Trimesoyl Chloride-Melamine Copolymer-TiO$_2$ Nanocomposites as High-Performance Visible-Light Photocatalysts for Volatile Organic Compound Degradation

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Abstract: Benzene is a typical volatile organic compound (VOC) and is found widely in industrial waste gases. In this study, trimesoyl chloride-melamine copolymer (TMP)-TiO$_2$ nanocomposites with excellent photocatalytic efficiency in visible-light degradation of gas-phase benzene were synthesized via an in situ hydrothermal synthesis. The optimal conditions for TMP-TiO$_2$ nanocomposite synthesis were determined by orthogonal experiments. The structural, physiochemical, and optoelectronic properties of the samples were studied by various analytical techniques. Ultraviolet-visible diffuse reflectance spectroscopy and surface photovoltage spectra showed that the positions of the light-absorbance edges of the TMP-TiO$_2$ nanocomposites were sharply red-shifted to the visible region relative to those of unmodified TiO$_2$. The most efficient TMP-TiO$_2$ nanocomposite was used for photocatalytic oxidative degradation of gas-phase benzene (initial concentration 230 mg m$^{-3}$) under visible-light irradiation (380–800 nm); the degradation rate was 100% within 180 min. Under the same reaction conditions, the degradation rates of unmodified TiO$_2$ (hydrothermally synthesized TiO$_2$) and commercial material Degussa P25 were 19% and 23.6%, respectively. This is because the Ti–O–N and Ti–O–C bonds in TMP-modified TiO$_2$ reduce the band gap of TMP-TiO$_2$. The amide bonds in the TMP decrease the TiO$_2$ nanoparticle size and thus increased the specific surface area. The conjugated structures in the TMP provide abundant active sites for trapping photogenerated electrons and promote the separation and transfer of photogenerated electrons and holes.

Keywords: TiO$_2$; visible light; volatile organic compound; benzene; gas degradation

1. Introduction

Volatile organic compounds (VOCs) are a kind of important class of air pollutants and are usually found in the air of industrial areas [1]. VOCs are crucial precursors in the formation of fine particulate matter (PM2.5), ozone, and photochemical smog. They are harmful to the human body and have strong carcinogenic, teratogenic, and mutagenic properties [2,3]. Benzene is a typical VOC. It is highly toxic, is generated in large amounts from various sources, and is difficult to degrade naturally [4]. Benzene has been used by many researchers as a representative VOC pollutant. Because of increasing pollution by VOCs, it is important to develop techniques for separating or removing VOCs. The most common removal methods include adsorption, thermal burning, photocatalytic degradation, and plasma degradation [5–7].

Among these methods, photocatalytic oxidation of VOCs is considered to be one of the most promising environmentally friendly purification techniques because of its great performance,
high stability, and cost effectiveness [8]. Among many catalysts, TiO₂ has become the most commonly used photocatalyst because of its low price, photostability, and thorough degradation ability. However, its shortcomings such as the wide band gap for photocatalysis and the recombination of photogenerated electron-hole pairs have limited its applications.

Studies of photocatalytic techniques have therefore focused on developing methods for improving the electron-hole separation efficiency of TiO₂ and expanding its response to visible light. Various strategies for modification of TiO₂ photocatalysts to decrease the band gap, and enhance the electronic activity and quantum efficiency have been investigated. Estrellan and Gao et al. modified TiO₂ by doping with metals and non-metals to decrease its band gap. However, the traditional doping modification process is complicated and the reaction conditions are uncertain. To improve the catalytic degradation efficiency of the catalyst under visible light, Mittal and Shayegan used noble metals and semiconductor oxides to construct heterojunctions or inorganic acids to further modify TiO₂ to improve the electronic activity and quantum yield. These modification methods are expensive, toxic, and environmentally unfriendly [6,8,9]. Modification of TiO₂ with polymers has caused widespread interest because the obtained catalyst has high efficiency, is non-toxic, environmentally benign, and the synthesis is convenient and cheap [10–15].

In this study, trimesoyl chloride-melamine copolymer (TMP)-modified anatase TiO₂ materials were prepared by an in situ hydrothermal synthesis with tetrabutyl titanate as the precursor. The TMP-TiO₂ nanocomposites were characterized by using XRD, Brunauer Emmett and Teller (BET), XPS, scanning electron microscopy (SEM), transmission electron microscopy (TEM), HR-TEM, UV-vis-DRS and surface photovoltage spectrum (SPS). Modification with TMP led to a 0.3-fold reduction in the particle size, better absorption in the visible-light range (400–800 nm), and increased the surface area ratio of the {001} crystal faces, which give strong oxidation. The photocatalytic efficiency of TMP-TiO₂ in gas-phase benzene degradation was 100% in 180 min. These results show that the special backbone structure and large number of TMP functional groups enabled TiO₂ to form Ti–O–C and Ti–O–N bonds, which decreased the TMP-TiO₂ band gap. The conjugated structures in TMP can provide abundant active sites for trapping photogenerated electrons to promote the separation and transfer of photogenerated electrons and holes. In this study, high-efficiency, visible-light catalytic oxidation by TMP-TiO₂ nanocomposites was achieved.

2. Results and Discussion

2.1. Optimal Conditions for TMP-TiO₂ Synthesis

In order to analyze the influence of various experimental factors on the degradation efficiency of gaseous benzene, Minitab-17 was used to fit the experimental results in Table 1 below, and the regression equations of four factors and RE % were obtained:

\[
\text{RE} \%(\%) = 36.85 + 17.55 A + 19.82 B - 31.72 C + 39.80 D - 3.735 A \times A - 4.485 B \times B + 8.850 C \times C - 9.110 D \times D. \tag{1}
\]

As shown in Table 1, the variance analysis is carried out for the experimental regression model, and all the main factors of the model are examined, without considering the interaction between various factors. From the overall effect of the fitting, these models have a significant impact on the probability level of 5%, and the experimental error is small. Therefore, this regression equation can predict the photocatalytic degradation performance of the sample. According to the value of F and the signal-to-noise ratio (Figure 1) of degradation efficiency, the optimal synthesis conditions are: hydrolysis reaction temperature 80 °C, TMP: TiO₂ precursor ratio 1:1, and then hydrothermal reaction at 180 °C for 8 h to prepare visible optical driven TMP-TiO₂ nanocomposites (A2B2C3D2). The order of importance of the four control factors affecting degradation efficiency is: factor D > factor C > factor B > factor A.
2.2. Fourier-Transform Infrared (FTIR) and XPS Analysis

FTIR spectroscopy and XPS were used to investigate the interactions between the unmodified TiO$_2$ and the TMP-TiO$_2$ nanocomposites. The FTIR spectrum are shown in Figure 2. The FTIR spectrum of the unmodified TiO$_2$ has peaks at 3360 and 1627 cm$^{-1}$, which correspond to the stretching and bending vibrations peaks, respectively, of OH groups in physically adsorbed water and surface OH groups [16–18]. The peaks at 3220, 1718, 1535, and 1449 cm$^{-1}$ in the TMP-TiO$_2$ spectrum are not observed in the unmodified TiO$_2$ spectrum and are respectively attributed to N–H stretching, C=O stretching, C–N–H bending vibrations, and COO–symmetric telescopic vibrations. All these new peaks indicate TMP adsorption on the TiO$_2$ surface. The two absorption bands at 1249 and 1022 cm$^{-1}$ are ascribed to Ti–O–C and Ti–O–N bonds, and suggest chemical bonding between the TMP and TiO$_2$ in the TMP-TiO$_2$ nanocomposites [19–21]. This was confirmed by XPS. The XP spectra (Figure 3a) show that the unmodified TiO$_2$ contains only Ti, O, and C elements. The carbon arises from the uncertain hydrocarbons in the XPS instrument. The TMP-TiO$_2$ nanocomposites (Figure 3a) contain Ti, O, N, and C elements, and the binding energies of Ti2p, O1s, N1s, and C1s are 460.7, 462.0, 401.9, and 284.8 eV, respectively. The total amount of nitrogen in the TMP-TiO$_2$ nanocomposites was approximately 13.9 at %. In addition, we also recorded the high-resolution Ti2p XPS of the unmodified TiO$_2$ and TMP-TiO$_2$ nanocomposites (Figure 3b). The peaks in the TMP-TiO$_2$ spectrum at 464.3 and 458.6 eV, which correspond to Ti2p1/2 and Ti2p3/2, are slightly transferred to higher binding energies compared with unmodified TiO$_2$. These results indicate that the chemical environment of Ti in TMP-TiO$_2$ has been altered by the formation of Ti–O–C and Ti–O–N bonds [22–24]. The O1s XP spectrum of TMP-TiO$_2$ (Figure 3c) can be fitted by three peaks, corresponding to Ti–O (529.4 eV),
O–H (531.2 eV), and N–O (532.7 eV) bonds, respectively. These results further confirm the presence of Ti–O–N bonds [25,26]. The C1s core levels (Figure 3d) of the TMP-TiO nanocomposites can be fitted by four peaks at binding energies of 285.0, 286.4, 288.3, and 289.2 eV, which are attributed to Ti–C–O, C–O, C–N, and O=C–O, respectively [14,27]. These results indicate that Ti–O–C bonds were formed in the TMP-TiO2 nanocomposites [28].

Figure 2. Fourier transform infrared (FTIR) of unmodified TiO2 and trimesoyl chloride-melamine copolymer (TMP)-TiO2.

Figure 3. (a) XPS of unmodified TiO2 and TMP-TiO2, (b) Ti2p XPS high resolution spectra of unmodified TiO2 and TMP-TiO2, (c) O1s XPS high resolution spectra of TMP-TiO2, and (d) C1s XPS high resolution spectra of TMP-TiO2.
2.3. XRD Analysis

The effects of TMP on the structure of TiO₂ synthesized by the hydrothermal method were studied by XRD; the patterns for the unmodified TiO₂ and TMP-TiO₂ nanocomposites are shown in Figure 4. The peaks at 25.3, 37.8, 48.2, 54.1, and 62.8 °C in the XRD pattern of the hydrothermally synthesized TiO₂ are attributed to the (101), (004), (200), (105), and (205) reflections of anatase TiO₂ (JCPDS No.84-1285). The rutile-phase diffraction peak at 28.2 °C (110) appeared in the XRD pattern of the TMP-TiO₂ nanocomposites [29,30]. This shows that the crystalline structures of the unmodified TiO₂ and the TMP-TiO₂ nanocomposites consisted mainly of the anatase phase, with a little amount of the rutile phase which appeared in the TMP-TiO₂. The rutile phase could be produced by interactions between the functional groups in TMP with hydroxyl groups on the TiO₂ surface during hydrothermal synthesis. Modification with TMP broadened the anatase peaks, which indicates that the crystallinity of the TMP-TiO₂ nanocomposites was lower than that of the unmodified TiO₂ and the particle size decreased correspondingly. This could be caused by the effect of TMP amide bonds and indicates that modification with TMP could affect the crystalline structures during the hydrothermal synthesis of TiO₂. Line-width analysis of the anatase (101) diffraction peak by the Scherrer formula showed that the estimated average crystallite sizes of the unmodified TiO₂ and TMP-TiO₂ nanocomposites are about 8.5 and 6.9 nm, respectively [31]. These results show that modification with TMP efficiently inhibits the TiO₂ crystal size, which improves the photocatalytic activity. The photocatalytic activity of the anatase phase is higher than the rutile phase, but a mixed anatase–rutile phase could have a synergistic effect and inhibit electron-hole pair recombination. These results show that modification with TMP improves the photocatalytic activity.

![Figure 4. XRD spectra of TiO₂ and TMP-TiO₂.](image)

2.4. BET Analysis

The nitrogen adsorption–desorption isotherm pore and the size distribution curves of unmodified TiO₂ and TMP-TiO₂ nanocomposites are shown in Figure 5, respectively. According to the classification of IUPAC, the unmodified TiO₂ and TMP-TiO₂ nanocomposites belong to the type IV isotherm with hysteresis loops, which indicates that the material has a porous like structure. The specific surface area of unmodified TiO₂ and TMP-TiO₂ are 37.44 and 67.29 m²g⁻¹, and the average adsorption pore diameter is 16.9 and 9.7 nm, respectively. It can be seen that the specific surface area of TMP-TiO₂ is higher than 55 m²g⁻¹ of Degussa P25 TiO₂ material [32]. Therefore, the high specific surface area of TMP-TiO₂ is one of the reasons for its excellent photocatalytic degradation.
Figure 5. N₂ adsorption–desorption isotherm pore and the size distribution curves of unmodified TiO₂ and TMP-TiO₂ nanocomposites.

2.5. SEM and TEM Investigations

The morphologies and structures of the unmodified TiO₂ and TMP-TiO₂ nanocomposites were researched by SEM and TEM. The SEM image of the unmodified TiO₂ in Figure 6a clearly shows that the particle size distribution of the unmodified TiO₂ is not uniform and there is considerable aggregation. The SEM image in Figure 6b shows that the TMP-TiO₂ particles are smaller than those of the unmodified TiO₂ and better distributed. The TMP-TiO₂ surface is rougher than that of unmodified TiO₂, and the sample has a high degree of intraparticle porosity. The SEM images indicate that the TMP-TiO₂ nanocomposites had excellent dispersion and intraparticle porosity compared with those of the unmodified TiO₂.

Figure 6. (a) Scanning electron microscopy (SEM) images of TiO₂, and (b) SEM images of TMP-TiO₂.

The morphologies and crystal structures of the unmodified TiO₂ and TMP-TiO₂ nanocomposites were investigated by TEM. Figure 7a shows that the unmodified TiO₂ particles have irregular shapes and are of non-uniform size. The TEM image of TMP-TiO₂ in Figure 7c shows that the crystallite size of TMP-TiO₂ is clearly smaller than that of the unmodified TiO₂ and evenly distributed. Figure 7b,d shows the particle size histogram of TiO₂ and TMP-TiO₂, respectively. A random selection of 100 nanoparticles was made, and the crystallite sizes were determined by using ImageJ software. The crystallite sizes of the unmodified TiO₂ is 6–13 nm, the average crystallite size is 9.71 nm, the crystallite sizes of TMP-TiO₂ are 4–11 nm, and the average crystallite size is 6.84 nm. These values are consistent with those calculated by XRD through Scherrer formula. High-resolution TEM images are shown in Figure 7e. Three types of lattice are present, with lattice spacings of 0.19, 0.235, and 0.345 nm, consistent with the (200), (004), and (101) crystal planes of anatase TiO₂ [24,30]. The corresponding selected-area electron diffraction (SAED) pattern (Figure 7f) confirms exposure of the (200), (004), and (101) crystal planes. In addition, according to previous reports, the (200) and (004) crystal planes both belong to the [001] crystal system, and their photooxidation activities are stronger than that of the
(101) crystal plane [33,34]. This is one of the reasons for the strong catalytic activity of TMP-TiO$_2$ in benzene degradation.

![Figure 7](image)

**Figure 7.** (a) Transmission electron microscopy (TEM) images of TiO$_2$. (b) particle size histogram of TiO$_2$. (c) TEM images of TMP-TiO$_2$, (d) particle size histogram of TMP-TiO$_2$, (e) HR-TEM of TMP-TiO$_2$, and (f) selected-area electron diffraction (SAED) pattern of TMP-TiO$_2$.

### 2.6. UV-Vis Diffuse Reflectance Spectra

Photo-absorption is one of the important factors in the performances of photocatalysts. Figure 8a shows that the unmodified TiO$_2$ shows almost no absorption above 400 nm, whereas TMP-TiO$_2$ shows obvious absorption in the visible-light region of 400–800 nm. In addition, the band gap energies of the unmodified TiO$_2$ and TMP-TiO$_2$ (Figure 8b), which were to be 3.05 and 2.30 EV, respectively, are shown using the Kubelka Munk function transformation. The chemical bonding between the hydrothermally synthesized TiO$_2$ and TMP forms Ti–O–N and Ti–O–C bonds, which significantly reduces the band gap of TMP-TiO$_2$ nanocomposite; thereby this could enhance its photocatalytic activity under visible-light irradiation [35].
with the UV-Vis results. This is attributed to the conjugated system in TMP trapping photogenerated electrons, which leads to the effective separation of photogenerated electron-hole pairs of TMP-TiO$_2$.

![Figure 8](image.png)

**Figure 8.** (a) UV-Vis DRS of TiO$_2$ and TMP-TiO$_2$, and (b) plots of transformed Kubelka-Munk function versus the energy of absorbed light.

### 2.7. SPS Analysis

In order to investigate the separation and recombination of photogenerated electrons and holes in TiO$_2$ and TMP-TiO$_2$ nanocomposites, the surface photovoltage spectra (SPS) were measured. As shown in Figure 9, we can clearly see that TiO$_2$ has an obvious SPS response at 300–370nm, which is caused by the electron transition from the valence band to the conduction band of TiO$_2$. In addition, we can see that the SPS response of the TMP-TiO$_2$ nanocomposite is red-shifted to 550 nm, which is consistent with the UV-Vis results. This is attributed to the conjugated system in TMP trapping photogenerated electrons, which leads to the effective separation of photogenerated electron-hole pairs of TMP-TiO$_2$.

![Figure 9](image.png)

**Figure 9.** Surface photovoltage spectrum (SPS) spectra of TiO$_2$ and TMP-TiO$_2$.

### 2.8. Photocatalytic Efficiency

The CO$_2$ gas production rates and benzene conversion rates with increasing irradiation time are shown in Figure 10. Under dark conditions, TMP-TiO$_2$ reached adsorption saturation in 20 min, the removal rate of gaseous benzene was 13.2%, and CO$_2$ was not produced. After 180 min of visible-light irradiation, the photodegradation rates of gaseous benzene by the unmodified TiO$_2$ and P25 were only about 19% and 23.6%, respectively, and the produced CO$_2$ contents were about 195 and 157 mg m$^{-3}$, respectively. This shows that the photodegraded gaseous benzene cannot be effectively converted to CO$_2$ and water when unmodified TiO$_2$ and P25 are used as photocatalysts. TMP-TiO$_2$ has better visible light photocatalytic performance. Gas-phase benzene was completely converted to CO$_2$ and water under visible-light irradiation in 180 min; the amount of produced CO$_2$ was 960 mg m$^{-3}$ (Figure 10b). Moreover, the stability of visible light photocatalytic performance of the TMP-TiO$_2$ nanocomposites were examined during four cycle experiments, and the results are shown in Figure 10c,d. At the same time, TMP-TiO$_2$ after catalytic reaction was collected and washed by water and alcohol for many times, and then dried for characterization. We can see the FTIR, XPS, and XRD spectra before and after the photocatalytic reaction in Figure 11; the chemical bond composition and state of TMP-TiO$_2$, and
the crystal structure have not changed significantly, indicating that the TMP-TiO₂ nanocomposites are well-recycled photocatalysts. The results indicate that the Ti–O–N and Ti–O–C bonds formed between TMP and TiO₂ can improve the visible light absorption of TMP-TiO₂ nanocomposites, and the conjugated system in TMP can provide a rich active site for capturing photogenerated electrons, which promotes the separation and transfer of photogenerated electrons and holes, and enhances their catalytic degradation activity.

**Figure 10.** (a) Degradation rate of benzene gas concentration with visible light irradiation, (b) production rates for the CO₂ gas, (c) cycling degradation rate of benzene on TMP-TiO₂, and (d) CO₂ produced with cycling runs.

**Figure 11.** (a) XRD spectra of TMP-TiO₂ before and after photocatalytic reaction, (b) XPSpectra of TMP-TiO₂ before and after photocatalytic reaction, and (c) FTIR of TMP-TiO₂ before and after photocatalytic reaction.
2.9. Relationship between Physicochemical Properties and Photocatalytic Activity of TMP-TiO$_2$ Nanocomposites

Scheme 1 shows a proposed mechanism of enhanced photocatalytic activity of the TMP-TiO$_2$ nanocomposite photocatalysts under visible-light irradiation. The above results suggest that the special chemical structures of the TMP-TiO$_2$ nanocomposites play crucial roles in improving the photocatalytic activity under visible-light irradiation. There are a lot of C=C, hydroxyl, amidogen, carboxyl, and amide bonds on the surface of TMP [12,24,36]. Under high pressure and temperature, the amide bond and carboxyl group on the surface of TMP can form Ti–O–C and Ti–O–N bonds through chemical bond with the hydroxyl group on the TiO$_2$ surface [21–23,37]. The amide bonds in the TMP cause the TiO$_2$ nanoparticle size to decrease, and the relative surface area of the TiO$_2$ nanomaterial increases. The Ti–O–N and Ti–O–C bonds between TiO$_2$ and the TMP decrease the TiO$_2$ band gap, and the conjugated system in the TMP provide abundant active sites for trapping photogenerated electrons; this promotes the separation and transfer of photogenerated electrons and holes [38]. The TMP-TiO$_2$ nanocomposites therefore have high catalytic activity in benzene degradation under visible-light irradiation, and the mechanism of TiO$_2$ modification by TMP is confirmed.

![Scheme 1. Proposed mechanism for enhancement of the photocatalytic activity of the TMP-TiO$_2$ nanocomposite photocatalysts under visible-light irradiation.](image)

3. Materials and Methods

3.1. Chemicals and Materials

Melamine and benzene (AR) were purchased from the Sinopharm Chemical Reagent Co., Ltd. (Tianjin, China). Absolute ethanol was purchased from the Tianjin FuYu Fine Chemical Co., Ltd. (Tianjin, China). Trimesoyl chloride was purchased from the Shanghai Aladdin Reagent Co., Ltd. (Shanghai, China). CuCl$_2$ was purchased from the Xi Long Chemical Co., Ltd. (Shantou, China). A commercial TiO$_2$ sample (P-25) was purchased from the Degussa Co., Ltd. (Steinheim, Germany). All these reagents were AR grade and could be used without purification, and all experiments used deionized water.

3.2. Preparation of Trimesoyl Chloride-Melamine Copolymer (TMP)

The TMP was synthesized according to the literature method [39–41]. Melamine (2.52 g) was added to a 100 mL three-necked, round-bottomed flask, which contained trimesoyl chloride (5.35 g) as both a reactant and the solvent. CuCl$_2$ (0.1 g) was added as a catalyst. The mixture was refluxed at 95 °C with continuous stirring. After 6 h of reaction, the system was naturally cooled to room temperature. The resulting TMP was washed with a large amount of absolute ethanol and deionized water.
water until the washing liquid was colorless. The TMP was collected by centrifugation and dried in a constant temperature blast furnace at 105 °C for 2 h.

3.3. Preparation of TMP-TiO$_2$ Nanocomposites

Orthogonal experiment, factor design and signal-to-noise (S/N) ratio are used to optimally combine different selection factors to determine the most influential factors. The object of the research was to degrade gaseous benzene under visible-light irradiation by using the TMP-TiO$_2$ nanocomposites as photocatalysts. The selected quality characteristic was therefore “the higher-the-better”, and the S/N ratio was determined from the following equation:

$$
\frac{S}{N} = -10 \log \left( \frac{1}{n} \sum_{i=1}^{n} \frac{1}{y_i^2} \right)
$$

where $y$ is the measured value and $n$ the number of measurements (in the present study $n = 3$).

Before the design experiment, we conducted a single factor experiment to prepare the visible light-driven TMP-TiO$_2$ nanocomposites by an in situ hydrothermal method [42–45]. In the first part of the hydrolysis reaction, a molar ratio of 1:1 TMP and tetrabutyl titanate were added to a 100 mL three-necked round-bottom flask with anhydrous ethanol as the solvent, a certain amount of hydrochloric acid was added to adjust the pH of the reaction system to 3, and the mixture was heated at 80 °C for 4 h. In the second part of the hydrothermal reaction, the hydrolysis reaction product solution was transferred from the three-necked, round-bottomed flask to a Teflon autoclave. The autoclave was heated at 160 °C for 8 h, and then cooled naturally to room temperature. The products were collected by centrifugation and washed with a large amount of deionized water until the washing liquid was colorless. The products, i.e., the TMP-TiO$_2$ nanocomposites, were dried at 105 °C for 2 h in an electro-thermostatic blast oven. There were four controllable factors: hydrolysis reaction temperature, TMP:TiO$_2$ precursor ratio, hydrothermal reaction temperature and hydrothermal reaction. We conducted a four factors three levels center combination design, and ran the experiment 3 times. The experimental factor level design and results are shown in Tables 2 and 3.

### Table 2. Levels and codes of variables chosen for the experimental design.

| Coded Level | Hydrolysis Reaction Temperature (°C) | TMPs:TiO$_2$ Precursor Ratio (−) | Hydrothermal Reaction Temperature (°C) | Hydrothermal Reaction Time (h) |
|-------------|--------------------------------------|-----------------------------------|----------------------------------------|-------------------------------|
| 1           | 60                                   | 1:2                               | 140                                   | 6                             |
| 0           | 80                                   | 1:1                               | 160                                   | 8                             |
| 1           | 100                                  | 2:1                               | 180                                   | 10                            |

### Table 3. Experimental designs and results.

| Run | Coded Levels | Real Values of Parameters | Response | Average S/N Ratio for RE |
|-----|--------------|---------------------------|----------|--------------------------|
|     | A | B | C | D | A (°C) | B (-) | C (°C) | D (h) | Removal Efficiency (RE/%) |
| 1   | −1 | −1 | −1 | −1 | 60     | 1:2   | 140    | 6     | 72.83          |
| 2   | −1 | −1 | −1 | −1 | 60     | 1:2   | 140    | 6     | 77.50          |
| 3   | −1 | −1 | −1 | −1 | 60     | 1:2   | 140    | 6     | 71.16          |
| 4   | −1 | 0  | 0  | 0  | 60     | 1:1   | 160    | 8     | 86.50          |
| 5   | −1 | 0  | 0  | 0  | 60     | 1:1   | 160    | 8     | 87.30          |
| 6   | −1 | 0  | 0  | 0  | 60     | 1:1   | 160    | 8     | 88.70          |
| 7   | −1 | 1  | 1  | 1  | 60     | 2:1   | 180    | 10    | 92.68          |
| 8   | −1 | 1  | 1  | 1  | 60     | 2:1   | 180    | 10    | 90.23          |
| 9   | −1 | 1  | 1  | 1  | 60     | 2:1   | 180    | 10    | 92.13          |
3.4. Photocatalytic Activity Tests

The photocatalytic performances of the TMP-TiO$_2$ nanocomposites, the hydrothermally synthesized TiO$_2$ (unmodified TiO$_2$), and P25 were determined from the decrease in the gaseous benzene concentration (initial concentration 230 mg m$^{-3}$) at room temperature in an experimental reactor by using the experimental system designed in our laboratory.

A schematic diagram of the static experimental reactor is shown in Figure 12. The reactor was a 7.7 L cylindrical glass reactor. The outside of the reactor consisted of a water-bath sleeve to control the temperature of the catalytic reaction system. An internal 400 W halogen lamp (i.e., 38 mW cm$^{-2}$) was used as a visible-light source (380–800 nm) and the light source was cooled by a cold trap. A cylindrical quartz catalyst carrier with a diameter of 11 cm and a height of 15 cm was placed outside the light source and a temperature sensor was placed on the quartz carrier. The reactor was kept completely sealed and high-purity air was used as the carrier gas in the degradation experiments. The concentration of gas-phase benzene was determined with a GC 2010 Plus system.

![Figure 12. Benzene gas photocatalytic reactor.](image)

| Run | A  | B  | C  | D  | A (°C) | B (-) | C (°C) | D (h) | Removal Efficiency (RE(%)) | Average S/N Ratio for RE |
|-----|----|----|----|----|--------|-------|--------|-------|----------------------------|--------------------------|
| 10  | 0  | −1 | 0  | 1  | 80     | 1:2   | 160    | 10    | 82.73                      |                          |
| 11  | 0  | −1 | 0  | 1  | 80     | 1:2   | 160    | 10    | 82.35                      | 38.24763                 |
| 12  | 0  | −1 | 0  | 1  | 80     | 1:2   | 160    | 10    | 80.11                      |                          |
| 13  | 0  | 0  | 1  | −1 | 80     | 1:1   | 180    | 6     | 94.91                      |                          |
| 14  | 0  | 0  | 1  | −1 | 80     | 1:1   | 180    | 6     | 92.38                      | 39.45424                 |
| 15  | 0  | 0  | 1  | −1 | 80     | 1:1   | 180    | 6     | 94.44                      |                          |
| 16  | 0  | 1  | −1 | 0  | 80     | 2:1   | 140    | 8     | 95.41                      |                          |
| 17  | 0  | 1  | −1 | 0  | 80     | 2:1   | 140    | 8     | 97.32                      | 39.68244                 |
| 18  | 0  | 1  | −1 | 0  | 80     | 2:1   | 140    | 8     | 96.50                      |                          |
| 19  | 1  | −1 | 1  | 0  | 100    | 1:2   | 180    | 8     | 98.19                      |                          |
| 20  | 1  | −1 | 1  | 0  | 100    | 1:2   | 180    | 8     | 98.77                      | 39.90305                 |
| 21  | 1  | −1 | 1  | 0  | 100    | 1:2   | 180    | 8     | 99.71                      |                          |
| 22  | 1  | 0  | −1 | 1  | 100    | 1:1   | 140    | 10    | 91.14                      |                          |
| 23  | 1  | 0  | −1 | 1  | 100    | 1:1   | 140    | 10    | 93.11                      | 39.19418                 |
| 24  | 1  | 0  | −1 | 1  | 100    | 1:1   | 140    | 10    | 92.17                      |                          |
| 25  | 1  | 1  | 0  | −1 | 100    | 2:1   | 160    | 6     | 77.35                      |                          |
| 26  | 1  | 1  | 0  | −1 | 100    | 2:1   | 160    | 6     | 78.26                      | 37.80283                 |
| 27  | 1  | 1  | 0  | −1 | 100    | 2:1   | 160    | 6     | 77.34                      |                          |
The weight of catalyst powder used in each set of experiments was kept at 0.5 g, dissolved using anhydrous ethanol, and uniformly applied to the quartz catalyst carrier. Prior to the experiments, the temperature of the water-bath sleeve was set at 25 °C, high-purity air was injected into the reactor, and then benzene (2 µL) was injected into the reactor by using a microsyringe. The light source was turned on for the photocatalytic degradation experiment, and samples (1 mL) were removed at a defined time interval (20 min). The gas-phase benzene content was determined by gas chromatography with nitrogen as the carrier gas.

3.5. Characterization

The morphologies of the unmodified TiO\textsubscript{2} (the hydrothermally synthesized TiO\textsubscript{2}) and the TMP-TiO\textsubscript{2} nanocomposites were investigated by transmission electron microscopy (TEM) (JEM2100, JEOL, Tokyo, Japan) and field-emission scanning electron microscopy (SEM) (Regulus8220, Hitachi, Tokyo, Japan). The unmodified TiO\textsubscript{2} and TMP-TiO\textsubscript{2} nanocomposites were examined by powder XRD (Shimadzu XRD-6100, Tokyo, Japan) with Cu Kα radiation. The chemical structures of the unmodified TiO\textsubscript{2} and TMP-TiO\textsubscript{2} nanocomposites were investigated by Fourier-transform infrared (FTIR) spectroscopy (Shimadzu IRAffinity-1s, Tokyo, Japan) at a resolution of 2 cm\(^{-1}\) and using KBr pellets. The surface compositions of the unmodified TiO\textsubscript{2} and TMP-TiO\textsubscript{2} nanocomposites were investigated by XPS (Thermo Fisher ESCALAB Xi+, Waltham, MA, United States). All binding energies were referenced to the C1s peak (284.8 eV) from adventitious carbon. UV-vis diffuse reflectance spectroscopy was performed with a UV spectrophotometer (Agilent CARY 300/PE lambda 750S, Waltham, MA, United States) equipped with an integrating sphere attachment. The surface photovoltage spectrum (SPS) was measured by the built equipment. The powder sample was sandwiched between two ITO glass electrodes and placed in an atmosphere control vessel with a quartz window. The monochromatic light was obtained by using the light from the 500W Xenon lamp (CHF XQ 500W, Beijing, China) through the biprism monochromator (SBP3000, Beijing, China). A Geminiv2380 adsorption instrument was used, with N\textsubscript{2} as adsorbate to record isotherms at 77 K. The specific surface area of TiO\textsubscript{2} and TMP-TiO\textsubscript{2} nanocomposites were calculated by using the Brunauer Emmett and Teller (BET) method from the adsorption desorption isotherms of nitrogen, and the pore sizes distribution of isotherm desorption branch were estimated.

4. Conclusions

In this study, we synthesized TMP-TiO\textsubscript{2} nanocomposites by an in situ hydrothermal method and achieved efficient photocatalytic oxidation of gas-phase benzene under visible-light irradiation. The optimal conditions were a hydrolysis reaction, temperature set at 80 °C, a TMP:TiO\textsubscript{2} precursor ratio 1:1, a hydrothermal reaction temperature of 180 °C, and a hydrothermal reaction time of 8 h. TEM images showed that the TMP-TiO\textsubscript{2} nanocomposite prepared under the optimal conditions had a particle size of about 7 nm. A combination of Ti–O–N and Ti–O–C bonds in TMP-TiO\textsubscript{2} was confirmed by FTIR spectroscopy and XPS. XRD patterns and high-resolution TEM images showed that the crystal structure of the TMP-TiO\textsubscript{2} nanocomposites retained the anatase form and the {001} crystal system appeared. UV-vis diffuse reflectance spectroscopy and surface photovoltage spectra showed that the light-absorbance edge of the TMP-TiO\textsubscript{2} nanocomposites clearly shifted to the visible-light region. The TMP-TiO\textsubscript{2} nanocomposites completely degraded benzene gas under visible-light irradiation within 180 min; the photocatalytic activity was significantly higher than those of P25 and unmodified TiO\textsubscript{2}. Through the catalytic cycle experiments and XRD, XPS, FTIR characterization, TMP-TiO\textsubscript{2} is a catalytic degradation material with excellent cycle stability. The TMP-TiO\textsubscript{2} nanocomposites have a narrower band gap and smaller particle size, and the photogenerated electrons and holes are more effectively separated and transferred, compared with those in unmodified TiO\textsubscript{2}. This study shows that TMP-TiO\textsubscript{2} nanocomposites are highly efficient visible-light- driven photocatalysts for gas-phase benzene degradation.
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