

## Hydrothermal Synthesis of Dy Doped TiO<sub>2</sub>(B) Nanowires

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### Abstract

This study aimed to synthesize and then characterize the physical property of dysprosium doped TiO<sub>2</sub>(B) nanowires powders (Dy/TiO<sub>2</sub>(B) NWs). This composite was prepared by hydrothermal method. Phase formation of TiO<sub>2</sub> was characterized by XRD. Morphology of the TiO<sub>2</sub> nanowires powders (NWS) was observed by using field emission scanning electron microscope (FESEM). Optical absorption of the composite had been measured employing UV-Vis spectrophotometer. The result of the physical properties showed a smaller size of Dy/TiO<sub>2</sub>(B) NWs crystal 13.8 nm than of TiO<sub>2</sub>(B) crystal 20.7 nm by the x-ray diffraction test. Only the TiO<sub>2</sub>(B) phase was found at the calcination temperature of 400 °C. The 0.1 mole% dysprosium has good electrical properties. The expected overall properties of Dy/TiO<sub>2</sub>(B) NWs may open the way towards new applications of high-performance materials, leading to an innovative product development in the solar cell, electronics batteries and many other applications.

**KEYWORDS:** TiO<sub>2</sub>(B) phase nanowire; Hydrothermal; Dysprosium (Dy)

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### Introduction

TiO<sub>2</sub> is a semiconductor material used widely for studies due to photochemical stability, electronic properties, high photocatalytic activity, non-toxicity and low cost. However, applications of TiO<sub>2</sub> are used in energy as an excitation source. In general, TiO<sub>2</sub> has 4 crystal forms, anatase, rutile, brookite, and monoclinic TiO<sub>2</sub>(B) structure. TiO<sub>2</sub>(B) structure has been higher voids oxygen vacancies and lower density [1 – 5]. TiO<sub>2</sub> can be synthesized using the application of several procedures, such as chemical vapor deposition (CVD) [6], sol-gel [7, 8], microwave [9], electrospinning [10, 11] and hydrothermal [8, 12, 13].

Rare earth (RE) metal ions are usually employed by the researchers as catalyst for the incompletely occupied 4f and empty 5d orbitals [14]. Some experimental results have indicated that the photocatalytic activity of TiO<sub>2</sub> could be promoted by the modification of RE metals [15]. Among the lanthanide series, the Dy doped materials have attracted much attention due to their white light emission. Based on the host environment, Dysprosium has a single oxidation state (Dy<sup>3+</sup>), the 4f electrons give dysprosium an advantage for various functional luminescence

applications. Dysprosium's fluorescence spectrum subsists of numerous traces that are observed, especially in the 470 – 500 nm and 570 – 600 nm regions in host lattices. Alternative, TiO<sub>2</sub>, a well-known huge band gap semiconductor [16, 17], has confirmed the possibility to be a good sensitizer to take in light and transfer energy to RE ions [18]. Therefore, the fabrication of structurally pure, concentration managed, TiO<sub>2</sub>: RE nanostructures with an emission conduct is still a challenging project for their utilization in optoelectronics [19].

To date, dysprosium doped TiO<sub>2</sub>(B) composites have been investigated; however, to our knowledge, there have been no reports regarding the Dy doped TiO<sub>2</sub>(B) composites nanowire (NWS) particularly by novel hydrothermal method. Hydrothermal is a method involving a wet chemical process with relatively low temperature and autogenously pressure. This has the advantage of ease of controlling the synthesis process, low energy consumption, cost-effectiveness, and is environmentally safe.

In this paper, synthesis of Dy/TiO<sub>2</sub>(B) NWS by hydrothermal method and characterized will be reported in detail. Crystallization,

microstructure and optical properties of the powders were characterized. The photocatalytic properties of the Dy/TiO<sub>2</sub>(B) NWs were investigated. Also, the mechanism for improving the photocatalyst activity and electrical property was discussed.

## Materials and Methods

### Synthesis of Dy/TiO<sub>2</sub>(B) NWs by hydrothermal method

In a typical preparation procedure, Degussa P25 TiO<sub>2</sub> nano powder mixed with 30 mL of 10 M sodium hydroxide (NaOH, 98%, Loba-chemie) and Dysprosium Nitrate (DyN<sub>3</sub>O<sub>9</sub>, 99.9%, Sigma-Aldrich) corresponding to different Dy/Ti proportioning of (0 and 0.1 at mol.%) were sonicated for 60 minutes in an ultrasonic. The mixture was transferred to a 50 mL teflon-lined autoclave container and heated at 220 °C for 24 h. After cooling to room temperature, the mixtures were taken out, and then were rinsed extensively with 0.1 M HCl, deionized water and subsequently with ethanol. Then, the mixture was annealed at 400 °C for 2 h.

### Characterization of TiO<sub>2</sub>(B) NWs

The X-ray diffraction (XRD) patterns were characterized in terms of phase compositions and crystallite size by using an X-ray diffractometer (Phillips E'pert MPD, CuK<sub>α</sub>). The surface morphology of the prepared powders was characterized by field emission scanning electron microscope (FESEM, Apreo, FEI). The band gap energy value of TiO<sub>2</sub> in the powder form UV-vis absorption spectra were obtained by UV-vis spectrophotometer (UV-2401, Shimadzu by using BaSO<sub>4</sub> as reference). The study of DC electrical conductivity property of powder samples used an LCR-meter (Agilent 4285A Precision) in the frequency test range 75 kHz – 30 MHz, with 100 Hz steps at room temperature.

## Results and Discussion

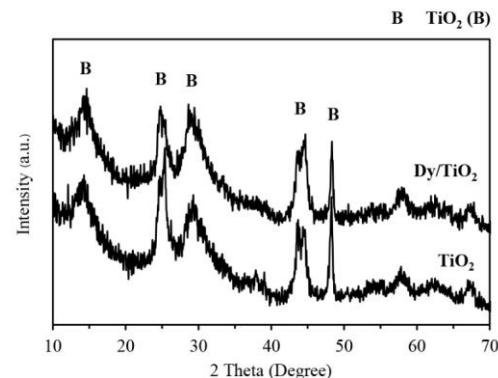
### XRD Analysis

The XRD patterns of TiO<sub>2</sub> powders calcined at 400 °C by hydrothermal method are presented

in Fig. 1. It was found that only the TiO<sub>2</sub>( B) phase can be seen at 0 and 0.1 mol.% Dy doping in TiO<sub>2</sub>. The diffraction peaks which appear in undoped TiO<sub>2</sub> sample at 2θ are 14.18, 25.32, 29.26, 44.39 and 48.29 respectively. According to the JCPDS 46-1238 patterns of TiO<sub>2</sub>( B) phase form TiO<sub>2</sub> monoclinic structure requirements and no found position of Dy. The crystallite size was determined from XRD peaks using the Scherer equation (1) [20],

$$D = 0.9\lambda / \beta \cos \theta \quad (1)$$

where  $D$  is the crystalline size (nm),  $\lambda$  is the wavelength of the X-ray radiation (CuK<sub>α</sub> = 0.15406 nm),  $\beta$  is the angle width at half maximum height, and  $\theta$  is the half diffraction angle in degree of the centroid of the peak. The Dy doping seems to affect the crystal phase from the Scherrer formula, the average crystallite sizes of Dy/TiO<sub>2</sub>(B) NWs are estimated to be about 13.8 nm (Table 1), Dysprosium retards the grain size. In addition, lattice parameter of TiO<sub>2</sub> can be calculated from XRD patterns [11], The difference in lattice constant suggests that Dy<sup>3+</sup> ions are doped in to the crystal lattice of TiO<sub>2</sub> [21]. However, there is a distinction between the lattice parameters of the pure TiO<sub>2</sub> and Dy/TiO<sub>2</sub>(B) NWs, which may be due to the formation of stresses by the difference in ionic size between Ti (~0.6 Å) and Dy (~0.91 Å) (Table 1) [22, 23], which cause the increase of the unit cell.



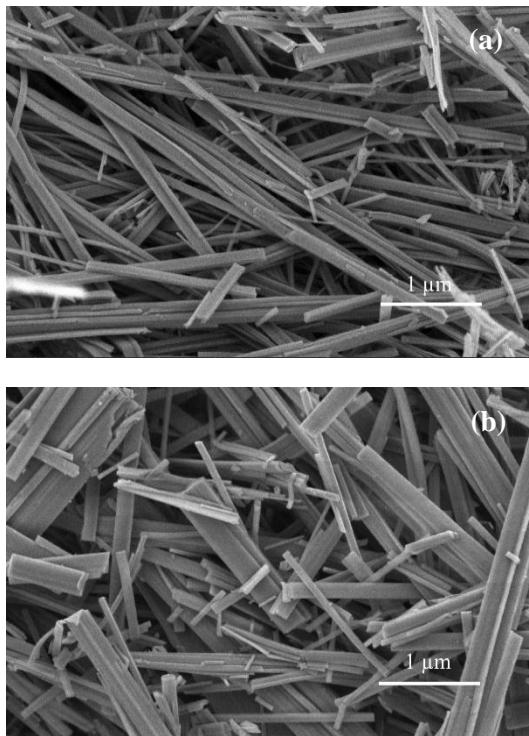
**Fig.1** XRD patterns of pure TiO<sub>2</sub> NWs and Dy/TiO<sub>2</sub>(B) NWs calcined at 400 °C.

**Table 1** Crystallite size, Lattice parameters and Volume of cell of pure TiO<sub>2</sub> and Dy/TiO<sub>2</sub>(B) NWs.

Sample	Crystalline size (nm)	Lattice parameters (Å)				Volume of cell (Å <sup>3</sup> )
		a	b	c	β	
TiO <sub>2</sub> NWs	20.7	12.20	3.75	6.53	107.36°	286.13
Dy/TiO <sub>2</sub> NWs	13.8	13.44	3.76	6.56	107.36°	316.40

### Morphology of Dy/TiO<sub>2</sub> (B) NWs

Morphology of the Dy/TiO<sub>2</sub>(B) NWs prepared by hydrothermal method for 24 h at 220 °C and calcined 400 °C was observed by FESEM illustrated in Fig. 2. It can be seen that Dy/TiO<sub>2</sub>(B) NWs nucleated are homogeneous. The average diameter and length of Dy/TiO<sub>2</sub>(B) NWs are about 86.3 – 251.2 nm and 0.6 – 5.1 μm, respectively.



**Fig. 2** FESEM images of (a) pure TiO<sub>2</sub> NWs and (b) Dy/TiO<sub>2</sub>(B) NWs

### Energy gap measurement

The UV-vis spectra of TiO<sub>2</sub>(B) NWs and Dy/TiO<sub>2</sub>(B) NWs are shown in Fig. 3a. The band gap energies ( $E_g$ ) of the samples was determined and analyzed by intercept x of the linear portion of  $(\alpha h\nu)^2$  as a function of  $E$  to  $\alpha E = 0$  (where  $E = E_g$ )

of following equation (2) [24],

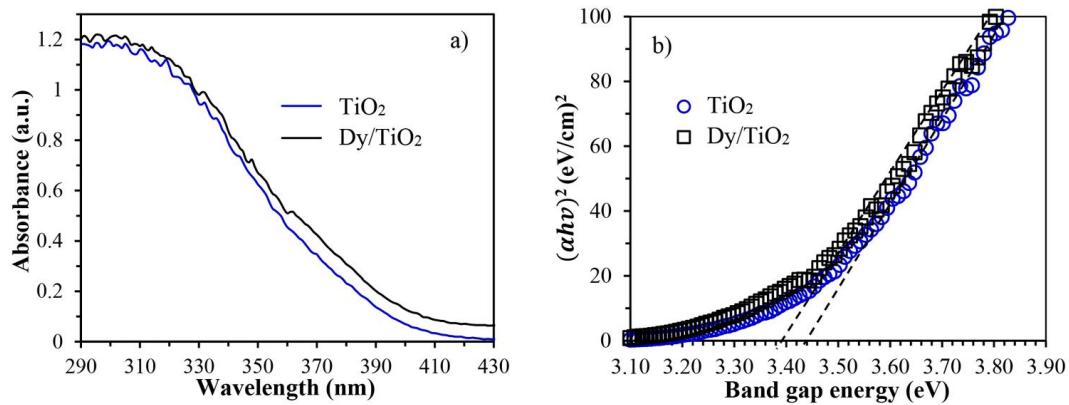
$$\alpha E = A' (E - E_g)^m \quad (2)$$

where  $E_g$  is the band gap energy (eV) of the sample and  $\lambda$  is the wavelength of the on set of the spectrum (nm). ( $E = hc/\lambda$ ), respectively.  $M = 1/2$  for direct band gap and  $m = 2$  for indirect band gap. The absorption coefficient ( $\alpha$ ) was calculated by  $\alpha = A/d'$  where  $A$  is the measured absorbance (nm),  $d'$  is the thickness of samples in UV-vis cell (0.4 cm).

Figure 3(b) shows the direct band gap of the pure TiO<sub>2</sub> NWs is 3.44 eV [8]. It is decreased to 3.39 eV with the addition of dopant Dy<sup>3+</sup>. Decrease in the optical band gap of the nanostructure observed can be attributed to the reduction of the crystallite size. The optical band gap shift of Dy/TiO<sub>2</sub> NWs from the optical band gap of pure TiO<sub>2</sub> NWs indicates the red shift. Furthermore, since Dy doping causes narrower band gap energy of the photocatalyst as depicted in Fig 3, formations of electron-hole pairs on the photocatalyst surface also increase, resulting in the highest photocatalytic activity because the absorption wavelength range is towards visible light and hence the increase in absorption intensity. From the results, it is ascertained that photocatalytic activity of Dy/TiO<sub>2</sub> NWs photocatalyst is strongly dependent on the amount of doped Dy concentration [25, 26]. This effect of Dy doping in TiO<sub>2</sub> on enhancement of visible light absorption capacity agrees well with the previous works [13]. In addition we discuss the probable reason of band gap narrowing in TiO<sub>2</sub> with Dy doping in hydrothermal treatment. As reported, the Dy dopant acts as an acceptor impurity in TiO<sub>2</sub> lattice [13]. Thus when the TiO<sub>2</sub> is doped with Dy, the acceptor levels of Dy along with oxygen vacancies are created in the band gap of TiO<sub>2</sub>. In our case, as discussed above Ti<sup>3+</sup> is also formed which creates energy level in the band gap, contributing to the reduction of band gap (Table 2).

**Table 2** Band gap energy and Oxygen vacancy of samples

Sample	Band gap energy (eV.)	Oxygen vacancy
TiO <sub>2</sub> NWs	3.44	2.76
Dy/TiO <sub>2</sub> NWs	3.39	2.91



**Fig. 3** (a) UV-vis spectra and (b) evolution of  $(\alpha h\nu)^2$  versus photon energy curves of pure TiO<sub>2</sub> NWs and Dy/TiO<sub>2</sub> NWs calcined at 400 °C for 2 h.

#### Electrical properties

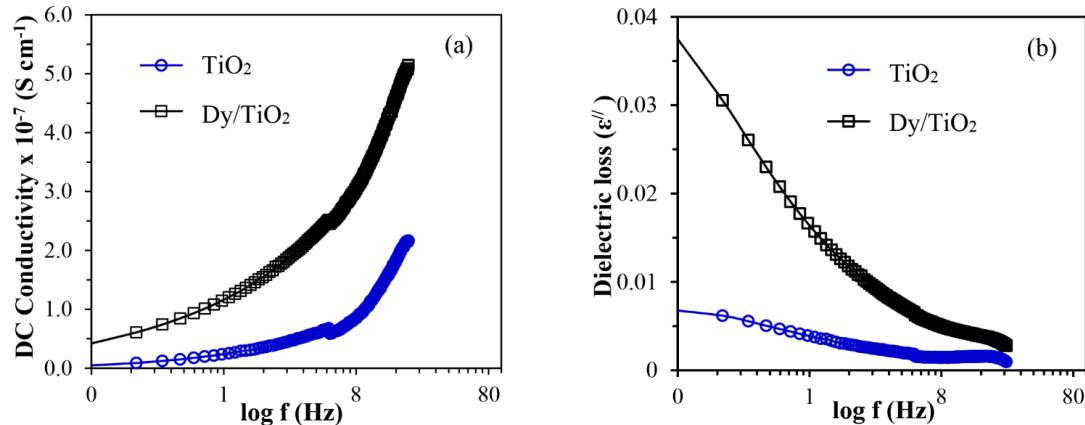
The DC electrical conductivity and dielectric loss of nanocomposite Dy/TiO<sub>2</sub> sample powder using LCR-meter in the range frequency test 75kHz – 30MHz at room temperatures can be calculated by the following equation (3) and (4) [27],

$$\sigma_{DC} = 1 / \rho_{DC} = (1 / R) \cdot (L / A) \quad (3)$$

where  $\sigma_{DC}$  is the DC conductivity,  $\rho_{DC}$  is the resistivity of the sample,  $R$  is the resistance,  $L$  is the thickness and  $A$  is the area of the samples.

$$\varepsilon'' = 1 / 2\pi F \cdot C_p \cdot R_p \quad (4)$$

where  $\varepsilon''$  is dielectric loss,  $F$  is the frequency,  $C_p$  is the capacitance in parallel and  $R_p$  is the resistance in parallel.



**Fig. 4** Electrical properties of pure TiO<sub>2</sub> and Dy/TiO<sub>2</sub> NWs (a) DC Conductivity and (b) Dielectric loss

conductivity. This may be the reason for higher conductivity and strong frequency dispersion on Dy [13, 34]. As expected, the conductivity increases with doped Dy. The conductivity of Dy/TiO<sub>2</sub> NWs was increased by  $0.42 \times 10^{-7}$  S cm<sup>-1</sup> relative to  $0.05 \times 10^{-7}$  S cm<sup>-1</sup> for pure TiO<sub>2</sub> NWs. The Dy crystal dispersion of TiO<sub>2</sub>(B) phase particles is due to the phase action of Dy/TiO<sub>2</sub> NWs. It helps in controlling the internal individual dipoles in the presence of electric field and hence, controls the conductivity properties of the composite.

## Conclusion

We have successfully fabricated single crystalline Dy/TiO<sub>2</sub> NWs using the hydrothermal process. This method produced a large quantity of single crystalline NWs at relatively high purity and very low cost. The Dy/TiO<sub>2</sub> NWs have very strong electrical properties. The Dy/TiO<sub>2</sub> NWs may have many potential applications in photocatalysts and photoelectronics.

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