both the electrical conductivity and OEP were enhanced compared to the aligned CNFs membrane electrode [23]. The SnO₂-Sb₂O₄ anode was modified with CNTs and Cr₃C₂, resulting in a reduction of the particle size on the electrode surface from 18 nm to 8 nm. This modification increased the effective catalytic area of the electrode and enhanced exposure of its active sites, leading to an improved removal efficiency of COD from phenol solution by 18% [24].

A variety of rare earth elements, including Ce, Nd, Gd, Eu and Er were introduced by researchers into the SnO₂ catalytic coating [25–27]. Song et al. [28] introduced the Nd element into the SnO₂ catalytic coating, wherein the impact of the ratio of Nd/Sn on the electrode performance was studied. The results demonstrated that incorporating 1% Nd

into the electrode led to improved crystallinity and a higher oxygen evolution potential, consequently resulting in enhanced electrocatalytic activity compared to that without Nd doping. The electrochemical removal of clothianidin was investigated on a Ti/Sb-SnO₂ electrode co-doped with graphene and europium (Eu). This dual doping strategy effectively enhanced the apparent morphology and electrochemical properties [29].

The aforementioned literature analysis has indicated that modifying the electrode substrate or doping exogenous substances can both enhance the performance of electrodes in wastewater treatment. However, due to variations in the preparation process, even when utilizing the same doping substance, distinct effects in the apparent morphology and crystal structure of the electrode can be observed. Consequently, the underlying mechanism governing the augmentation in electrocatalytic activity and stability also exhibits dissimilarities.

Hence, in this study, a vertically aligned TiO₂ nanotube (TNT) array layer was utilized as the electrode substrate in order to enhance both the stability of the electrode and the loading capacity of the catalyst. Two nanoscale SnO₂-Sb composites doped with Nd and Gd elements were embedded into the TNTs substrate using an in situ solvothermal method. The impact of incorporating Nd and Gd into the precursor solution on the structural and electrochemical properties of SnO₂-Sb electrodes was compared. The morphology, structure and chemical composition of rare earth-modified electrodes were characterized and analyzed in order to elucidate the structure–activity relationship of these electrodes. Special attention was given to the correlation between oxygen vacancy concentration and reactive radical formation on the rare earth-doped electrodes. Additionally, this paper introduced rare earth-doped electrodes into an electrocatalytic degradation system, thereby providing fundamental data and technical support as well as guidance for controlling organic wastewater pollution.

2. Materials and Methods

2.1. Fabrication of Titanium Nanotube (TNT) Arrays as the Substrate for TNTs/SnO₂-Sb Electrodes

The TNT array on a Ti substrate as the substrate for TNTs/SnO₂-Sb electrodes was fabricated using an anodization technique, and the detailed preparation procedure was described as follows: A titanium sheet (20 mm × 20 mm) was rinsed with absolute ethyl alcohol in an ultrasonic cleaner several times prior to the anodization process.

A mixed solution comprising 70 mL of glycerol and 30 mL of H₂O was utilized in the anodization process as a corrosive electrolyte, with NH₄F dissolved at a concentration of 0.5 wt.%. This experimental procedure employed a two-electrode system, wherein titanium and stainless steel plates of equal surface area were designated as the anode and cathode, respectively. The anodization process lasted for 2 h with a voltage of 25 V applied. Following this, the resulting titanium sheet underwent ultrasonic cleaning before being subjected to crystallization through annealing in atmosphere at 500 °C for another 2 h, resulting in a vertically grown titanium dioxide nanotube (TNT) array substrate.

2.2. Preparation of TNTs/SnO₂-Sb Electrodes

The rare earth doped TNTs/SnO₂-Sb electrodes were synthesized through a solvothermal method. The precursor solution for the TNTs/SnO₂-Sb electrode was freshly prepared by dissolving SnCl₄·5H₂O and SbCl₃ in a mixture of ethanol and concentrated hydrochloric acid, maintaining a Sn:Sb molar ratio of 10:1. The substrate of TNT arrays obtained from the anodization process was immersed and sealed in the aforementioned solution for a solvothermal process at 180 °C with continuous stirring. After a 12 h reaction, the resulting substrate of TNT arrays was extracted from the solution and subsequently subjected to air-drying. An annealing process was then carried out in a muffle furnace at 550 °C for 3 h, leading to the formation of a TNTs/SnO₂-Sb electrode.

The Nd and Gd contents in the doped TNTs/SnO₂-Sb electrodes were achieved by incorporating Nd(NO₃)₃·6H₂O (with a molar ratio of Nd/Sn at 3:100) and Gd(NO₃)₃·6H₂O (with a molar ratio of Gd/Sn at 2:100), respectively, into the precursor solution, while

keeping the remaining steps unchanged. The obtained electrode samples were denoted as TNTs/SnO₂-Sb-Nd and TNTs/SnO₂-Sb-Gd.

2.3. Characterization of Electrodes

The morphology of the TNTs/SnO₂-Sb electrodes with and without rare earth were analyzed via scanning electron microscopy (SEM, S4700, Hitachi Ltd., Kyoto, Japan). The crystalline patterns and lattice parameters of the present electrodes were tested using X-ray diffraction (XRD, D/max-rB, Rigaku, Tokyo, Japan) with Cu K α radiation, and the grain size of the catalytic coating was calculated according to the Scherrer formula [30]. The surface chemical environment element was analyzed via X-ray photoelectron spectroscopy (XPS, PHI5700, ESCA, Carrollton, TX, USA) (Al K α radiation; $h\nu = 1486.6$ eV). The percentages of different species present in the surface coating of the electrodes were determined by analyzing the intensities and sensitivities of the diffraction characteristic peak. The oxygen vacancy concentrations were detected using Electron paramagnetic resonance measurements (EPR, ER200D-SRC, Bruker, Billerica, MA, USA), and the detailed operating parameter are shown in Ref. [31].

2.4. Electrochemical Experiments

The oxygen evolution potential was assessed by conducting linear sweep voltammetry (LSV) utilizing a three-electrode system and an electrochemical workstation: the prepared electrode was utilized as the working electrode with a working area of 10 mm $\times$ 10 mm, a platinum sheet measuring 15 mm $\times$ 15 mm served as the counter electrode, and a saturated Ag/AgCl reference electrode was employed. The tested solution consisted of 0.5 mol/L H₂SO₄, and the kinetic potential scan rate was set at 1 mV/s. The double electrode layer structure was analyzed via an electrochemical impedance spectroscopy (EIS) measurement, which was also carried out in the above system. The tested solution comprised a 0.25 mol/L Na₂SO₄ solution, and the frequency range ranged from 10⁵ to 10⁻¹ Hz under an impedance amplitude signal of 5 mV.

2.5. Analysis of Hydroxyl Radicals ($\bullet$ OH) Generation

The presence of hydroxyl radicals ($\bullet$ OH) generation in a Na₂SO₄ solution (0.25 mol/L) with terephthalic acid (0.5 mmol/L) as the trapping agent was determined using fluorescence spectroscopy technology (FP-6500, JASCO, Oklahoma City, OK, USA). The detailed procedure for electrolysis experiment could be found elsewhere [13].

2.6. Electro-Catalytic Oxidation Experiments

The electrocatalytic degradation of phenol was conducted in a cylindrical reactor at room temperature. The experimental setup ensured that the initial concentration of phenol remained constant at 100 mg/L throughout all the runs. To facilitate the electrocatalytic degradation process, a supporting electrolyte consisting of Na₂SO₄ at a concentration of 0.25 mol/L was used.

The as-prepared samples, with dimensions of 20 mm $\times$ 20 mm, were employed as the working anode. A stainless steel plate of identical size was utilized as the cathode and positioned at a distance of 10 mm from the working anode. All degradation experiments were carried out under a controlled stirring speed, ensuring uniform mixing and distribution within the reactor. Additionally, a current density of 10 mA/cm² was applied using a DC power supply to sustain the electrochemical reactions effectively. To monitor and quantify changes in phenol concentration over time during electrolysis, UV-Vis spectrophotometry (TU-1810PC, PERSEE, Lyon, France) was employed. Additionally, the alteration of total organic carbon (TOC) in the simulated wastewater was concurrently monitored throughout the degradation process.

2.7. Electrode Stability Analysis

The stability of the electrode was investigated through an accelerated life test conducted at a high current density of 100 mA/cm² using a DC potentiostat. The prepared electrode, serving as the working anode (20 mm × 20 mm), was paired with a stainless steel cathode of the same size. Both electrodes were immersed in a 0.5 mol/L H₂SO₄ solution with a gap distance of 10 mm. The service time was recorded when the electrode voltage exceeded 10 V. Additionally, the variation in cell voltage during phenol electrolysis was monitored to evaluate electrode stability.

3. Results and Discussion

3.1. Electrocatalytic Activation Test

The electrocatalytic activity of different electrodes on the phenol removal was compared as shown in Figure 1a. The results showed that the TNTs/SnO₂-Sb-Nd (2 h) and TNTs/SnO₂-Sb-Gd (1.5 h) exhibited significantly reduced time requirements for complete phenol degradation compared to the TNTs/SnO₂-Sb (2.5 h).

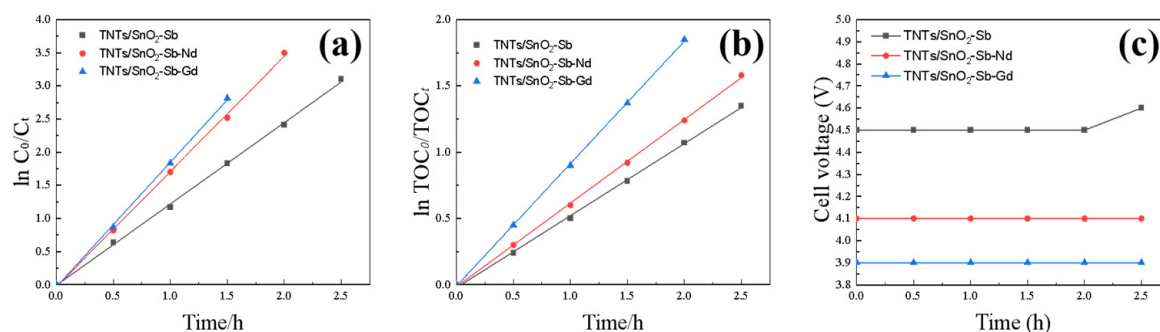


Figure 1. Impact of different rare earth-doped electrodes on phenol degradation: (a) phenol removal; (b) TOC removal; (c) voltage fluctuations.

The logarithmic relationship between phenol concentration and electrolysis time was analyzed using a pseudo-first-order kinetics model. The kinetic rate constant (k) of the electrode for phenol degradation was determined using the equation

$$\ln \frac{C_0}{C_t} = kt \quad (1)$$

where C_0 represents the initial concentration of phenol and C_t is its concentration at a given time t .

The fitting results presented in Table 1 demonstrated that the rates of phenol removal on TNTs/SnO₂-Sb-Nd and TNTs/SnO₂-Sb-Gd electrodes exhibited a significant increase of 45.0% and 60.0%, respectively, compared to the control (TNTs/SnO₂-Sb). The logarithmic relationship between total organic carbon (TOC) and the electrolysis time was also analyzed using a pseudo-first-order model, as depicted in Figure 1b. Among the three electrodes, the highest rate of TOC removal was observed on the TNTs/SnO₂-Sb-Gd electrode, followed by the TNTs/SnO₂-Sb-Nd electrode. The rates of TOC removal on the TNTs/SnO₂-Sb-Nd and TNTs/SnO₂-Sb-Gd electrodes were 22.2% and 66.7% higher than that of the control electrode, respectively. The aforementioned findings indicated that the incorporation of rare earth elements could effectively enhance the electrocatalytic activity of the electrode for organic compound removal.

Table 1. Kinetic parameters of phenol degradation in electrochemical process by different SnO₂ anodes.

Electrode Samples	Phenol		TOC	
	k (min ^{−1})	R ²	k (min ^{−1})	R ²
TNTs/SnO ₂ -Sb	0.020	0.9995	0.009	0.9986
TNTs/SnO ₂ -Sb-Nd	0.029	0.9995	0.011	0.9994
TNTs/SnO ₂ -Sb-Gd	0.032	0.9996	0.015	0.9997

The variation in the cell voltage during phenol electrolysis was monitored as shown in Figure 1c. The TNTs/SnO₂-Sb electrode voltage of 4.5 V, while varying degrees of reduction were observed on the TNTs/SnO₂-Sb-Nd (4.1 V) and TNTs/SnO₂-Sb-Gd (3.9 V), indicated a higher carrier concentration and conductivity on the electrode surface due to the rare earth doping. Additionally, a slight increase in the electrolytic cell voltage of TNTs/SnO₂-Sb was observed after 2 h of degradation, whereas no change was observed in the electrolytic cell voltage of TNTs/SnO₂-Sb-Nd and TNTs/SnO₂-Sb-Gd. It indicated that the incorporation of rare earth elements also could effectively enhance the stability of the electrode during the process of degrading organic compounds.

3.2. Surface Morphology and Crystal Structure

The TNT array substrate had been successfully fabricated via the anodization process as shown in Figure 2a. The internal bore diameters of TNT arrays was approximately 98 nm and the length of nanotube array was approximately 950 nm. A comparative SEM image of SnO₂-Sb electrodes based on the TNT array substrate with and without doping rare earth is shown in Figure 2b–d. The oxide layer on all the electrodes exhibited a film composed of clusters arranged in a sphere-stacking pattern. The surface of the TNTs/SnO₂-Sb doped with Nd and Gd exhibited an increasingly refined distribution of catalytic particles compared to the TNTs/SnO₂-Sb. The combination of the results obtained from the phenol degradation test suggested that the modification of electrode morphology through doping rare earth could potentially enhance electrocatalytic reactions by facilitating a greater number of active sites.

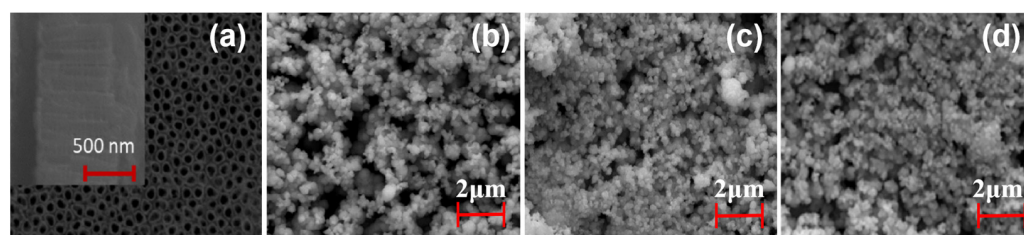


Figure 2. SEM images of (a) TNTs; (b) TNTs/SnO₂-Sb; (c) TNTs/SnO₂-Sb-Nd; (d) TNTs/SnO₂-Sb-Gd.

The rare earth doping exerted a significant influence on the structural characteristics of SnO₂-Sb electrode, as depicted in Figure 3. Comparing the obtained diffraction peak positions to standard cards (PDF#41-1445), the SnO₂ was in the form of tetragonal rutile crystalline [30]. Due to the strong overlap by SnO₂ diffraction peaks, the diffraction peaks corresponding to TiO₂, as shown in Figure 3a, were not observed in Figure 3b. Additionally, loading with a SnO₂ catalytic coating resulted in weaker peak intensity of Ti metal at approximately 71° on the TNT array substrate, indicating an enhanced coverage of SnO₂-Sb coating during the solvent process.

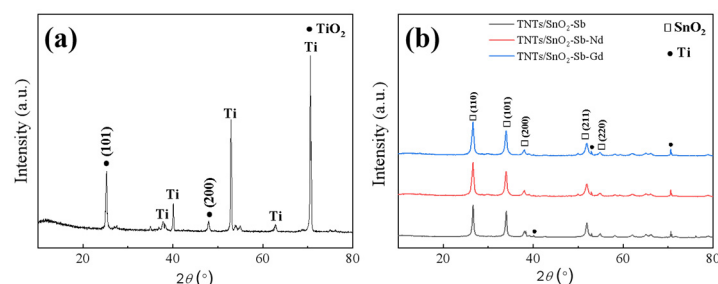


Figure 3. XRD patterns of (a) TNTs substrate; (b) different TNTs/SnO₂-Sb electrodes.

The XRD pattern did not reveal the presence of any oxide phases corresponding to Nd, Gd and Sb, suggesting that Nd, Gd and Sb might have been incorporated into the SnO₂ lattice through displacement or gap addition mechanisms, or they could be uniformly dispersed as small clusters within the SnO₂ particles. The lattice parameters (i.e., *a*, *b*, and *c*) of the TNTs/SnO₂-Sb-Nd and TNTs/SnO₂-Sb-Gd were found to be larger than those of TNTs/SnO₂-Sb in Table 2. This suggested that the rutile SnO₂ lattice experienced a slight expansion upon doping with rare earth elements, as the larger ions of rare earth elements entered the unit cell of SnO₂ and replaced the smaller Sn⁴⁺ ions [32]. The smaller the radius of the doped ion, the more easily it could penetrate into the lattice interior. Consequently, the lattice parameters of TNTs/SnO₂-Sb-Gd were larger than those of TNTs/SnO₂-Sb-Nd.

Table 2. Lattice parameters and grain size of the electrodes.

Electrode Samples	Lattice Parameters		Average Grain (nm)	Ionic Radius (nm)
	<i>a</i> = <i>b</i>	<i>c</i>		
TNTs/SnO ₂ -Sb	4.717	3.154	16 ± 0.4	Sn = 0.071
TNTs/SnO ₂ -Sb-Nd	4.724	3.169	10 ± 0.2	Nd = 0.098
TNTs/SnO ₂ -Sb-Gd	4.747	3.175	9.5 ± 0.3	Gd = 0.094

The diffraction peak of SnO₂ corresponding to the (110) and (101) crystallographic planes began to broaden upon doping with Nd and Gd, indicating a reduction in the grain size of SnO₂ after doping, which could be proven by the subsequent calculation results in Table 2. The mean size of the crystals of the electrode's surface doped with rare earth elements was found to be smaller than that of the undoped one, as determined by Scherrer's formula. The particle size of TNTs/SnO₂-Sb-Gd was found to be smaller than that of TNTs/SnO₂-Sb-Nd based on the aforementioned analysis, which could likely be attributed to the smaller ionic radius of the doped elements facilitating their incorporation into the SnO₂ lattice and impeding grain growth, consequently resulting in a finer electrode grain size.

3.3. Electrochemical Properties of the Electrodes

A comparative investigation was conducted on the linear sweep voltammograms of the TNTs/SnO₂-Sb electrodes with and without rare earth doping, as illustrated in Figure 4. The equilibrium potential of the three electrodes was essentially identical; however, when the oxygen evolution reaction occurred, the potential under the same current density exhibited noticeable variations, indicating distinct differences in their oxygen evolution potential. In a redox reaction, the electrode should consume the solute of the nearby electrolyte, resulting in a decrease in the concentration of the electrolyte. If the electrode reaction rate exceeds the diffusion rate of the electrolyte, it will lead to a reduction in the current density. To maintain the original current density, the electrode potential must increase. Therefore, a faster electrode reaction rate determines a higher oxygen evolution overpotential. As for the analysis above, the variation in oxygen evolution potential was attributable to the disparate reaction rates exhibited by different electrodes [30].

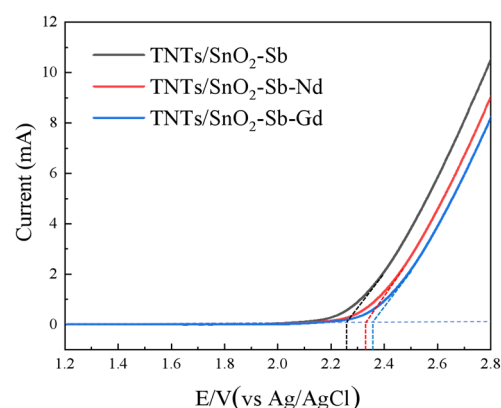


Figure 4. Linear sweep voltammograms of different electrodes.

The lower the potential for oxygen evolution, the greater the likelihood of occurrence of the oxygen evolution side reaction. This may lead to a reduced current efficiency in organic matter degradation. Additionally, it could result in reduced electrode stability to deactivation caused by the Ti substrate reacting with O^{2-} ions from the reaction. Therefore, an ideal electrode material for electrocatalytic oxidation technology must be characterized by a high oxygen evolution potential. The oxygen evolution potentials of TNTs/SnO₂-Sb-Nd (2.33 V) and TNTs/SnO₂-Sb-Gd (2.36 V) exhibited higher values compared to that of the TNTs/SnO₂-Sb electrode (2.26 V). It could be speculated that the highest current efficiency was obtained on TNTs/SnO₂-Sb-Gd, suggesting that this was the reason for the significantly reduced time required for complete phenol degradation compared to TNTs/SnO₂-Sb-Nd and TNTs/SnO₂-Sb in Figure 1.

The double electrode layer structure was analyzed via EIS measurement, as shown in Figure 5. The impedance arc radius exhibited varying degrees of reduction on the doped electrodes compared to the undoped one, with a minimum observed on the TNTs/SnO₂-Sb-Gd electrode. The impedance spectrum was analyzed by fitting it with an equivalent circuit consisting of R(CR)(CR), and the corresponding results are presented in Table 3. The introduction of rare earth elements into the catalytic coating resulted in a lower charge transfer resistance (R_t) compared to the electrode without doping, indicating an enhanced electron diffusion path for an efficient charge transfer between the electrode and solution. In addition, the electronic double-layer capacitance (C_t) of TNTs/SnO₂-Sb doped with Nd or Gd was found to be higher than that of TNTs/SnO₂-Sb, suggesting an increased presence of anions in the electronic double-layer due to the inclusion of rare earth elements [33].

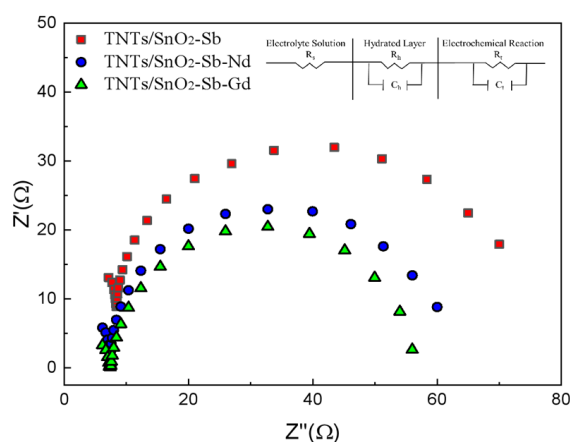


Figure 5. EIS spectrums of the electrodes with and without rare earth elements.

Table 3. EIS fitting results of electrodes with and without rare earth elements.

Sample	R_s (Ω)	C_h (F)	R_h (Ω)	C_t (F)	R_t (Ω)	R_s (Ω)
TNTs/SnO ₂ -Sb	4.72	5.8×10^{-8}	43.5	2.14×10^{-5}	65	4.72
TNTs/SnO ₂ -Sb-Nd	4.70	7.8×10^{-8}	37.7	2.53×10^{-5}	46	4.70
TNTs/SnO ₂ -Sb-Gd	4.68	8.1×10^{-8}	34.5	2.67×10^{-5}	38	4.68

The TNTs/SnO₂-Sb-Gd electrode exhibited the lowest charge transfer and highest electronic double-layer capacitance among the three electrodes. The increase in the number of anions in the tight layer leads to a corresponding rise in the redox potential of the oxygen evolution phenomenon, rendering it more challenging for oxygen evolution. Therefore, the sequence of the oxygen evolution potential is TNTs/SnO₂-Sb-Gd > TNTs/SnO₂-Sb-Nd > TNTs/SnO₂-Sb, and this finding is consistent with the polarization curve results.

3.4. Primary Reactive Species and Reaction Mechanisms

The surface chemical environment element was analyzed using XPS to further elucidate the structure–activity relationship (Figure 6). The surface coatings of the three electrodes were composed of elements Sn, Sb and O. Moreover, characteristic diffraction peaks of Nd4d and Nd3d were observed in the TNTs/SnO₂-Sb-Nd (Figure 6a), while Gd4d and Gd3d characteristic diffraction peaks were observed in TNTs/SnO₂-Sb-Gd (Figure 6b), indicating that Nd and Gd elements were successfully doped into the electrode coating. A comparison of the Sn3d spectra is shown in Figure 6c. The presence of Sn element on the coating was confirmed to be in the form of Sn⁴⁺ based on the observed Sn3d binding energies, which were consistent with the standard value for Sn⁴⁺ (486.65 eV) [33]. TNTs/SnO₂-Sb-Nd and TNTs/SnO₂-Sb-Gd exhibited a decrease in Sn3d binding energies compared to the control, indicating the presence of a higher average electron configuration surrounding Sn⁴⁺ with doping rare earth elements. The increased electron density surrounding Sn⁴⁺ led to a reduced number of O^{2−} ions within the crystal lattice that were capable of attracting electrons, owing to the nonstoichiometric nature of SnO₂. The result was an increased generation of oxygen vacancies, enabling the adsorption of a larger quantity of oxygen species to ensure charge equilibrium. The aforementioned analysis implied that the introduction of rare earth dopants might lead to an increase in surface defects, specifically an elevation in the quantity of oxygen vacancies present on the surface.

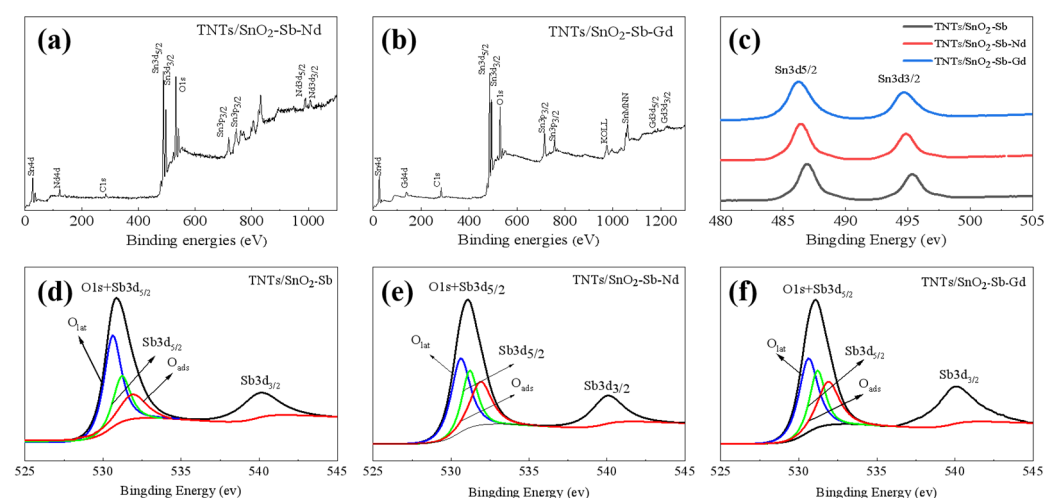


Figure 6. XPS patterns of (a) TNTs/SnO₂-Sb-Nd; (b) TNTs/SnO₂-Sb-Gd; (c) Sn3d on different electrodes; and the fitted curves of O1s and Sb3d of different electrodes: (d) TNTs/SnO₂-Sb; (e) TNTs/SnO₂-Sb-Nd; (f) TNTs/SnO₂-Sb-Gd.

Additionally, the relative peak area of Sb3d in the doped electrodes was found to be higher than that in the undoped one, indicating that doping with rare earth elements could

lead to a Sb enrichment coating surface. Since Sb is pentavalent and positively charged, its substitution for tetravalent Sn on the electrode surface creates new oxygen vacancies to compensate for the excess positive charge, which can adsorb external oxygen and maintain the charge balance. The increase in Sb content may account for the elevated concentration of oxygen vacancies, consequently resulting in an increased amount of adsorbed oxygen on the electrode surface.

This was confirmed by the fitted curves of O1s of different electrodes (Figure 6d–f). The O1s spectrum displayed two distinct peaks: one corresponding to lattice oxygen (O_{lat}), existing in the SnO_2 crystal structure, and another corresponding to adsorbed oxygen (O_{ads}). The TNTs/ SnO_2 -Sb-Nd and TNTs/ SnO_2 -Sb-Gd samples demonstrated a significantly elevated O_{ads} content, exhibiting respective increases of 62.8% and 74.7% compared to the control sample (Table 4).

Table 4. XPS analysis of different TNTs/ SnO_2 -Sb electrodes.

Electrode Samples	Binding Energies of $Sn3d_{5/2}$	Atom Ratio of O_{ads} (%) ¹
TNTs/ SnO_2 -Sb	486.63	21.5
TNTs/ SnO_2 -Sb-Nd	486.22	35.0
TNTs/ SnO_2 -Sb-Gd	486.18	37.5

$$^1 \text{ At\% } (O_{ads}) = \frac{O_{ads}}{Sn + Sb + Nd + O_{ads} + O_{lat}} \times 100\%.$$

The confirmation was further supported by the analysis of electron paramagnetic resonance (EPR), which revealed variations in oxygen vacancy across different electrodes (Figure 8). Due to the absence of unpaired electrons in either the Sn^{4+} or Sb^{5+} structures, oxygen vacancies were anticipated to be the exclusive source of EPR signals in all samples, and a higher relative intensity of EPR indicated a greater content of oxygen vacancies [34]. The relative intensity of the EPR signals for TNTs/ SnO_2 -Sb electrodes doped with rare earth elements was found to be higher than that of undoped one, indicating an increase in surface defects (oxygen vacancies) resulting from the incorporation of rare earth dopants.

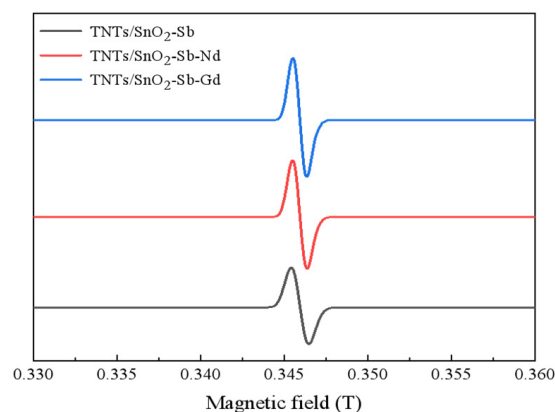
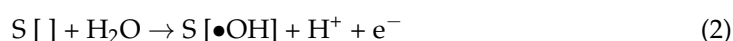
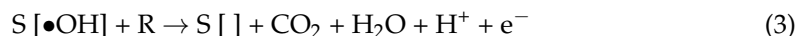


Figure 7. The accelerated life of different electrodes.

The presence of more oxygen vacancies in the electrode meant an increased number of unbonded valence electrons within the metal atoms. When subjected to an electric field, these valence electrons migrated into the conduction band, leading to a higher concentration of charge carriers. As the charge carriers transition from the surface to the body phase of the electrode, a positive charge center was formed at the oxygen vacancy. Consequently, this increase in oxygen vacancy content will provide more positive charges and adsorb more anions as the surface active sites, so that the doped electrode surface had a higher ability to adsorb the oxygen content to generate hydroxyl radicals($\bullet OH$) to react with the pollutants (R) as shown in Equations (2) and (3) [35]:





where S represents the SnO₂ electrode's surface active sites for adsorption of •OH species.

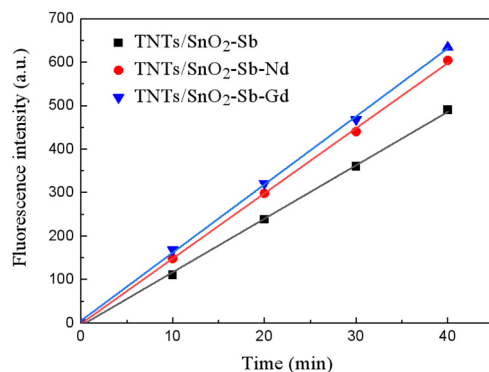


Figure 8. EPR spectra of different electrodes.

In order to validate the aforementioned analysis, the hydroxyl radical (•OH) generation capacity of the three electrodes was examined, as illustrated in Figure 9. The observed rate of •OH formation exhibited a strong correlation with the trend in oxygen vacancies content as shown in Figure 8, namely TNTs/SnO₂-Sb-Gd > TNTs/SnO₂-Sb-Nd > TNTs/SnO₂-Sb. The results demonstrated that a higher proportion of oxygen vacancies could effectively enhance the ability to generate •OH for efficient degradation of the targeted contaminant. The aforementioned analysis also elucidated the rationale behind the superior electrocatalytic activity observed in TNTs/SnO₂-Sb-Gd, which was subsequently followed by TNTs/SnO₂-Sb-Nd and then TNTs/SnO₂-Sb, as depicted in Figure 1.

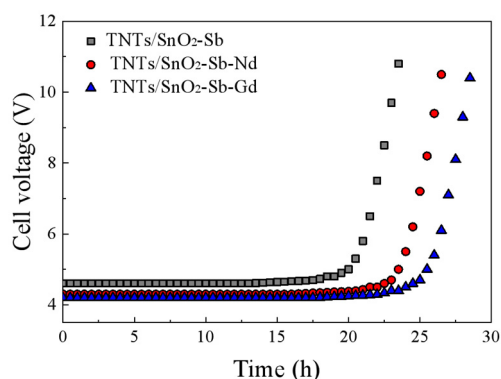


Figure 9. Hydroxyl radical generation ratios of different electrodes.

3.5. Electrode Stability Analysis

The stability of the three electrodes was assessed using an accelerated life test, as depicted in Figure 7. It was observed that the potentials of all the electrodes initially exhibited a gradual increase, followed by a sudden surge in voltage for three electrodes at different time points, indicating a decrease in the electrode stability. According to the definition of electrode accelerated service life in section of 2.6, the accelerated service life followed the following order: TNTs/SnO₂-Sb-Gd (28.5 h) > TNTs/SnO₂-Sb-Nd (26.5 h) > TNTs/SnO₂-Sb (23.5 h). It was consistent with the aforementioned experimental results obtained from monitoring the voltage of the electrolytic cell, namely, the incorporation of rare earth elements could effectively enhance the stability of the electrode during the process of degrading organic compounds.

4. Conclusions

A solvothermal synthesis technique was employed to embed SnO₂-Sb into the vertically aligned TNT substrate, serving as anode material for electrocatalytic degradation of phenol. The influence of doping Gd and Nd into the precursor solution on the structure and properties of SnO₂-Sb electrodes was compared through an experimental analysis:

- (1) The electrodes doped with rare earth elements demonstrated enhanced electrocatalytic activity and stability compared to the undoped electrode. Among the two doped electrodes, TNTs/SnO₂-Sb-Gd exhibited a higher phenol and TOC removal rate, surpassing that of the TNTs/SnO₂-Sb-Nd electrode by 10.3% and 36.4%, respectively. Additionally, the accelerated service life of TNTs/SnO₂-Sb-Gd was extended by 7.5% in comparison to that of the TNTO₂-Sb-Nd electrode.
- (2) The TNTs/SnO₂-Sb-Gd composite exhibited a finer grain size and increased active sites compared to TNTs/SnO₂-Sb-Nd, attributed to the smaller ionic radius of the Gd element. This facilitated its incorporation into the SnO₂ lattice interior and inhibited grain growth, resulting in a significant enhancement in the exposure of more active sites.
- (3) The enhanced electrocatalytic activity observed in the Gd-doped electrode can be attributed to the increased generation of oxygen vacancies on its surface, which act as active sites for enhancing the adsorption of oxygen species and promoting •OH generation.

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