Adsorption and visible-light-derived photocatalytic kinetics of organic dye on Co-doped titania nanotubes prepared by hydrothermal synthesis

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1. Introduction

Recently, tubular type of titanium dioxide (TiO2) has attracted considerable attention because of a variety of technological and scientific applications, involving organic light-emitting diodes, photocatalysts, gas sensors, and dye-sensitized solar cells [1–6]. Several approaches to prepare TiO2 nanotubes (TNTs) are believed to positively raise the applicability of the titania nanotubes. Among these approaches, the hydrothermal synthesis of nanotubes is an emerging method as a result of its convenience and cheapness. Generally, these TNT samples show not only high aspect ratio but also vast pore structure owing to their unique tubular-type nanos-structure. Therefore, the titania-based nanotube becomes one of the promising candidates for use in photocatalytic (e.g., de-NOx catalysis) [5] and photoelectrochemical (e.g., electrodes of dye-sensitized solar cell) systems [7]. To make it more commercial, some important characteristics of TNTs, such as adsorption and photocatalysis, still require a better understanding.

Doping metal or nonmetal has been extensively applied to improve the properties of oxide nanoparticles in catalysis and gas sensing [8,9]. Accordingly, doping transition metals into anatase-type titania crystallites leads to tune the optical band gap, thus shifting UV absorption to visible-light absorption. Pervious studies have reported doping of TiO2 with various species such as a number of metal ions such as Pt, V, Ni, Mn, Cr and Fe [10–13], or nonmetals like N atoms [14–17]. They have been demonstrated to improve the photocatalytic reactivity toward organic molecules under visible-light illumination. Very recently, we have reported a hydrothermal route for preparation of titania nanoparticles with Fe, Co, and Ni dopants, showing a photocatalytic capability of organic dye under visible illumination [9]. However, to our knowledge, little work has been reported on probing the photocatalysis of dye on the metal-doped TNT nanostructures.

In this work, our interest focuses on adsorption and photocatalytic abilities of organic dye on metal-doped TNTs in aqueous solution. We aim to synthesize a novel titania nanostructure that behaves not only as high porosity but also as visible-light-derived photocatalysis. A hydrothermal route combined with metal doping was employed to prepare highly porous Co-doped TiO2 nanotubes (TNTs) for enhancement of adsorption and visible-light-driven photocatalysis capabilities of basic violet 10 (BV10) from liquid phase. The specific surface area of prepared TNTs can reach the maximal value of ~379 m²/g. These tubes are hollow scrolls with a typical outer diameter of about 10–15 nm, inner diameter 5–10 nm and length of several micrometers. The anatase-type of TNTs has an average Co-dopant concentration of $5 \times 10^{20}$ ions/cm³, determined by an electron dispersive X-ray spectrometer. The adsorptive surface coverage on TNTs was found to be ca. 7.61–7.63%, showing a low affinity between BV10 molecules and TNTs. A pseudo-second-order reaction model was used to fit with the experimental data of adsorption and photocatalytic kinetic curves. The adsorption rate constant has one order higher than the photocatalytic rate constant, reflecting that the photocatalysis of the basic dye is the rate-determining step during the adsorption/photocatalysis process. These novel Co-doped TNTs are believed to be a promising candidate in a variety of photocatalysis applications because of the combination effect of a high porosity with a photocatalysis under visible illumination.

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unit operation because this dye is a mutagen and mitotic poison [18,19]. Here, we discover two pathways for removal of the dye on highly porous TNTs: adsorption and visible-light-derived photocatalysis. Thus, this effort to examine the adsorption and photocatalysis kinetics (e.g., rate constant) and equilibrium parameters (e.g., adsorption and photocatalytic capacities) is devoted. In addition, the influence of porous characteristics on these parameters is also discussed.

2. Experimental

2.1. Preparation of Co-doped TNTs

The hydrothermal method combined with Co-doping was employed here for the synthesis of Co-doped TNTs. Briefly, commercial TiO₂ nanoparticles (2 g) were mixed in an aqueous solution, containing 10 M NaOH + 0.01 M Co(NO₃)₂, and charged into a Teflon-lined autoclave. The autoclave was then oven-heated at 135 °C for 24 h. The precipitate was filtered and the pH value of the slurry was adjusted with a diluted 0.1 M HNO₃. To obtain anatase-type titania, the pH value of the slurry was adjusted to 1.6 by HNO₃ washing [20]. The final products were obtained by filtration with subsequent drying at 110 °C overnight. For comparison, different TNT samples were prepared to examine the effect of porous characteristics on the photocatalytic capability. Three types of TNT samples with different porosities were obtained through various calcination temperatures, ranging from 300 °C to 400 °C.

2.2. Characterization of Co-doped TNTs

A UV spectrometer (Varian Cary100) was applied to analyze the reflectance spectra of TNT samples, ranging from 200 nm to 800 nm in wavelength. The phase identification of TiO₂ nanotubes was characterized by XRD with Cu Kα radiation using an automated X-ray diffractometer (Philips PW 1700). High-resolution transmission electron microscopy (HR-TEM, JEOL JEM-6500F) was

![Fig. 1. Adsorption (solid symbol)/desorption (empty symbol) isotherms of N₂ onto (a) TiO₂ nanoparticles (P25), (b) TNT-1, (c) TNT-2, and (d) TNT-3 at −196 °C. Pore size distributions of (e) TiO₂ nanoparticles (P25) and (f) TNT-1, (g) TNT-2, and (h) TNT-3, determined from BJH method.](image)
used for morphological observations of the Co-doped TNTs. Specific surface areas and pore volumes of the derived nanotubes were determined by gas adsorption. An automated adsorption apparatus (Micromeritics, ASAP 2000) was employed for these measurements. Adsorption of N2, as a probe gas, was performed at –196 °C. Nitrogen surface areas and micropore volumes of the samples were determined from Brunauer–Emmett–Teller (BET) and Dubinin–Radushkevich (DR) equations, respectively. The amount of N2 adsorbed at relative pressures near unity were used for morphological observations of the Co-doped TNTs. Specific surface areas and pore volumes of the derived nanotubes were determined by gas adsorption. An automated adsorption apparatus (Micromeritics, ASAP 2000) was employed for these measurements. Adsorption of N2, as a probe gas, was performed at –196 °C. Nitrogen surface areas and micropore volumes of the samples were determined from Brunauer–Emmett–Teller (BET) and Dubinin–Radushkevich (DR) equations, respectively. The amount of N2 adsorbed at relative pressures near unity (P/P0 = 0.98 in this work) has been employed to determine the total pore volume, which corresponds to the sum of the micropore and mesopore volumes. The peak pore diameter of nanotubes can be estimated according to pore size distribution, determined from Barrett–Joyner–Halenda (BJH) method.

2.3. Adsorption and photocatalysis of BV10 on Co-doped TNTs

Analytical-grade basic dye, BV10 (molecular formula: C28H31ClN2O3; molecular weight: 478.5; supplier: Sigma Chemical Co.) was served as the target organic pollutant for adsorption and photocatalysis experiments. To clarify the effects of adsorption and photocatalysis, adsorption experiments of BV10 in complete darkness were performed before photocatalysis. We placed a slurry of 100 mg of Co-doped TNTs into a glass-stoppered flask at 30 °C for 5 h, employing a fluorescent lamp. To ensure no UV light illumination, the irradiation from the fluorescent lamp was filtered through a UV cut filter. This allowed for the visible light > 400 nm to pass through the filter. The slurries were also illuminated at 400 nm to mimic a UV–visible spectrometer (Shimadzu UV-2550). Based on the Beer–Lambert law, the dye concentration is linearly proportional to the absorbance of measured spectrum within the linear range of 0.001 to 0.050 absorbance units. The Beer–Lambert law has been well examined and reported elsewhere. This result is consistent with the previous studies, confirming the anatase-type TNTs.

Electrode dispersive X-ray spectrometer (EDS) was used to confirm the composition of TNT samples, as shown in Fig. 3. The EDS analysis has shown the presence of Co in TiO2 crystallites, and the average dopant concentration of TNTs is found to be 5 × 1020 ions/cm3. Fig. 4 compares the typical XRD patterns of TNTs and P25. It is known that the precursor P25 has ca. 70% anatase and ca. 30% rutile phases. In the case of TNTs, the XRD patterns that represent peaks are anatase [1 0 1], [0 0 4], [2 0 0], [1 0 5], and [2 0 4] diffractions at scattering angles (2θ) of 25.3°, 36.6°, 48.0°.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>S_Bet⁹ (m²/g)</th>
<th>V₁⁹ (cm³/g)</th>
<th>Pore size distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>45.8</td>
<td>0.121</td>
<td>0.016 (16) 0.102 (84)</td>
</tr>
<tr>
<td>TNT-1</td>
<td>379</td>
<td>0.934</td>
<td>0.117 (13) 0.816 (87)</td>
</tr>
<tr>
<td>TNT-2</td>
<td>350</td>
<td>0.975</td>
<td>0.118 (12) 0.857 (88)</td>
</tr>
<tr>
<td>TNT-3</td>
<td>289</td>
<td>0.685</td>
<td>0.118 (17) 0.567 (83)</td>
</tr>
</tbody>
</table>

³ S_Bet: specific surface area computed using BET equation.
⁹ V₁: total pore volume estimated at a relative pressure of 0.98.
⁴ V_micropore: micropore volume determined from DR equation.
⁴ V_mesopore: mesopore volume determined from the subtraction of micropore volume from total pore volume.
54.5° and 62.6°, respectively. Apparently, the rutile of P25 has been transformed to anatase-type. The anatase phase with a longer c-axis has been reported to be the preferred phase in TiO₂ nanotubes [20,22]. Additionally, the peak intensity becomes vague after the formation of nanotubes. This is presumably due to the small number of crystalline layers or the small wall thickness of the tubes.

Diffuse reflection spectra of TNTs and P25 are shown in Fig. 5. Generally, anatase-type TiO₂ crystalline has a strong absorption edge below ca. 380 nm [10]. In comparison, the absorption edge of Co-doped TNTs shows a shift to visible-light region, i.e., > 400 nm in wavelength. After that, an obvious peak appears within the wavelength region 550–650 nm, which can be ascribed to the formation of impurity energy level within the band gap. This proves that the hydrothermal doping technique has modified the UV–visible absorption characteristics of titania catalysts. In Fig. 5, both the absorption edges are extrapolated to the axis of wavelength, producing two intersections: (A) and (B) at 385 nm and 590 nm, respectively. Generally, the intersection represents the optical band gap of titania samples according to the formula of band gap (optical band gap = 1240/wavelength). After calculations, P25 has a typical band gap of 3.20 eV, whereas the Co-doped TNT shows a significant drop of the magnitude of band gap smaller than 3.20 eV; that is, only ca. 2.14 eV for all Co-doped TNTs. The above results disclose one crucial finding that the Co-dopant effectively make the band gap narrower. Also, this confirms that the hydrothermal synthesis of Co-doping in TNTs leads to a pathway of “communicated electrons” between these crystals. How the Co doping in TNTs affects the visible-light photocatalysis of organic dye will be investigated in the following section.

We now turn to the main subject of this paper, that is, the adsorption and visible-light photocatalysis behaviors of the Co-doped TNT samples. The adsorption and photocatalytic kinetics as functions of time are shown in Fig. 6. To figure out both the effects, the adsorption experiment in complete darkness was carried out first, followed by the photocatalysis of BV10 under visible illumination. The adsorption equilibrium of BV10 is reached within 2 h, and the equilibrium adsorption capacities have an order as follows: TNT-1 (10.6 mg/g) > TNT-2 (9.8 mg/g) > TNT-3 (8.1 mg/g) > P25 (0.35 mg/g). These total adsorption capacities of TNTs are much greater than that of P25 nanoparticles [23]. In the case of adsorption of BV10 on the Co-doped TNTs, this order is generally followed by the magnitude of specific surface area of nanotubes, indicating different numbers of active sites for the liquid-phase adsorption of dye molecules.

The adsorptive surface coverage θₜₐ₅, i.e., the fraction of BET area covered by BV10 molecules, can be estimated by assuming that the area occupied by a BV10 molecule is estimated to be 217 Å² [24]. The calculated surface coverage θₜₐ₅ for TNTs ranges between 7.61% and 7.63%, showing that all Co-doped TNTs have the same number of active sites for adsorption of BV10. However, such low θₜₐ₅ value (≪100%) reflects that basic dyes only partially wet titania surface (or low affinity between BV10 molecules and TNTs), indicating the presence of surface heterogeneity for BV10 adsorption. It is generally recognized that the adsorption of basic dyes on adsorbents is dominated by ion-exchange process [25]. Since TiO₂ surface favors a more hydrophilic behavior due to surface hydroxyl (–OH) groups [3], whereas the polarity of BV molecule seems to be weak, thus resulting in the weak interaction between TNTs and BV10. Another
way to interpret the above result is probably due to the fact that the large basic dyes may screen TNT porosity. This would induce the inaccessibility for BV10 into the entrance or channel of TNTs, decreasing available N$_2$-BET surface area for adsorption of the basic dye.

Fig. 6 also shows visible-light photocatalytic kinetics of BV10 on Co-doped TNTs after attaining adsorption saturation. As expected, P25 does not show any photocatalytic capability under visible irradiation. On the contrary, Co-doped TNTs are found to give an excellent photodecomposition performance of BV10 in liquid phase. This demonstrates that the hydrothermal synthesis of Co-doped TNTs is an efficient approach in promoting not only adsorption but also photocatalysis ability under visible illumination. Their photocatalytic capacities after 10 h visible illumination have an order as follows: TNT-1 (43.0 mg/g) > TNT-2 (39.2 mg/g) > TNT-3 (29.5 mg/g) > P25 (∼0.1 mg/g). This sequence of photocatalysis is identical with adsorption capacity, which is strongly related to the porosity of TNT samples. The results disclose two important messages: (i) the photocatalysis of BV under visible illumination belongs to a surface-catalyzed reaction, and (ii) the pore structure of Co-doped TNTs may play a major factor in removing the dye form aqueous solution.

Here, we estimate the photocatalytic surface coverage, $\theta_{\text{photo}}$, according to the above assumptions. These calculated $\theta_{\text{photo}}$ values are 30.87%, 30.48%, and 29.47% for TNT-1, TNT-2, and TNT-3, respectively. This little difference indicates a resembling amount of active sites over TNTs for visible-light-derived photocatalysis of BV10. It is of interest that the $\theta_{\text{ads}}$ has a much smaller value than the $\theta_{\text{photo}}$. Which can be attributed to two possible reasons: (i) the number of adsorptive sites cannot match that of photocatalytic sites at an equal rate constant or (ii) the equilibrium rate constant of adsorption exceeds that of visible-light photocatalysis. Generally, the photocatalytic reaction is considered as a surface-catalyzed reaction that would take place on the dye-adsorbed sites over photocatalysts. This means that the surface coverage of photocatalytic sites should be identical with that of adsorptive sites based on equal rate constants. However, this result seems to violate the above assumption in our case. Thus, we infer that reason (ii) suits to the adsorption/visible-light photocatalysis hybrid behavior of BV10 on Co-doped TNTs. To prove this, the adsorption and photocatalysis kinetic parameters will be investigated in further section.

Table 2 presents a well description on the dependency of photocatalytic reaction rates of organic compounds [26–28]. However, this model cannot agree with the adsorption/photocatalytic kinetics of BV10 on TNTs based on the above deduction. Accordingly, a simple reaction rate expression is performed with the aid of pseudo-second-order equation [25,29] as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2$$  \hspace{1cm} (1)

where $q_e$ and $q_t$ are the amount of BV10 adsorbed or visible-light photocatalyzed per unit mass of TNT at steady state and any time $t$, respectively, and $k_{\text{ads}}$ is the rate constant for adsorption ($k_{\text{ads}}$) and photocatalysis ($k_{\text{photo}}$) of BV10. This adsorption rate expression can be definitely integrated by applying the two initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t$.

$$t = \frac{1}{k_{\text{ads}}} q_e^2 + \frac{t}{q_e}$$ \hspace{1cm} (2)

A linearity plot of $t/q_t$ versus $t$ would determine $q_e$ and $k_{\text{ads}}$ from the slope and intercept, respectively. The calculated values, together with the correlation factor ($r^2$), are given in Table 2. The $r^2$ value, approximately close to unity, indicates an excellent fitting result for the adsorption of BV10 on TNTs using the pseudo-second-order kinetic model. As shown in Table 2, all $q_e$ values are nearly identical with the equilibrium adsorption capacities determined from Fig. 6. These rate constants, $k_{\text{ads}}$, are found to have an increasing function of BET specific surface area, ranging between 6.6 × 10$^{-3}$ g/min mg and 8.9 × 10$^{-3}$ g/min mg. Basically, Eq. (1) is an apparent reaction formula; that is, the rate constant is possibly governed by diffusion and adsorption in the BV10 adsorption step. Since all TNTs show the similar pore size distribution (Fig. 1) and tubular size (Fig. 2), we infer that pore diffusion resistance has the same basis during the adsorption process. Thus, the increase in the adsorption rate constant can be ascribed to the fact that the vaster porosity of TNTs provides more active sites, allowing BV10 accessibility into nanotubes.

Similarly, Eqs. (1) and (2) are employed to estimate the kinetic parameters of visible-light photocatalysis once again. It is noticed that the initial conditions should be modified since each TNT has its own adsorption capacity at steady state. The apparent rate constant for visible-light photocatalysis ($k_{\text{photo}}$) and photocatalytic capacity ($q_e$) can be determined from the intercept and slope of linearity plot of $t/q_t$ versus $t$, respectively. The two parameters, together with correlation factor ($r^2$), of pseudo-second–order reaction are also collected and listed in Table 2. The $r^2$ values (>0.995) demonstrate that

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**Table 2**

Ad sorption and visible-light photocatalytic parameters on Co-doped TNTs determined from the pseudo-second-order reaction kinetic model.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Dark adsorption</th>
<th>Visible-light-derived photocatalysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$ (mg/g)</td>
<td>$k_{\text{ads}}$ (g/min mg)</td>
</tr>
<tr>
<td>TNT-1</td>
<td>10.9</td>
<td>0.0089</td>
</tr>
<tr>
<td>TNT-2</td>
<td>10.2</td>
<td>0.0076</td>
</tr>
<tr>
<td>TNT-3</td>
<td>8.6</td>
<td>0.0066</td>
</tr>
</tbody>
</table>
the linear fits are fairly good for photocatalytic kinetic behavior of BV10. These kinetic parameters in Table 2 are used to predict the adsorption and photocatalysis kinetic curves of Co-doped TNTs, and the prediction curves are presented in Fig. 6 to predict with the experimental data. Fig. 6 clearly shows that Eq. (1) provides equally good fits for all the TNT samples over the entire reaction period.

From the data in Table 2, the visible-light photocatalytic capacity, \( q_{\text{photo}} \), is expected to have an increasing trend of the specific surface area of TNTs. Again, this proves that the specific surface area significantly promotes the number of active sites for photocatalysis under visible illumination. As for the value of \( k_{\text{ads}} \), it also depends on the specific surface area of TNTs, showing an increase in \( k_{\text{ads}} \) value with the porosity. To compare with the \( k_{\text{ads}} \) value, the two rate constants as function of the specific surface area are illustrated in Fig. 7. This figure shows that both the rate constants tend to gradually increase with surface area. Reasonably, this positive effect infers that more active sites over photocatalysts facilitate the adsorption and photocatalytic rates. Additionally, we note that the \( k_{\text{ads}} \) value has one order higher than the \( k_{\text{ads}} \), this finding can support our previous argument that the equilibrium rate constant of adsorption exceeds that of visible-light photocatalysis, thus resulting in adsorptive surface coverage smaller than photocatalytic coverage. Based on the result, we infer that the photocatalysis of BV10 under visible illumination becomes the rate-determining step during the adsorption/photocatalysis hybrid process.

As mentioned above, it is generally admitted that the adsorption of basic dye on adsorbents is a simple physisorption [25,29,30]. However, visible-light photocatalysis is a serial of complicated reactions, consisting of photoinduction, electron (e\(^{-}\))/hole (h\(^{+}\)) pair generation, radical formation, and BV10 degradation. Briefly, the formation of (e\(^{-}\))/hole (h\(^{+}\)) pairs on Co-doped TNTs requires a photocatalytic energy of 2.14 eV, which is about seven times higher than the photodesorption of BV10 on titane nanotubes (~0.295 eV) [31]. This induces that the visible photocatalysis of BV10 would take a very long period in comparison with the physisorption; that is, \( k_{\text{ads}} \ll k_{\text{ads}} \), as shown in Fig. 7. After the adsorption of BV10 takes place on adsorptive site rapidly, the BV10-adsorbed site is slowly photocatalyzed under visible illumination, thus decomposing the dye into one ionic compound. After that, next BV10 molecule immediately occupies the site, and the photocatalysis then repeats to degrade next +BV10 molecule. Owing to the well-developed tubular nanostructure, dye diffusion and adsorption resistance seem to be negligible. When the photocatalysis period prolongs, the number of photactive species is enough to photodecompose the basic dyes, thus leading to higher visible-light photocatalytic activity. We believe that Co-doped nanotubes show not only a fairly good adsorption capacity in liquid phase but also a dye-photocatalysis capability under visible illumination.

4. Conclusions

(1) We have successfully developed a hydrothermal route for the preparation of Co-doped TNTs that markedly enhance the adsorption and visible photocatalytic capabilities of basic dye in aqueous solution.

(2) The prepared TNTs exhibit high specific surface areas of ca. 289–379 m\(^2\)/g and total pore volumes of 0.685–0.934 cm\(^3\)/g. HR-TEM observation showed that these tubes are hollow scrolls with a typical outer diameter of about 10–15 nm, inner diameter 5–10 nm and length of several micrometers.

(3) The crystalline structure of TNTs showed anatase-type crystal-\( \bar{c} \)ite, and the dopant concentrations of cobalt had an average value of \( 5 \times 10^{20} \) ions/cm\(^3\), determined from XRD and EDS analysis, respectively. In UV absorption spectra, the adsorption edge of Co-doped TNTs shows a shift to visible-light region, followed by an obvious adsorption peak at 550–650 nm. This transformation can be ascribed to the formation of impurity energy level within the band gap, improving the visible-light photocatalysis of basic dye.

(4) Adsorption and visible-light photocatalysis capacities are increasing functions of the BET-specific surface area, showing that (i) the photocatalysis of BV under visible illumination belongs to a surface-catalyzed reaction, and (ii) the pore structure of Co-doped TNTs may play a major factor in removing the dye form aqueous solution.

(5) The adsorptive surface coverage (\( \Theta_{\text{ads}} \)) on TNTs was found to be ca. 76.1–76.3%, showing the low affinity between BV10 molecules and TNTs. Based on the surface-catalyzed reaction, the photocatalytic surface coverage, \( \Theta_{\text{photo}} \), ranges between 29.47% and 30.87%, which is much higher than \( \Theta_{\text{ads}} \).

(6) A pseudo-second-order reaction expression was found to have an excellent fitting with the experimental data of adsorption and photocatalytic kinetic curves. The \( k_{\text{ads}} \) value has one order higher than the \( k_{\text{photo}} \) value, reflecting that the photocatalysis of the basic dye is the rate-determining step during the adsorption/photocatalysis process.

(7) The hydrothermal synthesis of Co-TiO\(_2\) tubes is an efficient approach in enhancing not only specific surface area but also photocatalysis capability under visible illumination. These novel Co-doped TNTs are believed to be a promising candidate in a variety of photocatalysis applications because of the combination effect of a high porosity with a photocatalysis under visible illumination.

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References


