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RSM-Based Preparation and Photoelectrocatalytic Performance Study of RGO/TiO₂ NTs Photoelectrode

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Abstract: In this paper, reduced graphene oxide (RGO) was prepared by a modified Hummers method and chemical reduction method, and an RGO/TiO₂ NTs (RGO/TiO₂ nanotubes) photoelectrode was prepared by the electrochemical deposition method. The as-prepared RGO/TiO₂ NTs were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD), and their photocatalytic activities were investigated by measuring the degradation of methylene blue (MB) under simulated solar light irradiation. The SEM and XRD results indicated that the original tubular structure of TiO₂-NTs was not changed after RGO modification. The surface of the TiO₂ NTs photoelectrode was covered with a non-uniform, flake-shaped reduced graphene oxide film. The thickness of the RGO/TiO₂ NTs was increased to about 22.60 nm. The impedance of the RGO/TiO₂ NTs was smaller than that of the TiO₂ NT photoelectrode. The optimal preparation conditions of RGO/TiO₂ NT photoelectrodes were investigated by using a single factor method and response surface method. The best preparation conditions were as follows: deposition potential at 1.19 V, deposition time of 10.27 min, and deposition temperature at 24.94 °C.

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Keywords: methylene blue; photoelectrocatalysis; response surface method; RGO/TiO₂ NTs

1. Introduction

In recent years, the discharge of a large amount of dye wastewater has caused a huge threat to the environment, due to the toxicity, mutagenicity and carcinogenicity of dyes [1,2]. Among various dyes, methylene blue is one of the most common pollutants to prevent wastewater [3]. In terms of ecological environment, MB blocks sunlight from penetrating the water body, thereby posing a threat to aquatic life; in terms of public health, MB may burn eyes and cause irreversible damage [4]. Therefore, it is extremely necessary to remove dyes in wastewater. Commonly used methods for removing dyes include biosorption, electrocoagulation, redox, photocatalysis, etc. [5–9]. Photoelectrocatalysis (PEC) is an electrochemical advanced oxidation process (EAOP) combining photocatalysis with electrolysis [10]. Considering the renewable source of solar energy, research on photocatalysis has been rapidly expanding in recent years [11]. However, compared with photocatalysis, PEC can effectively solve the problem of the recombination of photogenerated electron–hole pairs in photocatalysis, so it has been widely used in the removal of pollutants in wastewater in recent years [12,13].

In 1972, Fujishima and Honda et al. [14] found that water could be decomposed into H₂ and O₂ by the TiO₂ photoelectrode under light conditions. Since then, TiO₂ has been thought to be an ideal semiconductor close to photocatalysis due to its high stability, low cost, harmlessness, high electron mobility, and excellent photoactivity [15–17]. However, TiO₂ has a wide band gap (3.0–3.2 eV) [18]. Therefore, it is slightly difficult to use sunlight as an external light source for catalytic titanium dioxide. This limitation can be overcome by changing the form of titanium dioxide or doping with other materials. TiO₂ nanotubes have been proven to have great research potential in photoelectric decomposition,

optoelectronics, photocatalysis, and sensors [19–24]. Compared with all other forms of TiO_2 , TiO_2 nanotubes show higher stability in morphology, structure, and photoelectric degradation performance [25,26]. In order to improve the photoelectric catalytic activity of TiO_2 , researchers have carried out a large number of modification studies. The main methods include non-metallic element doping, precious metal deposition, and semiconductor compounding. Dandan Cao et al. [27] synthesized Ag-AgBr nanospheres on the tubular surface of TiO_2 nanotube arrays (TiO_2 NTA/Ag-AgBr). Due to the sensitization of Ag-AgBr nanospheres, the visible light response region was significantly extended and the photoelectric conversion activity was improved. The visible photovoltage and transient photocurrent density of the TiO_2 NTA/Ag-AgBr (0.025) photoelectrode were -0.17 volts and 0.12 mA/cm^2 . Maryline et al. [28] prepared RGO/ TiO_2 nanofibers as photocatalytic materials and used the degradation rate of methyl orange to observe its catalytic efficiency. The results showed that the reaction rate of RGO/ TiO_2 (2 wt.%) nanofibers was significantly higher than that of commercial TiO_2 -P25. Yuyuan Zhang et al. [29] introduced visible light-activated cadmium sulfide flowers onto the titanium dioxide nanotube array film on the titanium foil substrate to effectively separate the photo-excited electron-hole pairs and to improve the photocatalytic efficiency and water splitting in photoelectrochemical conversion, and the yield of hydrogen production. The excellent enhancement effect of graphene oxide nanosheets on the photocatalytic performance of TiO_2 was attributed to its thin two-dimensional sheet support, large specific surface area, greatly increased adsorption capacity, and a good electron acceptor favoring the transfer of photo-generated electrons from the conduction band of TiO_2 to the graphene oxide sheet [30–32]. The above qualities make graphene oxide nanosheets one of the candidate materials in the effort to improve the catalytic activity of titanium dioxide [33].

Response surface methodology (RSM) comprises a set of mathematical and statistical techniques based on polynomial equation fitting with experimental data, which describes the behavior of data sets and aims at statistical prediction. It is suitable for optimizing system performance when one or more responses are affected by several variables [34]. Box and Behnken et al. [35] suggested how to select points from a three-level factorial arrangement, which allows the efficient estimation of the first- and second-order coefficients of the mathematical model. These designs are more efficient and economical, particularly for a large number of variables.

In order to improve the visible light photocatalytic activity of TiO_2 NT photoelectrode, RGO was loaded onto the electrode. Due to the strong carrier mobility, optical transparency, and flexibility of sp^2 hybrid graphene, it is currently used in many fields, such as photocatalysis, sensors, and solar materials. In this experiment, the response surface experiment was designed. RGO was deposited onto TiO_2 NTs by the electrochemical deposition method, and the samples were analyzed by SEM, EDS, XRD, and Raman. The photoelectrocatalytic properties of RGO/ TiO_2 NTs photoelectrode materials under external light were studied, which can provide a reference for the preparation of high-performance photoelectrocatalytic materials.

The purpose of this study is to deposit RGO onto TiO_2 NTs by electrochemical deposition, and to study the effect of active free radicals on the photocatalytic oxidation reaction and the stability of the photoelectrode. The specific objectives are as follows: (1) to prepare TiO_2 NTs photoelectrode material by anodizing method; (2) to prepare RGO by a modified Hummers method and chemical reduction method, and prepare an RGO/ TiO_2 NT photoelectrode by the electrochemical deposition method; (3) to optimize the RGO/ TiO_2 NT photoelectrode. This achievement is considered to provide a theoretical basis and reference for the preparation of high-performance catalytic materials.

2. Materials and Methods

2.1. Materials

Reagents: C, P_2O_5 , $\text{K}_2\text{S}_2\text{O}_8$, CH_3COOH , KI, $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , $\text{NH}_3 \cdot \text{H}_2\text{O}$, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, Na_2SO_4 .

Instruments: Desktop high-speed centrifuge (Shanghai Luxiang Instrument Co., Ltd., Harbin, China), Raman spectrometer (HORIBA Jobin Yvon, Harbin, China).

2.2. Synthesis of RGO/TiO₂ NTs

2.2.1. Synthesis of GO

Graphene oxide (GO) was prepared by a modified Hummers method. Firstly, graphite powder (1 g) was treated with 80 mL H₂SO₄, 1 g K₂S₂O₄, 1 g P₂O₅ and slowly heated to 80 °C for 5 h. Then, a large amount of deionized water was used to wash repeatedly until it was neutral to obtain pre-graphite oxide, and the pre-oxidized graphite was dried at 6 °C for 12 h. A mixture of 40 mL H₂SO₄ and graphite was added to the ice water bath in the flask. Secondly, 4 g KMnO₄ was slowly added to the solution, heated to 35 °C to react for 2 h. Then, deionized water was added and heated to about 98 °C. After 15 min, deionized water and 10 mL H₂O₂ were added and then centrifuged when the color of the solution gradually changed into golden yellow. The obtained solid was washed with dilute hydrochloric acid and deionized water to remove residual acid on the surface. Finally, the GO sample was dried by vacuum at 60 °C for 12 h.

2.2.2. Synthesis of RGO

RGO was prepared by the chemical reduction method. Graphene oxide (GO) was added to deionized water and ultrasonically treated for 1 h. Ammonia was added and the pH was adjusted to 10. A total of 250 mL hydrazine hydrate (35%) was added to the treated GO and heated at 95 °C for 4 h. The black solution was filtered, followed by washing with dilute hydrochloric acid and deionized water to remove residual acid on the surface. RGO was obtained by vacuum drying at 70 °C for 12 h.

2.2.3. Fabrication Method of RGO/TiO₂ NTs

In this study, a TiO₂ NT photoelectrode grown on Ti foils was prepared by the anodic oxidation method, and the synthesis progress and experiment parameters are provided in our previous papers [36]. The RGO/TiO₂ NTs photoelectrode was prepared by electrochemical deposition. The electrodeposition solution was a mixture of 100 mg·L^{−1} RGO solution and 0.5 mol·L^{−1} Na₂SO₄. A three-electrode system was adopted with the TiO₂ NTs electrode as the anode, Pt as the cathode, and SEC as the reference electrode. Electrodeposition was conducted at a certain voltage for a period of time. After the reaction was completed, the sample was repeatedly rinsed with deionized water and then vacuum dried at 70 °C for 4 h. Finally, the RGO/TiO₂ NTs was obtained.

2.3. Photoelectric Catalytic Activity Tests

The photoelectric catalytic property of RGO/TiO₂ NT photoelectrode was evaluated by photoelectric catalytic oxidation degradation of 5 mg/L methylene blue aqueous solution. At room temperature, 80 mL methylene blue solution was added to a 100 mL quartz beaker. The mercury lamp was used as the external light source and placed parallel to the Ti sheet, with an interval of 10 cm. The 35 W external light source and the 15 V DC regulated power supply were turned on. At regular intervals of 30 min, a 5 mL sample was taken and the absorbance was checked at 664 nm through a UV–vis spectrophotometer. The degradation efficiency (η) was calculated using the following equation:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%$$

where C_0 is the initial concentration of MB (mg/L) and C_t is the instantaneous concentrations (mg/L) in the solution.

2.4. Single Factor Test

Single factor test was used to design the photoelectric catalytic performance experiments of RGO/TiO₂ NTs photoelectrodes. The deposition potential, deposition time, and

deposition temperature were taken as research targets. The voltages were 0.6, 0.8, 1.0, 1.2, and 1.4 V, the deposition times were 4, 6, 8, 10, and 12 min, and the deposition temperatures were 15, 20, 25, 30, and 35 °C, respectively.

2.5. Response Surface Experimental Design

RSM was used to regulate and control the photoelectric catalytic performance of RGO/TiO₂ NTs photoelectrodes. Box–Behnken with the software Design Expert 8.0 was employed to evaluate the combined effects of the three independent variables: deposition potential, deposition time, and deposition temperature. The coded and actual values of the three independent variables together with the responses are shown in Table 1.

Table 1. The design of RSM and the corresponding experimental and predicted values.

Run	Deposition Potential/V		Deposition Time/min		Deposition Temperature/°C		MB Degradation Rate (%)	
	A	Code	B	Code	C	Code	Experimental	Predicted
1	1.4	1	10	0	20	−1	51.2	46.87
2	1.4	1	8	−1	25	0	51.2	52.15
3	1	−1	8	−1	25	0	47.9	55.45
4	1.2	0	10	0	25	0	65.8	49.63
5	1.2	0	10	0	25	0	64.1	54.14
6	1.2	0	10	0	25	0	66.5	49.66
7	1	−1	10	0	20	−1	54.7	50.84
8	1.2	0	10	0	25	0	64.9	53.76
9	1.4	1	10	0	30	1	53.2	52.79
10	1	−1	12	1	25	0	56.4	58.61
11	1.2	0	10	0	25	0	65.4	56.49
12	1.2	0	8	−1	30	1	58	55.71
13	1.2	0	8	−1	20	−1	52.2	65.34
14	1.4	1	12	1	25	0	49.6	65.34
15	1	−1	10	0	30	1	49.3	65.34
16	1.2	0	12	1	20	−1	57.1	65.34
17	1.2	0	12	1	30	1	56.3	65.34

3. Results and Discussion

3.1. Analysis of Single Factor Test Results

The RGO/TiO₂ NTs photoelectrode was prepared by depositing for 10 min with different deposition potentials and then used for photoelectric catalytic degradation of MB, as shown in Figure 1. It was found that the catalytic effect of the photoelectrode on MB was significantly improved, showing a trend of first increasing and then decreasing. When the voltage was 1.2 V, the photoelectrode had the best degradation effect on MB, and the degradation rate reached 65.7%. This may be due to the high deposition potential and to a large amount of RGO deposited on the surface of the nanotubes, which reduces the light absorption performance (Figure 1).

When the deposition potential is 1.2 V, the photoelectric catalytic degradation effect of RGO/TiO₂ NTs photoelectrode on MB is studied under different times. It can be seen from Figure 2 that when the deposition time is 10 min, the photoelectric catalytic degradation effect is the best, and the MB degradation rate reaches 66.1%. However, a longer deposition time causes too much RGO to accumulate on the surface of the nanotubes, which reduces the light absorption performance, resulting in a decrease in the degradation rate of MB (Figure 2).

Figure 1. Effect of deposition voltages on the methylene blue degradation.

Figure 2. Effect of deposition time on the methylene blue degradation.

When the deposition potential was 1.2 V and the deposition time was 10 min, the photoelectrodes were prepared under the conditions of different deposition temperatures. As shown in Figure 3, the photoelectric catalytic performance of the photoelectrode is proportional to the deposition temperature. When the deposition temperature was 25 °C, the photoelectric catalytic performance was at its best, and the degradation rate of MB reached 66.8%. However, when the temperature rises further, the degradation of MB decreases. This may be due to a large amount of RGO accumulated on the surface of the nanotubes caused by the high temperature, which affects the photocatalytic activity (Figure 3).

Figure 3. Effect of deposition temperature on the methylene blue degradation.

3.2. Optimization Conditions of RGO/TiO₂ NTs Production

In the Equation (1), Y is the degradation rate of MB (%), and A, B, C are the code values of deposition potential, deposition time, and deposition temperature. The positive and negative signs before each item represent synergistic and antagonistic effects. The model was evaluated based on the correlation coefficient R². The R² of the model is 0.9761, which is close to 1, indicating that the predicted value of the model was similar to the measured value. Table 1 showed the initial conditions of fermentation and the actual and predicted responses.

$$Y = +65.34 - 0.39 \times A + 1.26 \times B + 0.20 \times C - 2.53 \times A \times B + 1.85 \times A \times C - 1.65 \times B \times C - 8.93 \times A^2 - 5.13 \times B^2 - 4.31 \times C^2 \quad (1)$$

In the ANOVA results of RSM, shown in Table 2, those model terms with a “*p*-value” less than 0.05 were significant (Table 2). The model *p*-value was less than 0.0001, which was extremely significant. The lack of fit was 0.0762 (>0.05), which was not significant, indicating that the model fit well within the regression area. As the F-values in Table 2 show, the order of the impact of three conditions on RGO/TiO₂ NTs production was: B > A > C. Moreover, the error statistical analysis of the regression equation showed that the R² value was 0.9454 and R_{adj}² was 0.6900, indicating that the 69% change in response value could be explained by the model. The precision was 15.193, more than 4, and proved reasonable; the CV was 2.64%, less than 10%, indicating the high reliability and accuracy of the test. The analysis results showed that the regression equation model was in good agreement with the actual test, which can effectively predict the test results. It is recommended to use this model to predict the optimal conditions for the preparation of RGO/TiO₂ NTs.

Table 2. ANOVA results of RSM.

Source	Sum of Squares	Degree of Freedom	Mean of Square	F-Value	<i>p</i> -Value Prob > F	Significant
Model	642.52	9	71.39	31.78	<0.0001	Significant
A	1.2	1	1.2	0.53	0.4884	
B	12.75	1	12.75	5.68	0.0487	
C	0.32	1	0.32	0.14	0.7170	
AB	25.5	1	25.5	11.35	0.0119	
AC	13.69	1	13.69	6.09	0.0429	
BC	10.89	1	10.89	4.85	0.0436	
A ²	335.96	1	335.96	149.56	<0.0001	
B ²	110.92	1	110.92	49.38	0.0002	
C ²	78.12	1	78.12	34.78	0.0006	
Residual	15.72	7	2.25			Not significant
Lack of Fit	12.43	3	4.14	5.04	0.0762	
Pure Error	3.29	4	0.82			
Cor Total	658.25	16				

The regression equation can be effectively represented by the response surface three-dimensional graph. The relationship between the response value of each variable and the test value is shown in Figure 4, which further evaluates the relationship between each variable and the best conditions. According to the analysis of Design Expert 8.0 software, the best preparation conditions for loading RGO onto TiO₂ NTs photoelectrodes were: deposition potential at 1.19 V, deposition time of 10.27 min, and deposition temperature at 24.94 °C, and the predicted value of MB degradation rate was 65.43%. Considering the actual situation, the optimal preparation conditions were identified as: deposition potential at 1.1 V, deposition time of 10 min, and deposition temperature at 25 °C (Figure 4).

Figure 4. (a) Response Surface of deposition potential and deposition time to methylene blue degradation rate; (b) response surface of deposition potential and deposition temperature to methylene blue degradation rate; (c) response surface of deposition potential and deposition temperature to methylene blue degradation rate.

Figure 5 is the SEM image of the RGO/TiO₂ NT photoelectrode under the conditions of deposition potential of 1.1 V, deposition time of 10 min, and deposition temperature of 25 °C. It can be seen from the figure that after RGO modification, the surface of the TiO₂ NTs photoelectrode was covered with a sheet of RGO film, which covered most of the nanotube surface. Part of the wall of the RGO/TiO₂ nanotube became thicker: measured by nano measurer 1.2.5, the wall was 22.60 nm. Therefore, the RGO/TiO₂ NTs photoelectrode had a better photoelectrocatalytic performance with RGO than without it (Figure 5).

Figure 5. The SEM pattern of RGO/TiO₂ NT photoelectrode.

Figure 6a is the XRD diffractogram of the photoelectrode prepared under the optimal preparation conditions. Cu K α rays (λ was 0.15418 nm), the characteristic diffraction peak of anatase phase A (101), appeared when $2\theta = 25.3^\circ$, and the characteristic diffraction peak of rutile phase R (101) appeared when $2\theta = 27.4^\circ$. It can be seen from the figure that there were three crystal phases at the same time, and the diffraction peak position was the same as that of TiO₂ NTs. After RGO modification, the characteristic diffraction peak of graphene (002) appeared at $2\theta = 24.9^\circ$, indicating that RGO had been successfully modified [37]. In order to further test whether RGO was successfully modified on the surface of the TiO₂ NTs photoelectrode, Raman spectroscopy was used. In the Raman spectrum of TiO₂, the Raman peaks at 148, 198, 397, 515, and 638 cm⁻¹ correspond to the anatase-induced A1g⁺2B1g⁺3Eg mode [38]. As shown in Figure 6b, the four Raman peaks caused by RGO are located at 1365, 1585, 2749, and 2938 cm⁻¹. This was caused by the D band related to the defects in the hexagonal graphite sheet and the G band related to the E2g mode. In addition, the G band was also related to the sp² hybridized carbon atoms [39]. Therefore, it is further proved that RGO has been successfully modified on TiO₂ NTs (Figure 6).

Figure 6. (a) XRD diffractogram of RGO/TiO₂ NTs photoelectrode; (b) XRD diffractogram and Raman spectrum of RGO/TiO₂ NTs photoelectrode.

In order to study the performance of RGO/TiO₂ NT photoelectrodes prepared under the best conditions, the photoelectrocatalytic MB (80 mL, 5 mg/L) degradation test was carried out under three different conditions, and the reaction time was 120 min. As shown in Figure 7, when the electrode was illuminated by a 35 W mercury lamp, the photocatalytic degradation rate of MB was 17.2%; when the electrode was protected from light under a 15 V bias voltage, the photocatalytic degradation efficiency of MB was 32%; when the electrode was irradiated by a 35 W mercury lamp and a 15 V bias voltage was applied, the MB degradation efficiency was significantly increased to 64% (Figure 7).

Figure 7. Degradation of methylene blue by RGO/TiO₂ NT photoelectrode.

It can be seen from Figure 8 that the MB degradation rate of TiO₂ NTs photoelectrode under mercury lamp irradiation is 54%, and the MB degradation rate under the catalysis of RGO/TiO₂ NTs photoelectrode is 63%, indicating that the degradation efficiency of the RGO modified TiO₂ NTs photoelectrode has been significantly improved (Figure 8).

Figure 8. Photocatalytic degradation of methylene blue on RGO/TiO₂ NTs and TiO₂ NT photoelectrode.

3.3. Analysis of Photoelectrocatalytic Mechanism

In the process of RGO/TiO₂ NTs photoelectrode photoelectrocatalysis of MB, the active intermediates participating in the reaction mainly include $\cdot\text{OH}$, h^+ and $\cdot\text{O}_2^-$. To study the catalytic mechanism of RGO/TiO₂ NTs photoelectrode to MB, we conducted free radical scavenging experiments. It can be seen from Figure 9 that $\cdot\text{OH}$ and h^+ are the main active substances in the photoelectric catalytic reaction.

Figure 9. Effects of free radical scavengers on the degradation efficiency of methylene blue.

In order to study the stability of RGO/TiO₂ NTs photoelectrode photoelectrocatalysis, a series of cyclic experiments were carried out. The result, as shown in Figure 10, was that the RGO/TiO₂ NTs photoelectrode has excellent stability: after repeated use for five times, the degradation efficiency of MB was still above 58%.

Figure 10. Stability study on RGO/TiO₂ NT photoelectrode.

Figure 11 shows the catalytic activity mechanism of RGO/TiO₂ NTs photoelectrodes. When light is irradiated, electrons in the valence band of TiO₂ are excited to transition to the conduction band, leaving a hole in the valence band. At the same time, electrons in the valence band of RGO are excited to transition to the conduction band, also leaving holes in the valence band. Due to its good conductivity of RGO, it can promote the flow of photogenerated electrons from the conduction band of TiO₂ to the conduction band of RGO. These electrons can react with O₂ to produce $\cdot\text{O}_2^-$. In addition, the holes in the conduction band of TiO₂ and RGO can react with H₂O to generate $\cdot\text{OH}$. In this way, electrons are transferred to the conduction band of RGO to react with O₂, and holes react with H₂O, effectively inhibiting the recombination of electrons and holes. Moreover, the applied voltage accelerates the migration rate of photo-generated electrons in the system, which greatly improves the photocatalytic effect. In addition, this method not only has excellent degradation effects but also has a simple process and is easy to characterize compared with photocatalytic oxidation reactions.

Figure 11. Photoelectric catalytic mechanism diagram.

4. Conclusions

Through single factor experiments, the optimal preparation conditions for RGO/TiO₂ NTs were found to be: deposition voltage at 1.1 V, deposition time of 10 min, and deposition temperature at 25 °C. According to the analysis and optimization of the response surface experiment design, the significance of the catalytic activity of RGO/TiO₂ NTs photoelectrode was in the order of deposition time > deposition voltage > deposition temperature. The optimal preparation conditions obtained by optimization were: deposition voltage at

1.19 V, deposition time of 10.27 min, and deposition temperature at 24.94 °C. The predicted value of MB degradation rate was 65.43%. Compared with the actual value (63%), the error value was 2.43%, indicating that the preparation parameters optimized by RSM have practical application value. The results provide a reference for the large-scale application of RGO/TiO₂ NTs photoelectrodes in engineering. Through SEM and XRD characterization analysis, it can be seen that after RGO modification, the original tubular structure of TiO₂ nanotubes was not changed. The surface of the TiO₂ NTs photoelectrode was covered with a non-uniform flake-shaped reduced graphene oxide film. The impedance of RGO/TiO₂ NTs was smaller than that of TiO₂ NTs photoelectrode.

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References

- King, T.C. *Azo Dyes and Human Health: A Review*; Taylor & Francis: Washington, DC, USA, 2016; pp. 233–261.
- Wang, X.L.; Rong, X.; Lin, H.Y.; Liu, D.N.; Wang, X.; Liu, G.C.; Song, G. A series of novel polyoxometalate-based Ag I -complexes constructed from asymmetric pyridyl-monoamide ligand: Synthesis, structures and selective separation of cationic dyes. *Inorg. Chim. Acta* **2017**, *461*, 279–289. [[CrossRef](#)]
- Zhu, M.T.; Kurniawan, T.A.; Song, F.; Ouyang, T.; Othman, M.H.D.; Rezakazemi, M.; Shirazian, S. Applicability of Ba-TiO₃/graphene oxide (GO) composite for enhanced photodegradation of methylene blue (MB) in synthetic wastewater under UV-vis irradiation. *Environ. Pollut.* **2019**, *255*, 113182.
- Reddy, B.S.; Ramana, K.V.; Ravindhranath, K. Extraction of methylene blue dye from polluted waters using some bio-adsorbents. *Int. J. Appl. Biol. Pharm. Technol.* **2012**, *3*, 215–224.
- Bhattacharjee, C.; Dutta, S.; Saxena, V.K. A review on biosorptive removal of dyes and heavy metals from wastewater using watermelon rind as biosorbent. *Environ. Adv.* **2020**, *2*, 100007. [[CrossRef](#)]
- Hussein, T.K.; Jasim, N.A. A comparison study between chemical coagulation and electro-coagulation processes for the treatment of wastewater containing reactive blue dye. *Mater. Today Proc.* **2021**, *42*, 1946–1950.
- Khandelwal, N.; Tiwari, E.; Singh, N.; Marsac, R.; Schäfer, T.; Monikh, F.A.; Darbha, G.K. Impact of long-term storage of various redox-sensitive supported nanocomposites on their application in removal of dyes from wastewater: Mechanisms delineation through spectroscopic investigations. *J. Hazard. Mater.* **2021**, *401*, 123375. [[CrossRef](#)] [[PubMed](#)]
- Anantha, M.S.; Jayanth, V.; Olivera, S.; Anarghya, D.; Venkatesh, K.; Jayanna, B.K.; Sachin, H.P.; Muralidhara, H.B. Microwave treated Bermuda grass as a novel photocatalyst for the treatment of methylene blue dye from wastewater. *Environ. Nanotechnol. Monit. Manag.* **2021**, *15*, 100447.
- Espinola-Portilla, F.; Navarro-Mendoza, R.; Gutiérrez-Granados, S.; Morales-Muñoz, U.; Brillas-Coso, E.; Peralta-Hernández, J.M. A simple process for the deposition of TiO₂ onto BDD by electrophoresis and its application to the photoelectrocatalysis of Acid Blue 80 dye. *J. Electroanal. Chem.* **2017**, *802*, 57–63. [[CrossRef](#)]
- García-Segura, S.; Brillas, E. Applied photoelectrocatalysis on the degradation of organic pollutants in wastewaters. *J. Photochem. Photobiol. C Photochem. Rev.* **2017**, *31*, 1–35. [[CrossRef](#)]
- Licht, S.; Wang, B.; Mukerji, S.; Soga, T.; Umeno, M.; Tributsch, H. ChemInform Abstract: Efficient Solar Water Splitting, Exemplified by RuO₂-Catalyzed AlGaAs/Si Photoelectrolysis. *Chem. Inform.* **2001**, *104*, 8920–8924. [[CrossRef](#)]
- Zhang, Y.; Xiong, X.; Han, Y.; Zhang, X.; Shen, F.; Deng, S.; Xiao, H.; Yang, X.; Yang, G.; Peng, H. Photoelectrocatalytic degradation of recalcitrant organic pollutants using TiO₂ film electrodes: An overview. *Chemosphere* **2012**, *88*, 145–154. [[CrossRef](#)]
- Ye, S.; Chen, Y.; Yao, X.; Zhang, J. Simultaneous removal of organic pollutants and heavy metals in wastewater by photoelectrocatalysis: A review. *Chemosphere* **2021**, *273*, 128503. [[CrossRef](#)] [[PubMed](#)]
- Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37–38. [[CrossRef](#)]
- Gupta, S.M.; Tripathi, M. A review of TiO₂ nanoparticles. *Chin. Sci. Bull.* **2011**, *56*, 1639. [[CrossRef](#)]
- Sun, C.; Wu, Y.; Zhang, W.; Jiang, N.; Jiu, T.; Fang, J. Improving Efficiency by Hybrid TiO₂ Nanorods with 1,10-Phenanthroline as A Cathode Buffer Layer for Inverted Organic Solar Cells. *ACS Appl. Mater. Interfaces* **2013**, *6*, 739–744. [[CrossRef](#)] [[PubMed](#)]

17. Yang, H.G.; Sun, C.H.; Qiao, S.Z.; Zou, J.; Liu, G.; Smith, S.C.; Cheng, H.M.; Lu, G.Q. Anatase TiO₂ single crystals with a large percentage of reactive facets. *Nature* **2008**, *453*, 638. [[CrossRef](#)] [[PubMed](#)]
18. Mena, E.; José, M.D.V.M.; Mesones, S.; Marugán, J. Influence of anodization mode on the morphology and photocatalytic activity of TiO₂-NTs array large size electrodes. *Catal. Today* **2017**, *313*, 33–39. [[CrossRef](#)]
19. Adachi, M.; Murata, Y.; Harada, M.; Yoshikawa, S. ChemInform Abstract: Formation of Titania Nanotubes with High Photocatalytic Activity. *Chem. Inform.* **2000**, *31*, 942–943. [[CrossRef](#)]
20. Chu, S.Z.; Inoue, S.; Wada, K.; Li, D.; Awatsu, S. Highly Porous (TiO₂-SiO₂-TeO₂)/Al₂O₃/TiO₂ Composite Nanostructures on Glass with Enhanced Photocatalysis Fabricated by Anodization and Sol-Gel Process. *Chem. Inform.* **2003**, *107*, 6586–6589. [[CrossRef](#)]
21. Zhang, Z.; Yuan, Y.; Fang, Y.; Liang, L.; Ding, H.; Shi, G.; Jin, L. Photoelectrochemical oxidation behavior of methanol on highly ordered TiO₂ nanotube array electrodes. *J. Electroanal. Chem.* **2007**, *610*, 179–185. [[CrossRef](#)]
22. Jeon, M.S.; Chun, Y.G.; Chang, S.J.; Kim, J.H.; Kang, B. Formation of Titania Nanotubes and Application for Dye-Sensitized Solar Cell. *J. Electrochem. Soc.* **2003**, *150*, G488.
23. Mor, G.; Shankar, K.; Varghese, O.; Grimes, C. Photoelectrochemical properties of titania nanotubes. *J. Mater. Res.* **2004**, *19*, 2989–2996. [[CrossRef](#)]
24. Chakraborty, I.; Chatterjee, S.; Ayyub, P. Field emission from hydrogen titanate nanotubes. *Appl. Phys. Lett.* **2011**, *99*, 1179. [[CrossRef](#)]
25. Mor, G.K.; Varghese, O.K.; Paulose, M.; Shankar, K.; Grimes, C.A. A Review on Highly Ordered, Vertically Oriented TiO₂ Nanotube Arrays: Fabrication, Material Properties, and Solar Energy Applications. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2011–2075. [[CrossRef](#)]
26. Li, L.; Zhou, Z.; Lei, J.; He, J.; Zhang, S.; Pan, F. Highly ordered anodic TiO₂ nanotube arrays and their stabilities as photo(electro)catalysts. *Appl. Surf. Sci.* **2012**, *258*, 3647–3651. [[CrossRef](#)]
27. Cao, D.; Wang, Q.; Liu, Z.; Zhang, H.; Gao, S. Enhanced the photoelectrocatalytic performance of TiO₂ nanotube arrays by the synergistic sensitization of Ag-AgBr nanospheres. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2019**, *227*, 117674. [[CrossRef](#)]
28. Maryline, N.; Sébastien, B.; Cynthia, E.; Roland, H.; Philippe, M.; Mikhael, B. Enhanced Visible-Light Photocatalytic Performance of Electrospun rGO/TiO₂ Composite Nanofibers. *J. Phys. Chem. C* **2017**, *121*, 261–269.
29. Zhang, Y.; Hu, H.; Kang, W.; Qiu, G.; Liang, R.; Deng, L.; Yuan, H. Enhancing hydrogen evolution by photoelectrocatalysis of water splitting over a CdS flowers-loaded TiO₂ nanotube array film on the Ti foil substrate. *Ceram. Int.* **2020**, *46*, 17606–17613. [[CrossRef](#)]
30. Lavanya, T.; Satheesh, K.; Dutta, M.; Victor Jaya, N.; Fukata, N. Superior photocatalytic performance of reduced graphene oxide wrapped electrospun anatase mesoporous TiO₂ nanofibers. *J. Alloys Compd.* **2014**, *615*, 643–650. [[CrossRef](#)]
31. Nainani, R.K.; Thakur, P. Facile synthesis of TiO₂-RGO composite with enhanced performance for the photocatalytic mineralization of organic pollutants. *Water Sci. Technol.* **2016**, *73*, 1927–1936. [[CrossRef](#)]
32. Fan, W.; Lai, Q.; Zhang, Q.; Wang, Y. Nanocomposites of TiO₂ and Reduced Graphene Oxide as Efficient Photocatalysts for Hydrogen Evolution. *J. Phys. Chem. C* **2011**, *115*, 10694–10701. [[CrossRef](#)]
33. Jiang, G.; Lin, Z.; Chen, C.; Zhu, L.; Chang, Q.; Wang, N.; Wei, W.; Tang, H. TiO₂ nanoparticles assembled on graphene oxide nanosheets with high photocatalytic activity for removal of pollutants. *Carbon* **2011**, *49*, 2693–2701. [[CrossRef](#)]
34. Bezerra, M.A.; Santelli, R.E.; Oliveira, E.P.; Villar, L.S.; Escalera, L.A. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta* **2008**, *76*, 965–977. [[CrossRef](#)]
35. Box, G.; Behnken, D.W. Some New Three Level Designs for the Study of Quantitative Variables. *Technometrics* **1960**, *2*, 455–475. [[CrossRef](#)]
36. Zuo, J.L.; Li, Y.W.; Li, J.S.; Xia, Z.; Tan, C.; Jiang, L.M.; Sun, Y.Q.; Tian, S.L. Optimized preparation of TiO₂-NTs photoelectrode by response surface method and its property of photocatalytic degradation. *Res. Environ. Sci.* **2020**, *33*, 677–684.
37. Gao, G.Y.; Guo, D.J.; Li, H.L. Electrocatalytic oxidation of formaldehyde on palladium nanoparticles supported on multi-walled carbon nanotubes—ScienceDirect. *J. Power Sources* **2006**, *162*, 1094–1098. [[CrossRef](#)]
38. Tian, G.; Fu, H.; Jing, L.; Xin, B.; Pan, K. Preparation and Characterization of Stable Biphasic TiO₂ Photocatalyst with High Crystallinity, Large Surface Area, and Enhanced Photoactivity. *J. Phys. Chem. C* **2008**, *112*, 3083–3089. [[CrossRef](#)]
39. Zickler, G.A.; Smarsly, B.; Gierlinger, N.; Peterlik, H.; Paris, O. A reconsideration of the relationship between the crystallite size La of carbons determined by X-ray diffraction and Raman spectroscopy. *Carbon* **2006**, *44*, 3239–3246. [[CrossRef](#)]