

Co²⁺ doped TiO₂ Nanotubes Visible Light Photocatalyst Synthesized by Hydrothermal Method for Methyl Orange Degradation

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Abstract - Co²⁺ doped TiO₂ nanotubes was successfully synthesized using simple hydrothermal method. The synthesized doped TiO₂ nanotubes were characterized by X-ray diffractometer (XRD), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX) and ultra violet diffuse reflectance spectroscopy (UV-DRS) for band gap measurements. XRD pattern shows that after Co ion doping the phase structure of anatase TiO₂ nanotubes transformed to hexagonal TiO₂ with the nanotubes morphology remained as proved by TEM micrographs. The band gap energy of Co²⁺ doped TiO₂ nanotubes gave as low as 2.06 eV compared to undoped TiO₂ nanotubes (3.20 eV). This resulted Co doped TiO₂ nanotubes exhibited higher rate for methyl orange degradation (MO) than the undoped TiO₂ nanotubes.

Key Words: Nanomaterials, Titania, Catalyst, Photodegradation

1. HEADING 1

Studies have indicated that TiO₂ nanotubes have displayed enhanced photocatalytic performance compared to other forms of TiO₂ for degradation of organic chemicals. Guo et al. (2011) found the nanotubular of TiO₂ has a better efficiency for photocatalytic degradation of Rhodamine B and methyl orange under solar illumination than the commercialized nano P25 TiO₂ [1]. While, Li et al. (2011) synthesized Ag-doped TiO₂ nanotubes for photocatalysis of gaseous toluene. The composites exhibited a degradation efficiency of 98%, which was higher than those of pure P25 TiO₂ and Ag-doped P25 TiO₂ [2]. The large surface area and unique tubular structure suggested that TiO₂ nanotubes would be suitable as photocatalyst. Moreover, nanotubes materials are expected to have faster electron transport and lower charge recombination due to 1D channel for electron transportation and decrement of

inter-crystalline contacts, respectively [3]. Even though TiO₂ nanotubes shows novel properties and exhibit better photocatalytic activities compared with other forms of TiO₂, however it is only photocatalytically active under UV irradiation region due to their wide band gap energy. Xu et al. (2011) reported the band gap energy of anatase TiO₂ nanotubes is 3.25 eV, being slightly larger than bulk TiO₂ anatase (3.2 eV) and rutile TiO₂ (3.0 eV) [4]. Due to their large band gap energy the TiO₂ only become active under UV light, thus limits the efficiency of solar photocatalytic reaction, as UV light accounts for only a small fraction (< 10%) of the incoming solar energy compared to visible light (45%) [5]. Thus, more research has been conducted in recent years to modify and develop TiO₂ photocatalyst that can work with high efficiency under UV and visible light irradiation such as via metal ion doping. The cobalts (Co) doping into TiO₂ nanocatalysts has been confirmed to exhibit superior photodegradation capability under visible light irradiation. For instance, Wang et al. (2012) had found that hydrothermal synthesized Co doped TiO₂ nanotubes managed to decompose methylene blue (MB) in liquid phase under visible light irradiation [6]. They reported the synergetic effect that is high porosity and optical band gap are the two key factors in affecting the photocatalytic activity of Co doped TiO₂ nanotubes under visible light. Co-doped TiO₂ nanotubes exhibit not only visible-light derived photodegradation but also liquid-phase adsorption ability of MB in aqueous solution. Despite the fact that the increase of the photocatalytic activity of Co doped TiO₂ has been demonstrated, there is still a lack of comprehension of dopant chemical environment and the processes involved.

2. EXPERIMENTAL

2.1 Preparation

2.00 g of the commercial TiO₂ powder precursor (Merck) was mixed with 100 mL of aqueous solution consists of 10 M NaOH and 5.00 mmol Co(NO₃)₂·3H₂O. The mixture was stirred for 30 minutes and subjected to hydrothermal treatment at 150°C for 24 hours in an autoclave. When the

reaction was completed, the white solid was collected and washed with 0.1 M HCl (200 ml). This followed by washing with distilled water until a pH 7 of washing solution was obtained. The final product was obtained by filtration and subsequently dried at 80°C for 24 hours. The resulting powder then calcined for 2 hours at 300 °C respectively.

2.2 Characterization

Paragraph X-Ray powder diffraction (XRD) analysis was performed using a Bruker D8 Diffractometer with Cu-K α ($\lambda = 1.54021 \text{ \AA}$) and scans were performed in step of 0.2°/second over the range of 2 θ from 10 to 90°. ZEISS SUPRA™ 35VP field emission scanning electron microscope (FESEM) coupled with EDX and Philips CM12 transmission electron microscope (TEM) was used to investigate the morphology of the sample.

2.3 Photocatalytic Study

Photocatalytic study of the samples was studied for methyl orange degradation (MO). The experiment was carried out by adding 0.1 g of samples into 100 ml of 20 ppm MO dye solution. The suspension was subjected to visible light irradiation for 3 hours. The visible light source was provided by 500W tungsten-halogen lamp (OSRAM, Germany), in which the 420 nm cut-off filter was used to cut off UV light below 420 nm. Throughout the experiment, the aqueous suspension was magnetically stirred. At every 30 minutes of time intervals 5 ml of aliquot was taken out using syringe and then filtered through 0.45 μm millipore syringe filter. Then absorption spectra were recorded via UV-Vis spectrophotometer (Perkin Elmer Lambda 35 UV-Vis) and the percentage of MO degradation was calculated using the formula in Eq. 1 [7,8].

$$\text{Degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad \text{Eq. 1}$$

Whereby, C_0 the absorbance of the solution at 270 nm wavelength before illumination, and C_t is the absorbance of solution at 270 nm wavelength after t times illumination.

3. RESULTS AND DISCUSSION

Fig-1 shows the XRD patterns of TiO₂ nanotubes (undoped) and Co²⁺ doped TiO₂ nanotubes. Undoped TiO₂ nanotubes revealed XRD patterns with peaks appeared at 2 $\theta = \sim 25.25^\circ, 37.52^\circ, 48.02^\circ, 53.58^\circ, 54.88^\circ, 62.61^\circ, 68.65^\circ, 70.22^\circ, 75.07^\circ$ and 82.71° which are assigned to anatase TiO₂ (Fig-1(a)) (PDF: 98-000-5225) [9]. While, XRD patterns for Co²⁺ doped TiO₂ nanotubes samples, relating them to TiO₂ hexagonal based on the three peaks presence at 2 θ about $19.89^\circ, 24.57^\circ$ and 48.30° (Fig-1(b)) (PDF: 98-005-5018) [9]. The XRD results clearly indicates that the addition of Co ion dopant alter the crystal structure phase of TiO₂ from anatase TiO₂ (tetragonal) to

TiO₂ hexagonal. The lattice parameters of anatase crystal structure of undoped TiO₂ nanotubes and hexagonal TiO₂ for Co²⁺ doped TiO₂ nanotubes based on the XRD patterns were collected and listed in Table 1.

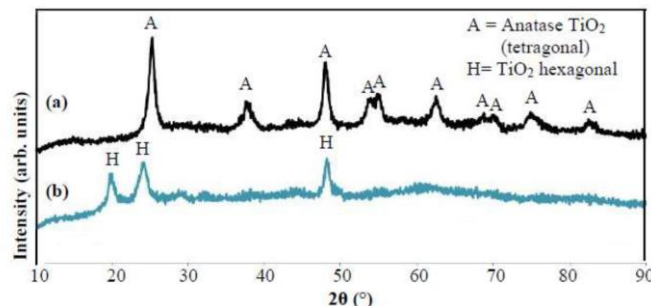


Fig -1: XRD patterns of (a) undoped TiO₂ nanotubes and (b) Co²⁺ doped TiO₂ nanotubes.

As can be seen in Table 1, the undoped TiO₂ nanotubes have lattice parameters (a - and c -axis) of 3.781 \AA and 9.509 \AA , respectively. On the other hand, for Co²⁺ doped TiO₂ nanotubes, the a and c lattice parameter values were significantly different, in comparison with the undoped TiO₂ nanotubes. This differences as well as the formation of new phase after cobalt ion doping is probably due to the incorporation of metal ion (Co²⁺) into interstitial positions of the TiO₂ lattice, as suggested by other [10]. The interstitial diffusion metal ion into the TiO₂ lattice can modify the nanotube lattice. Moreover, no additional peaks corresponding to the dopants were observed proving those dopants ions are successfully incorporated into the of TiO₂ lattice site. Larger ionic radius of Co²⁺ (0.89 \AA) than Ti⁴⁺ (0.745 \AA), thermodynamically supported Co ions to reside in the interstitial positions of TiO₂ lattice [11,12].

Table 1: Lattice parameters, phase structure and phase content of undoped TiO₂ nanotubes and Co²⁺ doped TiO₂ nanotubes

Samples	$a=b$ (\AA)	c (\AA)	Phase	Phase content (wt %)
Undoped TiO ₂ nanotubes	3.781	9.509	Anatase TiO ₂ (tetragonal)	100
Co ²⁺ doped TiO ₂ nanotubes	5.05	6.51	TiO ₂ hexagonal	100
Anatase TiO ₂ (tetragonal)	3.784	9.515	PDF: 98-000-5225	
TiO ₂ hexagonal	5.29	6.13	PDF: 98-005-5018	

In order to study the effect of Co ion doping on morphology of the samples, FESEM and TEM analyses was carried out. Fig-2 shows the FESEM micrographs of undoped TiO₂ nanotubes and Co²⁺ doped TiO₂ nanotubes, respectively. Fibrous-like structures with the diameter is about 10 nm and several hundred nanometers in length was obtained for undoped TiO₂ nanotubes (Fig-2(a)). After Co ion doping similar morphological characteristics are observed with little variation (Fig-2(b)). This indicated

that the cobalt ion doping had no effect on fibrous-like structure as metal ion loading was small, although the small addition had affected the phase formation of the doped nanotubes. The amount of cobalt ion loading presence in the TiO₂ matrix will be further discussed in EDX analysis.

cobalt dopant is also traced. The result indicates that TiO₂ based (99.3 at%) composed of small amount of cobalt (0.7 at%) as dopant.

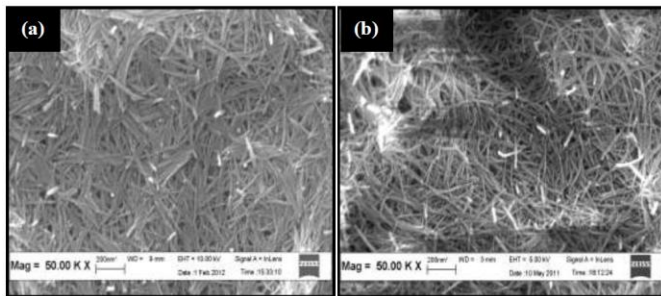


Fig -2: FESEM micrographs of (a) undoped TiO₂ nanotubes and (b) Co²⁺ doped TiO₂ nanotubes.

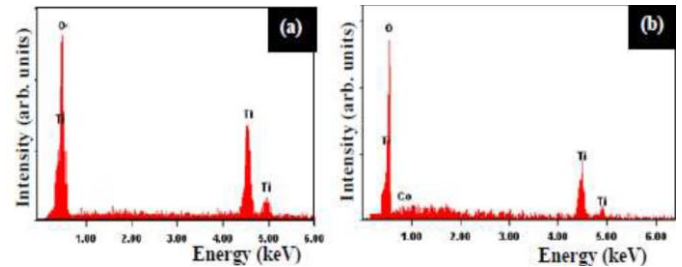


Fig -4: of (a) undoped TiO₂ nanotubes and (b) Co²⁺ doped TiO₂ nanotubes.

TEM micrographs of the undoped and doped TiO₂ nanotubes are shown in Fig-3. Fig-3(a) shows the TEM images of the undoped TiO₂ nanotubes. The existence of hollow inside the fibrous-like structures indicated the nanotubes. The inner and outer diameters of the nanotubes are about 4 nm and 10 nm respectively. After being doped with cobalt ion there were no obvious changes in their surface morphology. Samples of Co²⁺ doped TiO₂ nanotubes also showed the existence of hollow inside the fibrous-like structure indicating that nanotubular morphology were retained (Fig-3(b)). The nanotubular configuration owns large specific surface area due to both the internal and external areas of the nanotubes, thus it can enhance the adsorption of the organic molecules onto the surface of photocatalyst. Moreover, such nanotubular architecture also provides channels for enhanced electron transfer and offers a unidirectional electrical channel for photogenerated charge carrier transport [13]. These characteristics are good for the photocatalytic degradation of organic pollutant.

The band gap energy of synthesized samples was determined using ultra violet visible diffuse reflectance spectroscopy (UV-Vis DRS). The band gap energy of undoped TiO₂ nanotubes was determined to be 3.20 eV (Fig-5(a)), being similar with the band gap value that was reported in the literature for pure TiO₂ anatase [14]. For Co²⁺ doped TiO₂ nanotubes, their band gap energy were found significantly reduce to 2.06 eV as illustrated in Fig-5(a). This is due to the formation new phase of hexagonal TiO₂ after cobalts ion doping. The incorporation of Co (II) into the lattice of TiO₂ introduces a dopant energy level below the conduction band of TiO₂. Its subsequently creates intra-band gap states close to the valence band edges and leads to a narrower band gap.

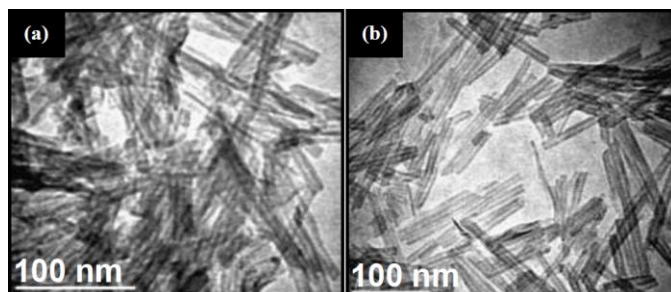


Fig -3: TEM micrographs of (a) undoped TiO₂ nanotubes and (b) Co²⁺ doped TiO₂ nanotubes.

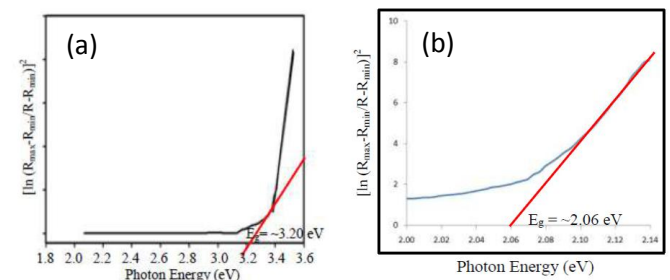


Fig -5: Band gap energy of (a) undoped TiO₂ nanotubes and (b) Co²⁺ doped TiO₂ nanotubes.

Fig-6 shows the percentage of MO degradation in the presence of different samples of undoped TiO₂ nanotubes and doped TiO₂. The degradation of MO were about 24%, and 85% for undoped TiO₂ nanotubes, Co²⁺ doped TiO₂ nanotubes, respectively after 3 hours reaction.

The EDX spectra of the samples were illustrated in Fig-4. As can be seen in Fig-3(a), only oxygen and titanium elements were present, while in Fig-3(b) the presence of

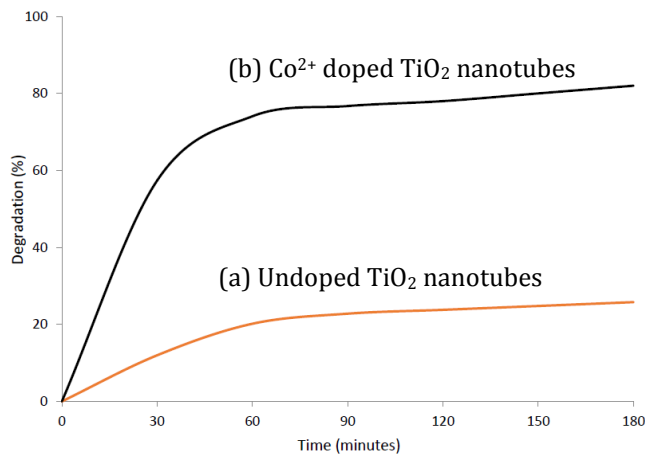
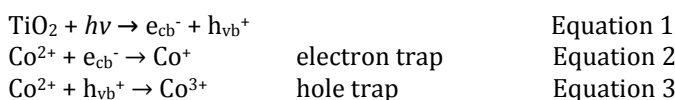


Fig -5: Degradation of methyl orange using (a) undoped TiO₂ nanotubes and (b) Co²⁺ doped TiO₂ nanotubes

It is evident that the Co²⁺ doped TiO₂ nanotubes gave higher degradation of MO than undoped TiO₂ nanotubes due to their low band gap energy. The undoped TiO₂ nanotubes only managed to degrade 24% of MO after 3 hours reaction because the TiO₂ nanotubes inactive under visible light region due to their large band gap energy. There are no formation of positive hole and photo-generated electron for degradation process. Thus only small loss of MO was obtained most probably due to the adsorption of MO into nanotubes. In contrast for the Co²⁺ doped TiO₂ nanotubes, about 80% degradation of MO was achieved after 3 hours reaction attributed to low band gap energy of the sample. Since the band gap energy level Co²⁺ doped TiO₂ nanotubes is about 2.06 eV, which is lower the undoped TiO₂ nanotubes (3.2 eV), the electrons can be injected from the valence band to the conduction band of Co²⁺ doped TiO₂ nanotubes, when the samples is illuminated by visible light irradiation. Then, the electrons are simultaneously transport to the surface to react with absorbed O₂ and H₂O to generate ·O₂⁻ and ·OH. The formation of reactive species of ·O₂⁻ and ·OH radicals will contribute to the oxidative pathways for degradation of methyl orange. The excited electron and positive hole could also recombine, in which can occur in the volume and at the surface of the particle especially on bare TiO₂ nanotubes, hence reduce the photocatalytic activity of the samples. Thus, the presence of Co ion in doped TiO₂ nanotubes can reduce the recombination rate by acting as electron and hole trappers through the process shown in Equations 1-3 [15];



These processes can restrain the recombination rate of photogenerated electrons and holes thus improving the photocatalytic activity.

3. CONCLUSIONS

Co²⁺ doped TiO₂ nanotubes exhibited outstanding photocatalytic activity for MO degradation under visible light irradiation. The high photocatalytic activity attributed to their low band gap energy (2.06 eV) as compared to 3.2 eV for undoped TiO₂ nanotubes. Co²⁺ doping created intra-band gap states close to the valence band edges and leads to a narrower band gap energy. On top of that, doping resulted in the formation of hexagonal TiO₂ phases due to the incorporation of Co²⁺ into TiO₂ lattice. The presence of Co²⁺ as well can reduce the recombination rate of photogenerated electrons and holes thus enhances the photocatalytic activity.

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BIOGRAPHIES



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