Morphological, Structural and Optical Properties Study of Transition Metal Ions Doped TiO_2 Nanotubes Prepared by Hydrothermal Method

Mohd Hasmizam Razali, Ahmad-Fauzi M. N., Abdul Rahman Mohamed, and Srimala Sreekantan

***Abstract*—Undoped TiO_2 nanotubes and doped titanium dioxide nanotubes with various transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}) were prepared by hydrothermal method. The samples were characterized using X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), nitrogen gas adsorption and UV-Vis diffuse reflectance spectroscopy. The structural and morphological studies showed that the transition metal ion dopant was incorporated into interstitial positions of the TiO_2 lattice to form a new phase of TiO_2 (hexagonal) instead of anatase TiO_2 (tetragonal) for undoped TiO_2 nanotubes. It could be expected that doped TiO_2 nanotubes active under visible light due to their small band gap.**

***Index Terms*—Doped, photocatalyst, TiO_2 nanotubes, transition metal ion.**

I. Introduction

Recently, extensive researches have been conducted on the synthesis and characterization of TiO_2 nanotubes because of their novel properties such as unique shape, size confinement in radial-direction, large specific surface area and large pores volumes [1]. They also have high interfacial charge transfer rate, resulting in the carriers being free to move throughout the length of these nanostructures thus, reduce the e^-/h^+ recombination probability [2]. However, due to the their large band gap energy (~ 3.25 eV) [3], it only active only under UV-light spectral range, which is a small fraction (5–6) % of whole solar-light spectrum [4], [5]. Therefore, doped titanium dioxide nanotubes photocatalyst have been extensively investigated due to their capability to extend the wavelength response of TiO_2 nanotubes into the visible region and inhibits phase transformation. Moreover, doping could enhance its photoactivity by reducing the recombination of e^- and h^+ pair and enhancing the interfacial charge transfer [6], [7]. So far, various transition metal ions [8], [9], noble metal [10], and non-metals [11]-[13] doped TiO_2 have been successfully prepared and investigated. However, there is a considerable controversy on the effect doping metal-ions on photocatalytic performance. Some papers reported that the doping of metal-ions such as W^{6+} and Cu^{2+} in TiO_2 increased the photocatalytic performance [14], [15], whereas Nagaveni *et al.*, demonstrated that TiO_2 doping with these metal-ions through solution combustion method showed weaker photocatalytic performance than pure TiO_2 [16]. Such wide variations in reported literatures should be mainly due to different preparation methods and doping elements which resulted in different physical properties of TiO_2. Thus, in this present work, various transition metal ions doped TiO_2 nanotubes were synthesized by hydrothermal method and were characterized using FESEM, TEM, XRD, nitrogen gas sorption and UV-Vis diffuse reflectance spectroscopy.

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II. Experimental

A. Preparation of Undoped and Doped TiO_2 Nanotubes

To synthesis undoped TiO_2 nanotube, 2 g of the commercial TiO_2 powder precursor (merck) was mixed with 100 mL of 10 M NaOH. The mixture was subjected to hydrothermal treatment at 150 ℃ for 24 hours in autoclave. When the reaction was completed, the white solid was collected and washed with 0.1 M HCl (200 ml) followed by distilled water until a pH 7 of washing solution was obtained. The final products were obtained by the filtration with subsequent drying at 80 ℃ for 24 hours. Then, sample was heated at 300 ℃ for 2 hours in the air. In order to synthesis Co^{2+}, Ni^{2+} and Cu^{2+} doped nanotubes, similar procedure was repeated with 2 g of TiO_2 precursor was mixed with 100 mL of 10 M NaOH consists of 0.25 mmol of $Co(NO_3)_2$, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ aqueous solution as metal ions source respectively.

B. Characterization

ZEISS SUPRA^{TM} 35VP field emission scanning electron microscope (FESEM) and Philips CM12 transmission electron microscope (TEM) was used to investigate the morphology of the sample. X-Ray powder diffraction (XRD) analysis was performed using a Bruker D8 Diffractometer with Cu-Kα (λ = 1.54021 Å) and scans were performed in step of 0.2°/second over the range of 2θ from 10 up to 80°. Quantachrome ASiQwin - nitrogen gas adsorption was used to determine the surface area and UV-Vis was carried out

using Perkin Elmer Lambda UV-Vis spectrometer for band gap measurements.

III. Result and Discussion

The XRD patterns of undoped TiO_2 nanotubes and doped TiO_2 nanotubes with different metal ion shown in Fig. 1. TiO_2 nanotubes revealed the presence of the peaks at 25.25 °, 37.52 °, 48.02 °, 53.58 °, 54.88 °, 62.61 °, and 75.07 ° which are assigned to TiO_2 anatase. Meanwhile for Co^{2+}, Ni^{2+}, Cu^{2+} doped TiO_2 nanotubes at 0.25 mmol, only three peaks at about 19.89 °, 24.57 ° and 48.30 ° was observed. These peaks were due to the hexagonal phase of TiO_2.

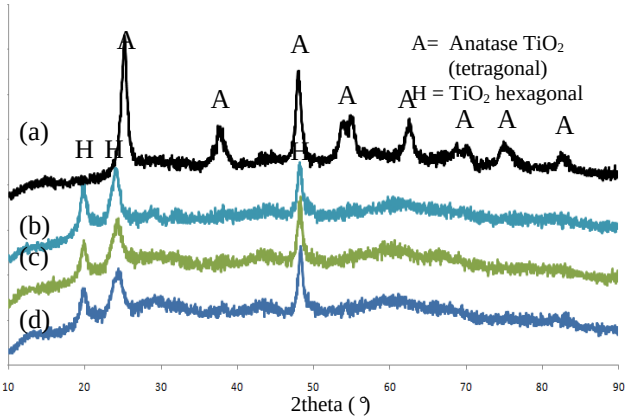

Fig. 1. XRD patterns of (a) undoped TiO_2 nanotubes and 0.25 mmol doped TiO_2 nanotubes with (b) Co^{2+} (c) Ni^{2+} (d) Cu^{2+} metal ion

The lattice parameters of TiO_2 nanotubes and various transition metal ion doped TiO_2 nanotubes based on the XRD patterns are listed in Table I.

TABLE I: Lattice Parameters and Phase Content of the Samples

Sample	*a* (Å)	*c* (Å)	Phase content (%)
TiO_2 nanotubes	3.781	9.509	100 anatase TiO_2
Co^{2+} doped TiO_2 nanotubes	5.05	6.51	100 TiO_2 hexagonal
Ni^{2+} doped TiO_2 nanotubes	5.11	6.45	100 TiO_2 hexagonal
Cu^{2+} doped TiO_2 nanotubes	5.12	6.38	100 TiO_2 hexagonal
Anatase TiO_2 (tetragonal)	3.784	9.519	-
TiO_2 hexagonal	5.29	6.13	-

It can be seen that TiO_2 nanotubes have lattice parameters (a- and c-axis) of 3.781 Å and 9.509 Å, respectively, in the unit cell based on the tetragonal Bravais lattice. In comparison with doped titania nanotubes, there exists derivations of *a* and *c* values. This derivation as well as formation of new phase after metal ion doping is most probably due to the incorporation of metal ion into interstitial positions of the TiO_2 lattice. The interstitial diffusion of metal ion into the TiO_2 lattice can strongly modify the lattice parameters. In addition, no additional peaks corresponding to the dopants were observed proving those dopants ions are successfully incorporated into the lattice site of TiO_2. However, researchers [17], [18] reported that no peaks of dopant were observed in XRD pattern due to low concentration of dopant loading into TiO_2 nanotubes. The XRD cannot identify the dopant peaks because of their detection limit.

In order to study the effect of transition metal ion doping on morphology of nanotubes, the FESEM and TEM was carried out. Fig. 2 represents the FESEM micrographs of undoped TiO_2 nanotubes and doped TiO_2 nanotubes with different metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}). Fibrous-like structures is shown by FESEM image for undoped TiO_2 nanotubes (Fig. 2a). The diameter of the fibrous is about 12 nm. On the other hand, after doping with different metal ion of Ni^{2+} (Fig. 2b), Co^{2+} (Fig. 2c) and Cu^{2+} (Fig. 2d), similar morphological characteristics was observed. This indicating that, the metal ion doping had little effect on fibrous-like structure may be due to small amount of metal ion loading.

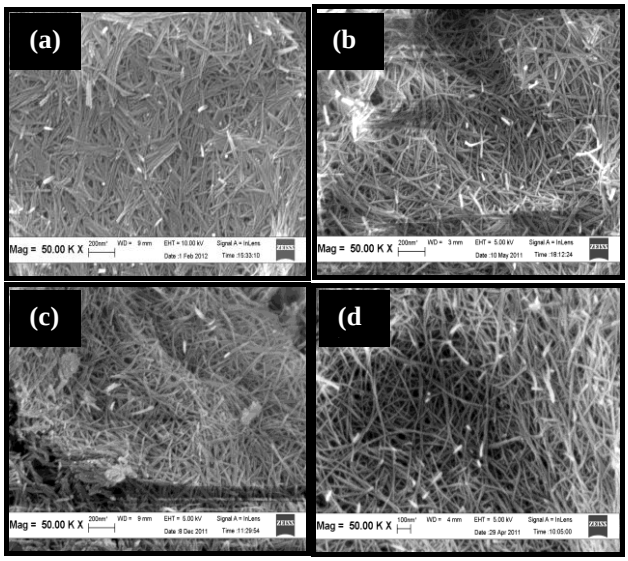

Fig. 2. FESEM micrographs of (a) undoped TiO_2 nanotubes, and 0.25 mmol doped TiO_2 nanotubes with (b) Co^{2+} (c) Ni^{2+} (d) Cu^{2+} metal ion

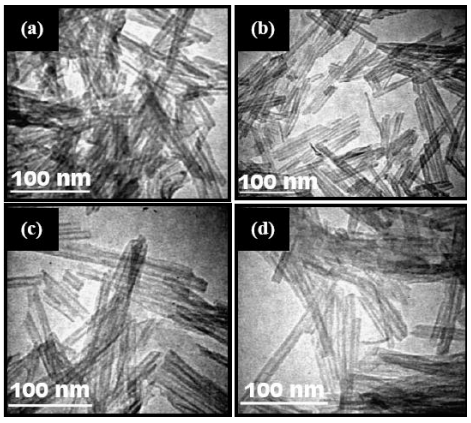

Fig. 3. TEM micrographs of (a) undoped TiO_2 nanotubes and 0.25 mmol doped TiO_2 nanotubes with (b) Co^{2+} (c) Ni^{2+} (d) Cu^{2+} metal ion

Meanwhile, TEM micrographs of the undoped and doped TiO_2 nanotubes are shown in Fig. 3. Fig. 3a shows TEM images of the undoped TiO_2 nanotubes. The existence of hollow inside the fibrous-like structures indicated for nanotubes formation. The inner and outer diameters of the nanotubes are 4 nm and 12 nm respectively. After doping with metal ion, there were no obvious changes in their morphological structure. All doped TiO_2 nanotubes also showed the existence of hollow inside the fibrous-like structure indicating that nanotubes structures were retained (Fig. 3b, 3c, 3d). The nanotubes structures were connected

randomly. This will promotes the diffusion of reactants and products, thus enhancing the photocatalytic activity by facilitating access to the reactive sites on the surface of the photocatalyst [19]. In addition, photocatalytic reactions are believed to take place on the illuminated surface. The tube-like structure increases the surface areas significantly and, consequently, helps rapid mass transfer of the adsorbed molecules from bulk solution onto the catalyst surface, causing the photocatalytic process to be accelerated [20].

TABLE II: BET SURFACE AREA OF TiO_2 PRECURSOR, UNDOPED TiO_2 NANOTUBES AND DOPED TiO_2 NANOTUBES

Samples	BET surface area (m^2/g)
TiO_2 precursor	9.280
Undoped TiO_2 nanotubes	226.521
Co^{2+} doped TiO_2 nanotubes	240.441
Ni^{2+} doped TiO_2 nanotubes	242.262
Cu^{2+} doped TiO_2 nanotubes	245.075

As shown in Table II the BET surface area of the TiO_2 precursor is 9.280m^2/g. However for undoped TiO_2 nanotubes, the value increases drastically to 226.521 m^2/g. It is predicted that the inner and outer surfaces of tubes structure are the major reason for the increase in surface area, which was one of the new attribute of the TiO_2 nanotubes compared with TiO_2 precursor. On the other hand, the BET surface areas of doped TiO_2 nanotubes are larger than undoped TiO_2 nanotubes due to the presence of dopant, which can reduced TiO_2 crystallization and grain growth during the heat decomposition step, thus producing larger surface area material [21]. For doped material, the trends show that the BET surface area increases from 240. 441 m^2/g to 241.262 m^2/g and 245.075 m^2/g upon the addition of transition metal ion series from left to right of the periodic table (Co^{2+}, Ni^{2+}, Cu^{2+}). The differential of transition metal ion size may be contributed to the deviation of surface area.

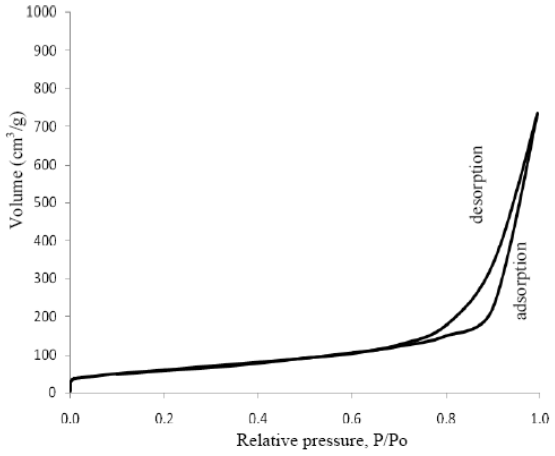

Fig. 4. Isotherm plot of undoped TiO_2 nanotubes

Fig. 4-7 shows the N_2 adsorption-desorption isotherms of undoped TiO_2 nanotube and doped TiO_2 nanotubes. The isotherm for all samples exhibits a typical IV-like isotherm with H1 hysteresis according to IUPAC classification [22]. The shapes of hysteresis loops have often been identified with specific pore structures. Type H1 hysteresis appearing in the multilayer range of physisorption isotherms is usually associated with capillary condensation in mesopore structures. Mesoporous structures allowed rapid diffusion of various reactants and product molecules passing through the pores during photodegradation reaction [22].

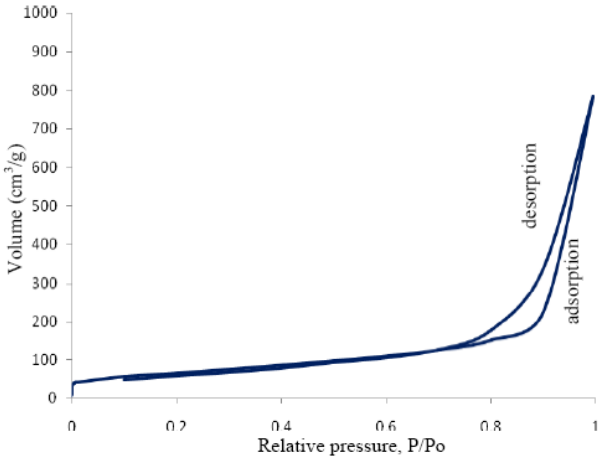

Fig. 5. Isotherm plot of 0.25 mmol Co^{2+} doped TiO_2 nanotubes

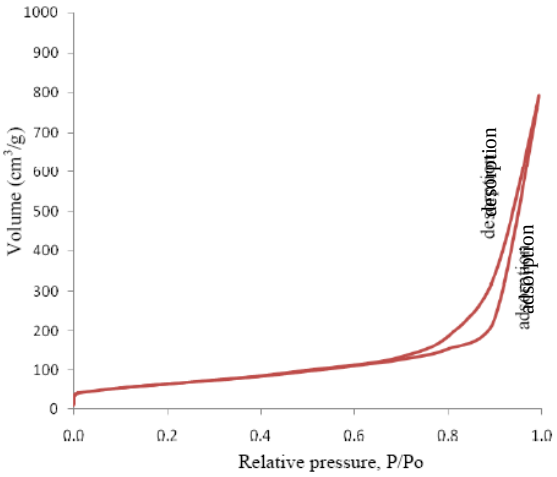

Fig. 6. Isotherm plot of 0.25 mmol Ni^{2+} doped TiO_2 nanotubes

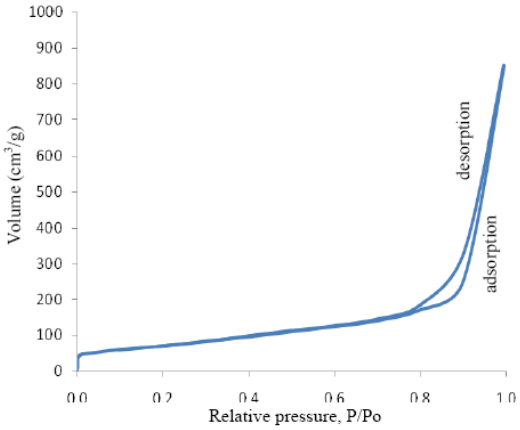

Fig. 7. Isotherm plot of 0.025 mmol Co^{2+} doped TiO_2 nanotubes

The band gap energy of the undoped titania nanotubes and doped nanotubes (copper ion) were determined from the reflectance data obtained in reflectance spectra [Fig. 8 and 10]. A graph of $[In (R_{max}-R_{min}/R-R_{min})]^2$ versus photon energy

(band gap energy) was plotted, where R_{max} represents the maximum reflectance value in desired wavelength and R_{min} represents the minimum reflectance value in desired wavelength. The energy band gap was determined based on the intersection from the extrapolation of the straight line of the curve to the y-axis = 0 [23]. In this study, the band gap energy of the undoped TiO_2 nanotubes is about ~3.27 eV (Fig. 9). The doped titanium dioxide nanotubes (with copper ion) on the other hand, show very small in their band gap energy (~2.06 eV) (Fig. 11), and shifted to the blue region wavelength in reflectance spectra. This probably due to the formation of a new phase (hexagonal) of TiO_2

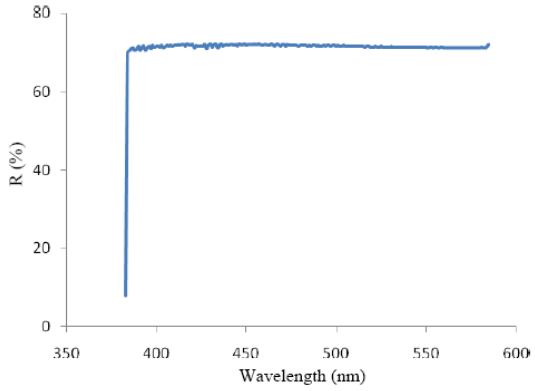

Fig. 8. Reflectance spectra of undoped TiO_2 nanotubes

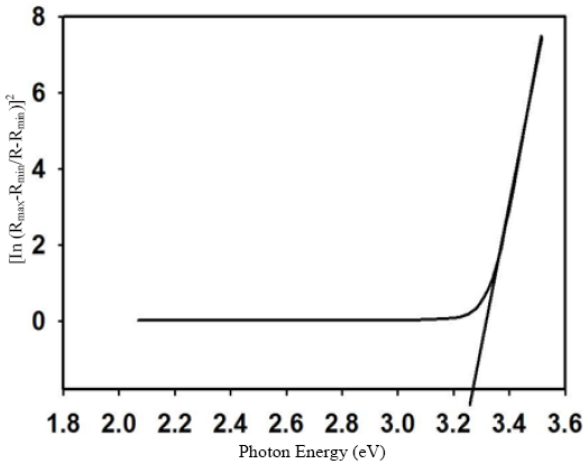

Fig 9. Energy band gap of undoped TiO_2 nanotubes

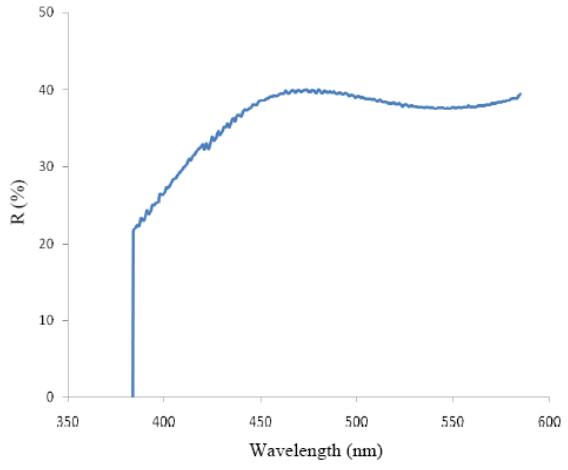

Fig. 10. Reflectance spectra of copper ion doped TiO_2 nanotubes

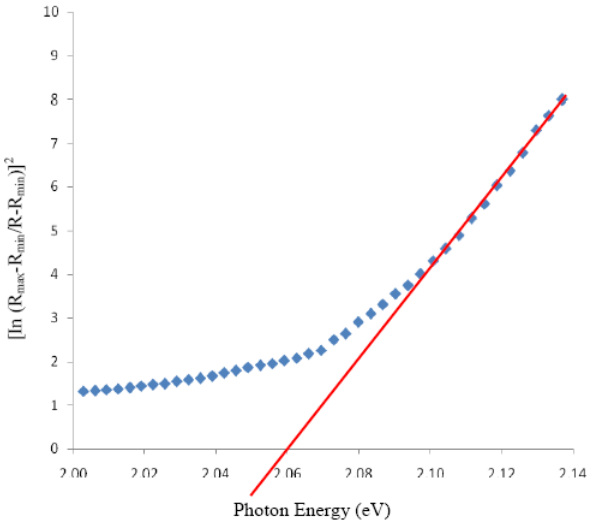

Fig. 11. Energy band gap of copper ion doped TiO_2 nanotubes

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