Immobilization of cobalt doped rutile TiO$_2$ on carbon nanotubes walls for efficient photodegradation of 2,4-dichlorophenol under visible light

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Abstract

In this work, we focused on improvement of rutile-type TiO₂ degradation efficiency by cobalt doping and decorating on carbon nanotubes walls (CNTs) (Co-TiO₂/CNTs). X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), field emission scanning electron microscopy (FESEM), diffuse reflectance spectroscopy (DRS), and nitrogen physisorption were used to characterize the prepared samples. The XRD results indicated after cobalt doping, we obtained rutile phase as the major phase for cobalt containing samples. The band gap energy of the synthesized samples were calculated by Kubelka-Munk equation using diffuse reflectance spectra. The surface area of the samples was obtained by BET model and average pore diameter and pore volume of the samples were extracted from desorption branch of BJH model. The effectiveness of the samples was examined through degradation of 2,4-dichlorophenol (2,4-DCP) as a model of organic pollutants under visible light. We achieved 27% and 50% visible light degradation of 2,4-DCP in the presence of pure TiO₂ and Co-TiO₂/CNTs after 180 min irradiation, respectively. The high visible light activity of Co-TiO₂/CNTs sample can be approved that the presence of cobalt and CNTs reduce the band gap energy and sensitize TiO₂ surface to visible light respectively. The mechanism for degradation of 2,4-DCP by Co-TiO₂/CNTs photocatalyst under visible light is proposed.

Keywords: Cobalt; CNTs; Rutile; TiO₂; visible light degradation; 2,4-dichlorophenol

1. Introduction:

The expansion of degradation efficiency of TiO₂ in the visible light region is essential for decontamination of water pollutants. Many researchers made the efforts on the alteration of TiO₂ for improving of its efficiency under visible light by doping of noble, transition and rare earth metals [1, 2] and immobilization on different supports including zeolite, alumina, activated carbon and carbon nanotubes (CNTs)[3-5]. Another objective of surface modification of TiO₂ is to restrain the electrons and holes recombination by encouraging the charge isolation to improve the degradation performance [6, 7]. Cobalt as one of the most valuable dopants among the transition metals can develop the light response and degradation activity of TiO₂. Recently,
Ebrahimian et al. [8] prepared cobalt doped TiO$_2$ nanoparticles by hydrothermal method and the synthesized samples showed a great absorption range in the visible region. Iwasaki et al. [9] reported that doping of Co$^{2+}$ into TiO$_2$ lattice could extend the absorption edge of TiO$_2$ and improve degradation performance of it under UV irradiation and visible light. The degradation performance of TiO$_2$ can be improved under UV by using CNTs in TiO$_2$ composite and surface features are changed to attain sensitivity to visible light [10]. Moreover, using CNTs in the structure of TiO$_2$ composite changes morphology and the particle dimension of TiO$_2$ [11]. Furthermore, the photocatalytic activity is greatly affected by CNTs as dispersing agent, adsorbent and photosensitizer[12].

The one dimensional nature of CNTs provides easy movement of charge carriers through nanotubes with no scattering causing ballistic transport that minimizes Joule heating and consequently, currents with very large densities transfer easily[13]. These transporting features of CNTs causes a suitable means of directing the flow of photoinduced electrons and holes and increase the life of them [14].

In our previous study[15], we investigated the effect of cobalt doping on the phase formation of TiO$_2$ and achieved anatase as the major phase for the prepared nanocomposites. In the current study, we focused on the synthesis of cobalt doped TiO$_2$ with rutile major phase and decorated on the walls of CNTs. The textural and morphology features of the obtained photocatalysts were characterized by XRD, FTIR, DRS, FESEM/EDX and N$_2$ physisorption analyses. The effectiveness of the obtained samples was assessed through degradation of synthetic wastewater containing 2,4-dichlorophenol (2,4-DCP) under visible light.

2. Materials and Methods

2.1. Materials and reagents

Cobalt (II) chloride hexahydrate (CoCl$_2$.6H$_2$O)(Merck, No.102539), Titanium isopropoxide (TIP) (Merck No. 8.21895), ethanol (Merck No. 818760), high-purity 2,4-DCP, 98%, (Merck No. 803774), and carboxylic groups-functionalized CNTs with diameter of the 10-20 nm and the
length of 0.5-2.0 μm provided by Neutrino Corporation (Iran) were used in this study. Deionized water was used in all experiments.

2.2. Preparation of Co-TiO$_2$/CNTs nanocomposite

Co-TiO$_2$/CNTs photocatalyst was synthesized through a modified sol-gel technique. 0.96 g of CoCl$_2$.6H$_2$O, 20 mL TIP and 60 mL ethanol were agitated for 2h (Solution A). Next, solution B, 40 mL ethanol, 10 mL deionized water, 4 mL hydrochloric acid and 0.08 g CNTs were poured into the solution A and agitated for 12h at ambient temperature. The sol was generated after stirring for 12h and aging at ambient temperature for 24h. Then it was evaporated at 80 °C for 8h to obtain the dried powder. Lastly, the Co-TiO$_2$/CNTs sample was obtained by calcinating the resulted powder at 450 °C under air for 2h. Pure TiO$_2$, Co-TiO$_2$ and TiO$_2$/CNTs samples were prepared through the similar method (Table 1).

2.3. Characterization

The XRD analysis was performed using a Siemens D5000 instrument (Germany) while Cu K$_\alpha$ radiation was employed as the X-ray source. The diffractograms were recorded in the 2θ = 20 - 80°. Morphology of the samples was identified by scanning electron microscopy (SEM) (Veigall-Tescan Company), which was coupled with an energy dispersive X-ray (EDX) detector. The diffuse reflectance UV–Vis spectra (DRS) of the samples were recorded by an Ava Spec-2048TEC spectrometer. Physisorption of nitrogen was studied by a Quantachrome Autosorb-1-MP (Micromeritics) in order to measure BET areas through static nitrogen physisorption. The samples were degassed at 200 °C for 2 h prior to the sorption measurement.

2.4. Photodegradation of 2,4-DCP

We selected 2,4-DCP as a model of organic pollutants to examine degradation performance of the obtained samples. We used Halogen, ECO OSRAM 500W lamp (350 to 800 nm, with the most intense peak at 575 nm) as visible light source. In each degradation experiment, the beaker containing optimum amount of photocatalyst and 100 mL 2,4-DCP aqueous solution (40 mg/L) was agitated first for 10 min, in the dark, for adsorption/ desorption equilibrium and after this
time, the lamp turned on for 180 min. At certain times, 2 mL of the solution was taken and filtered to eliminate the photocatalyst and analyzed using Rayleigh UV-2601 UV/VIS spectrophotometer ($\lambda_{\text{max}}$= 227nm).

3. Results & Discussion

3.1. X-ray diffraction analysis

The XRD patterns of the synthesized samples have been presented in Fig. 1. In XRD pattern of pure TiO$_2$ (Fig. 1a), the diffractions at $2\theta$= 27.48°, 36.14°, 41.24° and 54.34° with Miller indexes (110), (101), (111) and (211), respectively are the main diffractions of polycrystalline with a rutile structure[16]. The diffractions at $2\theta$= 37.80°, 48.18°, and 54.09° are the key peaks for the anatase crystalline phase of TiO$_2$ (JCPDS 21-1272). The XRD pattern showed the synthesized TiO$_2$ comprising predominant rutile crystalline phase and a small amount of anatase crystalline phase. Moreover, the XRD pattern of Co-TiO$_2$ sample (Fig. 1b) did not indicate any cobalt phase, so it can be concluded that cobalt ions homogenously dispersed into the TiO$_2$ crystallites and represented rutile phase as major phase for TiO$_2$ [17, 18].

In XRD pattern of TiO$_2$/CNTs (Fig. 1c), the main diffraction of CNTs at $2\theta$=25.5°[19] has not been detected and it may be overlapped with the main diffraction of anatase TiO$_2$ at $2\theta$=25.3°. Furthermore, it may be attributed to the significant difference between the mass percent of CNTs and TiO$_2$ and the low crystallinity of CNTs [13]. In the XRD pattern of Co-TiO$_2$/CNTs (Fig. 1d), the main diffractions of rutile crystalline phase were detected for TiO$_2$.

The mean TiO$_2$ crystal size for each samples was calculated at $2\theta$= 27.48° by using Scherrer's equation (Eq. (1))[20]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad \text{(eq. 1)}$$

Where $D$ represents the mean crystallite size of TiO$_2$ in nm, $\lambda$ is the wavelength of X-ray (1.54056 Å), $\beta$ refers to the diffraction full width at half maximum (FWHM) in radian, $K$ represents a coefficient (0.89) and $\theta$ is the diffraction angle at $2\theta$= 27.48°. The TiO$_2$ crystal size for all the obtained samples is in the nanosized range (Table 2). The mean crystallite size of TiO$_2$ in Co-TiO$_2$ and Co-TiO$_2$/CNTs samples is smaller compared with pure TiO$_2$, it can be stated that adding cobalt
to titania delays the growth of TiO$_2$ nanoparticles. It seems that cobalt ions form complex with the TiO$_2$ surface oxygen, hence, suppress the growth of TiO$_2$ crystallite[21].

The lattice parameters ($a=b\neq c$) of tetragonal crystalline structure were obtained for (110) crystal plane of rutile phase using Eq. (2):

\[
\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \tag{eq. 2}
\]

Considering the interplanar spacing ($d_{hkl}$), the distance between adjacent planes in the set ($hkl$) can be determined using the Bragg law (Eq. (3)):

\[
d_{hkl} = \frac{\lambda}{2 \sin \theta} \tag{eq. 3}
\]

The volume of cell (tetragonal one) was computed by Eq. (4):

\[
V = a^2c \tag{eq. 4}
\]

Where $a$ and $c$ are considered lattice factors. Table 2 displays the lattice factors of the synthesized samples. The achieved values for the lattice factors of TiO$_2$ in the synthesized samples matched well with the TiO$_2$ rutile structure [16]. The calculated values for the lattice factors of pure TiO$_2$ are in well matched with the rutile phase of TiO$_2$ [16]. No other impurity peaks are detected, which ensure high purity of TiO$_2$ powder used for Co doping. The diffraction patterns of the synthesized samples do not show any extra peaks confirming that the rutile phase is not troubled upon Co doping in TiO$_2$. A significant difference between ionic radii of the dopant and the host ions (i.e., Co$^{2+}$: 0.745 Å and Ti$^{4+}$: 0.605 Å, with a coordination number of 6) is predictable to cause a small enhancement of the TiO$_2$ unit cell size.

3.2. Diffuse reflectance analysis

The solid-state UV-Visible spectra (Fig. 2A) were recorded for all the samples.

In the DR spectrum of pure TiO$_2$, absorption peak around 400 nm can be attributed to the charge-transfer from the valence band of the oxide anions to the conduction band of the Ti$^{4+}$ cations [21].
The diffuse reflectance spectra of the Co-TiO₂ and Co-TiO₂/CNTs samples (Figs. 2b, d), consist of additional broad absorption peak between 500 to 750 nm. The genesis of absorption peak is attributed to Co²⁺/Ti⁴⁺ charge-transfer interaction [22]. This may also be a reason for high degradation efficiency of these samples in the visible region compared with pure TiO₂.

We also measured the energy of band gap of the synthesized samples using the diffuse reflectance spectra according to Eq. (5)[23].

\[ (F(R) h\nu)^{0.5} = A (h\nu-E_{bg}) \]  \text{ (eq. 5) }

Where A is constant, F(R) is the function of Kubelka-Munk (Fig. 2B), and \( E_{bg} \) is the band gap. The \( E_{bg} \) data of samples have been presented in Table 3. The pure TiO₂ showed high reflection within the visible light region (>400 nm), while the samples comprising cobalt showed lower reflection in the visible region, meaning that visible light photoresponse of the cobalt doped samples was increased. Red shifts found for the cobalt doped TiO₂ samples showed that the band gap energy of the samples was decreased gradually (Table 3). The band gap of samples containing cobalt decreased compared with TiO₂. It can be clearly seen that doping cobalt in the TiO₂ structure affects the optical features of TiO₂ significantly. It is evident that, the degradation activity of the Co-TiO₂ and Co-TiO₂/CNTs is greatly shifted into the visible light region, and exhibits a band gap narrowing 2.375 and 2.200 eV compared with that of pure TiO₂ (2.880 eV). It is explained in literature that the presence of transition metals might introduce new intra band gap states, giving the TiO₂ the capacity to absorb light at lower energy levels, thus, promoting the absorption on the visible part of the spectrum. The incorporation of the transition metal provides d orbitals just below the conduction band. These d orbitals are then able to receive electrons from the valence band, thus lowering the band gap energy[24].

### 3.3. FESEM/EDX and TEM analyses

Fig. 3 displays the FESEM images of the synthesized samples. FESEM images show that all the samples are slightly agglomerated and in the case of TiO₂/CNTs and Co-TiO₂/CNTs samples (Figs. 3c, d), TiO₂ and Co-TiO₂ nanoparticles are decorated on the CNTs walls. The FESEM analysis and
XRD calculations (Table 2) display that the existence of cobalt and CNTs has prevented increasing the dimension of TiO$_2$ particles (Table 2).

The EDX results were utilized to study the elemental composition of the samples (Fig. 4 and Table 4). The elemental analysis confirms the existence of C, Ti, O and Co elements in these samples. The EDX patterns of the samples (Fig. 4) display two peaks about 0.2 and 4.5 keV. The strong peak is related to the bulk TiO$_2$ and the less strong one is related to the surface TiO$_2$. Fig. 4 shows the peaks of cobalt at 0.6, 6.9 and 7.5 keV. The less strong peak is allocated to cobalt in the TiO$_2$ lattices[21, 25]. Fig. 5 demonstrates elemental mapping images of the synthesized samples. According to the elemental mapping mode, cobalt was greatly and homogeneously dispersed in the TiO$_2$ lattice. This implies good interaction of cobalt and TiO$_2$ over the sol-gel synthesis procedure. The elemental analysis of the samples showed the existence of cobalt atoms and CNTs in the powder structure, as the opposite of XRD patterns.

Fig. 6 shows the TEM image of Co-TiO$_2$/CNTs nanocomposite. According to these images, Co-TiO$_2$ NPs are dispersed on the wall of CNTs.

3.4. \textbf{N$_2$ physisorption analysis}

The results of N$_2$ adsorption/desorption isotherms are shown in Fig. 7. The sorption isotherms for the prepared samples correspond to the type IV isotherm based on the classification of IUPAC[26]. Textural and structural parameters of the obtained samples have been presented in Table 5. The specific surface areas calculated according to BET and the average pore diameter and pore volumes were extracted from the desorption branch based on the BJH model. Cobalt addition resulted in a reduction in both surface area and pore volume for the Co-TiO$_2$ and Co-TiO$_2$/CNTs samples. These variations could be attributed to the developed sintering and/or agglomeration of TiO$_2$ or to the formation of CoTiO$_3$ compound[22].

3.5. \textbf{Degradation of 2,4-DCP}

The degradation activity of 2,4-DCP with the synthesized samples under visible light presented in Fig. 8. Amongst the prepared samples, the photocatalytic activity of the Co-TiO$_2$/CNTs was the
maximum and 50% degradation of 2,4-DCP achieved following 180 min irradiation under visible light. In the same conditions, we obtained 27%, 32% and 35% degradation of 2,4-DCP in the presence of pure TiO$_2$, Co-TiO$_2$ and TiO$_2$/CNTs samples respectively. The two basic factors that are responsible for the activity of photocatalysts include surface area and light absorption capacity[21]. The DRS analysis results (Fig. 2) show that light absorption capacities of the prepared samples are different and increase with addition of cobalt in visible region. Therefore, addition of cobalt has two opposite effects on the degradation activity of the samples; increasing light absorption capacity and decreasing surface area. The degradation activity depends on which one of these is the dominant factor[8].

The higher degradation activity of Co-TiO$_2$/CNTs can be noticed that the presence of CNTs and cobalt clearly led to a synergetic impact on 2,4-DCP degradation and caused a larger photocatalytic performance. The more degradation activity of Co-TiO$_2$/CNTs nanocomposite may be described as firstly, the Co doped into TiO$_2$ could efficiently capture the photo-induced electrons and holes, which controlled combining photoinduced charge carriers and increased the degradation performance. Secondly, there are more surface hydroxyl groups in Co-TiO$_2$/CNTs samples compared with the pure TiO$_2$ which would be helpful for 2,4-DCP adsorption. The creation of hydroxyl radicals could be facilitated by the abundant hydroxyl groups adsorbed on the catalyst surface that could optimize the degradation procedure of the 2,4-DCP adsorbed on the surface[5]. Moreover, there is a synergetic impact among CNTs and TiO$_2$, and CNTs playing role as a photosensitizer. The photo-induced electrons can be trapped by CNTs and so, superoxide radical ion and/or hydroxyl radical is formed on the TiO$_2$ surface that they play role in degrading the organic compound. It can be suggested that charge on the surface of TiO$_2$ in the combined catalysts is increased due to the presence of CNTs. The surface charge may cause alterations of the fundamental procedure of electron/hole pair creation while using visible light [13]. Therefore, it may be the single interaction between TiO$_2$ and CNTs that endows the ternary nanocomposite with a higher catalytic activity in the degradation of 2,4-DCP than pure TiO$_2$. In the case of samples comprising cobalt, the Co$^{2+}$ trapped electrons which then moved to he absorbed O$_2$ for reaching a greater photocatalytic activity. According to the literature [27], with the replacement for Ti$^{4+}$ by Co$^{2+}$in TiO$_2$ crystal structure, the catalyst can introduce a new levels
of impurity to the conduction band of TiO$_2$ and the electrons can be moved from the valence band to these impurity levels, causing a narrowing of the band gap. This fact shows the presence of higher number of photogenerated electrons and holes which can be introduced for participating in the photocatalytic reactions [28]. Though, recombining photogenerated electrons and holes is one of the most important parameters that decline the photoactivity of the TiO$_2$ catalyst. Any parameter, which suppresses the recombination of electron-hole, will increase the photocatalytic performance [29]. Generally, if the dimension of doping metal ion is very similar to Ti$^{4+}$, entering metal ion into the TiO$_2$ crystal interstitial site is very probable. The doping metal ion placed mostly on the shallow surface of TiO$_2$ can induce defects. These defects can become the centers of shallow electrons or holes traps, which would powerfully progress separation process of an electron-hole pair. Therefore, the photocatalyst will have a great photocatalytic performance[30]. Our suggested mechanism for photodegradation of 2,4-DCP by Co-TiO$_2$/CNTs photocatalyst is shown in Fig.9.

4. Conclusions

In summary, the photocatalytic efficiency of rutile-type TiO$_2$ was successfully improved by cobalt doping and decorating on CNTs walls. It was found that the Co-TiO$_2$/CNTs sample presented enhanced degradation of 2,4-dichlorophenol (2,4-DCP) and exhibited expansion in spectral response range shifted to the visible region. We obtained 27% and 50% visible light degradation of 2,4-DCP in the presence of TiO$_2$ and Co-TiO$_2$/CNTs respectively after 180min irradiation. The presence of CNTs and cobalt dopant in Co-TiO$_2$/CNTs nanocomposite promoted the separation of photoinduced charge carriers and extended the absorption spectrum of TiO$_2$ into visible region.

Acknowledgements

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References:


Table 1. Nomenclature of the prepared samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>TIP (ml)</th>
<th>HCl (ml)</th>
<th>CoCl$_2$$\cdot$6H$_2$O (g)</th>
<th>Ethanol (ml)</th>
<th>H$_2$O (ml)</th>
<th>CNTs (g)</th>
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<tbody>
<tr>
<td>TiO$_2$</td>
<td>20</td>
<td>4</td>
<td>-</td>
<td>100</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Co-TiO$_2$</td>
<td>20</td>
<td>4</td>
<td>0.96</td>
<td>100</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>TiO$_2$/CNTs</td>
<td>20</td>
<td>4</td>
<td>-</td>
<td>100</td>
<td>10</td>
<td>0.08</td>
</tr>
<tr>
<td>Co-TiO$_2$/CNTs</td>
<td>20</td>
<td>4</td>
<td>0.96</td>
<td>100</td>
<td>10</td>
<td>0.08</td>
</tr>
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</table>

Table 2. Phase, crystal size and lattice parameters of the prepared samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Major Phase</th>
<th>Crystal size (nm)</th>
<th>a=b (Å)</th>
<th>c (Å)</th>
<th>Cell volume (Å$^3$)</th>
</tr>
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<tbody>
<tr>
<td>TiO$_2$</td>
<td>Rutile</td>
<td>21.540</td>
<td>4.598</td>
<td>2.957</td>
<td>62.505</td>
</tr>
<tr>
<td>Co-TiO$_2$</td>
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<td>20.466</td>
<td>4.600</td>
<td>2.956</td>
<td>62.561</td>
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<tr>
<td>TiO$_2$/CNTs</td>
<td>Rutile</td>
<td>21.261</td>
<td>4.588</td>
<td>2.951</td>
<td>62.110</td>
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<td>18.190</td>
<td>4.593</td>
<td>2.951</td>
<td>62.266</td>
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Table 3. Color and band gap energy of the prepared samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_{bg}$ (eV)</th>
<th>Color</th>
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<tbody>
<tr>
<td>TiO$_2$</td>
<td>2.880</td>
<td>White</td>
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<tr>
<td>Co-TiO$_2$</td>
<td>2.375</td>
<td>Green</td>
</tr>
<tr>
<td>TiO$_2$/CNTs</td>
<td>2.970</td>
<td>Gray</td>
</tr>
<tr>
<td>Co-TiO$_2$/CNTs</td>
<td>2.200</td>
<td>Slime Green</td>
</tr>
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</table>

Table 4. Elemental chemical analysis of the prepared samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ti (wt%)</th>
<th>O (wt%)</th>
<th>Co (wt%)</th>
<th>C (wt%)</th>
<th>Cl (wt%)</th>
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<td>53.03</td>
<td>3.15</td>
<td>4.50</td>
<td>2.15</td>
</tr>
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Table 5. Textural and structural parameters of the prepared samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>Average pore diameter (nm)</th>
<th>Pore volume (cm$^3$/g)</th>
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<td>TiO$_2$</td>
<td>41.21</td>
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<td>0.20</td>
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<td>34.28</td>
<td>25.75</td>
<td>0.13</td>
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<td>46.84</td>
<td>21.10</td>
<td>0.25</td>
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<tr>
<td>Co-TiO$_2$/CNTs</td>
<td>33.70</td>
<td>17.27</td>
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Fig. 1 The XRD patterns of a) TiO$_2$, b) Co-TiO$_2$, c) TiO$_2$/CNTs and d) Co-TiO$_2$/CNTs
Fig. 2 A: Diffuse reflectance spectra and B: Kubelka-Munk plots for the band gap energy calculation of a) TiO$_2$ b) Co-TiO$_2$ c) TiO$_2$/CNTs and d) Co-TiO$_2$/CNTs.
Fig. 3 FESEM images of a) TiO$_2$, b) Co-TiO$_2$, c) TiO$_2$/CNTs and d) Co-TiO$_2$/CNTs
Fig. 4 EDX spectra of a) TiO$_2$, b) Co-TiO$_2$, c) TiO$_2$/CNTs and d) Co-TiO$_2$/CNTs
Fig. 5 Elemental mapping of a) TiO$_2$, b) Co-TiO$_2$, c) TiO$_2$/CNTs and d) Co-TiO$_2$/CNTs.
Fig. 6 TEM images of Co-TiO$_2$/CNTs nanocomposite at a, b) 50 nm and c, d) 100 nm
Fig. 7 N₂ adsorption–desorption isotherms for a) TiO₂, b) Co-TiO₂, c) TiO₂/CNTs and d) Co-TiO₂/CNTs
Fig. 8 Photodegradation of 2,4-DCP in the presence of the prepared samples under visible light. (Initial concentration of 2,4-DCP, 40 mg /L; volume, 100 mL; catalyst dosage, 10 mg and Irradiation time: 180 min).
Fig. 9 Suggested mechanism for 2,4-DCP degradation in the presence of Co-TiO$_2$/CNTs under visible light.