Multi Application Studies of Bi₂0₃-Tio₂ Nanocomposite Material Synthesized By Precipitation Method and Sonication Technique

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Received: 21 Novemberr 2018 / Received in revised form: 22 March 2019, Accepted: 28 March 2019, Published online: 12 April 2019 © Biochemical Technology Society 2014-2019 © Same Educational Society 2008

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Abstract

The Bi₂O₃-TiO₂ nanocomposite material were prepared by the precipitation method and sonication technique, and used Rhodamine 6G (Rh 6G) under UV-Light on 365 nm in the elevated photocatalytic activity of Bi2O3-TiO2that TiO2. The nanocomposite material was characterized by high-resolution scanning electron microscopy with elementary dispersive X-ray, high-resolution transmission electron microscopy, X-ray diffraction method, photoluminescence spectroscopy, and diffuse reflectance spectra. This nanocomposite material was used for photodegradation of Rh 6G dye at various parameters. The mineralization of dyes is confirmed by chemical oxygen demand measurements. An achievable mechanism is proposed for higher activity of Bi₂O₃-TiO₂ than that of TiO₂ nanocomposite material. This nanocomposite material was found to be stable and reusable. This Bi₂O₃-TiO₂ nanocomposite material had higher photocatalytic, antibacterial, and electrochemical activities than that of TiO₂.

Keywords: Rh 6G dye, Catalyst, Antibacterial activity, electrochemical activity.

Introduction

The Semiconduct oxide (CdO, TiO₂, ZnO, SnO₂ and Bi₂O₃), is an exceptional good and high photocatalyst, medicine and sensing for optoelectronic applications (Balachandran et al., 2014; Kalele et al., 2006; Manikandan, udithVijaya and Kennedy, 2013; Elbaramawi et al., 2018; Loganathan et al., 2014; Murugavelu and Karthikeyan, 2013; Yatmaz, Akyol and Bayramoglu, 2004; Lam et al., 2012; Cho et al., 2011). The high photocatalytic activity of a multisemiconct oxide system also depends on the synthetic procedure and their compositions. TiO₂/WO, TiO₂/MoO₃, TiO₂/SiO₂ and TiO₂/ZrO₂ have photocatalytic properties (Mahmoud et al., 2017; Mohamed and Ahmed, 2018;

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Do et al., 1994; Papp et al., 1994; Fu et al., 1996). Bi2O3 (Bismuth oxide) -doping Semiconduct oxide has very high photacatalytic activity (Tanmay K., Ghorai R., Niladri, 2013; El-Hashash et al., 2017; Muruganandham et al., 2012; Xie et al., 2013). In the cloth industry with about 10,000 dyes and pigments, azo dyes correspond to the common and most significant class of commercial dyes and environmental problems such as remediation of organic contaminants and damage of microbes (Balachandran and Swaminathan, 2012; Soliman et al., 2018; Clonts and McKetta, 1978; Subash et al., 2013; Fujishima and Honda, 1972). Rh 6G dye molecule very stability of modern dye complete degradation of dyes (Guo et al., 2011; Li et al., 2011). The present article studies high photocatalytic, antibacterial and electrochemical activity. The nanocomposite material was characterized by high-resolution scanning electron microscopy with elementary dispersive X-ray, high-resolution transmission electron microscopy, X-ray diffraction method, photoluminescence spectroscopy and diffuse reflectance spectra. The photodegradation of Rh 6G dye at various parameters are reported. The mineralization of dyes is confirmed by chemical oxygen demand measurements. An achievable mechanism is proposed for higher activity of Bi2O3-TiO2 than that of TiO2 nanocomposite material. This nanocomposite material was found to be stable and reusable. This Bi2O3-TiO2 nanocomposite material had higher photocatalytic, antibacterial, and electrochemical activities than that of TiO2.

Experimental Section

Materials

The synthesis of Bi₂O₃-TiO₂ nanocomposite material: Bismuth nitrate penta-hydrate, nitric acid, NH₄OH, Rhodamine 6G (Rh 6G) dye and ethanol solution were from Sigma Aldrich company, and were used as such, or solutions were prepared by using deionized water.

Preparation of Bi2O3-TiO2 nanocomposite material by precipitation method

The Bi_2O_3 -TiO₂ nanocomposite material was synthesized by precipitation method. Initially Bismuth nitrate penta-hydrate was dissolved in anhydrous ethanol (solution A), and tetraisopropyl

orthotitanate in ethanol was taken as solution B. The solution A was added to beaker containing Solution B and stirred well. The pH of the solution was adjusted to about 9 by the addition of nitric acid. 5 mL NH₄OH was added to the solution at room temperature under vigorous stirring until the precipitate formed. The obtained precipitate was filtered and washed with water and ethanol. Then the precipitate was collected and dried on oven at 100 °C for 12 hrs. The resulting powder was finally calcinated at 450 °C for 4 hrs (Scheme 1).

Characterization

Ultraviolet and visible (UV-vis) absorbance spectra were measured over a range of 800-200 nm with a Shimadzu UV-1650PC recording spectrometer using a quartz cell with 10 mm of optical path length. High resolution Scanning Electron Microscopy (HR-SEM) as well as Elementary Dispersive X-ray (EDX) evaluation experiments were carried out on a FEI Quanta FEG 200 instrument with EDX analyzer facility at 25 °C. The nanoparticle size and structure were verified by Transmission Electron Microscopy (HR-TEM) using PHILIPS CM200. Each spectrum was determined with an acquisition time of 18s. XRD spectrum was determined on the X'PERT PRO model X-ray diffractometer from Pan Analytical instruments operated at a voltage of 40 kV and also a current of 30 mA with Cu Ka radiation. Photoluminescence (PL) spectra at room temperature were determined utilizing a Perkin-Elmer LS 55 fluorescence spectrometer. UV spectral measurements were carried out by a Hitachi-U-2001 spectrometer. UV-vis absorbance spectra were determined over a range of 800-200 nm with a Shimadzu UV-1650PC recording spectrometer utilizing a quartz cell with 10 mm of optical path length. The antibacterial activity was assessed by disc diffusion method; the test compound was dissolved in DMSO (200 mg/mL) for about half an hour. Commercially available drug disc, Ciprofloxacin (10 mg/disc) was utilized as positive reference standard and Cyclic voltammetry (CV) measurements were performed by CHI 60 AC electrochemical analyzer (CHI Instruments Inc. USA).

Photocatalysis

The photocatalytic activities of Bi₂O₃-TiO₂ nanocomposite material were studied by the photodegradation of dye. The light source was UV lamp at 365 nm. The reaction was done at ambient temperature (303 K). The experiment, aqueous suspensions of dye (40 mL, 1×10^{-4} M) and 0.080 g of photocatalyst were loaded in 50 mL-reaction tube with a prior 45 min in the irradiation. The suspension was magnetically stirred in dark to guarantee the establishment of an adsorption or desorption equilibrium. The suspension was kept under constant airequilibrated condition. At the intervals of given irradiation time, the suspension was recorded spectrophotometrically within the theory to Beer–Lambert law limit.

Results and Discussion

HR -SEM with EDX analysis

The HR-SEM image of Bi₂O₃-TiO₂ nanocomposite material is shown in Fig. 1a. The image of particles is in from of aggregates and uniformly distributed in various sizes and nanospherical chain structure is shown in Fig.1. (b). EDX analysis confirm that only Ti, Bi and O are present in Bi₂O₃-TiO₂ nanocomposite material.

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HR-TEM analysis

The high-resolution transmission electron microscope measurements of Bi₂O₃-TiO₂ nanocomposite material are shown in Fig 2a, in which the presence of particles is depicted from HR-TEM micrographs of the mixed nanoparticles at 100 nm as nano-spherical shaped structure; Fig 2b shows an image profile; and Fig 2c shows particle size distribution (0.281 nm) in selected particle area.

XRD analysis

The XRD spectra of TiO₂ and Bi₂O₃-TiO₂ nanocomposite material are shown in Fig 3. According to the crystal structure spectra, the well-defined peaks typical of TiO₂ are clearly determined. This is in compliance with the reported norms of the Joint Committee on Powder Diffraction Standard JCPDS card no. 21-1272. Samples give six distinctive TiO₂ peaks in the Figure 4a at 25, 29.91, 38.0, 47.87, 56.92, 64.5 and 74.74 that are the diffractions of the TiO₂ (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 0 4) crystal planes (anatase TiO₂)

The XRD spectrum of peaks observed at 30.10, 33.5 and 46.3° shown in Fig 3 correspond to (012), (-122), (041) and (-104) diffraction planes of catalyst [JCPDS no 71-2274], respectively. X-ray diffraction pattern was measured by utilizing the Debye-Scherrer formula (Marimuthu et al., 2018), L=0.89 λ / β COS θ , where L is the crystalline size (nm), λ is the wavelength (nm), β is the full width at half maximum intensity (FWHM-in radian), and θ is the Bragg diffraction angle (°). The average crystalline sizes of the Bi₂O₃-TiO₂ nanocomposite material products were calculated to be about 25 nm.

PL analysis

PL spectra of prepared TiO₂ and Bi₂O₃-TiO₂ nanocomposite material are shown in Fig.4a and b respectively. As the photoluminescence occurs due to electron-hole recombination, its intensity is directly proportional to the rate of electron –hole recombination; it is directly proportional to the rate of electronhole recombination. The prepared TiO₂ gave two emissions at 425 and 480 nm. Prepared Bi₂O₃ with TiO₂ does not shift the emission of TiO₂, but the intensity of PL emission is less when compared to TiO₂ nanocomposite material. This is because of suppression of recombination of electron-hole pairs by which enhanced photocatalytic activity occurs.

UV-vis DRS Spectrum

UV-Vis-DRS analysis diffuse reflectance spectra analysis of TiO_2 and Bi_2O_3 - TiO_2 nanocomposite material are displayed in **Fig. 5**. The synthesis of Bi_2O_3 - TiO_2 nanocomposite material shows increased absorption in both UV and visible region; that of TiO_2 nanocomposite material can be used as a UV and Visible light active semiconductor photocatalytic nanocomposite material. The UV–vis spectra is transformed to the Kubelka–Munk function F(R) to separate the extent of light absorption from scattering. The band gap energy is obtained from the plot of the modified Kubelka–Munk function (F(R) E)1/2 versus the energy of the absorbed light E by the Eq. (1)

$$(F(r)E)^{1/2} = \left(\frac{(1-R)^{1/2}}{2R}Xh\nu\right)$$
(1)

The final result indicates band gab energy of the chemical synthesis of TiO_2 and Bi_2O_3 - TiO_2 nanocomposite material which are 3.3 eV and 3.1 eV correspondingly. The lower band gab energy supports a superior photo catalytic activity.

Photodegradation of (Rh 6G) dye

• Primary analysis: Photodegradation of (Rh 6G) dye with artificial UV- light

The pH analysis in photo degradation of Rh 6G dye compared to fast dye was investigated in the pH range of 3, 7, 9 and 11. It is observed that the degradation increases with an increase in pH up to 7 and then decreases.

The photodegradation of Rh 6G dye in aqueous medium in the presence of catalyst and the atmospheric air were studied using multi lamp photo reactor with mercury UV lamps of wavelength 365 nm. The initial dye concentration was 10⁻⁴ M and the pH of dye was neutral (pH=7). It was shown to be dark in color. After the photodegradation color changes at irradiation times of 45 min. The reaction time affords the photodegratation of Rh 6G dye. Thus Bi₂O₃-TiO₂ exhibited very superior photo catalytic activity when compared to that of TiO₂, Dark and Nil catalysts are shown in Fig. 6. The Rh 6G dye is resistant to photolysis with Bi₂O₃-TiO₂ nanocomposite material in the dark in dye (1 X 10⁻⁴) concentration was observed Rh 6Gdye undergoes % of degradation 0, 21, 47 and 92% that of TiO_{2%} of degradation 0, 8, 19 and 32 %. The result indicate nanocomposite material is very superior in photocatalytic activity (Margandan et al., 2017; Li et al., 2009; KonstantinouI and Albanis, 2004).

• Effect of catalyst loading

Experiments performed with different amounts of Bi_2O_3 -TiO₂ nanocomposite material showed that the photo degradation efficiency increased with an increase in amount up to 0.08 g/ 50 ml and then slightly decreased as observed in catalyst loadings of 0.05, 0.08 and 0.1 g/50 ml (Fig.7). Bi_2O_3 -TiO₂ caused Rh 6G dye

to undergo 21, 92 and 32 % of degradation. Among the catalyst loadings 0.08g showed the most advantageous photo catalytic activity.

Effect of different concentrations of Rh 6G dye

The effect of dye concentration on the photodegradation of Rh 6Gdye by Bi₂O₃-TiO₂ nanocomposite material was investigated, and 1×10^{-4} M had highest photo catalytic activity than that of 2×10^{-4} and 3×10^{-4} M concentration as shown in Fig. 8.

• Effect of different temperatures

The photo degradation of Bi_2O_3 -TiO₂ nanocomposite material using different calcination temperatures under UV-light absorption in 45 min resulted in 16% (200 °C), 36% (400 °C), and 92 % (500 °C) degradation (Fig. 9). High calcination temperature is more optimum for photo catalytic activity than low calcination temperature, so high calcination temperature clears morphology and high activity of photo catalyst.

Stability and Reusability photo catalyst

The photo catalytic degradation properties of the photo catalyst were investigated by repeating Rh 6G dye photocatalytic degradation experiments for five times. After each cycle, the photo catalysts were washed thoroughly with water, and a fresh solution of Rh 6G dye was made before each photo catalytic run in the photo reactor under UV- light and the results are shown in Fig. 10. In Bi₂O₃-TiO₂ nanocomposite material's 1st, 2nd, 3rd, 4th, and 5th cycles 100, 99, 98, 96 and 96 % degradations were obtained, respectively. After the fifth cycle the efficiency of catalysts decreased compared to the total degradation of Rh 6G dye. There is no significant alteration in reaction, revealing the stability of photo catalyst. This is because of the loss of catalysts (4 %), during the water washing of catalysts, which was not witnessed by the naked eye in this photo catalyst.

• Chemical oxygen demand analysis (COD)

Fig. 11. shows chemical oxygen demand analysis of Rh 6G dye on mineralization of 0.080 g Bi₂O₃-TiO₂ nanocomposite material photocatalyst loading on 40 mL dye suspension with the concentration of 1×10^{-4} (pH=7) and air passing with UV- light at 365 nm. Bi₂O₃-TiO₂ nanocomposite % of COD reduction of dye was 21, 47, and 92 % in 15, 30, and 45 min. The mineralization is also specific by formation of calcium carbonate when the evolved gas (carbon dioxide) through photo degradation is accepted and calcium hydroxide is obtained. This result indicates almost complete photo degradation of dye.

Mechanism for photo catalytic effect of Bi2O3-TiO2 nanoparticles

On the basis of these observations, a tentative mechanism for photo catalytic degradation of 6G dye is proposed as follows:

$${}^{1}(\mathbf{Rh}\ \mathbf{6G})_{0} + \mathbf{hv} \rightarrow (\mathbf{Rh}\ \mathbf{6G})_{1} \tag{1}$$

$${}^{1}(\operatorname{Rh} 6\mathrm{G})_{1} + \operatorname{ISC} \rightarrow {}^{3}(\operatorname{Rh} 6\mathrm{G})$$

$$\tag{2}$$

 $Bi_2O_3-TiO_2(SC) + h\nu \rightarrow e^{-}(CB) + h^{+}(VB)$ (3)

 $^{-}$ OH + h⁺ \rightarrow OH (4)

 $\bullet OH + {}^{3}(Rh \ 6G)_{1} \rightarrow Leuco(Rh \ 6G)$ (5)

 $Leuco(Rh 6G) \rightarrow Products \tag{6}$

Rh 6G dye absorbs radiation of desired wavelength and forms excited singlet state. Further, it undergoes intersystem crossing (ISC) to give its more stable triplet state. Along with this, the Bi_2O_3 -TiO_2 nanocomposite material (SC) also utilizes this energy to excite its electron from valence band to the conduction band. An electron can be abstracted from hydroxyl ion by hole (h⁺) present in the valence band of semiconductor producing 'OH radical. This hydroxyl radical will oxidize methyl green to its leuco form, which may finally degrade to products. It was confirmed that the 'OH radical participates as an active oxidizing species in the degradation of Rh 6G dye as the rate of degradation was appreciably reduced in presence of hydroxyl radical scavenger (2-propanol) (Kamalakkannan et al., 2016) as shown in Scheme 2.

OH° analysis

Fig. 12 shows the detection of **•**OH by the changes in the fluorescence spectra of a coumarin solution under visible-light irradiation as a function of irradiation time of 45 min. Fluorescence intensity arises due to hydroxyl radicals as the active species. Further, the formed hydroxyl radicals on the surface Bi₂O₃-TiO₂ nanocomposite material illuminated by visible-light were detected by fluorescence technique that of TiO₂nanocomposite material. The formation of **•**OH is directly related to the photo catalytic mechanism of the Bi₂O₃-TiO₂ nanocomposite material (Ahmed Abu-Dief and Mohamed, 2017; SameerahI et al., 2018; Kamalakkannan and Senthilvelan, 2017; Kamalakkannan et al., 2015; Chandraboss et al., 2015; Xiang, Yu and Jaroniec, 2011).

Electrochemical application

• Cyclic voltammogram (CV) analysis

CV analysis of prepared TiO₂ and Bi₂O₃-TiO₂ nanocomposite material was done by redox reaction of potassium ferrocyanide (3Mm concentration). A small amount of catalyst was dispersed in 0.1 % nafion solution on the glassy carbon electrode by evaporation for 20 min and drying in nitrogen atm for 20 min. The prepared TiO₂ does not have any anodic potential and current but anodic potential and current of Bi₂O₃-TiO₂ are E = 0.66V and I =2.6 X10⁻⁶ respectively; the increase in current indicates presence of metal ion in the catalyst (Bi) (Zhao et al., 2007) (Fig.13). Bi₂O₃-TiO₂ nanocomposite material has higher electrocatalytic activity (Kumar, Badrinarayanan and Sastry, 2000).

• Conductivity studies

Photoconductivity results of Bi₂O₃-TiO₂ nanocomposite material represent increased current and increased charge carriers act due to photocurrent compared with dark current. This nanocomposite material exhibit (+Ve) photoconductivity as well as solar cell application (Krishnakumar and Swaminathan, 2010; Ibrahim et al., 2017) (Fig.14).

Antibacterial activity

Antibacterial activity of TiO₂ and AC-CdO-TiO₂ nanocomposite material is shown in Fig 15. CdO-SnO₂ nanocomposite material showed activity against both gram-positive and gram-negative strains. 18 mm and 13 mm inhibition zone was developed against *Escherichia coli and Pseudomonas aeruginosa*. The AC-CdO-TiO₂ nanocomposite material was found to be effective against gram-positive bacteria rather than gram-negative. This was due to the differences in the cell wall composition of these bacteria (Balachandran et al., 2013; Balachandran, Thirumalai and Swaminathan, 2014; Laila et al., 2016). AC-CdO-TiO₂ nanocomposite material had high antibacterial activity on grampositive and gram-negative bacteria.

Conclusion

The photocatalyst Bi₂O₃-TiO₂ nanocomposite material prepared by precipitation method. The photo degradation efficiency was analyzed by Bi₂O₃-TiO₂ nanocomposite material employing various experimental parameters namely high photo catalytic effect in pH=7 and then decreases; the catalyst loadings that 0.080 g loading showed optimum photo catalytic activity when compared to TiO₂ nanocomposite material; Concentration of 1×10^{-4} M had highest photo catalytic activity; catalysis was stable; and reusability of material for the degradation of Rh 6G dye was studied. Bi₂O₃-TiO₂ nanocomposite material had higher electrochemical activity than that of TiO₂ nanocomposite material.

Conflict of Interest

The authors declare no competing financial interest.

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Fig. 1. HR-SEM image of (a) $Bi_2O_3\mbox{-}TiO_2$ nanocomposite material and (b) EDX analysis.





Fig. 2. HR-TEM analysis of Bi_2O_3 -TiO₂ nanocomposite material (a) TEM Image (b) Surface plot and (c) particle size in selected area highlighted fig (a)



Fig. 3. XRD pattern of Bi₂O₃-TiO₂ nanocomposite material



Fig. 4. PL analysis of (a) TiO_2 and (b) Bi_2O_3 - TiO_2 nanocomposite material



Fig. 5. UV-Vis DRS analysis of (a) TiO_2 and (b) Bi_2O_3 - TiO_2 nanocomposite material



Fig 6. The effect of pH = 7 Photodegradation of RB 5 dye under UV-light irradiation at 365 nm by (a) Dark (b) Nil catalysis (c) TiO₂ P25 (d) TiO₂ and (e) Bi₂O₃-TiO₂ nanocomposite material



Fig 7. The effects of catalyst loading Bi_2O_3 -TiO₂ nanocomposite material on RB 5 dye under UV-light irradiation at 365 nm



Fig 8. The effects of concentrations of Bi_2O_3 -TiO₂ nanocomposite material



Fig 9. The effects of temperature of Bi_2O_3 -TiO₂ nanocomposite material



Fig 10. Stability and reusability on Rh 6G dye degradation; Bi₂O₃-TiO₂ nanocomposite material



Fig 11. COD analysis of Bi₂O₃-TiO₂ nanocomposite material



Fig.12. Fluorescence spectra measured at $\lambda max = 310$ nm (a) TiO₂ and (b) Bi₂O₃-TiO₂ nanocomposite material obtained using various time 40 min in coumarin solution (sample was illuminated for 45 min of UV light).



Fig 13. CV analysis of (a) TiO_2 and (b) Bi_2O_3 - TiO_2 nanocomposite material GCE in 0.1 M KCl segment 5)



Fig.14. Photoconductivity of Bi_2O_3 -TiO₂ nanocomposite material. Applied field (V Cm⁻¹) Vs electric current (mA) (a) Dark and (b) photocurrent on irradiation with 100 W halogen lamp.



Sheme.1 Preparation of Bi2O3-TiO2 nanocomposite material



Scheme 2. Schematic representation for the photodegradation holes and electrons in the Bi_2O_3 -TiO₂ nanocomposite material under UV- light for successive mineralization of Rh 6G dye.