Physiochemical properties of n-n heterostructured TiO\textsubscript{2}/Mo-TiO\textsubscript{2} composites and their photocatalytic degradation of gaseous toluene

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**ABSTRACT**

The composite TiO\textsubscript{2}/Mo-TiO\textsubscript{2} were prepared by a modified sol-gel method. The prepared catalysts were characterized by X-ray diffraction, BET analysis, SEM, X-ray photoelectron spectroscopy, and UV-vis diffused reflectance spectroscopy techniques. The structural characterization results demonstrated that Mo was successfully doped into the TiO\textsubscript{2} lattice and caused slight changes in the physiochemical properties. The UV-vis DRS showed a red shift of the adsorption edge to the visible region. The photocatalytic decomposition efficiencies of the catalysts were examined with toluene as a typical VOC in a continuous flow reactor. The photocatalytic activity of the n-n heterogeneous TiO\textsubscript{2}/Mo-TiO\textsubscript{2} was greater than that of pure TiO\textsubscript{2} and Mo-TiO\textsubscript{2}, and the catalyst containing a Mo/Ti mole ratio of 2.5% exhibited optimum photocatalytic properties. In general, a relative humidity of 35%, a higher oxygen content, a lower initial toluene concentration, and a higher UV intensity were beneficial for toluene decomposition.

**1. Introduction**

Over the past few decades, the environment has suffered devastating damages owing to the overuse of fossil fuels, pharmaceuticals, cosmetics, surfactants, interior fitments, and other industrial chemical products [1]. Many of these pollutants are easily disseminated as air-volatile organic compounds (VOCs), which are the main pollutants contributing to indoor and outdoor air pollution [2]. To date, many conventional methods, including adsorption, catalytic combustion, corona treatment, and biological membrane consumption, have been used in attempts to degrade these harmful organic compounds [3]. More recently, advanced oxidation processes (AOPs, e.g. UV/H\textsubscript{2}O\textsubscript{2}, UV/O\textsubscript{3}, and UV/TiO\textsubscript{2}) have been proposed as optional methods for degrading many VOCs [4]. The mechanisms of these AOPs involve a hydroxyl radical (•OH), which is a strong oxidizing agent that can oxidize many organic compounds that contain unsaturated bonds [5]. Photocatalytic decomposition with TiO\textsubscript{2} as the photocatalyst is a typical AOP [6]. Since Fujishima and Honda discovered in 1972 that TiO\textsubscript{2} was an excellent catalyst for splitting water [7], researchers have lent much focus toward improving the photocatalytic activity of this preeminent semiconductor [8]. However, during the photocatalytic process, the generated electrons and holes (e\textsuperscript{-} and h\textsuperscript{+}, respectively) formed in the TiO\textsubscript{2} surface easily recombine and cause photonic deactivation, which is the main defect associated with this photo-degradation process [9].

Significant efforts have been undertaken to enhance the activity of TiO\textsubscript{2} by improving its photo-electro-catalytic attributes with the addition of doping ions. To this end, considerable studies involving both cation- and anion-doped photo-generated carriers have been carried out for the purpose of enhancing the e\textsuperscript{-}/h\textsuperscript{+} separation efficiency [10]. Doping with different elements is effective at encouraging the separation of photo-induced carriers by introducing lattice electron traps. Both metal cations (Cu\textsuperscript{2+}, Fe\textsuperscript{3+}, Ag\textsuperscript{+}, Cr\textsuperscript{3+}, etc.) [11–14] and non-metal anions (C, N, F, S, B, etc.) [15–18] have been utilized as dopants with some success. Recently, heterostructures (e.g. TiO\textsubscript{2}/ZnO, TiO\textsubscript{2}/CdS, TiO\textsubscript{2}/BiO\textsubscript{3}, TiO\textsubscript{2}/CeO\textsubscript{2}, and TiO\textsubscript{2}/LaVO\textsubscript{4}) [19–23] have been investigated for the purpose of degrading aqueous waste dyes (e.g. rhodamine B, methylene blue, and bisphenol A), but few have been examined for the elimination of VOCs [24]. In one such instance, Mo-TiO\textsubscript{2} was hybridized with TiO\textsubscript{2} to form an n-n heterojunction structure, and the resulting catalyst was found to have a higher photocatalytic mineralization capacity than did pure TiO\textsubscript{2} and Mo-TiO\textsubscript{2}. Mo\textsuperscript{6+} was easily
doped into the TiO$_2$ lattice, effectively introducing extrinsic defects due to its unique configuration and similar ionic radius to Ti$^{4+}$ and enhancing the photocatalytic property of TiO$_2$ [25,26].

In this study, toluene was chosen as a typical VOC to quantitatively evaluate the photocatalytic degradation activity of TiO$_2$/Mo-TiO$_2$ under varying conditions. The results were compared with those of known methods for toluene decomposition, namely TiO$_2$/UV, Mo-TiO$_2$/UV, and TiO$_2$/Mo-TiO$_2$/UV. The effect of reaction conditions on photocatalytic potency was examined by varying the experimental parameters like catalyst identity, initial toluene concentration, relative humidity, and O$_2$ concentration.

2. Experimental

2.1. Photocatalyst preparation

2.1.1. Preparation of TiO$_2$ and Mo-TiO$_2$

TiO$_2$ was prepared by a traditional sol-gel method. In brief, 30 mL tetrahydrozol titanate (Ti(OBu)$_4$, CP), 2 mL acetyl acetone (ACAC, AR), and 5 mL PEG 200 (CP) were dissolved in 90 mL of ethanol (AR) and stirred for 30 min. This was marked as solution ‘A’. Solution ‘B’ was prepared by compounding 10 mL deionized water, 45 mL ethanol, and enough concentrated nitric acid (AR) to adjust the pH to 3–4. ACAC was chosen as the chelant to inhibit the hydrolysis of tetrabutyl titanate by generating a stable titanium complex in the sol. The PEG was introduced as a template to suppress particle agglomeration and to form a porous structure. Solution ‘B’ was added into ‘A’ dropwise with vigorous stirring, which continued for another hour after the addition had ended. After aging at ambient temperature for 1 day, a wet gel was formed. The gel was then dried at 80 °C for 12 h to obtain the xerogel, which was then ground into a powder. The powder was baked at 500 °C for 3 h in a muffle furnace to obtain the xerogel, which was then ground into a powder. The powder was then ultrasound-treated for 30 min to form a stable powder-decentralized mixture, and it was constantly stirred until the mixture formed a gel. All remaining steps were the same as those performed for pure TiO$_2$, and the doping amount of Mo was calculated by the molar ratio of Mo/Ti and was denoted as x% Mo-TiO$_2$.

2.1.2. Preparation of heterostructured TiO$_2$/Mo-TiO$_2$

Mo-TiO$_2$ powders derived from the routine sol-gel method above were added into the TiO$_2$ sol. The mixture was then ultrasound-treated for 30 min to form a stable powder-decentralized mixture, and it was constantly stirred until the mixture formed a gel. All remaining steps were the same as those performed for pure TiO$_2$ and Mo-TiO$_2$. The composite heterojunction of Mo-TiO$_2$ was denoted as TiO$_2$/x% Mo-TiO$_2$, in which the mass ratio of Mo-TiO$_2$ to TiO$_2$ was 1:10.

2.1.3. Preparation of photocatalyst films

The photocatalyst films were prepared by the dip-coating method. 3 g of the synthesized catalyst powders were dispersed into 100 mL of a 1% solution of carboxymethyl cellulose (CMC, CP) in water and ultrasound-treated for 1 h to generate a uniform mixture. Purified quartz beads (approximately 4–5 mm in diameter) were immersed into the mixture, removed, and dried for 30 min at 80 °C. This process was repeated 5–7 times before a thin film could be obtained, and the loading amount was calculated according to the increased weight of beads. The coated beads were then dried in a vacuum oven for 5 h at 80 °C to remove any residual moisture.

2.2. Characterization of catalysts

The chemical compositions of the synthesized samples were characterized by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Scientific) with Al K$_\alpha$ radiation (300 W). The crystal structures of the prepared samples were determined by powder X-ray diffraction (XRD) (DX-2700 diffractometer, China) with Cu K$_\alpha$ (λ = 0.15406 nm) radiation over the 2θ range of 5°–80° with a step size of 0.02° and a scan rate of 5° min$^{-1}$. Surface morphology images of the samples were obtained by SEM (S4800, HITACHI) at an accelerating voltage of 5 kV and 10 mA of power. The films were coated onto silicon wafers in order to generate better SEM observations. Prior to SEM analysis, the catalysts were pretreated with a sputter-coater, adding a thin layer of platinum to improve their conductivity. The specific surface area, pore volume, and average pore diameter for each sample were obtained by nitrogen adsorption and desorption isotherms using BET analysis (ASAP 2020M, Micromeritics) at 77 K. The optical characteristics of the samples were determined by UV–vis diffuse reflectance spectroscopy (UV–vis DRS) (UV-2600, SHIMADZU) over a range of 190–800 nm at ambient temperature using a tablet pressing method with BaSO$_4$ as a reflectance standard.

2.3. Experimental design

The experimental design of the photoreactor apparatus used to evaluate the catalysts’ capacity for toluene decomposition is shown in Figure 1. The testing platform consisted of a simulated toluene gas supply system, vapor humidification equipment, a fixed bed flow reactor system, and an online GC system. The toluene gas was generated from a compressed gas cylinder containing toluene vapor in N$_2$. The O$_2$ source was used to control the oxygen concentration in the total gas flow. The N$_2$ source was distributed into two branches: one branch was used to adjust the toluene concentration, and the other passed through the water tank to facilitate gas humidification. The concentration of toluene could...
therefore be adjusted easily by regulating it proportionately with the mass flow controller.

The schematic of the fixed bed photoreactor is presented in Figure 2. The fixed bed photoreactor was custom-made as a cylindrical annular tube with openings to allow for filling with quartz beads and illuminating with an internal light source. It was equipped with a recirculator to keep the light source cool and the gas reaction temperature constant (30 ± 5 °C). The catalyst-coated quartz beads were fed into the photoreactor; the filling volume was 120 mL. The UV lamp with dominant intensities at 254 and 365 nm was installed in the tube center.

In these experiments, a GC (6890N, Agilent) equipped with an FID detector was used to measure the toluene concentration using high-purity N₂ as the carrier, H₂ as the burning gas, and an HP-5 (30 m × 0.32 mm × 0.50 μm) column (Agilent) for separation.

The decomposition efficiency of toluene is calculated according to Equation (1):

$$\eta(\%) = \frac{C_i - C_o}{C_i} \times 100$$

where $C_i$ and $C_o$ represent the concentration of toluene at the inlet and outlet of the fixed bed photoreactor, respectively.

3. Results and discussion
3.1. Catalyst characteristics
3.1.1. XRD and BET analysis

In order to determine the crystal phases and structures of the TiO₂, Mo-TiO₂, and TiO₂/Mo-TiO₂ powders, XRD examinations were conducted. The XRD patterns of the partial samples are illustrated in Figure 3, and those of the Mo-TiO₂ and TiO₂/Mo-TiO₂ samples were similar to that of pure TiO₂. The main diffraction peaks at 2θ = 25.4°, 37.0°, 37.9°, 38.7°, 48.1°, 54.1°, 55.0°, 62.7°, 68.8°, 70.4°, and 75.1° are assigned to diffractions from the (1 0 1), (1 0 3), (0 0 4), (1 1 2), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), (2 2 0), and (2 1 5) crystal planes, respectively, for anatase (JCPDS card No. 21-1272) [27]. There are no obvious diffraction peaks of the Mo species, which may be due to the low doping amount. Metallic molybdenum oxide (MoO₃) could have a great dispersion effect on TiO₂ with no formation of a crystal phase if the dosage of Mo remained below the critical value. In addition, the Mo and Ti ions exist in the form of Mo⁶⁺, Mo⁵⁺, and Ti⁴⁺, and their ionic radii are 62, 68, and 68 pm respectively [28]. Therefore, the Mo⁶⁺ and Mo⁵⁺ ions could embed into the TiO₂ crystal lattice by isomorphous substitution due to the similarity of their ionic radii. The characteristic peaks of the doped TiO₂ sample appear wider and weaker than those of pure
The density of the anatase was calculated according to Equation (5) [31].

\[
\text{Density} = \frac{n \times M}{(abc)N_a}
\]  

where \(n\) is the number of atoms per unit cell; \(M\) is the relative molecular mass; and \(N_a\) is Avogadro’s number.

The average crystallite size, crystal lattice parameters, and density of each synthesized catalyst are presented in Table 1. The Mo-TiO\(_2\) and TiO\(_2\)/Mo-TiO\(_2\) samples had structural parameters similar to pure TiO\(_2\), including smaller average crystallite size, smaller unit cell volume, and higher density. Moreover, the Mo-TiO\(_2\) samples, on average, displayed smaller average crystallite size, smaller unit cell volume, and higher density than did the TiO\(_2\)/Mo-TiO\(_2\) samples. These changes in the lattice parameters are likely related to the lattice defects that are generated as a result of the doping of Mo, again indicating that the Mo ions inserted into the lattice gap or substituted for Ti as impurities, thereby inhibiting the growth of the anatase crystalline domains.

The pore properties (specific surface area, total pore volume, and average diameter) obtained from the BET analysis are listed in Table 1. The specific surface areas and average pore diameters increased upon incorporation of Mo. However, the total pore volumes of the Mo-TiO\(_2\) and TiO\(_2\)/Mo-TiO\(_2\) powders were smaller than those of pure TiO\(_2\), which indicates that the micropores in TiO\(_2\) became oblate with the doping of Mo. In addition, the total pore volumes and average pore diameters remained practically unchanged among the Mo-TiO\(_2\) and TiO\(_2\)/Mo-TiO\(_2\) samples, confirming further that the Mo was homogeneously dispersed throughout the TiO\(_2\) system.

### Table 1. Physiochemical properties of the synthesized TiO\(_2\), Mo-TiO\(_2\), and TiO\(_2\)/Mo-TiO\(_2\) photocatalysts.

| Sample       | Average crystallite size (nm) | Unit cell parameters (Å) | Unit cell volume (Å\(^3\)) | Density (g/cm\(^3\)) | Specific surface area (m\(^2\)/g) | Total pore volume (cm\(^3\)/g) | Average pore diameter (Å) |
|--------------|------------------------------|--------------------------|-----------------------------|----------------------|-----------------------------------|---------------------------------|---------------------------|
| Pure         | 23.0                         | 3.780 9.512              | 136.21                      | 3.894                | 20.1                              | 0.21                            | 106.1                     |
| 0.5% Mo-TiO\(_2\) | 17.9                         | 3.782 9.513              | 136.06                      | 3.899                | 26.5                              | 0.17                            | 213.2                     |
| 1.0% Mo-TiO\(_2\) | 17.2                         | 3.782 9.503              | 135.93                      | 3.902                | 28.3                              | 0.15                            | 220.3                     |
| 2.5% Mo-TiO\(_2\) | 16.8                         | 3.780 9.491              | 135.62                      | 3.911                | 30.9                              | 0.16                            | 218.6                     |
| 4.0% Mo-TiO\(_2\) | 17.7                         | 3.779 9.498              | 135.62                      | 3.913                | 34.2                              | 0.18                            | 223.7                     |
| 5.0% Mo-TiO\(_2\) | 17.9                         | 3.781 9.515              | 136.03                      | 3.899                | 44.2                              | 0.18                            | 208.3                     |
| TiO\(_2\)/0.5% Mo-TiO\(_2\) | 18.2                         | 3.780 9.499              | 135.73                      | 3.908                | 32.3                              | 0.18                            | 209.4                     |
| TiO\(_2\)/1.0% Mo-TiO\(_2\) | 18.0                         | 3.779 9.502              | 135.61                      | 3.911                | 26.6                              | 0.19                            | 209.4                     |
| TiO\(_2\)/2.5% Mo-TiO\(_2\) | 17.8                         | 3.778 9.499              | 135.56                      | 3.913                | 27.8                              | 0.16                            | 212.5                     |
| TiO\(_2\)/4.0% Mo-TiO\(_2\) | 18.2                         | 3.782 9.515              | 136.10                      | 3.897                | 28.9                              | 0.16                            | 213.9                     |
| TiO\(_2\)/5.0% Mo-TiO\(_2\) | 18.3                         | 3.781 9.512              | 136.01                      | 3.900                | 28.4                              | 0.17                            | 209.8                     |

The micro-morphologies and structures of the TiO\(_2\), Mo-TiO\(_2\), and TiO\(_2\)/Mo-TiO\(_2\) powders were examined by FESEM, and the images are shown in Figure 4. Pure TiO\(_2\) (a) presented as a massive, layered structure with
which may be an indication that the amount present was lower than the critical detection limit for XPS.

### 3.1.4. Optical absorption properties

UV–vis DRS was conducted in order to investigate the optical absorption of the TiO$_2$, Mo-TiO$_2$, and TiO$_2$/Mo-TiO$_2$ powders. The UV–vis DRS curves (a) and Tauc plots (b) are shown in Figure 6. The Tauc plot in Figure 6(b) is a diagram of $(\alpha h \nu)^{1/2} - h \nu$ obtained by calculating the band gap using the Kubelka–Munk equation as defined below in Equations (6)–(9) [37].

$$A = -\lg(R)$$  

$$F(R) = \frac{\alpha}{s} = \frac{(1 - R)^2}{2R}$$  

$$h \nu = \frac{1240}{\lambda}$$  

$$((ah\nu)^{1/2} = (F(R) \ast h\nu)^{1/2}$$

$A$ is the absorbance; $R$ is the reflectance; $\alpha$ is the absorption coefficient; $s$ is the reflection coefficient; $\lambda$ is the wavelength of UV–vis spectra; and $h\nu$ represents the photon energy of the band gap.

The absorption edge and band gap values obtained from Figure 6 are shown in Table 2. The absorption edge of pure TiO$_2$ appears at its natural position (401.3 nm), which corresponds to a band gap of 3.09 eV. The UV–vis spectra (a) and Tauc plots (b) for the Mo-TiO$_2$ and TiO$_2$/Mo-TiO$_2$ samples are similar to those of pure TiO$_2$.

As shown in Figure 6, there is an inverse association between the band gap and the absorption edge, and

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**Figure 4.** SEM images of synthesized (a) TiO$_2$, (b) 0.5% Mo-TiO$_2$, (c) 2.5% Mo-TiO$_2$, (d) 5% Mo-TiO$_2$, (e) TiO$_2$/2.5% Mo-TiO$_2$, and (f) TiO$_2$/5% Mo-TiO$_2$. 

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large spaces between the gaps and layers. After incorporation of Mo, the Mo-TiO$_2$ (b–d) and TiO$_2$/Mo-TiO$_2$ (e and f) samples presented porous, reticular structures with rough and complicated surfaces, resulting in greater specific surface areas. The decreased particle size upon doping with Mo that was apparent in the XRD was also evident in the FESEM images, again suggesting that the molybdenum was distributed into the TiO$_2$ lattices both interstitially and substitutionally.

### 3.1.3. XPS analysis

Figure 5 shows the survey spectrum and the Ti 2p, O 1s, and Mo 3d XPS spectra of the synthesized 2.5% Mo-TiO$_2$ powders. The electron binding energies of all of the elements were calibrated against the contaminated carbon C 1s level (284.6 eV). The main peaks appearing at 458.9 and 464.7 eV are attributed to the Ti 2P$_{3/2}$ and Ti 2P$_{1/2}$ (c) of Ti$^{4+}$ in the TiO$_2$ lattice. The binding energies of 530.1 and 531.0 eV can be assigned to the O1s (d) of O$^{2-}$ from the lattice oxygen and to the O-Ti binding electrons in the sample, respectively [32]. As shown in the Mo 3d XPS spectrum (e), the peaks observed at 232.7 and 235.8 eV are typical of Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ for Mo$^{6+}$, and the peaks at 231.9 and 235.0 eV are characteristic of Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ for Mo$^{5+}$ [33,34]. These peaks can be assigned to the Mo-O bond, which indicates that Mo has taken the place of Ti in the TiO$_2$ lattice [35]. Moreover, the content of each valence state was calculated by fitting the peak areas of Mo$^{6+}$ and Mo$^{5+}$ and was found to be 65.6% and 34.4%, respectively. This indicates that Mo$^{6+}$ was the dominant doping species present in the TiO$_2$ lattice, and the presence of Mo$^{5+}$ may be attributed to the reduction of Mo$^{6+}$ by residual organics present in the raw materials or by Ti$^{3+}$ [36]. In addition, there were no significant peaks characteristic of Mo in TiO$_2$/Mo-TiO$_2$, which may be an indication that the amount present was lower than the critical detection limit for XPS.
possess poor photocatalytic activity due to fast recombination of the photo-generated electron/hole (e\(^{-}\)/h\(^{+}\)). The spectra of Mo-TiO\(_2\) and TiO\(_2\)/Mo-TiO\(_2\) exhibit a slight red shift after the incorporation of Mo, and the shift becomes larger as the doping concentration increases. This may be due to the disturbance of the electronic structure that is caused by Mo doping [38]. The lower band gap of Mo-doped TiO\(_2\) catalysts is a consequence of the energy level of the impurity conduction band of the Mo atom. Therefore, the photon energy required for stimulating an electron from the valence band to the fundamental absorption edge wavelength. However, materials with a narrow band gap (<3.0 eV) generally

| Sample            | Absorption edge | Band gap |
|-------------------|----------------|----------|
| Pure TiO\(_2\)    | 401.3          | 3.09     |
| TiO\(_2\)/2.5% Mo-TiO\(_2\) | 413.0          | 3.00     |
| 0.5% Mo-TiO\(_2\) | 416.7          | 2.98     |
| TiO\(_2\)/5.0% Mo-TiO\(_2\) | 427.0          | 2.90     |
| 2.5% Mo-TiO\(_2\) | 433.5          | 2.86     |
| 5.0% Mo-TiO\(_2\) | 443.6          | 2.80     |

Figure 5. XPS spectra of (a) survey, (b) Ti 2p, (c) O 1s, and (d) Mo 3d of synthesized 2.5% Mo-TiO\(_2\).

Figure 6. (a) UV–vis DRS spectra and (b) Tauc plot of the synthesized TiO\(_2\), Mo-TiO\(_2\), and TiO\(_2\)/Mo-TiO\(_2\) catalysts.
impurity band is smaller than to the conduction band, which results in a shift of the absorption toward the visible light region.

### 3.2. Photocatalytic activities

#### 3.2.1. Effect of Mo-TiO₂ and TiO₂/Mo-TiO₂ on the catalytic decomposition of toluene

Catalyst efficiency is one of the most significant factors affecting photocatalytic processes. Therefore, in this work, the catalytic properties of the prepared pure TiO₂, Mo-TiO₂, and TiO₂/Mo-TiO₂ photocatalysts were compared in a toluene degradation process. The flow-rate was 100 mL/min, the relative humidity was 35%, and the initial toluene concentration was 100 ppm. The efficiencies of these catalysts for the decomposition of toluene are illustrated in Figure 7. The decomposition of toluene for all of the samples increased with increasing irradiation time and plateaued after 80–100 min. For many of the catalysts, a brief plateau was observed around the 20–30 min time point, which was possibly due to high conversion caused by gas desorption and the increase in temperature.

The first obvious observation is that the photocatalytic efficiency of Mo-TiO₂ is poorer than that of pure TiO₂. In general, an increase in specific surface area is typically beneficial for improving photocatalytic activity, but this is not always the case [39]. In addition, the UV–vis DRS spectra indicated that the addition of Mo caused a red-shift in the optical absorption band of TiO₂, which could have been an indication of an increase in photocatalytic activity as well. Nevertheless, there is no direct correlation between photocatalytic activity and light absorption capability. Doping with Mo could influence charge separation, photo-induced electron-hole recombination, and interfacial charge transfer of the TiO₂, thereby affecting the photocatalytic efficiency. On the one hand, the Mo⁶⁺ impurity could act as a trap to capture the photon-induced carriers, inhibit the recombination of the photo-generated electrons and holes, and thereby enhance the photocatalytic activity. On the other hand, the Mo substitution in TiO₂ could act as a recombination center for the photo-generated carriers, which would decrease the photocatalytic activity of Mo-TiO₂. In the case of Mo-doped TiO₂, the substitutional Mo is more likely to be a recombination center. Therefore, increasing the doping concentration also increases the number of recombination centers that are present, which lowers the photocatalytic activity [33,40].

The photocatalytic experimental results indicated that most of the TiO₂/Mo-TiO₂ heterostructures exhibited improved photocatalytic activity over pure TiO₂ and Mo-TiO₂. As an n-type semiconductor, TiO₂ dominates the electronic conduction due to its oxygen vacancies, which is also true for Mo-TiO₂ [23,33]. During the preparation of composite TiO₂/Mo-TiO₂ semiconductors, the prepared Mo-TiO₂ powders were fully dispersed into the pure TiO₂ sol, and the two were thoroughly combined through the drying and calcinating processes. Consequently, the n-n heterojunction was formed at the interface between TiO₂ and Mo-TiO₂. Since the Fermi level of TiO₂ is higher than that of Mo-TiO₂, the internal electron moves from TiO₂ to Mo-TiO₂ creating a built-in electric field inside the TiO₂/Mo-TiO₂ catalyst. When the semiconductor is under irradiation, the photo-generated electron transfers to the higher potential (TiO₂), and the photo-generated holes transfer to the lower potential (Mo-TiO₂). Since the recombination of the photo-generated electrons and holes was inhibited, the photocatalytic activity was improved.

The TiO₂/2.5% Mo-TiO₂ sample performed the best of all of the catalysts tested. With the n-n heterojunction structure, the intensity of the built-in electric field increased with increased doping concentration. In general, a higher doping concentration of Mo led to a more intense electric field that facilitated the separation of photo-generated electrons and holes more quickly, which improved the photocatalytic activity. On the other hand, the Mo⁶⁺ present in the Mo-TiO₂ matrix diffuses interstitially or substitutionally into the lattice of pure TiO₂ during the preparation process. Since the extent of this diffusion is positively correlated with the Mo doping concentration, an optimum doping level exists and, in this study, was found to be a 2.5% mole ratio of Mo to Ti.

#### 3.2.2. Effect of the relative humidity

The effect of the relative humidity on toluene decomposition was investigated by mixing a humidified air stream, regulated from 10 to 60%, with the toluene flow. Figure 8(a) shows the photocatalytic efficiency of our most potent catalyst under various relative humidity conditions. It was found that the degradation efficiency increased greatly with the increase in the relative humidity up to 35% and then decreased steadily under more humid conditions. This data indicated that the photocatalytic activity can be enhanced by choosing suitable humidity conditions. In this study, when the relative humidity was 35%, the toluene conversion caused by gas desorption and the increase in temperature.

![Figure 7. Toluene decomposition efficiency as a function of irradiation time for synthesized TiO₂, Mo-TiO₂, and TiO₂/Mo-TiO₂.](image)
concentrations higher than that, no more \( \text{O}_2^- \) can be generated, resulting in an invariant oxidation efficiency.

### 3.2.4. Effect of initial toluene concentration

The initial toluene concentration was regulated in the range of 100–250 ppm, and decomposition efficiency was investigated as a function of initial concentration. As shown in Figure 8(c), toluene degradation is inversely proportional to its initial concentration. For this gas–solid photocatalytic process, molecular collision frequency between radicals and toluene is the major influence on the decomposition efficiency. Under light irradiation, when toluene molecules come in contact with the catalysts, \( \cdot \text{OH} \) and \( \text{O}_2^- \) radicals are generated and the photocatalytic oxidation process begins. Since the process conditions are constant, the numbers of radicals (\( \cdot \text{OH} \) and \( \text{O}_2^- \)) cannot be changed and are maintained at stable quantities. Therefore, at higher initial concentrations, less photo-electric energy is available to the toluene, and a lower decomposition efficiency is observed.

### 3.2.5. Effect of UV light wavelength

To investigate the effect of UV intensity on toluene decomposition, the experiments were conducted with two lamps of different wavelength (254 and 365 nm). Figure 8(d) shows the removal efficiency versus irradiation time for toluene decomposition. As seen from the curve, the toluene decomposition efficiency under...
254 nm UV light is higher than that of 365 nm. As is well known, there is a negative correlation between the wavelength and photonic energy of light. The UV irradiation from the 254 nm is stronger than that from 365 nm, which contributed to the differences in toluene decomposition efficiency.

4. Conclusions
Nanostructured TiO$_2$, Mo-TiO$_2$, and TiO$_2$/Mo-TiO$_2$ thin films were synthesized by a modified sol-gel method and dip-coating process. The photocatalysts were characterized by various analytical techniques, and the results showed that the molecular structure, physiochemical properties (e.g. crystallite size, lattice parameters and specific surface area), optical absorption properties, and photocatalytic activities were not significantly different. The toluene removal efficiencies of most of the TiO$_2$/Mo-TiO$_2$ heterocatalysts were higher than those for pure TiO$_2$ and Mo-TiO$_2$, primarily due to the n-n heterostructure present in TiO$_2$/Mo-TiO$_2$. This heterojunction provides a built-in electric field near the n-n heterostructure present in TiO$_2$/Mo-TiO$_2$. This heterojunction is important for understanding the properties of photocatalytic materials, and further research on this subject should be carried out.

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