

One Pot Synthesis of CoTiO₃-TiO₂ Composite Nanofibers and its Application in Dye Degradation

M. Shamshi Hassan, Department of Chemistry, Albaha University, Saudi Arabia

ABSTRACT

CoTiO₃-TiO₂ composite nanofibrous photocatalysts were synthesized by means of the one-step electrospinning method. The samples were characterized by a range of different methods (XRD, SEM, EPMA, FT-IR, UV-DRS, and TEM). Photocatalytic activity was performed for the degradation of rhodamine 6G under visible light. The results showed that CoTiO₃-TiO₂ composite photocatalysts were successfully synthesized. The average sizes of the diameters of the composite nanofibers were found to be 300 to 400 nm. The UV-Vis diffuse reflectance spectra of the CoTiO₃-TiO₂ composite showed an absorption wavelength, in the visible light region, having a band gap energy value of 2.21 eV. The CoTiO₃-TiO₂ composite showed higher photocatalytic efficiency than that of pristine TiO₂; which can be attributed to the heterojunctional interaction between CoTiO₃ and TiO₂.

KEYWORDS

Composite, CoTiO₃-TiO₂, Electrospinning, Nanofibers

INTRODUCTION

Water pollution is a matter of great concern in society. Photocatalysts are applied in order to degrade harmful organic pollutants into non-toxic compounds in water (Zhang et al., 2012). TiO₂ is one of the best-known photocatalysts so far. However, TiO₂ has a notable limitation in that its energy band falls in the ultraviolet zone, which makes it unsuitable to be applied for use in photodegradation under visible light. A lot of effort has been done in this regard in order to extend its activity in the visible region, by making various modifications. Scientists have shown immense curiosity in developing the modified titania; having its wavelength absorption in visible light region. One of the usual procedures is the doping of TiO₂ with elements like carbon, sulfur, and nitrogen; etc. (Chen, Jiang, Geng, Wang, & Yang, 2007; Guan et al., 2019; Ida et al., 2019; Luna, Gatica, Vidal, & Mosquera, 2019; Mahy et al., 2019; Park, Kim, & Bard, 2006; Pylnev & Wong, 2019; Sheydaei, Zangouei, & Vatanpour, 2019; Srisasiwimon, Chuangchote, Laosiripojana, & Sagawa, 2018; Tasbihi et al., 2019; Yoon et al., 2018). An alternative method is to combine TiO₂ with a semiconductor having a small bandwidth (Abdi, Yahyanezhad, Sakhaie, Vossoughi, & Alemzadeh, 2019; Chanhom, Charoenlap, Manipuntee, & Insin, 2019; Hendrix, Lazaro, Yu, & Brouwers, 2019; Ilieva, Nakova, & Tsakova, 2012; Jiang et al., 2018; Mahieu, Puzenat, Geantet, Cardenas, & Afanasiev, 2019; Mao et al., 2017; Ouyang,

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Chang, & Li, 2012; Ratova, Tosheva, Kelly, & Ohtani, 2019). By joining two semiconductors, a new photocatalytic material with a modified band gap can be developed, which will not merely lengthen the absorption of light to the visible spectrum but will, as well, put a check on the fast merging of electrons or holes during photoactivity.

Metal titanates like nickel titanate, cobalt titanate, ferrite titanate, zinc titanate, copper titanate, and lead titanate are famous functional materials which possess an assortment of uses. The titanate perovskites are the best recommended materials for use in photodegradation. Generally, titanate perovskites having band energy of (>3.0 eV) show photocatalytic activity under UV (ultraviolet) light (Ke, Cheng, Wang, Wang, & Pan, 2014; Zhu, Anzai, Yamamoto, & Yoshida, 2019). By doping the metal titanates, their wavelength can be modified from the UV to the visible light absorption range. CoTiO_3 is an ABO_3 -type perovskite oxide, having a narrow band gap semiconductor. Cobalt titanate (CoTiO_3) has been used in various applications such as Li-ion batteries (Jiang et al., 2014), gas sensors (Chuang et al., 2010), magnetic recorders (Toubal, Bensaha, & Yakuphanoglu, 2017) and photocatalysts (Wang, Guo, Wang, & Li, 2016). Cobalt titanate possesses a band width the in visible range ($E_g = 2.28$ eV). Currently, CoTiO_3 has been used as a catalyst under visible light (Singh et al., 2019). In the last few years, one-dimensional nanomaterials have gotten a tremendous response because of their unique size and shape. Developing materials with 1D (one-dimensional) morphology and nano-size range will not only increase their surface area but will also improve their properties. Therefore, it is believed that 1D nano-structures will exhibit superior thermal, optical, or electrical properties as compared to their nanoparticle counterparts (Choi, Kim, Lim, & Park, 2010; Pan et al., 2012).

The objective of the author's investigation was to synthesize one-dimensional TiO_2 - CoTiO_3 nanofibers by means of one-pot electrospinning. The crystal structure and surface organization of the CoTiO_3 - TiO_2 nanofibers have been described by different methods. Moreover, the photo-activity of the CoTiO_3 - TiO_2 nanofibers were also examined. The CoTiO_3 - TiO_2 composite showed better photodegradation efficiency as compared to pristine TiO_2 . This might be ascribed to the heterojunctional interaction between CoTiO_3 and TiO_2 .

EXPERIMENTAL WORK

Preparation of the CoTiO_3 - TiO_2 Nanofibers

Fabrication of CoTiO_3 - TiO_2 composite nanofiber was done via a one-step electrospinning method. Solution of 18 wt% Poly(vinyl acetate) (PVAc) was made in *N,N*-dimethylformamide (DMF) at 25 °C. Titanium isopropoxide (5 g) with some drops of acetic acid and homogeneous mixture of ethanol and $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1g) was added in a beaker. This solution was mixed with PVAc solution (6 ml), and the author kept on stirring it. The resultant sol-gel was electrospun at 15 kV. The fibrous mat was evaporated at 80 °C overnight and heated at 500 °C for 2 hours in standard atmosphere. PVAc was chosen as a template because of its easy availability, hydrophobicity, and its having no designed crosslinks. A new hybrid organic-inorganic solution was obtained by means of a chemical crosslinking reaction among titanium, cobalt precursor, and polyvinyl acetate. The experiment was done in *N,N*-dimethylformamide solution, by an organized crosslinking procedure which results in a uniform and clear solution.

Synthesis of pristine TiO_2 nanofibers was also done by dissolving titanium isopropoxide (5 g) with some drops of acetic acid in PVAc polymer solution (6 ml). The synthesized mat was oven-dried calcined at 500 °C in a muffle furnace.

Characterization

X-ray data of pure and composite nanofibers was examined by a Rigaku/Max-3A X-ray diffractometer having an angle range of 20 to 80°. The microstructure was examined by SEM (JSM6700, JEOL,

Japan) and TEM (H-7650 Hitachi, Co., Japan). The UV-DRS of powder samples were measured by Shimadzu spectrophotometer (UV-2501PC). The elemental distribution of samples was recorded by electron probe microanalysis (EPMA).

Photocatalytic Reaction

The photodegradation activity of TiO_2 and $\text{CoTiO}_3\text{-TiO}_2$ composite fibers was studied by the degradation of rhodamine 6G (R6G) in visible lamp. The photoactivity was done by dissolving 100 mg of the sample into a solution comprised of 100 ml of water and 10 ppm of dye. Prior to photocatalysis, the suspension was stirred in dark conditions for 30 minutes to establish absorption–desorption equilibrium with photocatalyst and rhodamine 6G dye. The nanofibers were added into the R6G solution and irradiated by a 125-W fluorescent mercury lamp having a UV filter of ($\lambda > 400$ nm). The concentration of R6G in solution was pipetted out in fixed time intervals. The photocatalytic activity of TiO_2 and $\text{CoTiO}_3\text{-TiO}_2$ composite nanofibers was compared.

RESULTS AND DISCUSSION

Figure 1 exhibits the XRD spectra of the calcined TiO_2 - and TiO_2 -coupled CoTiO_3 nanofibers. In Figure 1a, the characteristics of the X-ray peaks of the (101) (103) (004) (112) (200) (105) (211) (204) (116) reflections could be indexed for anatase TiO_2 phase (JCPDS no. 894921) (Li et al., 2013). No other peaks have been noticed in the spectra; therefore, this confirms its high purity—whereas, in Figure 1b, characteristics of the X-ray peaks of the (104) and (110) reflections attributed to the CoTiO_3 (JCPDS no. 330960) together with the anatase TiO_2 phase. Figures 2a and 2b demonstrate the SEM pictures of the fabricated TiO_2 and $\text{CoTiO}_3\text{-TiO}_2$ nanofibers, respectively. The TiO_2 nanofibers show even and smooth surfaces having an average diameter of 500–600 nm (Figure 2a); whereas, the $\text{CoTiO}_3\text{-TiO}_2$ composite nanofibers demonstrated a granular structure with a smaller diameter. The average diameter was found to be 300–400 nm (Figure 2b). Formation of the $\text{CoTiO}_3\text{-TiO}_2$ composite was further confirmed from EPMA dot images (Figure 3). The EPMA pictures noticeably demonstrated the homogenous presence of Co, Ti, and O, which were distributed over the composite's surface.

The simple TEM and high-resolution TEM images of the $\text{CoTiO}_3\text{-TiO}_2$ composite nanofibers were shown in Figure 4. The TEM image in Figure 4a shows the distribution of black particles along

Figure 1. XRD pattern of synthesized: (a) TiO_2 ; and (b) $\text{CoTiO}_3\text{-TiO}_2$ nanofibers calcined at 500 °C for 2 hours

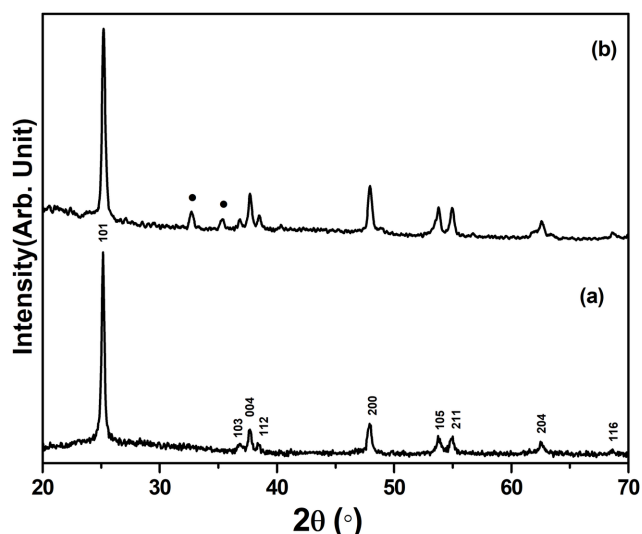


Figure 2. SEM image of synthesized: (a) TiO₂; and (b) CoTiO₃-TiO₂ nanofibers calcined at 500 °C for 2 hours

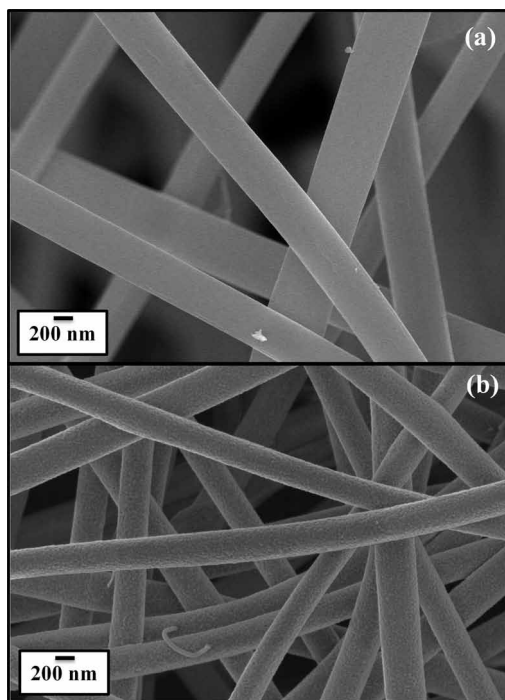


Figure 3. EPMA spectra of synthesized CoTiO₃-TiO₂ composite nanofibers

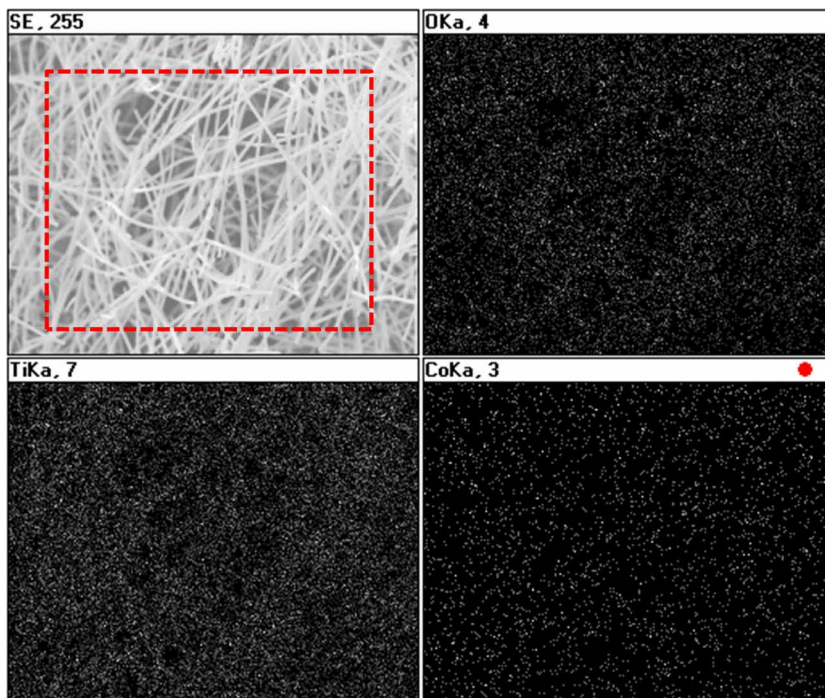
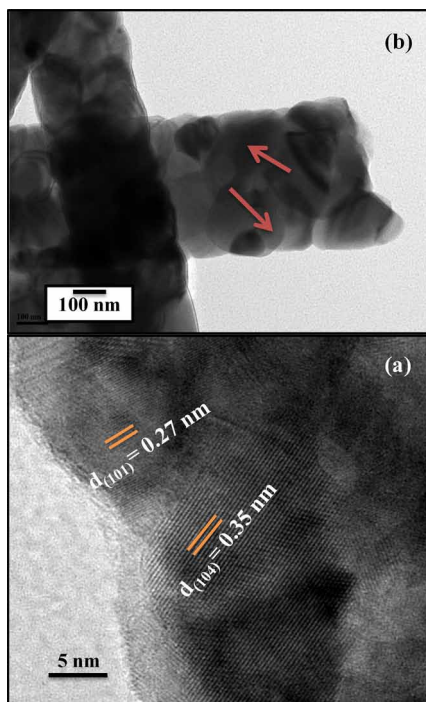


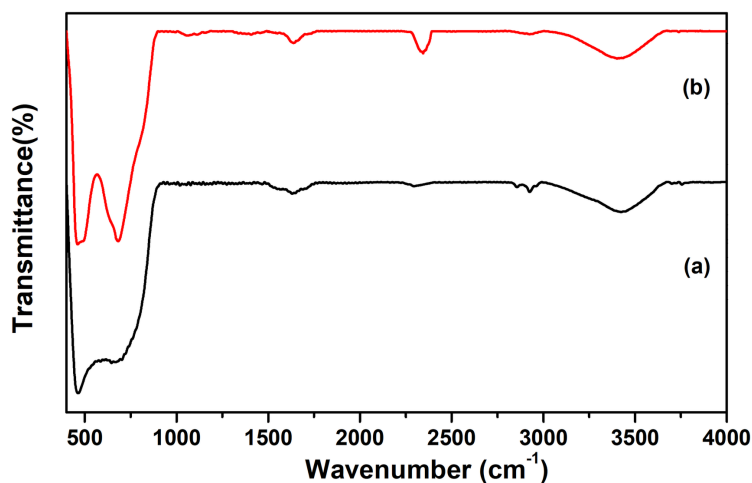
Figure 4. (a) HR-TEM; and (b) TEM micrographs of $\text{CoTiO}_3\text{-TiO}_2$ composite nanofibers



with the nanofibers. Upon closer inspection of the microstructure of these particles by HR-TEM, the presence of crystalline CoTiO_3 with TiO_2 (Figure 4b) has been confirmed. For CoTiO_3 , the interatomic spacing of the lattice plane (104) was found to be 0.27 nm; whereas for TiO_2 , the spacing for the lattice plane (101) was 0.35 nm.

The molecular structure of the pure TiO_2 and composite $\text{CoTiO}_3\text{-TiO}_2$ nanofibers has been characterized by FTIR spectroscopy (Figure 5) after calcination. FTIR spectra showed the total

Figure 5. FT-IR spectra of synthesized: (a) TiO_2 ; and (b) $\text{CoTiO}_3\text{-TiO}_2$ composite nanofibers



removal of the unwanted organics and the formation of metal oxide. Thus, above 2000 cm^{-1} , a very broad absorption peak around 3420 cm^{-1} endorsed to the $-\text{OH}$ stretching vibration mode was detected for both samples. A minor peak at 1635 cm^{-1} was observed due to the bending vibrations of absorbed molecular water. For both the samples of TiO_2 and $\text{CoTiO}_3\text{-TiO}_2$, the presence of a major peak before 1000 cm^{-1} is noticed. The absorption peaks between 400 and 1000 cm^{-1} could be allocated to the vibration of ions of metal. The aforementioned peaks were related to the stretching mode of $\text{Co}-\text{O}$ and $\text{Ti}-\text{O}$, corresponding to the presence of titania and cobalt titanate (Hashemian & Foroghimoqhadam, 2014; Yan, He, Evans, Zhu, & Duan, 2004).

Figure 6 shows the UV-DRS of pristine TiO_2 and nanocomposite $\text{CoTiO}_3\text{-TiO}_2$ nanofibers. As depicted here, the TiO_2 nanofibers possess an absorption edge at 387 nm ; and for the $\text{CoTiO}_3\text{-TiO}_2$ nanocomposite nanofibers, it appeared at 560 nm . The pure TiO_2 has demonstrated the spectra in the ultraviolet region; whereas the $\text{CoTiO}_3\text{-TiO}_2$ nanocomposite revealed extended optical absorption in the visible region. The spectra of $\text{CoTiO}_3\text{-TiO}_2$ nanocomposites demonstrated the combination of the spectra of CoTiO_3 and TiO_2 . It is known that TiO_2 absorbs UV light only. So, it can be said that the absorbance in the visible region is mainly because of the CoTiO_3 in the composite. The calculated band energy of the TiO_2 nanofibers is 3.2 eV , whereas the band gap of the $\text{CoTiO}_3\text{-TiO}_2$ composite is 2.21 eV . For TiO_2 , the position of the conduction band is around $\sim 0.3\text{ eV}$; and the position of the valence band is around $\sim 2.9\text{ eV}$ (Tahir & Amin, 2013). Meanwhile, the band gap of CoTiO_3 is reported to have 2.53 eV (Wang et al., 2016), whereas the conduction band is around $\sim 0.1\text{ eV}$ and the valence band is at $\sim 2.43\text{ eV}$. So, it can be said that the band position of CoTiO_3 lies in between the valence band and the conduction band of TiO_2 .

The photodegradation efficiency of the pure TiO_2 and $\text{CoTiO}_3\text{-TiO}_2$ composite samples were measured in the presence of visible light (Figure 7). The R6G dye removal efficiencies were found to be 9% and 56% for pure TiO_2 and $\text{CoTiO}_3\text{-TiO}_2$ composite nanofibers, respectively, within 5 h of the photocatalytic reaction. The better efficiency shown by the composite was mainly due to their photoabsorption properties in the presence of visible light. However, the dye removal efficiency of composite nanofibers was not very high as expected. This may be due to the fact that the band positions of CoTiO_3 lies in middle of the valence band and the conduction band of TiO_2 , which makes it difficult to transfer photoexcited charges to TiO_2 —and which ultimately leads to the decrease in the efficiency of a composite.

Figure 6. UV-Vis DRS spectra synthesized: (a) TiO_2 ; and (b) $\text{CoTiO}_3\text{-TiO}_2$ composite nanofibers

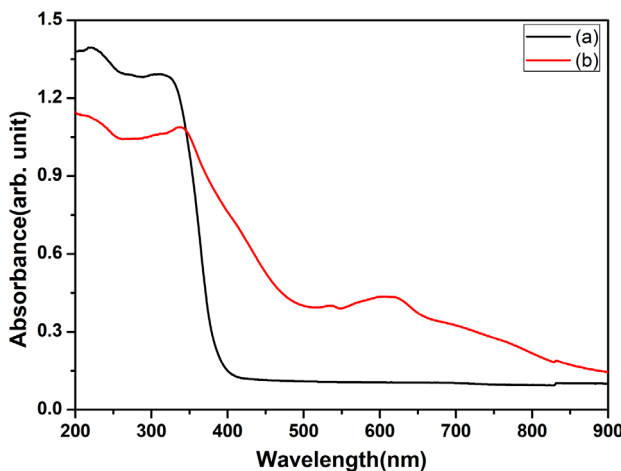
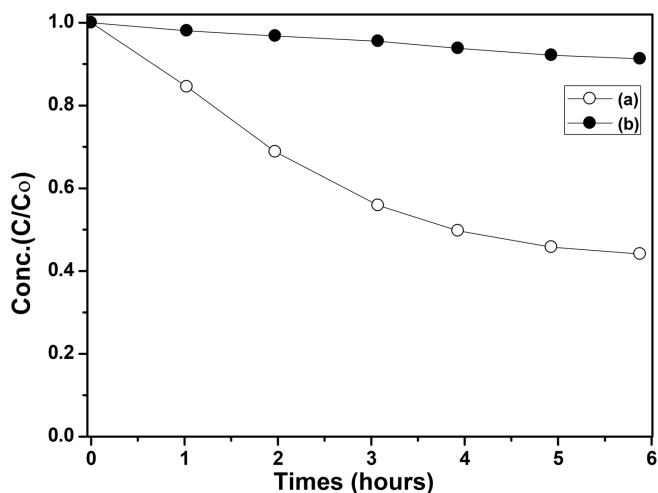


Figure 7. Photocatalytic activity of synthesized: (a) $\text{CoTiO}_3\text{-TiO}_2$ composite; and (b) TiO_2 composite nanofibers for R6G degradation

CONCLUSION

$\text{CoTiO}_3\text{-TiO}_2$ composite nanofibers were successfully prepared by electrospinning. The surface structure and the crystal formation of the samples were examined by different methods. The $\text{CoTiO}_3\text{-TiO}_2$ composite nanofibers were prepared by means of a simple and cost-effective single-step method. The $\text{CoTiO}_3\text{-TiO}_2$ composite nanofibers demonstrated better activity than the pure TiO_2 nanofibers did with regard to the degradation of R6G dye in the presence of visible light. The superior degradation efficiency of the $\text{CoTiO}_3\text{-TiO}_2$ composite nanofibers is primarily due to the heterojunctional interaction of CoTiO_3 and TiO_2 as well as to the low band energy of the composite photocatalyst. Nonetheless, the degradation efficiency of the composite nanofibers needs to be amplified further. This problem can be studied by doping with another element (such as Cu or Cr) in further study and can be applied to other applications (adsorption; sensing, etc.).

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M. Shamshi Hassan is currently working as an assistant professor in Albaha University in Department of Chemistry. He has completed his PhD and Post Doctorate from Chonbuk National University, South Korea. His research interests are in the synthesis of different morphology of pure or hybrid metal oxides and their applications.