Visible Light Photocatalysis of Ni-Deposited TiO₂ Nanotubes for Methyl Orange Degradation in Alkaline Medium

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Abstract The photocatalysis of TiO₂ nanotubes (Ti/TNT) and Ni-deposited TiO₂ nanotubes (Ti/TNT–Ni) for methyl orange degradation was investigated. Methyl orange was selected as the model pollutant, and its photocatalytic degradation was determined in 1 mol/L KOH solution. Ti/TNT was produced by anodizing method, and the electrodeposition of nickel on TNT was performed galvanostatically. The characterization of electrodes was performed by scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray diffraction analysis. The electrochemical behavior of the electrodes was determined by cyclic voltammetry and electrochemical impedance spectroscopy. The irradiation was applied by visible light source ($\lambda = 635$ nm) for 48 h. UV/vis spectroscopy was used for determination of the concentration of methyl orange. Furthermore, after 48-h irradiation, the solutions were analyzed by Fourier transform infrared spectroscopy. Results showed that the concentration of methyl orange decreased from 100 ppm (10^{-6}) to 16 ppm, after 48-h irradiation with the photocatalysis of Ti/TNT–Ni.

KEY WORDS: Photocatalysis; Ni-deposited TiO₂ nanotubes (Ti/TNT–Ni); Methyl orange

1 Introduction

The photocatalytic degradation of organic pollutants has been the subject of a great amount of studies related to air and waste water cleaning [1–4]. Some works highlight a few problems associated with improving the photocatalytic performance of semiconductors [5–9], such as, one-dimensional-nanostructure-based materials for versatile photocatalytic applications, hierarchically CdS decorated 1D ZnO nanorods-2D graphene hybrids which can be synthesized at low temperature and have enhanced photocatalytic performance, surface charge promotes the

synthesis of large, flat structured graphene–(CdS nanowire)–TiO₂ nanocomposites as versatile visible light photocatalysts and composites of titanate nanotube and carbon nanotube as photocatalyst with high mineralization ratio for gas-phase degradation of volatile aromatic pollutant. The titanium dioxide (TiO₂) has received much attention in this area, because of the excellent photocatalytic activity, stability, non-toxicity, low-cost, availability, etc. In many studies, TiO₂ has irradiated by UV radiation in order to degrade liquid and gas-phase pollutants [10–12]. TiO₂ is activated by a mechanism involving radical reactive species, through the following series reactions [3]:

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As a result, active radical species oxidize organic molecules are produced. In addition, the pH value of the solution is an important factor for the degradation of organic molecules [13–15]. Mozia et al. [13] studied the photocatalytic activity of nitrogen modified and calcined (at temperatures of 100–350 °C) TiO₂ toward degradation of 3-chlorophenol (3-CP) under irradiation of fluorescent UV lamp and incandescent lamp emitting mainly visible light. An increase in the calcination temperature resulted in an increase in the rate of $\cdot\text{OH}$ formation. Furthermore, decomposition of 3-CP was influenced by pH of the solution. A visible-light-mediated C-TiO₂ photocatalytic process (Vis/C-TiO₂) was employed by Chen and Chu [14] in order to degrade antibiotic norfloxacin. The influences of catalyst dosage, initial probe compound concentration and pH value were investigated. It was also found that the addition of slight OH[−] anions into the system could accelerate the reaction with producing more radicals. The degradation of neonicotinoid insecticides (thiacloprid and imidacloprid) was investigated by Cernigoj et al. [15]. The photocatalytic ozonation (O₃/TiO₂/UV) was obtained for this purpose. The synergistic effect between ozone and TiO₂ was noticed at acidic and neutral pH.

Catalytic wet air oxidation (CWAO) and solar TiO₂ photocatalysis were investigated to degrade trinitrophenol (TNP) by Katsoni et al. [16]. The commercially available P25 TiO₂ powder was used as a photocatalyst. 100% and 80% TNP degradation obtained after 120 min of irradiation for initial TNP concentrations of 64 and 144 mg/L, respectively. Asiltürk et al. [17] prepared Fe³⁺-doped TiO₂ particles by the hydrothermal process. The undoped and doped TiO₂ particles were examined with respect to their photocatalytic performance for degradation of malachite green (MG) in aqueous solution, under UV and vis-light irradiation. The results showed that photocatalytic performance of Fe³⁺-doped TiO₂ was higher than undoped TiO₂ under UV and visible lights.

However, there are various effective methods have obtained to produce TiO₂ with a convenient structure for photocatalysis applications [18–22], and the anodization process is the simplest technique [23–27]. Liang and Li [23] prepared titanium dioxide nanotube (TNT) by an anodic oxidation process with post-calcination. Photocatalytic activity of the TNT was investigated in terms of the degradation of 2, 3-dichlorophenol (2, 3-DCP) in aqueous solution under UV light irradiation. The results showed that anodized sample (TNT) exhibited better photocatalytic activity than TiO₂, which was prepared by the sol-gel method. Diamanti et al. [28] investigated photocatalytic efficiency of TiO₂ nanotubes in the degradation of

rhodamine B. TiO₂ nanotubes were grown in H₃PO₄/H₂SO₄ mixture also in fluoride containing Na₂SO₄ electrolytes. Several TiO₂ nanotubes were prepared to identify an optimal photocatalyst suitable for wastewater treatment reactors. The photocatalytic efficiency of anatase-enriched TiO₂ was higher in rhodamine B photodegradation. In another study, the photocatalytic degradation of rhodamine B was studied also by Zeng et al. [29]. Amphiphilic TiO₂ nanotubes were fabricated through electrochemical oxidation of Ti in solution containing H₃PO₄ and NaF. They concluded that the TiO₂ nanotubes had the capability of self-cleaning.

In this study, the TiO₂ nanotubes (Ti/TNT) and nano Ni particle-deposited TiO₂ nanotubes (Ti/TNT–Ni) will be produced and utilized as photocatalyst, for degradation of methyl orange (MO) in the alkaline medium under visible light.

2 Experimental

2.1 Preparation of Ti/TNT and Ti/TNT–Ni

TiO₂ nanotubes (TNT) were prepared following the previous work [30]. The cylindrical titanium (99.9% purity) had 0.785 cm² surface area. Ti electrodes were anodized in a two-electrode system with a platinum cathode in 0.1 mol/L HF solution at room temperature, 17.5 V applied for 30 min. The electrodeposition of nickel was performed galvanostatically using Iviumstat electrochemical interface (with serial number AO6063) with a three-electrode configuration. In this system, anodized titanium (Ti/TNT) was used as the working electrode, nickel (Ni) as the counter electrode and Ag/AgCl (3 mol/L KCl) electrode as the reference electrode. The 100 µg/cm² Ni was deposited on Ti/TNT electrode surface.

2.2 Characterization of Electrodes

The surface morphology of electrodes (Ti, Ti/TNT and Ti/TNT–Ni) was investigated by the scanning electron microscope (SEM). The SEM images were taken using a Leo 440 SEM instrument at high vacuum and 20.00 kV. The chemical composition of the electrode surfaces was determined by energy-dispersive X-ray spectrometer (EDX) which is part of SEM device. The X-ray diffraction (XRD) patterns of electrodes were recorded on a Bruker AXS D8 with CuK_α radiation (λ = 0.15406 nm) in the 2θ range of 10°–90°.

2.3 Electrochemical Behavior of Electrodes

The electrochemical behavior of electrodes was investigated by using a CHI 604A electrochemical analyzer

(serial number 6A721A). The counter electrode was a platinum sheet (with 2.0 cm² surface area), and the reference electrode was Ag/AgCl (3 mol/L KCl). The experimental tests were performed in 50 mL 1 mol/L KOH solution in the absence and presence of MO after 1-h immersion. In each experiment, a freshly prepared solution was used. The test solutions were opened to the atmosphere, and the temperature was 298 K which was controlled with thermostat (Nuve BS 302 serial number 03-0033). The cyclic voltammetry measurements were carried out in the potential ranges between −1.4 and 2.0 V with a scan rate of 0.1 V/s. The EIS experiments were employed at 0.8 V between 100 kHz and 0.006 Hz, and the amplitude was 0.005 V. The EIS parameters were calculated by fitting the experimental results to an equivalent circuit using Z-View software.

2.4 Photocatalytic Degradation

The initial concentration of methyl orange (C_{MO}) was 100 ppm in 1 mol/L KOH. Photocatalytic decomposition of MO was carried out in a glass beaker containing 50 mL solution. Ti, Ti/TNT, Ti/TNT–Ni electrodes were immersed in a glass beaker for 48 h. All samples were irradiated by visible light source (FA-373-FB-002-SM, $\lambda = 635$ nm). The concentration of methyl orange was determined by UV–vis spectrophotometer (Shimadzu RX 1 UV–VIS system, serial number A10934502639CD) during

the irradiation period. After 48-h irradiation, all solutions were analyzed by FT-IR spectrophotometer (Nicolet iS10 Thermoscientific, serial number AKX1200282).

3 Results and Discussion

3.1 Characterization of the Electrodes

Figure 1 shows the surface morphology of Ti, Ti/TNT and Ti/TNT–Ni before irradiation. The smooth, untreated Ti surface is observed in Fig. 1a. It can be found from Fig. 1b that TiO₂ nanotubes on Ti surface are well-ordered and uniform. The pore size is between 5 and 10 nm. In Fig. 1c, deposited Ni particles are located in the outside the mouth of the TiO₂ nanotubes, and the Ni particles are spherical and quite similar to each other with sizes in the range of 50–150 nm.

The surface micrographs of all electrodes after 48-h irradiation in MO + KOH solutions are presented in Fig. 2. It can be concluded that the alkaline medium influenced the electrodes, and several damages were detected which due to corrosion. In Fig. 2a, corrosion products disperse heterogeneously on Ti surface. Deformations and cracks are seen in Fig. 2b, and oxide particles are plugged into the TNT's mouth. Other sides, TNT–Ni surface was less influenced than the others (Fig. 2c).

Fig. 1 SEM images of Ti **a**, Ti/TNT **b** and Ti/TNT–Ni **c** electrodes before immersion, the *insets* are the cross-sectional views [25]

Fig. 2 SEM images of Ti **a**, Ti/TNT **b** and Ti/TNT–Ni **c** electrodes after 48-h irradiation

Fig. 3 EDX spectra of Ti **a**, Ti/TNT **b** and Ti/TNT–Ni **c** electrodes after 48-h irradiation

Figure 3 shows the EDX results of the electrodes after 48-h irradiation. The oxygen peak was detected in Ti electrode analysis, and the concentration of O was 43.75 wt% which means the titanium was oxidized in alkaline medium and TiO_2 was formed on the surface spontaneously (Fig. 3a). By comparing the surface morphology before (Fig. 1) and after (Fig. 2) immersion, the differences are easily spot, which can be correlated to the EDX results. In Fig. 3b, the concentration of O is higher (46.85 wt%) than bare Ti surface, because the anodizing process improved the oxide layer on Ti. In Fig. 3c, the Ni peaks are detected which illustrate that nickel was deposited on the surface of Ti/TNT.

Figure 4 presents the XRD patterns of the electrodes after 48-h irradiation. In Fig. 4a, the XRD peaks appear at $2\theta = 35^\circ, 40^\circ, 53^\circ, 63^\circ$ and 77° in bare Ti surface after 48-h irradiation in $\text{MO} + \text{KOH}$ solution, indicated that the untreated Ti has a hexagonal structure [31]. In Fig. 4b, peaks were seen at $28^\circ, 36^\circ, 38^\circ, 40^\circ, 53^\circ, 63^\circ$ and 77° , as Thamaphat et al. [32] suggested that peaks at $27^\circ, 36^\circ$ and 55° indicate rutile phase and at 25° and 48° indicate anatase phase. The XRD pattern of Ti/TNT–Ni electrode is presented in Fig. 4c. The peaks appeared at $29^\circ, 35^\circ, 39^\circ, 40^\circ, 45^\circ, 54^\circ, 64^\circ, 71^\circ$, and 78° . The peak at 45° indicated the presence of face centered cubic Ni particles.

3.2 Electrochemical Behavior of Electrodes

The cyclic voltammograms of Ti, Ti/TNT and Ti/TNT–Ni in the absence and presence of 100 ppm MO in 1 mol/L KOH solution are presented in Fig. 5. For Ti electrode, in the absence of MO, the anodic current density increased up to 0.8 V (Ag/AgCl, 3 mol/L KCl), it signals the formation of oxide (Fig. 5a). In the presence of MO, higher anodic current density values were detected in 0.8–2.0 V potential range which illustrates the oxidation of MO molecules. In Fig. 5b, in the forward scan, prolate anodic peaks were detected in the absence and presence of MO, between 0.1 and 2.0 V. According to Ref. [33], it was assigned the $\text{Ti}^{2+}/\text{Ti}^{3+}$, $\text{Ti}^{2+}/\text{Ti}^{4+}$ and $\text{Ti}^{4+}/\text{Ti}^{6+}$ redox transitions.

In Fig. 5b, the current density values were 0.32 and 0.44 A/cm^2 at 2.0 V, in the absence and presence of MO, respectively. The higher current density proved the oxidation of MO. In Fig. 5c, peak at -0.7 V , signaled to Ni/Ni^{2+} oxidation. The transformation of $\alpha\text{-Ni(OH)}_2$ to $\beta\text{-Ni(OH)}_2$ occurred between the potential range of -0.5 – 0.3 V . The peak at 0.4 V corresponded to the $\text{Ni}^{2+}/\text{Ni}^{3+}$ transition. The cyclic voltammograms showed that the anodic current density increase, which was illustrated with MO oxidation, followed the order: $\text{Ti/TNT–Ni} > \text{Ti/TNT} > \text{Ti}$. Consequently, fabrication of TNT and deposition of nano Ni particles on it, enhanced the catalytic efficiency of Ti.

The cyclic voltammograms showed that 0.8 V was a convenient potential for investigation of electrochemical degradation of MO. Ranking the electrocatalytic effect of electrodes for MO degradation, EIS measurements were achieved at 0.8 V.

The Nyquist plots of all electrodes which were obtained in 1 mol/L KOH solution in the absence and presence of MO are presented in Fig. 6. The depressed semi-circular shape was seen in plots, which indicates a charge-transfer process mainly controlled the reaction [34]. The diameter of Nyquist plot which was attributed a polarization resistance (R_p) and it increased with the presence of MO due to adsorption of molecules on the electrode surface. The lower R_p was detected for Ti/TNT–Ni which showed that photocatalytic degradation performance of titanium was enhanced with producing TNT–Ni layers. Maheswari and Venkatachalam [35] determined the parallel results in the electrochemical impedance spectra of the composite TNTs/TNPs (TiO_2 nanotubes with TiO_2 nanoparticles) film-based dye-sensitized solar cells (DSSCs), which had the lowest charge-transfer resistances and the longest electron lifetime. They concluded that the composite photoanode facilitated the charge transport rate and enhanced the efficiencies of DSSCs [35].

The EIS results were fitted according to the equivalent circuit (inset of Fig. 6). The R_s is the solution resistance, CPE is the constant phase element which is used in place of

Fig. 4 XRD spectra of Ti **a**, Ti/TNT **b** and Ti/TNT–Ni **c** electrodes after 48-h irradiation

double-layer capacitance (C_{dl}) to give non-ideal capacitive behavior. The capacitance fitted with using CPE, then it exchanged to C_{dl} [34].

$$Z_{CPE} = \frac{1}{Y_o(J\omega)^n} \quad (7)$$

where Y_o and n are frequency independent parameters and $-1 \leq n \leq 1$, ω is angular frequency for which imaginary part of the impedance $-Z''$ reaches it maximum.

$$\omega = \left(\frac{1}{R_{ct}Y_o} \right)^{1/n} \quad (8)$$

Double-layer capacitance (C_{dl}) should be given as:

$$C_{dl} = \frac{Y_o\omega^{n-1}}{\sin(n\pi/2)} \quad (9)$$

The calculated C_{dl} values are given in Table 1. It can be found that the C_{dl} values decrease due to decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer.

UV spectra of MO + KOH solutions are presented in Fig. 7. The peak between 550 and 350 nm is attributed the MO and the absorption decreased with decreasing MO concentration. The lowest MO concentration was determined for Ti/TNT–Ni electrode. The results show that photocatalytic performance of Ti/TNT–Ni for the degradation of MO is higher than that of Ti/TNT under visible light. Asiltürk et al. [17] affirmed that the photocatalytic activity of TiO_2 was improved by doping with various metal or non-metal ions. Liu et al. [36] suggested that Cu species with smaller band gap and higher work function than bare TiO_2 facilitates the light harvesting and charge carrier separation in samples and are highly regarded to improve photocatalytic reaction efficiencies. Furthermore, a uniform dispersion of the dopant on TiO_2 facilitates migration of electrons from its conduction band to that of CuO and improves the photocatalytic activity [36]. Consequently, metal ion dopants may act as electron or hole traps and, consequently, alter electron–hole pair recombination rates.

The irradiation time versus the MO concentration (C_{MO}) curves are given in Fig. 8. The C_{MO} decreases with the irradiation time increases. According to Eqs. (1–6), during the irradiation, active radical species occurs and oxidize the organic molecules. The Ni-doped TNT could product higher radicals than TNT. Therefore, minimum C_{MO} detected for Ti/TNT–Ni. Barka et al. [37] illuminated the TiO_2 particles by UV light ($\lambda = 365$ nm) for photocatalytic degradation of MO. Their results showed that 20 ppm MO concentration decreased to almost 0 ppm after 14 h UV irritation. In this study, we applied visible light, 100 ppm MO decreased to 63, 45 and 16 ppm after 48 h irritation, by Ti, Ti/TNT and Ti/TNT–Ni electrodes, respectively.

Fig. 5 Cyclic voltammograms of Ti **a**, Ti/TNT **b** and Ti/TNT–Ni **c** electrodes in the absence (open circle) and presence (filled circle) of 100 ppm MO in 1 mol/L KOH

Fig. 6 Nyquist plots of Ti (filled circle, open circle), Ti/TNT (filled square, open square) and Ti/TNT–Ni (filled triangle, open triangle) at 0.8 V (vs. Ag/AgCl) in the absence **a** and presence **b** of 100 ppm MO in 1 mol/L KOH, where the solid lines are the fitted lines, and the electrical equivalent circuit diagram in **a** is used to modeling the metal/solution interface

Table 1 Equivalent circuit elements for electrodes in 1 M KO in the absence and presence of 100 ppm MO

Electrode	KOH			MO + KOH		
	R_p (Ω/cm^{-2})	n	C_{dl} ($\mu\text{F}/\text{cm}^2$)	R_p (Ω/cm^{-2})	n	C_{dl} ($\mu\text{F}/\text{cm}^2$)
Ti	22,104	0.95	75.69	44,379	0.94	32.68
Ti/TNT	16,959	0.94	23.51	37,569	0.92	24.67
Ti/TNT–Ni	9920	0.94	5.01	2009	0.60	21.40

The degradation mechanism of MO is very complex. In the degradation mechanism which was clarified by Baiocchi et al. [38], several degradation products occur:

The active radical species, [Eq. (6)], oxidize the MO molecule. The reaction products are several organic radical molecules ($\cdot\text{C}_a\text{H}_b\text{N}_c\text{S}_d\text{O}_e$) and totally oxidized species (CO_2 , H_2O and SO_4^{2-}) [38, 39].

After 48-h irradiation, all electrodes were removed from the solutions, and then, the solutions were analyzed with FTIR spectroscopy technique. In order to compare the peak intensities and wave numbers, 100 ppm MO containing 1 mol/L KOH solution was illuminated under electrodeless condition, and the results are presented in Fig. 9. The peaks belong to SO_3^- , $\text{N}=\text{N}$, para-substituted benzene ring and tertiary amine are seen at 885, 1550, 1656 and 2980 cm^{-1} , respectively, according to the results in Refs. [39, 40]. The peaks intensities decreased with the decrease in C_{MO} . According to results, the photocatalytic efficiency of electrodes followed the order: Ti/TNT–Ni > Ti/TNT > Ti.

Fig. 7 UV spectra of MO + KOH solution after 48-h irradiation under the conditions of without electrode, with Ti, Ti/TNT and Ti/TNT-Ni electrodes

Fig. 8 Methyl orange concentration as a function of irradiation time

Fig. 9 FTIR spectra of MO + KOH solutions after 48-h irradiation under the conditions of without electrode, with Ti, Ti/TNT and Ti/TNT-Ni electrodes

4 Conclusions

1. 5- to 10-nm pore-sized, uniform, well-ordered TNT and nano Ni particle-deposited TNT electrodes were produced.

2. After 48-h irradiation, oxygen peak was detected in the EDX spectrum of Ti, which was a signal of self-ordered oxide film. The higher peak intensity was seen in Ti/TNT spectrum due to anodic oxide film. The Ni peak was determined in Ti/TNT-Ni spectrum, which proved the Ni particles were deposited over Ti/TNT.
3. The TNT was found to be of mixed structure (rutile and anatase) in XRD analysis.
4. The electrochemical measurements showed that photocatalytic performance of Ti/TNT-Ni was higher than Ti and Ti/TNT.
5. After 48-h irradiation, the MO concentration decreased from 100 to 16 ppm by Ti/TNT-Ni.
6. The FT-IR results proved that the photocatalytic efficiency of electrodes ordered as: Ti/TNT-Ni > Ti/TNT > Ti.

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