Preparation and characterisation of bismuth-doped TiO₂ nanotubes (Bi–TiO₂–NT) and its photocatalytic activity test for rhodamine B elimination under visible light

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Abstract. As a photocatalyst, TiO₂ nanotubes can effectively degrade dyes; thus, they exhibit a considerable potential to mitigate the problem of river pollution by dye waste originating from the textile industry. However, with a band gap of 3.2 eV (UV light energy range), such nanotubes cannot be completely utilizing under visible light from the sun. Therefore, in this study, the TiO₂ nanotubes are modified using bismuth to obtain bismuth-doped TiO₂–NT (Bi–TiO₂–NT), which exhibits an activity under visible light. Bi–TiO₂–NT was successfully synthesized by one-step anodization with Bi(NO₃)₃ as the dopant source. The optimum synthesis conditions obtained were as follows: 1.0 M Bi(NO₃)₃ in an ethylene glycol electrolyte with anodization at 40 V for 1 h. In this study, the synthesized photocatalyst was characterized using X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), UV–Vis Diffuse Reflectance Spectroscopy (DRS), Scanning Electron Microscopy–Energy Dispersive X-Ray Spectroscopy (SEM-EDS), and Linear Sweep Voltammetry (LSV). The results of the photocatalytic activity test indicated that under visible light illumination the prepared Bi–TiO₂–NT was able to eliminate rhodamine B from the tested water, better than bare TiO₂.

1. Introduction

Human activity has triggered an extensive environmental pollution, especially related to water. One of the main sources of aquatic pollution is the textile industry, which commonly disposes the waste of textile dye into various rivers. Traditional methods for dealing with water pollution by such dyes, e.g., flocculation, carbon adsorption, reverse osmosis, and activated sludge processes, may help at some level to overcome the problem, but are not considered to be highly effective yet [1].

Rhodamine B is a commonly used dye in the textile industry. It is highly soluble in water with a bluish-red color and is a potential pollutant of the aquatic environments. Rhodamine B is a carcinogenic substance, a mutagen, and causes teratogenesis in rats; therefore, it is a potential threat to the human health. Furthermore, its stability and resistance to biological or chemical degradation increases its potential detrimental effect on environmental health [2].

Recently, several researchers have proposed photocatalysts method as solutions to the problem of environmental pollution because they are capable of degrading the organic compounds via the process of photo degradation. So far titanium dioxide has been proved to be the most suitable photocatalysts for environmental applications since its chemical inertness, has a strong oxidizing potential, low cost and long-term stability [3]. However, TiO₂ exhibits less responsive to solar light that reach earth surface, due to its wide band gap energy (3.0–3.2) eV [2–4]. A bare TiO₂ exhibits a high recombination rate between electron (e⁻) and hole (h⁺) pairs [2], that lead to another weakness. In responding to that problems, many researchers attempted to modify the bare TiO₂ by doping the TiO₂, with other elements, such as N, S, C, I, Br, and Cl. Their efforts reveal some type of doped TiO₂,
which has the optical band gap narrower than that of the bare one, hence shifted its respond toward the visible light [4]. Some of the works of photocatalysis under visible light have focused on the bismuth as the dopant. Bismuth oxide nanomaterial itself is suitable to be used as a photocatalyst, since it has narrow band gap (1.8–2.4) eV, non-toxic nature, high chemical stability. The combination of bismuth on the surface of TiO2, may act as a sensitizer and act as a trap for the photo-generated e−, thus reducing the recombination of e− and h+ pairs and enhancing the photocatalytic activity of TiO2 under visible light irradiation [2].

A combination of anodization to prepare the TiO2 nanotubes (TNT) and a sol gel process [3], electrospinning [6], hydrothermal deposition [5] and dip-coating [7] to incorporate the bismuth species in to TNT has reported in the literature. These TNT modifications were performed in a two-step process, beginning with anodization of TNT followed by bismuth doping. To improve this two-step experimental process, Ali et al. [2] proposed a one-step synthesis method, which over an advantages, such as low energy consumption and requires less time.

In the preparation of a TiO2–NT (TNT) via the anodization method, a Pt electrode is typically used as the counter electrode due to its inertness. However, Pt electrodes are expensive, thus it is worthy to find other electrode as an alternative, such as stainless-steel, which is much more cheaper and at some level is quite inert [8].

In this study, we prepared bismuth-doped TiO2 nanotubes (Bi–TiO2–NT) using a one-step electrochemical anodization method with a stainless-steel counter electrode. Bismuth was doped onto the TiO2–NT using bismuth nitrate at different concentrations, anodization times, and pH values. The obtained Bi–TiO2–NT photocatalyst was characterized and tested its photocatalytic (PC) degradation activity toward rhodamine B under UV and visible light irradiation.

2. Experimental method

2.1. Material and chemicals
The materials used were as follow Ti sheet (1.5 × 4 cm), deionized (DI) water, NH4F (Merck), NaNO3 (Merck), ethylene glycol (Merck), a Pt electrode, ethanol absolute, acetone, an Ag/AgCl electrode, a stainless-steel electrode, rhodamine B, and Bi(NO3)3H2O. All the chemicals were of analytical grade and were used as received.

2.2. Preparation of Bi–TiO2–NT
The Ti sheet was brushed, cleaned, and sonicated in acetone, ethanol, and DI water for 10 min each to remove impurities. The electrolyte solution used was comprising of ethylene glycol with 0.3 wt.% NH4F, 2 wt.% DI water, and various bismuth nitrate concentrations. Ti foil was used as an anode and stainless-steel as a cathode. Anodization was performed at 40 V and various times (1–2) h using a power supply. Then, the Ti foil was annealed in a furnace for 2 h at 450 °C to obtain the anatase phase.

2.3. Characterization
The prepared photocatalyst was characterized with X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), UV–Vis Diffuse Reflectance Spectroscopy (DRS), Scanning Electron Microscopy–Energy Dispersive X-Ray Spectroscopy (SEM-EDS), and Linear Sweep Voltametry (LSV).

2.4. Photocatalysis activity tests
Photocatalytic activity tests were used to assess the photodegradation of rhodamine B. The rhodamine B solution to be degraded had a concentration of 0.3 ppm. Photodegradation was carried out for various treatments under 100 W visible light and 15 W UV lamps in a special reactor at the laboratory scale. The degradation of rhodamine B was monitored by using a UV–Vis spectrophotometer every 10 minutes for 1 h.

3. Results and discussion

3.1. Samples characterizations
The diffractograms obtained for TiO$_2$–NT and Bi–TiO$_2$–NT that had been calcined at 450 °C for 2 h are shown in figure 1a and figure 1b, respectively. The typical peak of the anatase crystals is seen at position at 2θ of 25.281°, 48.050°, 53.801° (JCPDS No. 00-021-1272), are consistently observed. No peaks related to Rutile and brookite are observed. It is shown in figure 1b, that none of the peaks represents the crystals of Bi$_2$O$_3$, as reported by Ali et al. [2] are observed. This may be due to the thinness of the Bi$_2$O$_3$ crystal layer, meaning it cannot be detected properly. There is a decrease in the intensity and peak shift of the anatase structure of TiO$_2$; this result is possibly due to the formation of a Bi–O–Ti bond [3,9]. Based on the calculations, the obtained crystallite anatase phases of TiO$_2$ without doping and of Bi–TiO$_2$–NT were 38.814 nm and 31.167 nm, respectively.

The FT–IR results in figure 2 show that there is some absorption at wavenumbers 400–550 cm$^{-1}$, 600–850 cm$^{-1}$, 1500–1700 cm$^{-1}$, and 3000–3600 cm$^{-1}$, representing the deformation and stretching of O–H bonds. Also observed are the additional peaks that are present in both spectra at 1500–1700 cm$^{-1}$ and 3000–3600 cm$^{-1}$, representing the vibration of the Ti–O–Ti bond of the octahedral TiO$_2$. Wavenumber 600–850 cm$^{-1}$ represents the vibration of the Ti–O–Ti bond of the octahedral TiO$_2$. Also observed are the additional peaks that are present in both spectra at 1500–1700 cm$^{-1}$ and 3000–3600 cm$^{-1}$, representing the deformation and stretching of O–H bonds.

Regarding the Bi–TiO$_2$–NT FT–IR spectrum, different peaks observed in the region of 400–550 cm$^{-1}$ wavenumber; this is attributable to stretching of the Bi–O bonds [10]. This indicates that bismuth doping on TiO$_2$ was successfully performed. The other absorption is thought to be an impurity in the form of carbon elements.

The UV–Vis DRS (figure 3) reveals a quite different reflectance pattern, between bare TiO$_2$ and the doped TiO$_2$, which indicates that the Bi–TiO$_2$–NT shows more responsive toward visible light that
Figure 3. DRS UV-Vis spectra of (a) bare TiO$_2$-NT and (b) doped TiO$_2$ (Bi-TiO$_2$-NT)

Figure 4. SEM images of (a) bare TiO$_2$-NT and (b) doped TiO$_2$ (Bi-TiO$_2$-NT)

of bare TiO$_2$-NT. The optical band gap derived from the UV-DRS spectra, via a well-known Tauc Plot, are 3.12 eV and 2.6 eV for bare TiO$_2$-NT and Bi–TiO$_2$–NT respectively. The reduction of the energy gap upon bismuth doping may indicate the involvement of valence electron structure of bismuth, on the metal oxide from work. Since the valence electron of bismuth orbital is lower than that of the conduction band of the Ti 3d orbitals, this may result in narrowing the Bi–TiO$_2$–NT photocatalytic gap band. As such, the photo generated electrons will be captured by Bi present on the surface of TiO$_2$ [2].

The images in figure 4 show that the tubes formed were not very uniform/homogeneous, but it is well distributed. This may have been due to an unstable electricity source. Therefore, the mobilization of F ions that play a role in TiO$_2$ dissolution was irregular. The inner diameter of the nanotubes formed for TiO$_2$-NT and Bi–TiO$_2$–NT have mean diameters of approximately 62.5 nm and 52.6 nm, respectively.

The results of elemental analyses TiO$_2$–NT and Bi–TiO$_2$–NT by EDS are shown in table 1. Both TiO$_2$–NT and Bi–TiO$_2$–NT contain oxygen and titanium. However, from the EDS characterization results, it can be seen that bismuth was also present in Bi–TiO$_2$–NT but not in TiO$_2$–NT. This indicates that bismuth was successfully doped on the TiO$_2$–NT at 0.68%. The observed carbon is thought to be originated from contamination during photocatalytic preparation stage.
Table 1. Elemental analyses of the EDS spectra of TiO$_2$–NT and Bi–TiO$_2$–NT.

|        | Ti  | O    | Bi  | C   |
|--------|-----|------|-----|-----|
| TiO$_2$–NT | 34.03 | 65.97 | -   | -   |
| Bi–TiO$_2$–NT | 32.98 | 62.05 | 0.68 | 4.29 |

Figure 5. LSV patterns of (a) bare TiO$_2$–NT and (b) doped TiO$_2$ (Bi–TiO$_2$–NT)

Figure 6. Photocatalytic degradation of rhodamine B (0.3 ppm in water) under UV and visible light.

Figure 5 shows the photocurrents measurement results for the prepared photocatalyst obtained using the LSV method. For TiO$_2$–NT, the current density values obtained without a potential bias were approximately 99.745 $\mu$A/cm$^2$ and 0.649 $\mu$A/cm$^2$ under UV and visible illumination, respectively. While for Bi–TiO$_2$–NT, the values were approximately 81.499 $\mu$A/cm$^2$ and 6.194 $\mu$A/cm$^2$ under UV and visible illumination, respectively. It is evidenced that doping bismuth on the bare TiO$_2$ increases the visible light responds up approximately 10 times higher (from 0.649 to 6.194 $\mu$A/cm$^2$).

3.2. Photocatalytic activity test

Figure 6 shows the decreasing concentrations observed over time in each rhodamine B photocatalytic degradation test. The decreasing rhodamine B concentrations in the photocatalytic tests follow the order of TiO$_2$–NT (UV) > Bi–TiO$_2$–NT (UV) > Bi–TiO$_2$–NT (visible) > TiO$_2$–NT (visible). This
evidence demonstrates that the bismuth doped TiO$_2$–NT (Bi–TiO$_2$–NT) resulted the shift photocatalytic activity toward visible light, even though both photocatalyst give more high activity under UV light.

4. Conclusions
Bi–TiO$_2$–NT was successfully prepared by using a one stage anodizing method followed by a heat treatment. The prepared photocatalyst has an anatase phase, crystallite size of 31.167 nm and energy gap of 2.6 eV. The Bi–TiO$_2$–NT showed a better photocatalytic activity toward rhodamine B, under visible light illumination than that of bare TiO$_2$–NT. Therefore, it can be concluded that doping the bismuth on the TiO$_2$ shifted the photocatalytic activity of TiO$_2$–NT to the visible light range.

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