Comparison of the photocatalytic performance of TiO$_2$/AC and TiO$_2$/CNT nanocomposites for methyl orange photodegradation

Liping Wang, Jingru Guo, Jingjing Dang, Xiaojun Huang, Si Chen and Weisheng Guan

ABSTRACT

To enhance the photocatalytic degradation efficiency of TiO$_2$ on methyl orange (MO) removal, TiO$_2$/AC (activated carbon) and TiO$_2$/CNT (carbon nanotube) composites were synthesized. The prepared catalysts were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). The photocatalytic performance of the obtained composites were investigated by the degradation of MO under UV irradiation (254 nm, 365 nm). The results revealed that the prepared nanocomposite showed higher MO degradation efficiency than pure nano-TiO$_2$. Additionally, batch experiments of influencing factors, including H$_2$O$_2$ dosage, metal dopants, inorganic anions, chloride ion concentration and ultraviolet wavelength on the MO removal efficiency were also conducted. The results demonstrated that metal dopant and the presence of H$_2$O$_2$ significantly enhanced MO removal efficiency.

Key words | MO removal, photocatalytic, TiO$_2$/AC, TiO$_2$/CNT

INTRODUCTION

Photocatalysis has been extensively studied as a promising environmental remediation technology for a variety of contaminants. Since nano-TiO$_2$ was first used for photoelectrodes and shown to have good photodegradation efficiency, researchers have paid much attention to the investigation of the catalytic performance of semiconductor-based TiO$_2$ nanocomposites (Pathania et al. 2016; Alqadami et al. 2018). Because of its semiconducting properties, photostability, and cost effectiveness, TiO$_2$ photocatalyst has been successfully applied in the fields of hydrogen production and pollutant degradation (Stylidi et al. 2004; Ahmed et al. 2010). However, the application of TiO$_2$ nanoparticles (NP) for photocatalytic processes suffers from a low quantum efficiency because of the rapid recombination of the photoinduced electrons and holes ($e^-/h^+$), mass transfer and photon transfer limitations (Kumar et al. 2018). In particular, the quantum efficiency of TiO$_2$ catalysts is low with a relatively wide band gap (3.20 eV of anatase and 3.03 eV of rutile), so only the light of radiant energy greater than the band gap can be utilized to activate the photocatalytic reaction (Mattsson & Österlund 2010). Therefore, most of the photons in the process do not take part in the reaction. Moreover, electron and hole are easy to recombine (Zhang et al. 2010). For these reasons, doping or modifying TiO$_2$ photocatalyst to promote its photocatalytic activity and maximize the use of sunlight have become urgent tasks, and will also benefit the popularization and application of heterogeneous photocatalytic technology.

Currently, the main technologies to improve TiO$_2$ photocatalytic activity include noble metal deposition on the surface, metal ion doping, anion doping, composite semiconductor and dye sensitization (Wang et al. 2016). Among all these technologies, composite semiconductor effects on the reactivity of TiO$_2$ have become a common subject of investigation. Extensive research into on composite semiconductor for the improvement of TiO$_2$ photocatalytic activity has been carried out especially for water cleaning applications (Pathania et al. 2015). The presence of composite semiconductor in the TiO$_2$ crystalline matrix significantly influences photoreactivity, charge...
carrier recombination rates, and interfacial electron-transfer rates. Additionally, composite semiconductors have also been observed to be capable of tuning the absorption spectrum of TiO2 nanoparticles (Lu et al. 2018).

Recently, it has been found that carbon-based TiO2 composites are the simplest and safest coupled semiconductors because of the carbon materials' stability and cost efficiency. The large specific surface area of carbon materials can provide more active reactive spots and enhance its adsorption performance (Miranda et al. 2014). Moreover, carbon materials have a large electron-storage capacity, which can accept the photon-excited electrons to promote the separation of photo-generated carriers and remarkably inhibit electron-hole recombination. In this regard, due to the well-developed porous structures, strong adsorption performance and excellent electrical properties, carbon nanotubes (CNT) and activated carbon (AC) have received tremendous attention as excellent carriers for loading nanoscale TiO2 (Moya et al. 2015). For these reasons, the relatively low-cost and available carbon-based materials and TiO2 NP, with the synergistic effect of adsorption and degradation were considered for this work.

The main aim of the present work was to prepare TiO2/AC and TiO2/CNT composites, investigate their structure, morphology, and discuss the adsorption-photodegradation synergistic mechanism. These catalysts were utilized for the photocatalytic degradation of aqueous methyl orange (MO). The microscopic morphology of the TiO2/AC and TiO2/CNT composites were observed using field emission scanning electronic microscopy (FESEM). X-ray photoelectron spectroscopy (XPS) was used to determine the chemical compositions and element valence states of these composites. Also, Fourier transform infrared spectroscopy (FTIR) was applied to characterize the composites' functional groups. The effect of important parameters including H2O2 dosage, metal dopant, inorganic anions, chloride ion concentration and ultraviolet wavelength on the MO removal efficiency were also investigated.

MATERIALS AND METHODS

Materials

In our experiments, the reagents used were of analytical reagent grade without further purification. AC powder, CNT, hydrochloric acid (HCl), nitric acid (HNO3), bismuth nitrate pentahydrate (Bi(NO3)3·5H2O), zinc nitrate hexahydrate (Zn(NO3)2·6H2O), manganese nitrate tetrahydrate (Mn(NO3)2·4H2O), nickel nitrate hexahydrate (Ni(NO3)2·6H2O), sodium chloride (NaCl), sodium sulfate (Na2SO4), potassium chloride (KCl), sodium nitrate (Na2NO3) utilized in the experiments were purchased from Hongyan Co. in Tianjin. Tetrapotyl orthotitanate (TBOT), 30% H2O2, MO, absolute ethyl alcohol(EtOH) were purchased from Tianjin Zhiyuan Chemical Reagent Co. Deionized water (DI) was used throughout this study.

Preparation of TiO2

In order to study the catalytic performance of the catalysts prepared by different methods, TiO2 was prepared by the sol-gel method and the slow hydrolysis method. The sol-gel method was as follows: 10 ml TBOT and 100 ml absolute ethyl alcohol were mixed under 15 min vigorous stirring to obtain solution A at room temperature. Then, 2 ml nitric acid was added dropwise to the mixture of 10 ml distilled water and 30 ml absolute ethyl alcohol to obtain solution B (pH up to 3–4). Solution A was then slowly dripped into solution B under magnetic stirring for 3 hours to prepare a faint yellow transparent gel followed by 12 hours aging.

The TiO2 slow hydrolysis preparation method was as follows: 20 ml TBOT was slowly added to 100 ml absolute ethyl alcohol under magnetic stirring for 1 hour. A kind of stable yellowish colorless solution C was obtained after standing for 12 hours.

Preparation of TiO2/AC catalyst

Pretreatment of AC

An acid washing procedure was used for the pretreatment of AC. Firstly, the raw AC powder (100 g) was sieved through 70, 100, 160, and 200 meshes. Subsequently, the sieved powder was immersed in HCl solution for acid treatment, and the mixture was ultrasound for 1 hour. After standing for 2 hours, the mixture was filtered in a vacuum. The obtained products were washed with DI several times until residual chloride ions were found, then dried in an oven for 24 hours at 353 K. Finally, the samples were calcinated at 873 K for 1 hour, thus obtaining treated AC samples denoted as C70, C100, C160, and C200.

Preparation of TiO2/AC composites

Firstly, 2 g C70, C100, C160, C200 were dispersed into 20 ml TiO2 gel followed by shaking at 293 K for 12 hours. Then the mixture was maintained at 293 K for another 12 hours,
the filtered in a vacuum. The precipitates were rinsed with absolute ethyl alcohol 3 times and dried for 12 hours at 353 K. Finally, these products were calcinated in muffle at 823 K for 2 hours. Thus the TiO\textsubscript{2}/AC composites (denoted as TiO\textsubscript{2}-C(70) TiO\textsubscript{2}-C(100) TiO\textsubscript{2}-C(160) TiO\textsubscript{2}-C(200)) were prepared successfully.

In addition, 2 g C\textsubscript{160} was dispersed in 20 ml solution C. Then the above steps were repeated. The composite TiO\textsubscript{2}-C(160)-1 was prepared successfully.

**Preparation of metal-modified TiO\textsubscript{2}-C(160)**

Bi, Mn, Zn and Ni were selected as modifying metals for TiO\textsubscript{2}-C(160) due to their excellent photocatalytic properties when recombining with TiO\textsubscript{2}. The specific preparation method and mechanism discussion have been fully explained in a separate investigation in our previous study (Qi et al. 2016). In summary, firstly, metal precursor solutions (0.1 mol/L) were prepared by dissolving Bi(NO\textsubscript{3})\textsubscript{3}, Mn(NO\textsubscript{3})\textsubscript{2}, Zn(NO\textsubscript{3})\textsubscript{2} and Ni(NO\textsubscript{3})\textsubscript{2} in DI water. Then the desired metal solutions were mixed in the ratio of 1:1:1, denoted as Bi-Mn-Zn, Bi-Ni-Mn and Bi-Bi-Bi. Subsequently, 0.2 g TiO\textsubscript{2}-C(160) was dispersed into the three mixed solutions followed by shaking at 293 K for 12 hours. The remaining steps were the same as for the preparation of TiO\textsubscript{2}/AC: standing, vacuum filtration, washing and calcination. The metal-modified composite TiO\textsubscript{2}/AC composites TiO\textsubscript{2}-C(160)-Bi-Mn-Zn, TiO\textsubscript{2}-C(160)-Bi-Ni-Mn and TiO\textsubscript{2}-C(160)-Bi were prepared successfully.

**Preparation of TiO\textsubscript{2}/CNT catalyst**

**Preparation of CNT\textsuperscript{G}**

Firstly, CNT was processed by an acid-washing pretreatment: 2.0 g raw multi-wall carbon nanotubes (MWCNT) was immersed in 50 ml concentrated nitric acid, and the mixture was ultrasonicated for 1 hour to form oxygenated functionalities on the MWCNT surface. The mixture was left until it had layered. The MWCNT was then filtered from the acid pickle, washed with DI several times to nearly neutral pH, and calcinated at 423 K for 24 hours. Thus, some acid-treated MWCNT was obtained. Then, 1.0 g treated MWCNT was sonicated in the distilled water for 1 hour to obtain a MWCNT suspension.

CNT film on a glass substrate was prepared using the coating method. A glass slide was selected as the substrate because of its chemical inertness and low cost. First, some glass slides (75 × 25 mm\textsuperscript{2}) were fully washed in sodium hydroxide (NaOH) aqueous solution (0.1 mol/L) and absolute ethyl alcohol several times, and then fully dried at room temperature. Then the as-obtained CNT suspension (1 ml) was coated evenly onto the surface of a glass substrate and baked for 30 min at 453 K. The obtained sample was rinsed with distilled water 2–3 times and fully dried for 1 hour at 533 K. CNT film on a glass substrate was prepared successfully (denoted as CNT\textsuperscript{G}).

**Preparation of TiO\textsubscript{2}/CNT composites**

TiO\textsubscript{2}/CNT composites were prepared by the sol-gel method. Firstly, some prepared TiO\textsubscript{2} (1 ml) was dripped slowly onto CNT\textsuperscript{G} and rinsed gently with EtOH after 24 hours’ adsorption. Then, the obtained samples were dried in a vacuum drier for 12 hours at 353 K and calcinated under nitrogen protection at 823 K for 2 hours. After that, the samples were washed with distilled water gently 2–3 times and dried for 1 hour at 353 K. TiO\textsubscript{2}/CNT composites attached to a glass substrate were obtained.

**Preparation of metal-modified TiO\textsubscript{2}-CNT**

Bi, Mn, Zn and Ni were selected as modifying metals for the TiO\textsubscript{2}/CNT composites. The specific preparation process is as follows. Firstly, metal precursor solutions (0.1 mol/L) were prepared by dissolving Bi(NO\textsubscript{3})\textsubscript{3}, Mn(NO\textsubscript{3})\textsubscript{2}, Zn(NO\textsubscript{3})\textsubscript{2} and Ni(NO\textsubscript{3})\textsubscript{2} in DI water. Then the desired metal solutions were mixed in the ratio of 1:1:1, denoted as Bi-Mn-Zn, Bi-Ni-Mn and Bi-Bi-Bi. Subsequently, the target mixed solutions were dripped slowly onto TiO\textsubscript{2}/CNT\textsuperscript{G}. The obtained samples were sealed in a moisturizing environment for 4 hours. After reaching adsorption equilibrium, the samples were washed with distilled water gently 3 times and fully dried at room temperature. After that, the samples were calcinated at 823 K for 2 hours. Metal-modified TiO\textsubscript{2}/CNT\textsuperscript{G} composites TiO\textsubscript{2}-CNT-Bi-Mn-Zn, TiO\textsubscript{2}-CNT-Bi-Ni-Mn and TiO\textsubscript{2}-CNT-Bi were prepared successfully.

**Characterization and measurement**

The microscopic morphology of the TiO\textsubscript{2}\textsuperscript{G}, composite material TiO\textsubscript{2}-C(160), TiO\textsubscript{2}/CNT were observed using FESEM (SEM, FEI Quanta200, US). Catalyst components were determined using XPS (AXIS, ULTRA, Kratos Analytical, Japan) equipped with an Ag K\textsubscript{α} source. The FTIR of TiO\textsubscript{2}, TiO\textsubscript{2}-C(160), and TiO\textsubscript{2}/CNT was analyzed with a Thermo Nicolet Avatar 360 FTIR spectrometer within the range of 500–4,000 cm\textsuperscript{-1}.
The photocatalytic activities of the prepared photocatalysts were evaluated by the degradation of aqueous MO under UV-irradiation. The initial concentration of MO dyes was 0.1 g/L. The fixed initial pH = 6.5. The source of UV light (6 W mercury vapor lamp with different wavelengths 254, 365 nm and different light quantity 90 lm/w, 70 lm/w) was sealed above the quartz glass to prevent direct contact with the dye solution. A specific reactor with a unique structure (see detailed explanation in our previous study, Qi et al. 2016) was designed to carry out the experiment. Prior to the photoreaction process, catalysts were placed in the reactor, then 10 ml MO solution was injected. The reaction system stood for 1 hour in the dark to achieve adsorption-desorption equilibrium before UV irradiation. H₂O₂ concentration, salt ions, UV wavelength and reaction time were considered as the process variables. Removal efficiency of MO (%) was the response of the degradation procedure. An ultraviolet spectrophotometer (756 type from Shanghai Spectrum Instruments Co. Ltd) was used to measure the MO absorbance, which was converted to the equivalent concentration of the solution. Degradation efficiency was calculated as follows:

\[ \eta = \frac{C_0 - C_t}{C_0} \times 100\% \]

where \( \eta \) is the degradation efficiency of MO, \( C_0 \) is the initial concentration of MO, and \( C_t \) is the residual concentration of MO after reaction over time \( t \). During photoreaction, 1.5 ml reactant solution was sampled at regular intervals (15 min). After the measurement of the absorption spectra of the sample, the sample solution was injected back into the reactor immediately.

RESULTS AND DISCUSSION

Characterization of prepared products

Figure 1 shows the adsorption capacity of the prepared composites which revealed that all the samples except TiO₂-CNT presented a similar capacity for MO adsorption. Remarkably, TiO₂-C(160)-1 exhibited the highest capacity among them.

Figure 2(a) and 2(b) show the SEM images of TiO₂-C(160). Figure 2(c)–2(e) show the SEM images of TiO₂/CNT. Figure 2(f) and 2(g) show the SEM images of TiO₂-G. Figure 2(f) and 2(g) confirm that TiO₂ existed as a microspheric aggregation distribution on the surface of the glass substrate. The TiO₂ nanoparticles exhibit regular granules (particle size: 10–40 nm). Additionally, there are some micropores on the surface of TiO₂-G. The micropores are able to improve the adsorption of dyes, which is an efficient way to promote the photodegradation efficiency of dyes. In Figure 2(a) and 2(b), the distribution of AC is platy, laminating and interlacing. Spherical TiO₂ is distributed evenly on the surface of the AC (the red circles in Figure 2(a) and 2(b)). The aggregates of AC tend to form plenty of macropores and mesopores where TiO₂ particles were mainly found. Hence, the macropores in the TiO₂-C(160) porous composites contributed to improving the adsorption efficiency of the target dye, accelerating the flow of MO throughout the porous composites. In Figure 2(c)–2(e), on account of fabricating on a glass substrate and sintering, cracks are visible, which explain an obvious surface consolidation phenomenon on TiO₂/CNT composites. In addition, due to the effect of strong acid, the apparent sharp edges of
CNT disappeared, leaving a smooth surface, which facilitates the adhesion of CNT on the glass slide. TiO$_2$ spherical nanoparticles on the surface of the CNT are marked as red spots through the SEM mapping function. Figure 2(c) shows that TiO$_2$ nanoparticles are uniformly fabricated on the surface of the CNT, showing that CNT possesses an increased surface area due to the presence of TiO$_2$ (Liu et al. 2011).

XPS spectra were used to characterize the chemical compositions and element valence states of composites TiO$_2$-C(160) and TiO$_2$/CNT, as shown in Figure 3(a) and 3(b). The wide-scan spectrum in Figure 3 shows that the
elements of the two composites were mainly composed of C, Ti and O. The XPS spectrum shows that the exact binding energies of these elements are slightly different for different samples (Murcia et al. 2015). A summary of these results is shown in Table 1. The Ti 2p core peaks exhibit a main component at around 460 eV in all the samples, and this is representative of the Ti$^{4+}$ ions in the TiO$_2$ lattice. Figure 3(a) shows two prominent Ti 2p and Ti 2p1/2 peaks at 459 eV and 465 eV with the energy difference of 6 eV. Figure 3(b) shows Ti 2p and Ti 2p1/2 peaks at 455 eV and 461 eV with the energy difference of 6 eV. The results indicate the binding energies of these composites’ elements are all shifted in comparison with pristine TiO$_2$ nanoparticles. We presume that carbon materials combined on the TiO$_2$ surface or create some defects in TiO$_2$ in the mixed system, which leads the shift of the binding energies. The chemical states of O 1 s species can be resolved into two peaks at 527 and 530 eV which was attributed to the adsorbed oxygen and the metallic oxygen in the form of Ti-O, respectively (Teng et al. 2014). The O 1 s peak located at around 529 eV could be observed for all the samples, and it was assigned to oxygen atoms in the TiO$_2$ lattice. The Ti 2p together with O 1 s peak location confirms the existence of TiO$_2$. Another observed peak of C 1 s located at 285 eV in TiO$_2$-C(160) and 281 eV in TiO$_2$/CNT, represented carbon atoms in AC and CNT, respectively. The binding energy of C 1 s had a certain deviation due to different bonding effects in TiO$_2$-C(160) and TiO$_2$/CNT. As shown in Table 1, from the calculated surface element compositions of the above two samples, the C atom percent of composite TiO$_2$-C(160) is obviously higher than TiO$_2$/CNT, which is caused by the immobilization and calcination of the TiO$_2$/CNT on the glass. The XPS profile curve in Figure 3(a) and 3(b) further confirms the successful preparation of composite TiO$_2$-C(160) and TiO$_2$/CNT.

Table 1 | Binding energies and surface element components of TiO$_2$-C(160) (C1) and TiO$_2$/CNT (C2)

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding energy (eV)</th>
<th>M atom percent (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti 2p1/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti 2p</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C 1 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti 3p3/2</td>
<td></td>
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</tr>
</tbody>
</table>

* Determined by XPS.

Figure 3 | X-ray photoelectron spectroscopy of (a) TiO$_2$-C(160), (b) TiO$_2$/CNT.

The FTIR spectra of TiO$_2$, TiO$_2$-C(160) and TiO$_2$/CNT composites for characterizing their functional groups. For the three samples, the bands at 3,430 cm$^{-1}$ were attributed to the stretching and bending vibrations of O-H of samples or physically adsorbed water. The peaks at 2,923 cm$^{-1}$ and 2,853 cm$^{-1}$ are assigned to the symmetric alkane stretching vibration of C-H bonds in the AC and CNT. The broad banding in the range of 500 cm$^{-1}$ and 800 cm$^{-1}$ belonged to the combination vibration of Ti-O-Ti and Ti-O-C bonds that appeared in TiO$_2$-C(160) and TiO$_2$/CNT (Noroozi & Safa 2014). The appearance of a peak at 1,631 cm$^{-1}$ was attributed to vibration of the H-O-H bond.
in adsorbed water. At the same time, the broad bands at 1,444 cm\(^{-1}\) and 1,258 cm\(^{-1}\) for the TiO\(_2\)/CNT composites were ascribed to C-H bending vibration and C-O-C vibration generated in the contact interface between CNT and TiO\(_2\) (Bao et al. 2010; Pajootan & Arami 2013).

**MO photodegradation**

The evaluation of the photocatalytic activity of the materials prepared in this work was carried out by following MO photodegradation as test reaction. Generally, the amount of reaction solution adsorbed onto the photocatalyst’s surface will have a great affect on the photocatalytic activity, so the adsorption efficiency was recorded when adsorption-desorption equilibrium was achieved before irradiation.

Figure 5 shows photocatalytic properties of TiO\(_2\)/AC composites for the degradation of MO under different conditions. Figure 5(a) and 5(b) display the removal efficiency (Rt) of MO under irradiation at 254 nm and 365 nm respectively. It is clear that the MO Rt at 254 nm wavelength was higher. This is mainly attributed to the higher energy of 254 nm UV being easily able to break the chemical bond (–N = N–) of the MO molecule. For each sample, the removal efficiency was increased by 30–40%. Notably, TiO\(_2\)\(_{C(160)}\) showed the highest catalytic activity among these TiO\(_2\)/AC composites. The MO Rt for TiO\(_2\)\(_{C(160)}\) could reach 80% even under 365 nm, and it reached 95% under 254 nm. Therefore, the properties of TiO\(_2\)\(_{C(160)}\) were investigated in all subsequent experiments.

The effect of the composite preparation method on MO degradation efficiency was also investigated. As shown in Figure 5(c), the catalytic activity of TiO\(_2\)\(_{C(160)}\) and TiO\(_2\)\(_{C(160)-1}\) was approximately similar. The MO Rt of TiO\(_2\)\(_{C(160)}\) was about 5% higher than for TiO\(_2\)\(_{C(160)-1}\). This could be attributed to the large size of titanium dioxide generated by direct hydrolysis of butyl titanate, and it is very possible that the agglomeration blocks the pores of the AC, which affected the catalytic efficiency of composite TiO\(_2\)\(_{C(160)-1}\).

**Effect of inorganic anions**

Inorganic anions occur naturally in wastewater or may be added to facilitate the dyeing process. Inorganic anions may induce or reduce the photodegradation process. For example: formation of â€OH radicals during the irradiation of nitrate ions may increase the rate of photo oxidation, while scavenging of hydroxyl radicals reduces the reaction rate. Elmorsi et al. discovered that the rate constant of MR73 degradation decreased by about 50% from 0.081 (in the absence of 0.05 g/L NO\(_3^-\)) to 0.041 min\(^{-1}\) (Elmorsi et al. 2010). Figure 5(d) shows the effect of inorganic anions (0.1 M Cl\(^-\), 0.1 M SO\(_4^{2-}\), 0.1 M NO\(_3^-\)) on the removal efficiency (Rt) of MO. It can be seen from the figure that, compared to the blank sample, i.e. the bare TiO\(_2\)\(_{C(160)}\), the MO Rt increased due to the addition of all three inorganic anions. Although previous reports showed that the presence of NaNO\(_3\) had a negligible effect on the photodegradation process, the results indicated that the promotion effect of NO\(_3^-\) on the MO removal efficiency was the most obvious. It could be explained by the...
fact that the irradiation of the NO$_3^-$ ion may produce •OH radicals due to the rapid protonation of produced ^\text{-} O• as follows:

$$\text{NO}_3^- + \text{hv} \rightarrow \text{NO}_3^{2-} \rightarrow \text{NO}_2^- + ^\text{-} O•$$  \hspace{1cm} (1)

$$- O• + \text{H}_2\text{O} \rightarrow •\text{OH} + \text{OH}^-$$ \hspace{1cm} (2)

$$\text{NO}_2^- + •\text{OH} \rightarrow •\text{NO}_2 + \text{OH}^-$$ \hspace{1cm} (3)

So the availability of •OH radicals for the photodegradation process was increased by 0.1 M NO$_3^-$, which contributed to enhancing decolorization rates. From Figure 5(d), it appears that all of these three anions facilitate the decolorization process. The promotion effect is in the order 0.1 M NO$_3^-$ > 0.1 M Cl$^-$ > 0.1 M SO$_4^{2-}$. The promotion effect under other anionic concentrations was not explored.

Figure 5 | Photocatalytic properties of TiO$_2$/AC composites for degradation of MO under different conditions. (a) Removal efficiency of samples under 254 nm UV irradiation; (b) removal efficiency of samples under 365 nm UV irradiation; (c) removal efficiency of TiO$_2$/C(160) prepared by different methods; (d) effect of anions on the removal efficiency (λ = 365 nm); (e) effect of H$_2$O$_2$ concentration on the removal efficiency (λ = 365 nm); (f) effect of metal dopants on the removal efficiency (λ = 365 nm).
Effect of H₂O₂

The addition of H₂O₂ as an important parameter in the photocatalytic processes is also investigated in Figure 5(e). Various amounts of H₂O₂ (0.5%, 1%, 3%) were added continuously to the reactor. The results revealed that the addition of H₂O₂ to the system significantly promoted the photocatalytic activity to reach complete decolorization. The complete decolorization time for 3% H₂O₂, 1% H₂O₂, 0.5% H₂O₂ was 45 min, 60 min, respectively. However, the Rt could only reach 80% after 120 min irradiation time in the absence of H₂O₂. The Rt increased with the amounts of H₂O₂ added in this range. Plenty of research has also confirmed that H₂O₂ addition during UV treatment is highly effective for improving the degradation of organics. In particular, it has been observed that H₂O₂ addition is more effective in the degradation of PPCPs with low k values in a UV treatment experiment (Kim et al. 2009). It has been reported that H₂O₂ can inhibit the recombination of electrons and holes (e⁻/h⁺), while further providing additional hydroxyl radicals, as described by the following mechanisms:

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{hv} & \rightarrow 2\text{HO•} \quad (4) \\
\text{H}_2\text{O}_2 & \rightarrow \text{HO}_2 + 2\text{H⁺} \quad (5) \\
\text{HO}_2 + \text{hv} & \rightarrow \text{HO•} + 1/2\text{O}_2• \quad (6) \\
\text{O}_2• + \text{H}_2\text{O} & \rightarrow \text{O}_2 + \text{HO•} + \text{HO⁻} \quad (7)
\end{align*}
\]

Meanwhile, further addition of H₂O₂ has been reported to decrease the reaction rate owing to the formation of less destructive hydroxyl radicals (Crittenden et al. 1999).

Effect of metal dopant on the removal efficiency

Figure 5(f) shows the effect of metal dopant on the catalytic performance of TiO₂-C(160). Doping with Bi-Mn-Zn and Bi-Ni-Mn made a significant improvement on the catalytic performance on TiO₂-C(160), and the performance of Bi-Ni-Mn was better than Bi-Mn-Zn. The Rt of TiO₂-C(160)-Bi-Ni-Mn reached 96% in 2 hours. However, the Rt of TiO₂-C(160)-Bi was about 10% lower than the control, TiO₂-C(160). The specific interface electron transfer and behavioral mechanism of multi-composites is complicated. Based on the above results, a photocatalytic mechanism for the degradation of MO catalyzed by TiO₂-C(160)-Bi-Ni-Mn composites was proposed. Because of diverse sizes and electronic properties, the MO molecule was adsorbed on the specific active sites of catalyst selectively, as well as the H₂O₂ oxidant. With the benefit of the excellent optical properties and light response of the TiO₂-C(160)-Bi-Ni-Mn composite surface, some high-energy charge carrier pairs (e⁻/h⁺) were photogenerated by light irradiation. With the aid of some synergistic effects of H₂O₂ excitation and the composites in the materials, the e⁻/h⁺ photogenerated charge carriers were separated from each other and migrated to diverse active sites at the semiconductor/liquid interfaces. The degradation mechanism was mainly as follows (Qi et al. 2016):

\[
\begin{align*}
\text{MxOy} + \text{hv} & \rightarrow \text{MxOy} + e⁻ + h⁺ (M = \text{Bi, Ni, Mn, Zn, Ti}) \\
\text{O}_2 + e⁻ & \rightarrow \text{O}_2•⁻ \quad (8) \\
\text{H}_2\text{O} + h⁺ & \rightarrow \bullet\text{OH} + \text{H⁺} \quad (9) \\
\text{O}_2•⁻ + \text{H⁺} & \rightarrow \bullet\text{OOH} \quad (10) \\
\bullet\text{OOH} + \text{H⁺} + e⁻ & \rightarrow \text{H}_2\text{O}_2 \quad (12) \\
\text{H}_2\text{O}_2 + e⁻ & \rightarrow \bullet\text{OH} + \text{OH⁻} \quad (13) \\
\text{OH⁻} + h⁺ & \rightarrow \bullet\text{OH} \quad (14)
\end{align*}
\]

The photocatalytic properties of TiO₂/CNT composites for the degradation of MO under different conditions is illustrated in Figure 6. As can be seen from Figure 6, the overall catalytic activity of TiO₂/CNT is lower than that of TiO₂-C(160). Only with the addition of hydrogen peroxide could the MO removal efficiency reach 100% within 1 hour. In the other reaction groups, even under 254 nm UV irradiation, the highest MO removal efficiency was only about 55%. This was mainly attributed to the use of an inert glass slide as the loading substrate. CNT and TiO₂ were immobilized on the surface of the slide, which covered the active sites, leading to a great decrease of the composite’s catalytic activity. Figure 6(b) indicates that the addition of chloride ions suppressed the catalytic activity of the sample. As the chloride ion concentration increased, the MO removal efficiency decreased. Figure 6(e) shows that metal dopants increased the catalytic activity of the sample to a certain extent, but the effect was not significant. Figure 6(f) implies that the TiO₂/CNT on the glass slide has poor recycling ability, and after four reaction cycles, the MO removal efficiency had dropped to around 11% in 2 hours. The adsorption principle of CNTG was different from that of AC. It mainly depended on its high surface activity and functional group combination for adsorption. Under ultra-short-wave ultraviolet radiation with extremely high
energy, it also has a destructive effect on the functional groups of the surface-bound catalyst. After a period of UV light irradiation, the catalyst was mostly detached from the slide, and MO removal efficiency was greatly decreased.

We also evaluated the reusability of the TiO₂/AC nanocomposites. For this purpose, the TiO₂-C(160) was typically reused four times under the same conditions in 254 nm UV irradiation. As shown in Figure 7, the TiO₂-C(160) was highly stable and maintained its high photocatalytic performance over four reaction cycles. The degradation efficiency of TiO₂-C(160) of the four cycling runs was 95%, 93%, 92%, 91% respectively. Compared to the
reusability of the TiO2/CNTG, it clearly demonstrated that the TiO2-C(160) was quite stable and had good photocatalytic repeatability.

Figure 8 illustrates the transfer behavior of the photo-generated e-/h+ in TiO2-C(160) and TiO2/CNT under UV-irradiation. Under the irradiation of external light, electron (e-) was excited from the valence band (VB) to the conduction band (CB) of TiO2, leaving behind h+ at the original sites. From the SEM spectra it can be seen that the AC acted as a support or carrier for TiO2. However, CNT was not only a supported material, but also a semiconducting material with a forbidden band width of 2.7 eV, which is narrower than that of TiO2. Thus, e- migrated to the conduction band of CNT at the same time. In addition, H2O as electron donors and oxygen as electron acceptor will form the hydroxyl radicals (·OH) and superoxide ion radicals (O2·-). These generated radicals, especially hydroxyl radicals, are nonselective strong oxidants which can fully mineralize MO into inorganic pollutants.

CONCLUSIONS

In summary, TiO2-C(160) and TiO2/CNTG porous composites with large surface area and high adsorption capacity were successfully fabricated for MO removal. A group of 3-metal dopants were innovatively synthesized to improve the photocatalytic performance of the composites. Photocatalytic activity of TiO2-C(160) could be significantly improved by a metal dopant. The MO Rt of TiO2-C(160)-Bi-Ni-Mn reached 96% in 2 hours. This appeared to be a promising alternative for TiO2 modification. However, due to TiO2/CNT immobilization on the inert glass substrate, the metal dopant enhancement effect was not obvious for TiO2/CNTG. The characterization of the photocatalytic composites were investigated using SEM images and FTIR analysis, showing the successful and stable preparation of the composites. The catalytic activity was also examined by studying the influence of effective parameters such as H2O2 dosage, inorganic anions, chloride ion concentration and ultraviolet wavelength on the MO removal efficiency. The results demonstrated that the MO photodegradation rate can be significantly improved by the addition of H2O2. Complete decolorization was achieved in only 45 min with the addition of 3% H2O2 for both composites. Carbon-based porous composites combining excellent adsorption properties and good photocatalytic activities have great application potentials for MO removal, especially with the modification of metal dopants.

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