Co$^{2+}$ doped TiO$_2$ Nanotubes Visible Light Photocatalyst Synthesized by Hydrothermal Method for Methyl Orange Degradation

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Abstract - Co$^{2+}$ doped TiO$_2$ nanotubes was successfully synthesized using simple hydrothermal method. The synthesized doped TiO$_2$ 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 TiO$_2$ nanotubes transformed to hexagonal TiO$_2$ with the nanotubes morphology remained as proved by TEM micrographs. The band gap energy of Co$^{2+}$ doped TiO$_2$ nanotubes gave as low as 2.06 eV compared to undoped TiO$_2$ nanotubes (3.20 eV). This resulted Co doped TiO$_2$ nanotubes exhibited higher rate for methyl orange degradation (MO) than the undoped TiO$_2$ nanotubes.

Key Words: Nanomaterials, Titania, Catalyst, Photodegradation

1. HEADING 1

Studies have indicated that TiO$_2$ nanotubes have displayed enhanced photocatalytic performance compared to other forms of TiO$_2$ for degradation of organic chemicals. Guo et al. (2011) found the nanotubular of TiO$_2$ has a better efficiency for photocatalytic degradation of Rhodamine B and methyl orange under solar illumination than the commercialized nano P25 TiO$_2$ [1]. While, Li et al. (2011) synthesized Ag-doped TiO$_2$ nanotubes for photocatalysis of gaseous toluene. The composites exhibited a degradation efficiency of 98%, which was higher than those of pure P25 TiO$_2$ and Ag-doped P25 TiO$_2$ [2]. The large surface area and unique tubular structure suggested that TiO$_2$ 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 TiO$_2$ nanotubes shows novel properties and exhibit better photocatalytic activities compared with other forms of TiO$_2$, 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 TiO$_2$ nanotubes is 3.25 eV, being slightly larger than bulk TiO$_2$ anatase (3.2 eV) and rutile TiO$_2$ (3.0 eV) [4]. Due to their large band gap energy the TiO$_2$ 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 TiO$_2$ photocatalyst that can work with high efficiency under UV and visible light irradiation such as via metal ion doping. The cobalts (Co) doping into TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ nanotubes under visible light. Co-doped TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ powder precursor (Merck) was mixed with 100 mL of aqueous solution consists of 10 M NaOH and 5.00 mmol Co(NO$_3$)$_2$.3H$_2$O. 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-Kα (λ = 1.54021 Å) and scans were performed in step of 0.2°/second over the range of 2θ 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].

\[
\text{Degradation (%) = } \frac{C_o - C_t}{C_o} \times 100 \quad \text{Eq. 1}
\]

Whereby, \( C_o \) 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 TiO\(_2\) nanotubes (undoped) and Co\(^{2+}\) doped TiO\(_2\) nanotubes. Undoped TiO\(_2\) nanotubes revealed XRD patterns with peaks appeared at 2θ = ~25.25°, 37.52°, 48.02°, 53.58°, 54.88°, 62.61°, 68.65°, 70.22°, 75.07° and 82.71° which are assigned to anatase TiO\(_2\) (Fig-1(a)) (PDF: 98-000-5225) [9]. While, XRD patterns for Co\(^{2+}\) doped TiO\(_2\) nanotubes samples, relating them to TiO\(_2\) hexagonal based on the three peaks presence at 2θ about 19.89°, 24.57° 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 TiO\(_2\) from anatase TiO\(_2\) (tетragonal) to TiO\(_2\) hexagonal. The lattice parameters of anatase crystal structure of undoped TiO\(_2\) nanotubes and hexagonal TiO\(_2\) for Co\(^{2+}\) doped TiO\(_2\) nanotubes based on the XRD patterns were collected and listed in Table 1.

![Fig -1: XRD patterns of (a) undoped TiO\(_2\) nanotubes and (b) Co\(^{2+}\) doped TiO\(_2\) nanotubes.](image)

Table 1: Lattice parameters, phase structure and phase content of undoped TiO\(_2\) nanotubes and Co\(^{2+}\) doped TiO\(_2\) nanotubes

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Phase</th>
<th>Phase content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped TiO(_2)</td>
<td>3.781</td>
<td>9.609</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO(_2) nanotubes</td>
<td>5.05</td>
<td>6.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(^{2+}) doped TiO(_2) nanotubes</td>
<td>3.784</td>
<td>9.515</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anatase TiO(_2) (tетragonal)</td>
<td>5.29</td>
<td>6.13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 TiO\(_2\) nanotubes and Co\(^{2+}\) doped TiO\(_2\) nanotubes, respectively. Fibrous-like structures with the diameter is about 10 nm and several hundred nanometers in length was obtained for undoped TiO\(_2\) 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 TiO$_2$ matrix will be further discussed in EDX analysis.

Fig -2: FESEM micrographs of (a) undoped TiO$_2$ nanotubes and (b) Co$^{2+}$ doped TiO$_2$ nanotubes.

TEM micrographs of the undoped and doped TiO$_2$ nanotubes are shown in Fig-3. Fig-3(a) shows the TEM images of the undoped TiO$_2$ 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 Co$^{2+}$ doped TiO$_2$ 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.

Fig -3: TEM micrographs of (a) undoped TiO$_2$ nanotubes and (b) Co$^{2+}$ doped TiO$_2$ nanotubes.

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 cobalt dopant is also traced. The result indicates that TiO$_2$ based (99.3 at%) composed of small amount of cobalt (0.7 at%) as dopant.

Fig -4: of (a) undoped TiO$_2$ nanotubes and (b) Co$^{2+}$ doped TiO$_2$ nanotubes.

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 TiO$_2$ 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 TiO$_2$ anatase [14]. For Co$^{2+}$ doped TiO$_2$ 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 TiO$_2$ after cobalts ion doping. The incorporation of Co (II) into the lattice of TiO$_2$ introduces a dopant energy level below the conduction band of TiO$_2$. Its subsequently creates intra-band gap states close to the valence band edges and leads to a narrower band gap.

Fig -5: Band gap energy of (a) undoped TiO$_2$ nanotubes and (b) Co$^{2+}$ doped TiO$_2$ nanotubes.

Fig-6 shows the percentage of MO degradation in the presence of different samples of undoped TiO$_2$ nanotubes and doped TiO$_2$. The degradation of MO were about 24%, and 85% for undoped TiO$_2$ nanotubes, Co$^{2+}$ doped TiO$_2$ nanotubes, respectively after 3 hours reaction.

Fig -6: (a) Percentage of MO degradation in the presence of different samples of undoped TiO$_2$ nanotubes and doped TiO$_2$. (b) Percentage of MO degradation in the presence of undoped TiO$_2$ nanotubes and Co$^{2+}$ doped TiO$_2$ nanotubes, respectively after 3 hours reaction.
It is evident that the Co$^{2+}$ doped TiO$_2$ nanotubes gave higher degradation of MO than undoped TiO$_2$ nanotubes due to their low band gap energy. The undoped TiO$_2$ nanotubes only managed to degrade 24% of MO after 3 hours reaction because the TiO$_2$ nanotubes inactive under visible light region due to their large band gap energy. There are no formation of positive hole and photogenerated 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 Co$^{2+}$ doped TiO$_2$ 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 Co$^{2+}$ doped TiO$_2$ nanotubes is about 2.06 eV, which is lower the undoped TiO$_2$ nanotubes (3.2 eV), the electrons can be injected from the valence band to the conduction band of Co$^{2+}$ doped TiO$_2$ nanotubes, when the samples is illuminated by visible light irradiation. Then, the electrons are simultaneously transport to the surface to react with absorbed O$_2$ and H$_2$O to generate -O$_2^-$ and -OH. The formation of reactive species of -O$_2^-$ 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 TiO$_2$ nanotubes, hence reduce the photocatalytic activity of the samples. Thus, the presence of Co ion in doped TiO$_2$ nanotubes can reduce the recombination rate by acting as electron and hole trappers through the process shown in Equations 1-3 [15];

\[
\begin{align*}
\text{TiO}_2 + h\nu & \rightarrow e_{cb}^- + h_{vb}^+ \quad \text{Equation 1} \\
\text{Co}^{2+} + e_{cb}^- & \rightarrow \text{Co}^+ \quad \text{electron trap} \quad \text{Equation 2} \\
\text{Co}^{2+} + h_{vb}^+ & \rightarrow \text{Co}^{3+} \quad \text{hole trap} \quad \text{Equation 3}
\end{align*}
\]

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

3. CONCLUSIONS

Co$^{2+}$ doped TiO$_2$ 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 TiO$_2$ nanotubes. Co$^{2+}$ 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 TiO$_2$ phases due to the incorporation of Co$^{2+}$ into TiO$_2$ lattice. The presence of Co$^{2+}$ as well can reduce the recombination rate of photogenerated electrons and holes thus enhances the photocatalytic activity.

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REFERENCES


**BIOGRAPHIES**

Dr Ahmad Fauzi Mohd Noor is a professor at Universiti Sains Malaysia. His research interests are in the areas of ceramics, composites materials and nanomaterials. He has published more than 50 international journal articles.

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