High Performance COD Detection of Organic Compounds Pollutants using Sulfurized-TiO₂/Ti Nanotubes Arrays Photoelectrocatalyst

Muhammad Nurdin (✉ mnurdin06@yahoo.com)

Universitas Haluoleo <https://orcid.org/0000-0002-6727-9283>

Muhammad Zakir Muzakkar

Maulidiyah Maulidiyah

Trisna Trisna

Zul Arham

La Ode Agus Salim

Irwan Irwan

Akrajas Ali Umar

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Abstract

Photoelectrochemical oxidation processes offer a highly sensitive method to detect organic pollutants from wastewaters. Photoactive semiconducting material is the key factor in this process that accelerates the oxidation of the organic pollutant agent for sensitive detection. Chalcogenide doped TiO_2 system has so far come up as a potential photocatalyst system for photoelectrochemical detection of organic compounds. Here, we report a highly sensitive detection of chemical oxygen demand of organic compound pollutant using sulfurized- TiO_2 (S- TiO_2/Ti) nanotube arrays (NTA) photoelectrocatalyst. S- TiO_2/Ti NTA that is prepared via consecutive anodization of Ti sheet and TiO_2 sulfurization process exhibited a high sensitivity to COD value of organic compounds pollutant, such as Red HE-3B (Reactive Red 120), Red HE-7B (Reactive Red 141), and Blue HE-RD (Reactive Blue 160). Our results indicated that the COD value is linearly correlated with the concentration of the organic compounds and is close to the COD theoretical value, inferring the high accuracy of the detection. This explains that the new S- TiO_2/Ti NTA photoelectrocatalyst effectively enhances the electron transfer dynamic during the electrochemical measurement of an organic pollutant that is reflected by an impressive proportionality of electrochemical current to the concentration of the pollutant sample. The S- TiO_2/Ti NTA promises a highly efficient pollutant detection in the environment.

1 Introduction

The rapid development of the industries can provide many benefits in improving the quality of life, but at the same time, it also generates a serious negative impact on the surrounding environment. This occurs because of in most cases the use of hazardous and toxic chemicals that are produced in large quantities, primarily from industrial waste, particularly textile, medicine, and food industries (1–3). Thus, the effort to develop effective systems that are capable to provide early information on the status of environmental conditions should be continuously demonstrated.

Early detection of organic pollutants in the environment can overcome future serious impacts produced by large concentrations of such toxic compounds. There has been a wide range of approaches available to monitor the quality of the environment, such as gas chromatography, high-performance liquid chromatography, etc (4–6). Nevertheless, photoelectrocatalytic has so far come up as a potential method for the high-sensitive detection of organic pollutant in the environment. The existence of highly active photocatalysts from various classes of semiconducting materials further advances the application of photoelectrocatalytic detection of organic pollutants in the environment. TiO_2 is amongst the most potential material for photoelectrocatalytic application due to its excellent optoelectrical properties and chemical stability (7–10). In addition, its photosensitivity can be modified by doping so that its photosensitivity can be shifted from its original UV region to the visible region (11–13). Potential dopants that show high efficiency in improving the photoelectrical sensitivity of TiO_2 can be from the groups of metal or non-metal, such as iron (Fe) (14, 15), cobalt Co (16), Nickel (Ni) (17, 18), Copper (Cu) (19, 20), silver (Ag) and Manganese (Mn) (21, 22) from metals group and nitrogen (N) (23), sulphur (S) (24),

phosphorus (P) (25) and fluorine (F) (26) from the non-metals group. Non-metals dopant, particularly from the chalcogen, has shown a remarkable effect in enhancing the visible photoactivity of TiO_2 (27). Therefore, a continuous attempt to further advance the non-metals dopant effect on the photoelectrocatalytic of TiO_2 should be demonstrated.

Here, we report the synthesis of sulfur-doped TiO_2 nanotube array for highly sensitive detection of organic pollutants in the environment by measuring the chemical oxygen demand (COD) of the organic pollutant. COD is a measure of the amount of oxygen required (mg/L) to degrade the organic compounds that are contained in water using strong oxidizing agents (28–30). Our results show that the S- TiO_2 NTA photoelectrode can determine COD of Red HE-3B (reactive red 120), Red HE-7B (reactive red 141), and Blue HE-RD (reactive blue 160) test compounds of which the result exhibits excellent linearity with the concentration of the organic compounds. The S- TiO_2 NTA should find extensive application in environmental quality monitoring.

2 Experimental

2.1 Preparation of S- TiO_2 nanotube arrays (NTA)

Preparation of sulphurized TiO_2 (S- TiO_2) NTA was carried out using our previously reported method of a two step-process, namely TiO_2 nanotubes arrays growth and S- TiO_2 coated TiO_2 NTA. Briefly, to prepare the TiO_2 NTA, we applied anodizing method as follow: A Ti plate of length and width of xxx and xxx cm, respectively, was immersed into a reactor that has been filled with an electrolyte solution of 0.27 M NH_4F in 98% glycerol. In the typical process, 0.99 g of NH_4F was dissolved in 4 mL of distilled water. Then, 96 mL of glycerol 98% was added to the solution and mixed by stirring properly. The anodizing process was conducted by placing the Ti plate as an anode and Cu plate as a cathode. We then applied 25 V direct current bias across the two electrodes. The anodizing process was performed for 4 h. Finally, the sample was taken out from the reaction, washed with a copious amount of distilled water, and then annealed at 500°C for 1.5 h. From this process, anatase TiO_2 NTA will be obtained.

We next doped the TiO_2 NTA with S by separately prepared S doped TiO_2 sol-gel and then treated the TiO_2 NTA in the sol-gel solution. The sol-gel of S- TiO_2 was prepared by mixing 15 mL ethanol, 2 mL of distilled water and 2 mL of 1 M glacial acetic acid into a reflux flask containing 4 mL of titanium tetra isopropoxide (TTIP), 0.5 mL acetylacetonate and 15 mL ethanol. The mixture is then refluxed for 3 h at 50°C. After that, 4 mL of 1 M sulfuric acid was added to the reaction to obtain a sulfur-containing TiO_2 sol. The as-prepared sole was then evaporated at room temperature for 48 h and then heated at 80°C for 30 min. Sol-gel was formed from this process. Finally, the S- TiO_2 NTA was obtained by coating the sol-gel onto the NTA by dipping for 5 min in the sol-gel. The sample was then calcined at a temperature of 150°C for 15 min.

2.2 Characterizations

The phase crystallinity of the sample was examined using X-ray diffraction spectroscopy using Bruker D8 XRD spectrophotometer with CuK α irradiation and scan rate 2°/min. The nature of S doping into the TiO $_2$ system was verified by Fourier transformed infra-red (FTIR) spectroscopy. The surface structure of the sample was evaluated with scanning electron microscopy (SEM) technique using FESEM Zeiss Supra 55VP FESEM model. The machine was operated at 3kV and had a resolution of 1.0 nm. It was also equipped with energy dispersive X-ray (EDX) auxiliary for elemental analysis.

2.3 Photoelectrochemical COD detection

Photoelectrochemical detection of organic compound COD was carried out using linear sweep voltammetry (LSV) method with S-doped TiO $_2$ /Ti electrode as working electrode. The counter and the reference electrodes were Cu plate and Ag/AgCl, respectively. During the measurement, we used a direct current bias with applied potential of 0.4 V. The Multi-Pulse Amperometry (MPA) mode was applied during the measurement. We used Xenon lamp with power of xxx Watts as the visible light source and Mercury lamp with power of 15 Watts as the UV light source (wavelength of 360 nm).

2.4 Determination of COD Value

Photoelectrocatalytic COD measurements are based on photoelectrocatalytic reactions that occurs on the surface of catalyst. In this case, the photocatalyst functions as a substitute for chemical oxidizing agents in the dichromate based method. Because the photoelectrocatalytic degradation is carried out in the reactor using an electrochemical system, the degradation time can be reduced and the degradation efficiency can be improved. In the photoelectrolysis method, the output is a photocurrent which is the result of a photocatalytic process that occurs on the surface of catalyst..

During the photoelectrocatalysis, photo current produce from blank sample (electrolyte) (i_{blank}) is small, which is associated with the oxidation of water. Meanwhile, photocurrent generated from the solution containing organic compounds (i_{tot}) is the current from the oxidation of organic compounds and water. Thus, the net photocurrent (i_{net}) obtained from the degradation process of organic compounds is given by (31).

$$i_{\text{net}} = i_{\text{tot}} - i_{\text{blank}} \quad (1)$$

From this relation, we can obtain the net charge (Q_{net}) that is produced from the reaction using the Faraday's law $Q = \int i dt = nFVC$ (3)

Where Q, i, n, F, V and C are charge (coulomb), photocurrent (A), the number of electron transferred, Faraday's constant, sample volume (L), and concentration (Molar), respectively.

The measured Q is the total number of electrons transferred during a complete degradation of the organic compounds in the reaction. The Q value can then be converted to the oxygen demand by considering that one oxygen molecule oxidation is equivalent to four electrons transferred to the photoelectrode surface. Because of strong oxidation ability of photo-generated holes in TiO $_2$ photoelectrode, photocatalytic

oxidation of organic compounds over TiO₂/Ti Nanotube Arrays (TiO₂-NTAs) electrodes will produce a stoichiometry of oxidation reactions of:

Where N and X are each nitrogen and halogen atoms. The concentration of carbon, hydrogen, oxygen, nitrogen, and halogens atoms are represented by y, m, j, k, and q (32).

If organic compounds undergo a complete mineralization, the oxidation of these organic compounds satisfies Eq. (2). Thus, the number of electrons transferred becomes:

$$n = 4y - 2j + m - 3k - q \quad (4)$$

Thus, the net charge according to Faraday's law becomes:

$$Q = nFVC = (4y - 2j + m - 3k - q) FVC = kC \quad (5)$$

(6)

When complete degradation, Q is a measure of the total number of electrons produced from perfect mineralization of all the compounds contained in the sample. This is because one oxygen molecule is equivalent to the electron transferred (in the oxygen reduction reaction: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$), then the Q value can be easily converted into oxygen concentration so that the COD value can be determined by the following equation:

$$[COD](mg.L^{-1}O_2) = \frac{Q}{4FV} \times 32000 \quad (7)$$

3 Results And Discussion

3.1 S doped-TiO₂ Nanotube Arrays (S-TiO₂ NTAs)

We have successfully realized the S doped TiO₂ NTA, its morphology was verified by SEM analysis that will be discussed later, on the surface of Ti substrate following anodizing and S-doped TiO₂ sol-gel coating process. XRD analysis has confirmed the formation of S-TiO₂ NTA prepared in this study. Figure 1 shows the typical XRD pattern of the samples. The XRD pattern exhibits the presence of eight diffraction peaks that can be associated with the anatase TiO₂ as they match well with Crystallography Open Database numbers [96-900-8217], [96-152-8779] and [96-100-8051] for anatase TiO₂. The peak are at 2θ of 24.95; 36.63; 37.40; 47.71; 53.57; 54.79, 62.28 and 69°. According to the standard diffraction for anatase TiO₂ given above, the peaks can be assigned as X-ray diffraction from (0 1 1), (0 1 3), (0 0 4), (0 2 0), (0 1 5), (1 2 1), (0 2 4) and (1 1 6) Bragg planes, respectively. No diffraction peaks related to the

sulfur or its complex with TiO_2 is observed (Fig. 1a). This could be related to an effective substitution of S into the TiO_2 lattice. Nevertheless, it is true that in general the XRD pattern for S- TiO_2 NTA is identical with the pristine TiO_2 NTA (Fig. 1b). However, the successful doping can be probed from the peaks position in S- TiO_2 NTA that are relatively shifted to the right if compared to those of the pristine TiO_2 NTA. This is an indication of lattice modification in the TiO_2 the result of S substitution that in turn causes straining or compressing in the lattice system. Thus, we can further remark that the S- TiO_2 NTA has been realized on the Ti substrate.

We then performed a scanning electron microscopy to analyse the structure and morphology of the sample surface. The results are shown in Fig. 2. Regarding the pristine TiO_2 NTA (Fig. 2a), in accordance with its label, the structure of the sample is composed of tubular structure that are homogeneously distributed over the entire of the surface. The dimension of the tubular structure is approximately 100 to 150 nm for the outer diameter and less than 100 nm for the inner diameter. This morphology is assumed to be promising for catalysis application due to its large-surface area for interaction. Nonetheless, the morphology of the sample changed to a rough and porous film structure after coating the S doped TiO_2 sol-gel on top of the TiO_2 NTA (Fig. 2b). Cracked film structure can also be observed on the sample the result of high-surface tension of the sol-gel during the film drying process. Despite the fact of morphology modification, the S- TiO_2 film should offer large-scale active area the result of vertically oriented coated tubular structure that may be potential for surface reaction.

While the XRD analysis result has provided an impressive indication of successful doping of sulfur into the TiO_2 lattice, we also conducted EDX elemental analysis to verify the presence of dopant element in the samples. Figure 3 shows the EDX elemental analysis result of the sample. As the figure reveals, the S along with the TiO_2 elements are clearly observed. The S elemental peak is seen at the energy of 2.35 keV with Ti and O are each at energy of 4.5 keV and 0.5 keV. Interestingly, the S concentration is almost similar with the O. Considering that there is no individual diffraction peaks of S in the XRD pattern that is related to the interstitial growth process, we remark that the S has effectively substituted the O site of the anatase TiO_2 .

We also further verified the effectiveness of the doping process by conducting a Fourier transform infrared spectroscopy on the sample. The result is shown in Fig. 4. In agreement with the XRD and the EDX analysis result, we also observed the presence of S-O vibration mode in the sample at wave number of $1000\text{--}1250\text{ cm}^{-1}$. The S-O vibration should come from the S substitution in the TiO_2 that binds to O in the lattice. Meanwhile, the TiO_2 phase itself is represented by the Ti-O vibration mode that appeared at the wave number of 1116 and 1153 cm^{-1} (33). However, C-H and O-H vibration modes are also obtained from the results at wave number of 3412 cm^{-1} and 2920 cm^{-1} , which are originated from titanyl group terminal of TiO_2 or water absorbed on the surface of TiO_2 and acetic acid (34), respectively. Thus, this result further confirm the successful doping of S into the TiO_2 system.

The formation of TiO_2 NTA films on the Ti plate surface is due to direct oxidation of Ti substrate. during the anodizing process. The Ti^{4+} ions migrate from the Ti metal to the bulk electrolyte and combine with the F^- ion to form the titanium hexafluoride complex $[\text{TiF}_6]^{2-}$. The decomposition of water that produces O^{2-} and OH^- anions in the reaction will then decompose the Ti complex, releasing F^- anion that flow to the anode direction. This will leave the Ti^{4+} cation to react with oxygen or hydroxyl ions, growing the oxide layer on the surface of Ti substrate. Meanwhile, the S doped TiO_2 formation was the result of hydrolysis of titanium tetra isopropoxide (TTIP) in the presence of S anion from sulphuric acid during the preparation of the sol-gel.

3.2 Photoelectrocatalytic properties of S- TiO_2 /Ti electrode

The photoelectrocatalytic properties of the S- TiO_2 /Ti electrode sample was then evaluated using linear sweep voltammetry (LSV). Figure 5 shows the typical LSV response of the electrode in 0.1 M NaNO_3 under dark and under UV light illumination. As the figure presents, the electrode of pristine TiO_2 NTA and S- TiO_2 NTA show photoactivity under the illumination of the UV light sources that is shown by the existence of current above the horizontal axis of the curve. As also shown in the figure, surprisingly the photocurrent produced by the S- TiO_2 /Ti electrode is approximately 2×10^4 times higher than that produced from the pristine TiO_2 /Ti electrode. This certainly reflects that the S doping to TiO_2 system modifies the photoelectrical properties of the TiO_2 , for example increases the density of state at the conduction band, enabling higher photocurrent generation under UV light irradiation. This is in accordance with the results of our earlier study (31)(35)(36). In addition, the doping may also reduce the band gap due to the formation of impurity level at the band gap near the conduction band edge that can upgrade the photoactivity of the TiO_2 NTA. Thus, enhanced photoelectrocatalytic performance is expected from the S- TiO_2 /Ti electrode.

3.3 Photoelectrical detection of organic compound COD

The photoelectrocatalytic performance of the electrode was then evaluated in the detection of organic compounds of reactive red 120 (Red HE-3B), reactive red 141 (Red HE-7B) and reactive blue 160 (Blue HE-RD). The measurement was carried out using multi-pulse amperometry (MPA) method. This method enables to determine the changes in current in time that is caused by the flow of electrons. The measurement was carried out at a bias potential of 500 mV with the as-prepared electrode as working electrode, Pt wire as counter electrode and Ag/AgCl as reference electrodes. Each test organic compounds were prepared up to four different concentration, namely 1 μM , 3 μM , and 4 μM . Figure 7 shows the typical amperogram of organic compounds samples measured using pristine TiO_2 /Ti NTA working electrode. As can be seen from the figure, the pristine TiO_2 NTA electrode exhibit a linearly increase photocurrent response with the increase of concentration of all the organic compound samples. The results also indicate that the photocurrent value recorded for all the organic sample are relatively similar to each other. A more or less similar results were also obtained from the photoelectrocatalytic detection of these organic samples using S- TiO_2 /Ti NTA electrode (Fig. 8). Nevertheless, as expected, the

S-TiO₂/Ti electrode generates relatively higher photocurrent than that of pristine TiO₂ NTA. This is in excellent agreement with the result presented in Fig. 6.

As the resulting photocurrent is correlated to the charges produced during the oxidation of organic compounds, by using Faraday's law, we can quantify the net charge (Q_{nett}) released by the test compound. Figure 9 shows the relationships between the calculated Q_{nett} and the concentration of the organic compounds samples obtained using pristine TiO₂/Ti NTA and S-TiO₂/Ti NTA electrodes. According to the figure, as expected, the Q_{nett} value obtained from the photoelectrocatalytic degradation of organic compounds over S-TiO₂/Ti NTA electrode is much higher than that of the TiO₂/Ti NTA electrode. This certainly further verifies that the S-TiO₂/Ti NTA electrode much higher photoelectrocatalytic activity than the TiO₂/Ti NTA electrode. This phenomenon is further confirmed by the fact that the Q_{nett} value is close to the theoretical Q_{nett} value if using the S-TiO₂/Ti NTA electrode, reflecting highly photoelectrocatalytic activity of this electrode in the degradation of the organic compounds.

From the Q_{nett} value, the chemical oxygen demand (COD) of the reaction were determined. In a complete degradation reaction, the Q_{nett} value is a measure of the total number of electrons produced from the perfect mineralization of organic compounds. Because one oxygen molecule consumption is equivalent to four electrons transferred, the Q_{nett} can be converted into oxygen concentration by using Eq. 9. We found that the COD of the reaction linearly increase with the increase of the organic compounds concentration in the reaction. In accordance with the value of Q_{nett} of the reaction, the COD value in the photoelectrocatalytic degradation of all organic compounds over S-TiO₂/Ti NTA is higher as well as much closer to the COD theoretical value than that of the pristine TiO₂/Ti NTA electrode (Fig. 10). These results reflect that the S-TiO₂/Ti NTA electrode may offer a better sensitivity and accuracy in determining the COD value of the reaction than the pristine TiO₂/Ti NTA electrode.

4 Conclusion

Photoelectrocatalytic detection of COD in organic compounds degradation over S-TiO₂/Ti NTA electrode has been successfully demonstrated. Photoactivity analysis under UV irradiation indicated that the S-TiO₂/Ti NTA electrode can generate much higher photocurrent than that of the pristine TiO₂/Ti NTA electrode. We also discover that the S-TiO₂/Ti NTA electrode produced photocurrent that is correlated linearly with the concentration of the organic compounds during the photoelectrocatalytic degradation. This is also manifested in the COD value of the reaction. Our result further revealed that the COD value of all organic compounds samples are close to the COD theoretical value, inferring the high accuracy of the detection. This could be the result of enhanced electron transfer dynamic during the electrochemical measurement of the organic pollutant over the photoelectrocatalyst surface that is reflected by an impressive proportionality of electrochemical current to the concentration of the pollutant sample. The S-TiO₂/Ti NTA should find potential application in pollutant detection in the environment.

Declarations

Acknowledgment

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Conflict of Interest Statement

The authors declare that we have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Mani S, Chowdhary P, Bharagava RN. Textile wastewater dyes: toxicity profile and treatment approaches. In: Emerging and Eco-Friendly Approaches for Waste Management. Springer; 2019. p. 219–44.
2. Kaur H, Kainth GS. Mutagenicity Assessment of Textile Dyes Using AMES Test. *Int J Adv Study Res Work*. 2020;3(1):1–6.
3. Natsir M, Putri YI, Wibowo D, Maulidiyah M, Azis T, Bijang CM, et al. Effects of Ni–TiO₂ Pillared Clay–Montmorillonite Composites for Photocatalytic Enhancement Against Reactive Orange Under Visible Light. *J Inorg Organomet Polym Mater*. 2021;1–11.
4. Cernosek T, Eckert KE, Carter DO, Perrault KA. Volatile organic compound profiling from postmortem microbes using gas chromatography–mass spectrometry. *J Forensic Sci*. 2020;65(1):134–43.
5. Zheng F, Zhao X, Zeng Z, Wang L, Lv W, Wang Q, et al. Development of a plasma pseudotargeted metabolomics method based on ultra-high-performance liquid chromatography–mass spectrometry. *Nat Protoc*. 2020;15(8):2519–37.
6. Posselt M, Jaeger A, Schaper JL, Radke M, Benskin JP. Determination of polar organic micropollutants in surface and pore water by high-resolution sampling-direct injection-ultra high performance liquid chromatography-tandem mass spectrometry. *Environ Sci Process Impacts*. 2018;20(12):1716–27.
7. Ritonga H, Basri M, Rembon F, Ramadhan LOA, Nurdin M. High performance of chitosan-co-polyacrylamide-TiO₂ crosslinked glutaraldehyde hydrogel as soil conditioner for soybean plant (*Glycine max*). *Soil Sci Annu*. 2020;71(3):194–204.
8. Maulidiyah M, Susilowati PE, Mudhafar NK diyah, Salim LOA, Wibowo D, Muzakkar MZ, et al. Photo-inactivation staphylococcus aureus by using formulation of mn-n-tio₂ composite coated wall paint. *Biointerface Res Appl Chem*. 2022;12(2):1628–37.
9. Orudzhev FF, Isaev AB, Shabanov NS, Gasanova FG, Idrisova AK, Babaeva DP. Photoelectrocatalytic Oxidation of Phenol on Silver Loaded TiO₂ Nanotube Array at High Oxygen Pressure under Luminescent Light Irradiation. *Int J Electrochem Sci*. 2018;13:4548–60.

10. Muzakkar MZ, Azis T, Rajiani MSP, Maulidiyah M, Irwan I, Mustapa F, et al. The effect of calcogenate sulfur on the performance of the S-TiO₂/Ti electrode as a photoelectrocatalytic sensor for phenolic compounds . J Phys Conf Ser. 2021;1763(1):012069.
11. Nurdin M, Azis T, Maulidiyah M, Aladin A, Hafid NA, Salim LOA, et al. Photocurrent Responses of Metanil Yellow and Remazol Red B Organic Dyes by Using TiO₂/Ti Electrode. In: IOP Conference Series: Materials Science and Engineering. 2018.
12. Gao B, Sun M, Ding W, Ding Z, Liu W. Decoration of γ-graphyne on TiO₂ nanotube arrays: Improved photoelectrochemical and photoelectrocatalytic properties. Appl Catal B Environ. 2021;281:119492.
13. Fatimah I, Nurillahi R, Sahroni I, Muraza O. TiO₂-pillared saponite and photosensitization using a ruthenium complex for photocatalytic enhancement of the photodegradation of bromophenol blue. Appl Clay Sci. 2019;183(February):105302.
14. Maulidiyah, Azis T, Nurwahidah AT, Wibowo D, Nurdin M. Photoelectrocatalyst of Fe co-doped N-TiO₂/Ti nanotubes: Pesticide degradation of thiamethoxam under UV–visible lights. Environ Nanotechnology, Monit Manag. 2017;8.
15. Cheng G, Liu X, Song X, Chen X, Dai W, Yuan R, et al. Visible-light-driven deep oxidation of NO over Fe doped TiO₂ catalyst: Synergic effect of Fe and oxygen vacancies. Appl Catal B Environ. 2020;277:119196.
16. Magdalane CM, Priyadharsini GMA, Kaviyarasu K, Jothi AI, Simiyon GG. Synthesis and characterization of TiO₂ doped cobalt ferrite nanoparticles via microwave method: Investigation of photocatalytic performance of congo red degradation dye. Surfaces and Interfaces. 2021;101296.
17. Nurdin M, Ramadhan LOAN, Darmawati D, Maulidiyah M, Wibowo D. Synthesis of Ni, N co-doped TiO₂ using microwave-assisted method for sodium lauryl sulfate degradation by photocatalyst. J Coatings Technol Res. 2018;15(2):395–402.
18. Opra DP, Gnedenkov S V, Sinebryukhov SL, Gerasimenko A V, Ziatdinov AM, Sokolov AA, et al. Enhancing lithium and sodium storage properties of TiO₂ (B) nanobelts by doping with nickel and zinc. Nanomaterials. 2021;11(7):1703.
19. Natsir M, Maulidiyah M, Watoni AH, Arif J, Sari A, Salim LOA, et al. Synthesis and characterization of Cu-doped TiO₂(Cu/TiO₂) nanoparticle as antifungal phytophthora palmivora. J Phys Conf Ser. 2021;1899(1).
20. Wang M, Zhao Q, Yang H, Shi D, Qian J. Photocatalytic antibacterial properties of copper doped TiO₂ prepared by high-energy ball milling. Ceram Int. 2020;46(10):16716–24.
21. Mursalim LO, Ruslan AM, Safitri RA, Azis T, Maulidiyah, Wibowo D, et al. Synthesis and photoelectrocatalytic performance of Mn-N-TiO₂/Ti electrode for electrochemical sensor. IOP Conf Ser Mater Sci Eng. 2017;267(1).
22. Toshikj N, Politakos N, Veloso A, de San Román EG, Cordero-Lanzac T, Qin Z, et al. Visible light photocatalysts based on manganese doped TiO₂ integrated within monolithic reduced graphene oxide/polymer porous monolith. ChemistrySelect. 2020;5(20):5873–82.

23. Darzi SJ, Mahjoub AR, Sarfi S. Visible-light-active nitrogen doped TiO_2 nanoparticles prepared by sol-gel acid catalyzed reaction. *Iran J Mater Sci Eng*. 2012;9(3):17–23.
24. Park CS, Bangi UKH, Park HH. Effect of sulfur dopants on the porous structure and electrical properties of mesoporous TiO_2 thin films. *Mater Lett*. 2013;106:401–4.
25. Feng X, Wang P, Hou J, Qian J, Ao Y, Wang C. Significantly enhanced visible light photocatalytic efficiency of phosphorus doped TiO_2 with surface oxygen vacancies for ciprofloxacin degradation: Synergistic effect and intermediates analysis. *J Hazard Mater*. 2018;351:196–205.
26. Mukherjee K, Acharya K, Biswas A, Jana NR. TiO_2 nanoparticles co-doped with nitrogen and fluorine as visible-light-activated antifungal agents. *ACS Appl Nano Mater*. 2020;3(2):2016–25.
27. Mathew S, Ganguly P, Kumaravel V, Harrison J, Hinder SJ, Bartlett J, et al. Effect of chalcogens (S, Se, and Te) on the anatase phase stability and photocatalytic antimicrobial activity of TiO_2 . *Mater Today Proc*. 2020;33:2458–64.
28. Wibowo D, Nurdin M. Determination of COD based on Photoelectrocatalysis of FeTiO_3 . TiO_2/Ti Electrode. In: *IOP Conf Ser Mater Sci Eng*. 2017. p. 12007.
29. Nurdin M, Zaeni A, Rammang ET, Maulidiyah M, Wibowo D. Reactor design development of chemical oxygen demand flow system and its application. *Anal Bioanal Electrochem*. 2017;9(4).
30. Nurdin M, Ritonga H, Astria M, Salim LOA, Annisa D, Maulidiyah M. Photocatalytic sensor for chemical oxygen demand flow system using $\text{N-TiO}_2/\text{Ti}$ electrode: Determination of glucose and potassium hydrogen phthalate. *J Phys Conf Ser*. 2021;1899(1).
31. Si H, Pan N, Zhang X, Liao J, Rumyantseva MN, Gaskov AM, et al. A real-time on-line photoelectrochemical sensor toward chemical oxygen demand determination based on field-effect transistor using an extended gate with 3D TiO_2 nanotube arrays. *Sensors Actuators B Chem*. 2019;289:106–13.
32. Zhao H, Jiang D, Zhang S, Catterall K, John R. Development of a direct photoelectrochemical method for determination of chemical oxygen demand. *Anal Chem*. 2004;76(1):155–60.
33. Nam SH, Kim TK, Boo JH. Physical property and photo-catalytic activity of sulfur doped TiO_2 catalysts responding to visible light. *Catal Today*. 2012;185(1):259–62.
34. Jagadale TC, Takale SP, Sonawane RS, Joshi HM, Patil SI, Kale BB, et al. N-doped TiO_2 nanoparticle based visible light photocatalyst by modified peroxide sol-gel method. *J Phys Chem C*. 2008;112(37):14595–602.
35. Liang L, Yin J, Bao J, Cong L, Huang W, Lin H, et al. Preparation of Au nanoparticles modified TiO_2 nanotube array sensor and its application as chemical oxygen demand sensor. *Chinese Chem Lett*. 2019;30(1):167–70.
36. Si H, Zhang X, Lin S. A simple flow injection sensing system for the real-time on-line determination of chemical oxygen demand based on 3D Au-NPs/ TiO_2 nanotube arrays. *Front Mater*. 2019;6:238.

Figures

Figure 1

XRD TiO₂ Spectrum on Ti Plate Surface

Figure 2

Surface morphology of (a) TiO_2 -NTAs) electrodes; (b) S- TiO_2 /Ti-NTAs

Figure 3

Spectra EDX S- TiO_2 /Ti-NTAs composite electrodes

Figure 4

Spectra of FTIR S-TiO₂/Ti-NTAs composite electrodes

Figure 5

(a) Voltamogram of TiO_2/Ti NTAs electrodes in 0.1 M NaNO_3 solution, (b) Volta-mogram of S- TiO_2/Ti -NTAs electrodes in 0.1 M NaNO_3 solution

Figure 6

Photocurrent response NaNO₃ 0.1 M

Figure 7

Amperogram of TiO_2/Ti Nanotube Arrays ($\text{TiO}_2\text{-NTAs}$) electrodes; (a) Red HE-3B (reactive red 120) test compounds, (b) Red HE-7B (reactive red 141) test compounds, and (c) Blue HE-RD (reactive blue 160) test compound.

Figure 8

Amperogram of S-TiO₂/Ti-NTAs electrodes against test compounds; (a) Red HE-3B (reactive red 120) test compounds, (b) Red HE-7B test compounds (reactive red 141), and (c) Red HE-RD (reactive blue160)

Figure 9

Q_{net} relationship to the concentration; (a) reactive red test compounds 120, (b) reactive red 141, and (c) reactive blue 160

Figure 10

The relationship of the concentration of the test compound to PECOD for, (a) reactive red test compounds 120, (b) reactive red 141, and (c) reactive blue 160