

Synthesis of cobalt doping titanium dioxide fiber supported by reduced graphene oxide for photocatalytic degradation of toluene in air

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Abstract

Titanium dioxide has been widely used for photocatalytic degradation of organic pollutants in air, while problems like low utilization rate of sunlight and easy recombination of photogenerated electrons and holes are the main drawbacks for its application. In this study, a combination of Co doping and graphene supporting was used to synthesize cobalt doping titanium dioxide fiber supported by reduced graphene oxide (Co-TiO₂/RGO) using processes including electrospinning, heating and freeze-drying. The structural and textural features of Co-TiO₂/RGO were characterized by different techniques, and toluene was used as a model pollutant to test its photocatalytic performance. Results show that Co-TiO₂ is uniformly dispersed in reduced graphene oxide and the specific surface area of Co-TiO₂/RGO is higher than that of TiO₂ and Co-TiO₂. Further, under the conditions of Co doping amount of 1%, calcination of 600°C for 4 h, gas residence time of 100 min, relative humidity of 100%, and the Co-TiO₂ loading amount of 1 g, the degradation percentage of toluene by Co-TiO₂/RGO was the highest, up to 99.1%. This study confirms the possibility of synthesizing Co-TiO₂/RGO for the degradation of organic pollutants in air.

1. Introduction

Volatile organic compounds (VOCs) in air have aroused widely concern because of their great variety and harm (McDonald et al., 2018). Among these, toluene is one of the most representative substances, which is toxic and carcinogenic, may cause serious damage to the nervous system and internal organs (Feng et al., 2021). Photocatalytic oxidation, with the advantages of thorough reaction, few by-products, low cost and easy to operate, is currently one of the widely used methods to treat VOCs in air. The commonly used photocatalysts mainly include TiO₂, ZnO, Fe₂O₃, etc., among which TiO₂ is the promising photocatalyst due to its strong photocatalytic ability, cost-effectiveness, physical and chemical stability (Li and Li, 2020). However, problems such as large forbidden band width, limited ultraviolet light, and low specific surface area hinder its application (Low et al., 2018).

Various strategies have been employed to solve these problems of TiO₂, such as doping metal or nonmetal elements (Shayegan et al., 2020, 2021), coupling with semiconductors (Low et al., 2019), and recombination with carbon-based materials like carbon nanotubes (Li et al., 2018), graphite oxide (Kusiak-Nejman et al., 2020), and graphene (Padmanabhan et al., 2021). Karafas et al. (2019) prepared cobalt-doped TiO₂ array film, and found that the incorporation of Co improved the absorption of visible light and promoted the separation of photo-generated electro-hole pairs, leading to the better photocatalytic reduction performance compared with the film of TiO₂. Because of the good conductivity due to the unique structure of graphene, it is of great interest to synthesize semiconductor-graphene (Padmanabhan et al., 2020). Song et al. (2019) used poly(3-hexylthiophene) (P3HT) to modify graphene, and added TiO₂ powder to the P3HT/graphene solution to form a P3HT/TiO₂/graphene composite. The presence of graphene improves the charge transport capacity, reduces the e⁻-h⁺ recombination rate and further enhances its light catalytic activity of TiO₂. In addition, graphene combined with metal-modified

TiO₂ has shown the stable and efficient photocatalytic degradation property. Xie et al. (2021) prepared graphene oxide/TiO₂-Bi₂WO₆ to degrade ethylene, and found that the catalytic property of TiO₂-Bi₂WO₆ was significantly improved. However, the aggregation of TiO₂ or metal doped TiO₂ particles will lead to a decrease of the reactivity. In this study, Co-TiO₂ fibers were synthesized by electrospinning and heating, and loaded on graphene to enhance the dispersion of Co-TiO₂ particles, various technics are used to determine the structure and properties of the synthesized catalyst. Toluene was chosen as a typical pollutant to test the catalytic activity of the catalyst. To the best of our knowledge, it is the first time preparing Co-TiO₂ fibers loaded on graphene (Co-TiO₂/RGO), thereby obtaining a new type of photocatalyst.

2. Experimental

2.1. Chemicals

Analytical grade reagents including HNO₃, tetra-n-butyl titanate, absolute ethanol, ethylenediamine, cobalt nitrate hexahydrate and sodium tetraborate decahydrate were obtained from Sinopharm Chemical Reagent Co., Ltd. Reduced graphene oxide was obtained from Jiangsu Yueda Group Co., Ltd. Polyvinylpyrrolidone of analytical grade was obtained from Aladdin Biochemical Technology Co., Ltd. All these chemicals were without further purification, and experimental solutions were prepared with deionized water.

2.2. Synthesis of Co-TiO₂ fiber using electrospinning

Firstly, 5 g of polyvinyl pyrrolidone was added to 20 g of absolute ethanol to obtain precursor A. Secondly, 15 mL of glacial acetic acid and 15 mL of tetrabutyl titanate were added to 15 mL of ethanol to obtain precursor B. Then, PVP/Co-TiO₂ fiber was obtained by electrospinning the mixture of A and B on the negative iron plate. After that, the PVP/Co-TiO₂ fiber was calcined in a muffle furnace for 4 hours, and the temperature was set at 500°C, 600°C, 700°C, and 800°C, respectively. After the calcination, it was cooled to room temperature, and Co-TiO₂ fiber was obtained after grinding.

2.3. Synthesis of Co-TiO₂/RGO

60 mL of graphene oxide dispersion was mixed with 0.36 mL of ethylenediamine and 0.003 g of sodium borate. The mixture was sonicated for 10 minutes and then reacted in a vacuum oven. After that, the mixture was soaked in an ethanol aqueous solution for 3 hours to obtain a clean graphene hydrogel. According to a mass ratio of Co-TiO₂ fiber and graphene of 5:100, the Co-TiO₂ fiber and graphene gel were mixed uniformly, and then placed in a vacuum freeze dryer for 35 h to obtain Co-TiO₂/RGO.

2.4. Material characterization

Morphology of the samples was characterized by a Hitachi S-4800 scanning electron microscope (SEM). Elemental composition of materials was analyzed using an EDAX TEAM Apollo Energy Dispersive

Spectroscopy (EDS). Crystal structure of the samples was determined by a Bruker D8 Advanced X-ray diffractometer (XRD). Ultraviolet-visible (UV-vis) absorption spectra of the samples were obtained from a Shimadzu UV-2550 spectrophotometer. The Brunauer-Emmett-Teller (BET) surface area of samples were measured by a TriStar II analyzer. The photoluminescence (PL) spectrums of materials were tested with a Hitachi F7000 Fluorescence Spectrophotometer.

2.5. Photocatalytic degradation experiments

The processes and devices for photocatalytic degradation of toluene is shown in Fig. 1, which mainly includes the gas distribution part, gas flow control part, photocatalytic degradation part, gas sampling and detection part, and an exhaust gas treatment part.

Toluene standard gas (300 ppm) was used as the model pollution gas. The simulated exhaust gas distribution is divided into 2 routes, which are controlled by the flow controllers in the gas-phase photocatalytic system. Samples were taken from the inlet and outlet and the gas samples were detected by a Shimadzu GC9800 gas chromatograph (GC). The calculation formula for the removal percentage of toluene is as follows:

$$\eta(\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (1)$$

in which C_{in} and C_{out} are the concentrations of toluene at the gas inlet and the outlet, η is the removal percentage. All the experiments are conducted for 3 times, and the mean value is used for further analysis.

3. Results And Discussion

3.1. Morphology and phase characterization

The SEM-EDS results of Co-TiO₂ and Co-TiO₂/RGO are showed in Fig. 2. The morphology of Co-TiO₂ fiber is rod-like structure, with regular shapes and uniform protrusions on the surface (Fig. 2a, b). Further, Co disperses uniformly in the TiO₂ fibers (Fig. 2e-h). The RGO sheet is almost covered by the Co-TiO₂ rod-shaped particles (Fig. 2c, d, i-l), due to the reaction between the large number of oxygen-containing functional groups distributed in the middle and edge of the RGO sheet and the hydrolyzed butyl titanate through hydrogen bonding and electrostatic adsorption. Using these oxygen-containing functional groups as sites, Co-TiO₂ fibers generated after hydrolysis will be uniformly covered on the GO sheet (Zhou et al., 2011). Further, after low-temperature reduction, the unoccupied oxygen-containing functional groups of GO could be reduced and form RGO, which is a very stable composite that could be formed between Co-TiO₂ and RGO.

Figure 3a shows the XRD pattern of Co-TiO₂ fiber calcined at 600°C for 4 h. The diffraction peaks at $2\theta = 25.4^\circ$ (101) and $2\theta = 48.2^\circ$ (200) are typical characteristic peaks of anatase, and the diffraction peaks at

$2\theta = 27.6^\circ$ (110) and $2\theta = 54.3^\circ$ (220) are typical characteristic peak of rutile, showing both samples calcined at 600°C for 4 h could form two crystal forms of anatase and rutile. Compared with the XRD curve of TiO_2 , the diffraction peaks of Co/TiO_2 fibers have the same angle, which indicates that Co doping does not affect the crystal form of TiO_2 . The diffraction peaks of Co-TiO_2 , at $2\theta = 42.4^\circ$, correspond to the crystal plane diffraction peaks of CoO standard card (PDF#75-0393). The Co element may be introduced into the TiO_2 lattice, and CoO may be incorporated. Compared with TiO_2 , the peak intensity of Co-TiO_2 fibers increases at $2\theta = 25.4^\circ$, and decreases at $2\theta = 27.6^\circ$, indicating that Co changes the internal structure of TiO_2 and doping has a stabilizing effect on anatase TiO_2 (Wang et al., 2012).

Figure 3b is the UV-vis absorption spectra of Co-TiO_2 fibers at different calcination temperatures. It can be seen that the absorption edge of all samples has a significant redshift compared with TiO_2 , showing that the addition of Co can effectively extend the light absorption to the visible light range. Specifically, due to the influence of the wide band gap, TiO_2 can only absorb ultraviolet light less than 387 nm, which makes its light applicability very low. However, in the case of Co-TiO_2 fibers, the visible light absorption ranges from 400 to 700 nm have been significantly improved, due to the surface plasmon resonance (SPR) effect of the space-limited electrons of Co, and this redshift is related to the interaction between Co and TiO_2 . This is mainly caused by the hybridization of the d orbital of the doped metal with the 3d orbital of Ti and the 2p orbital of O, which causes the conduction band and valence band to move to the low energy region. In summary, Co moves the absorption range of the photocatalyst to the visible light direction, which effectively enhances light absorption and improves the separation efficiency of electrons and holes.

Figure 3c shows the PL spectrum of Co-TiO_2 fibers at 350 nm. It can be seen that the PL spectrum of the prepared samples all contain two characteristic peaks, and the characteristic peaks produced by different samples are basically in the same wavelength range. The luminescence peak of TiO_2 is the strongest at 474nm, indicating that the recombination probability of photogenerated electrons and holes generated by the distribution of TiO_2 is the highest. The intrinsic luminescence intensity of Co-TiO_2 fibers is the weakest, that is, the lifetime of its carriers is the longest. The possible reason is that the capture of photo-generated carriers by cobalt can inhibit the recombination of photo-generated carriers, resulting in a decrease in the intensity of the PL spectrum. However, when the Co doping amount is excessive, the more luminescent centers (such as oxygen vacancies, etc.) will promote the recombination of photogenerated carriers, emit fluorescence, and enhance the intensity of the PL spectrum (Chanda et al., 2018).

Table 1

Table 1
Specific surface area, pore size and pore volume of three photocatalysts.

Photocatalysts	Specific surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
TiO ₂	142.37	33.10	0.311
Co-TiO ₂	131.56	37.91	0.387
Co-TiO ₂ /RGO	168.86	21.66	0.401

Table 1 shows the N₂ adsorption/desorption results of TiO₂, Co-TiO₂ fibers and Co-TiO₂/RGO. The specific surface area of Co-TiO₂/RGO is the largest, reaching 168.86 m²/g. The loading of graphene increases the specific surface area of the catalyst, accelerates the enrichment of target pollutants on the surface during the photocatalysis process, and accelerates the degradation rate. For Co-TiO₂ fibers, the BET surface area, being 131.56 m²/g, is smaller than 142.37 m²/g of TiO₂. However, the pore volume of Co-TiO₂ is larger than that of TiO₂, being 0.401 m³/g. This indicates that the Co framework increases the pore volume inside the catalyst.

3.2. Photocatalytic degradation of toluene

Figure 4a shows the effects of Co-TiO₂/RGO photocatalysts with Co/TiO₂ molar ratios of 0, 0.005, 0.010, 0.015, and 0.020 on the degradation of toluene under the conditions of calcination at 500°C and degradation for 40 minutes. As the Co doping ratio increases, the photocatalytic performance of Co-TiO₂/RGO first increases and then decreases. When the molar ratio of Co: TiO₂ = 1: 100, the degradation performance of toluene was the best, reaching 82.6%. With a further increase of the Co doping ratio, the degradation efficiency does not increase but decrease. The photocatalytic activities of Co-TiO₂ in low concentration were higher than the undoped TiO₂ samples. When the concentration of Co exceeds 2.5%, the photocatalytic rate was lower than undoped TiO₂. This is because the excess dopants would lead to photon scattering (Qi et al., 2016).

Figure 4b shows the degradation performances of toluene, in 60 min, by catalysts synthesized with different Co/TiO₂ molar ratios at different calcination temperatures. With the increase of calcination temperature, the photocatalytic performance of Co-TiO₂/RGO first increases and then decreases. The best degradation performance was reached when the calcination temperature is 600°C, and 1% Co-TiO₂/RGO, being 93.4%. When the calcination temperature is lower than 600°C, the PVP fiber is not completely carbonized, and the organic components attach to the Co-TiO₂ fiber, hindering the contact between the catalyst and light, thereby reducing the performance of photocatalytic degradation of toluene. When the calcination temperature is higher than 600°C, catalyst agglomeration and compaction may occur, which reduces the specific surface area of the catalyst and decreases the active center, thereby making the activity of the catalyst decline.

Figure 4c shows the degradation of toluene by photocatalysts synthesized with different Co/TiO₂ molar ratios at a calcination temperature of 600°C under different gas residence times. The photocatalytic performance of Co-TiO₂/RGO gradually increases with the increase of gas residence time. After 80 min, the degradation percentage of toluene infinitely approaches 100%, showing that with the increase of gas residence time, the photocatalytic reaction of Co-TiO₂/RGO with toluene will be completed. However, considering the cost, practicality and other factors, 100 minutes of degradation should be enough.

Figure 4d shows the effect of relative humidity on the degradation of toluene in 60 min, by Co-TiO₂/RGO synthesized under the conditions of calcination at 600°C. As the relative humidity increases, the catalytic activity of Co-TiO₂/RGO increases gradually, showing that the increasing of relative humidity is positively correlated with the degradation rate of toluene. The increase can enhance the activity of the catalyst hydroxyl radicals, thereby improving the photocatalytic activity of the catalysts (Shayegan et al., 2018). The degradation percentage of 1% Co-TiO₂/RGO for toluene increased from 86.5–99.1%.

Figure 4e shows the effect of TiO₂/RGO, 1% Co-TiO₂/RGO, and TiO₂ on the degradation of toluene under conditions of calcination at 600°C and degradation for 40 min. The 1% Co-TiO₂/RGO has the highest degradation percentage, reaching 95.6%, showing the loading improves the photocatalytic reaction of toluene. Nevertheless, considering the cost and practicability, the loading of the Co-TiO₂ should be selected at about 1 g.

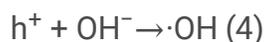
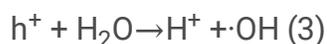
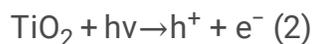
Table 2 lists the removal values of toluene reported in literature using different materials. The data indicates that the Co-TiO₂/RGO system shows competitive removal performance of toluene in shorter reaction time.

Table 2
Toluene removal by different catalyst.

Catalyst	Degradation percentage (%)	Condition	Reference
TiO ₂ -Cu ₂ O	78.3%	171.6 mg/m ³ , 30 mg catalyst, xenon lamp of 180 W, 3h	(Cheng et al., 2018)
TiO ₂ (Evonik P25, Cristal PC105, Kronos 1077, and Cristal AT-1); Support: flat glass disk	52% for P25; 50% for PC105; 46% for Kronos1077; and 46% for Cristal AT-1	400 ppm, 50 mg catalyst, 40% relative humidity, iron halogenide lamp of 500 W, 6 h	(Bianchi et al., 2014)
TiO ₂ /SiO ₂	65%	700 ppm, 0.68 g catalyst, 50% relative humidity, UV Lamp of 3 W, 3 h	(Paušová et al., 2020)
Activated carbon fiber coated TiO ₂	86%	500 ppb, 40% relative humidity, mercury lamp of 15 W, 3 h	(Guo et al., 2008)
Co-TiO ₂ /RGO	99.1%	1% Co, 1g catalyst, 100% relative humidity, 100min	This study

3.3. The photocatalytic mechanism of toluene

The doping of Co introduces a new energy level, generates more electron capture centers, and separates more electron-hole pairs. Figure 5 shows the photocatalytic degradation mechanism of toluene using Co-TiO₂/RGO. After being supported on graphene, the larger specific surface area further improves the photocatalytic activity of the catalyst. Toluene, used as the model pollutant, is firstly absorbed on the surface of Co-TiO₂/RGO. After that, Co-TiO₂/RGO is activated by light and the photogenerated electron-hole pairs are separated, and the photogenerated electrons are quickly transferred to the graphene surface. Then a series of reactions occur with oxygen molecules and water molecules (Eq. 2–4). After that, the active ·OH and ·O₂⁻ react with the toluene adsorbed on the graphene aerogel to undergo a photocatalytic oxidation reaction, and finally achieve the effect of degrading pollutants.



4. Conclusions

The Co-TiO₂/RGO was prepared by electrospinning, heating and freeze-drying. Toluene was used as a model pollutant, and the photocatalytic degradation experiment was carried out to evaluate the performance of the catalyst. Results show that under the conditions of Co doping molar ratio of 1%,

calcination temperature of 600°C for 4 h, gas residence time of 100 min, relative humidity of 100%, and the loading amount of Co/TiO₂ molar ratio of 1%, the degradation percentage of toluene of Co-TiO₂/RGO photocatalyst was the highest, up to 99.1%. This study confirms the possibility of synthesizing Co-TiO₂/RGO for the degradation of pollutants from air.

Declarations

Ethics Approval

Not applicable

Consent to Participate

Not applicable

Consent for Publication

Not applicable

Authors' Contributions

Conceptualization: Guilan Gao, Shuai Chen.

Investigation: Fei Long, Shuai Chen.

Data curation: Fei Long, Shuai Chen.

Writing—original draft preparation: Fei Long, Shuai Chen.

Formal analysis: Shuai Chen, Guilan Gao.

Validation: Shuai Chen, Guilan Gao.

Writing—reviewing and editing: Shuai Chen, Jie Guan, Yaoguang Guo, Li Zhang, Lian Duan.

All authors read and approved the final manuscript.

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Competing Interests

The authors declare that they have no competing interests.

Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

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Figures

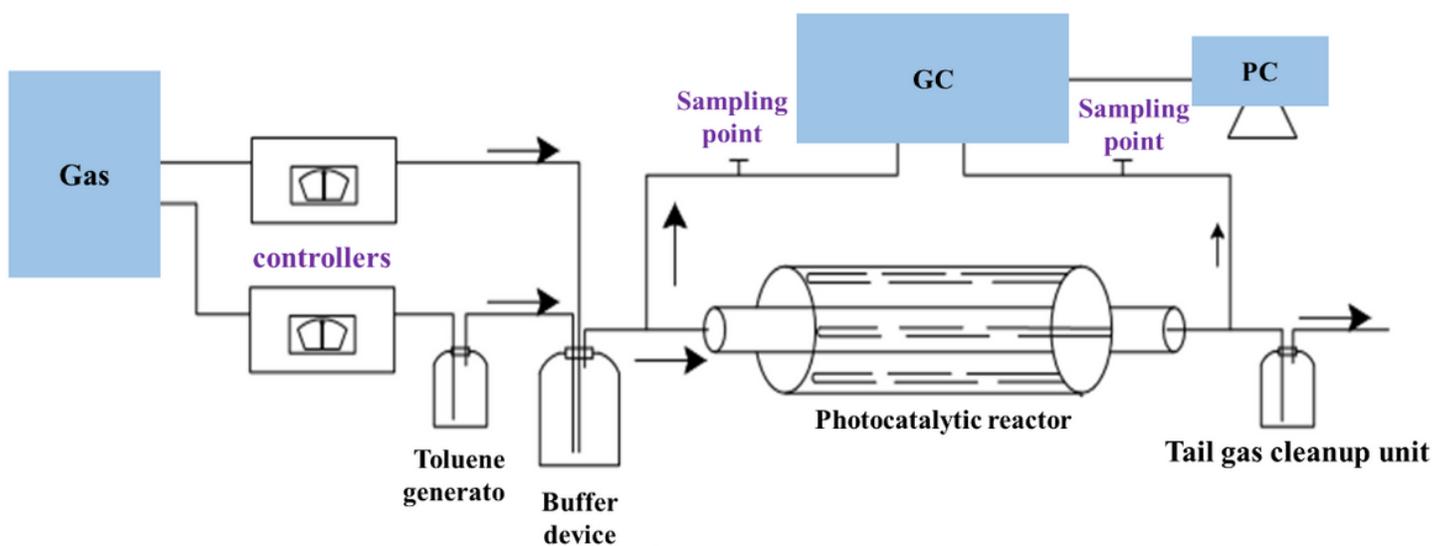


Figure 1

The process of photocatalytic degradation of toluene.

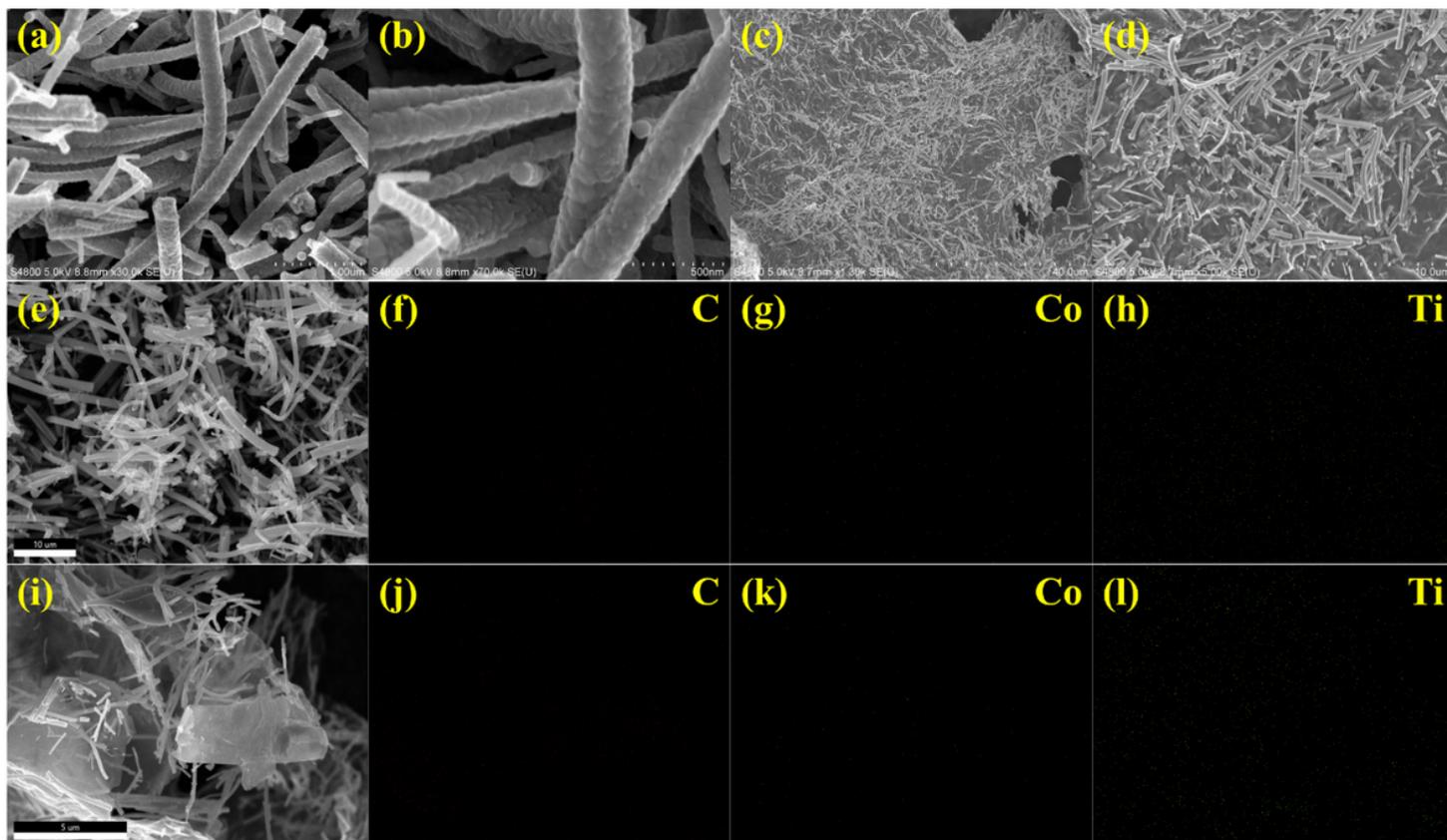


Figure 2

SEM and SEM-EDS results of Co-TiO₂ (a, b, e-h) and Co-TiO₂/RGO (c, d, i-l).

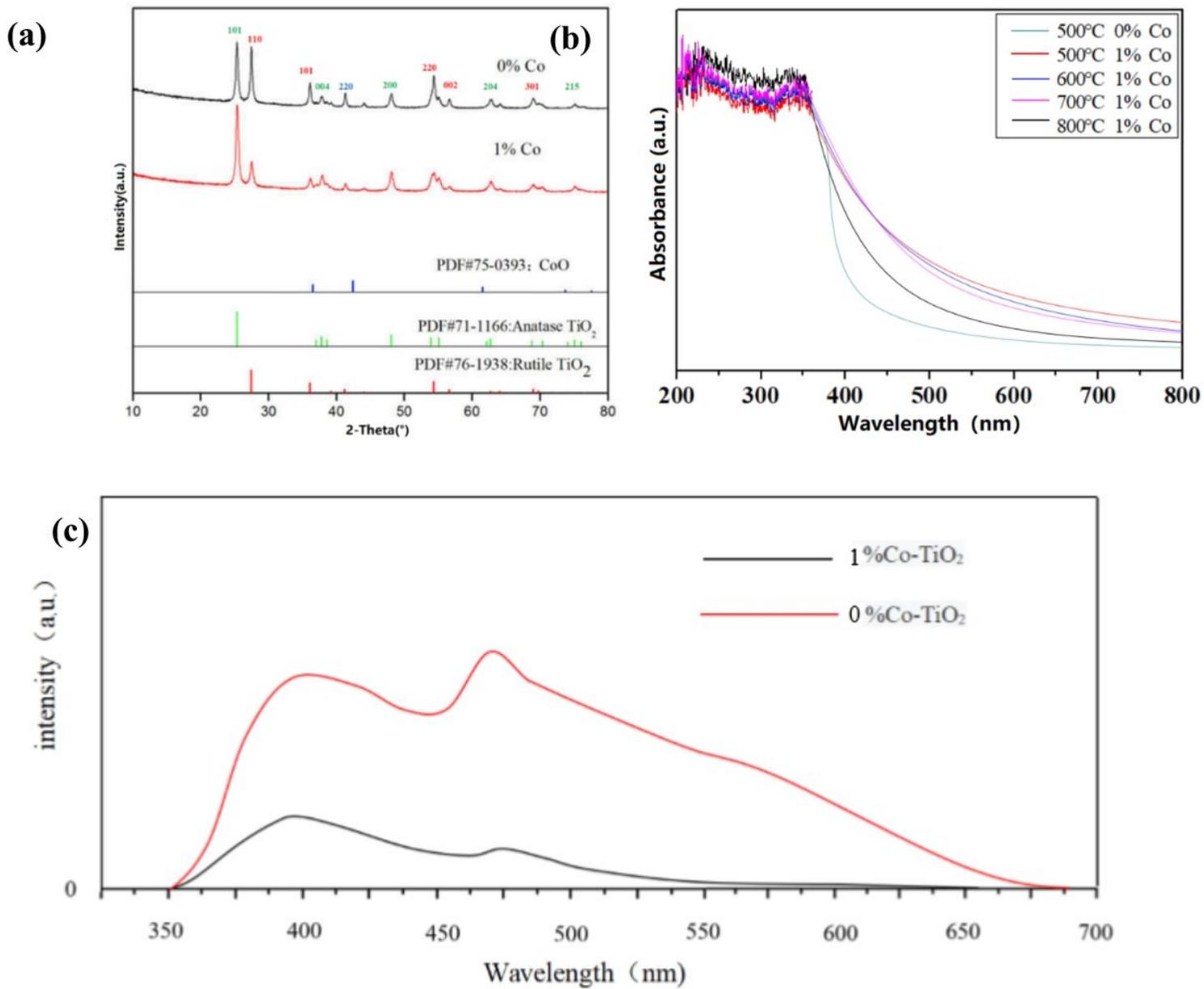


Figure 3

Photoluminescence spectrum (a), UV-vis absorption spectra (b) and XRD spectra (c) of catalysts.

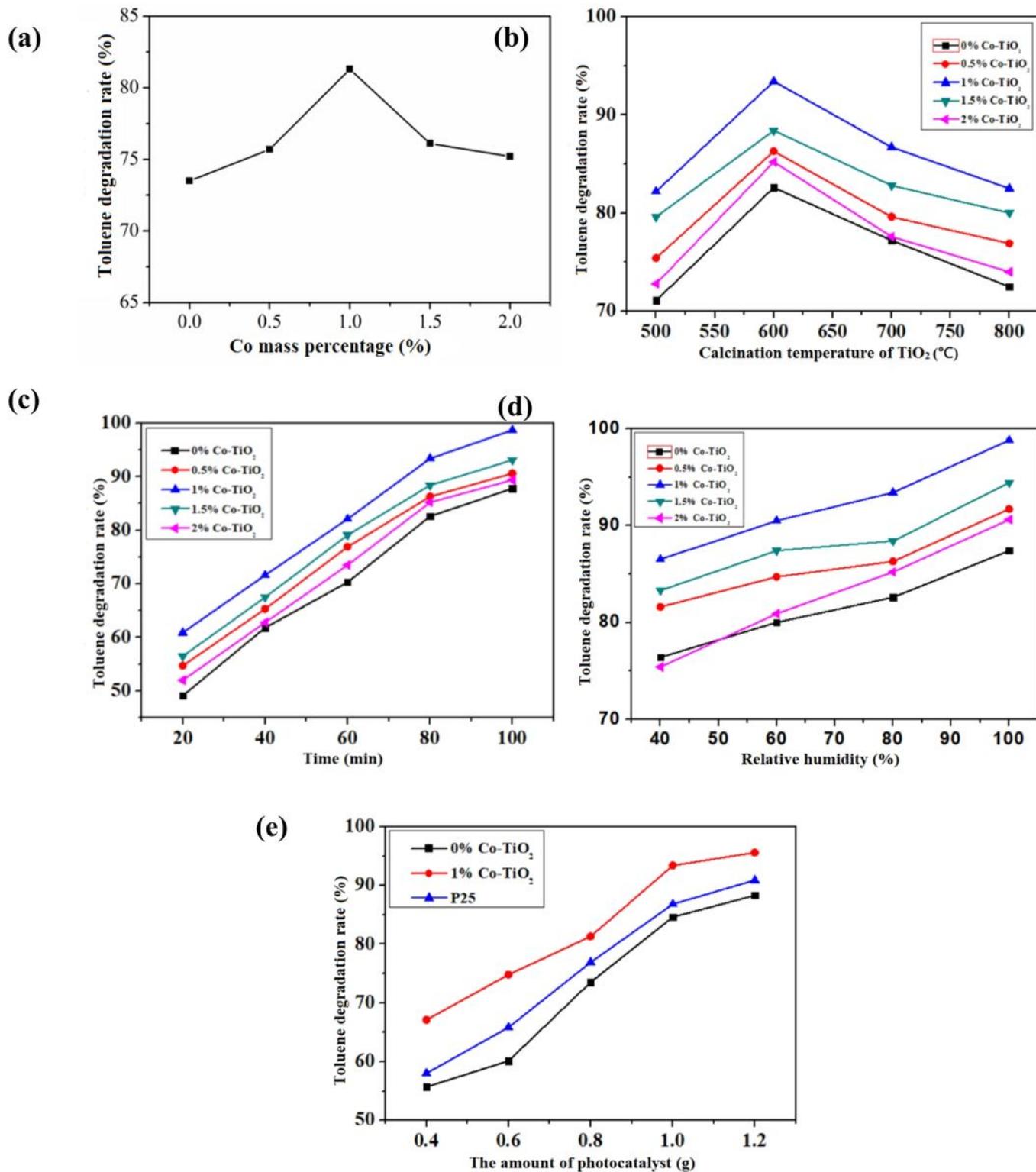


Figure 4

Degradation of toluene with different Co doping (a), calcination temperatures (b), gas residence time (c), relative humidity (d), and catalysts.

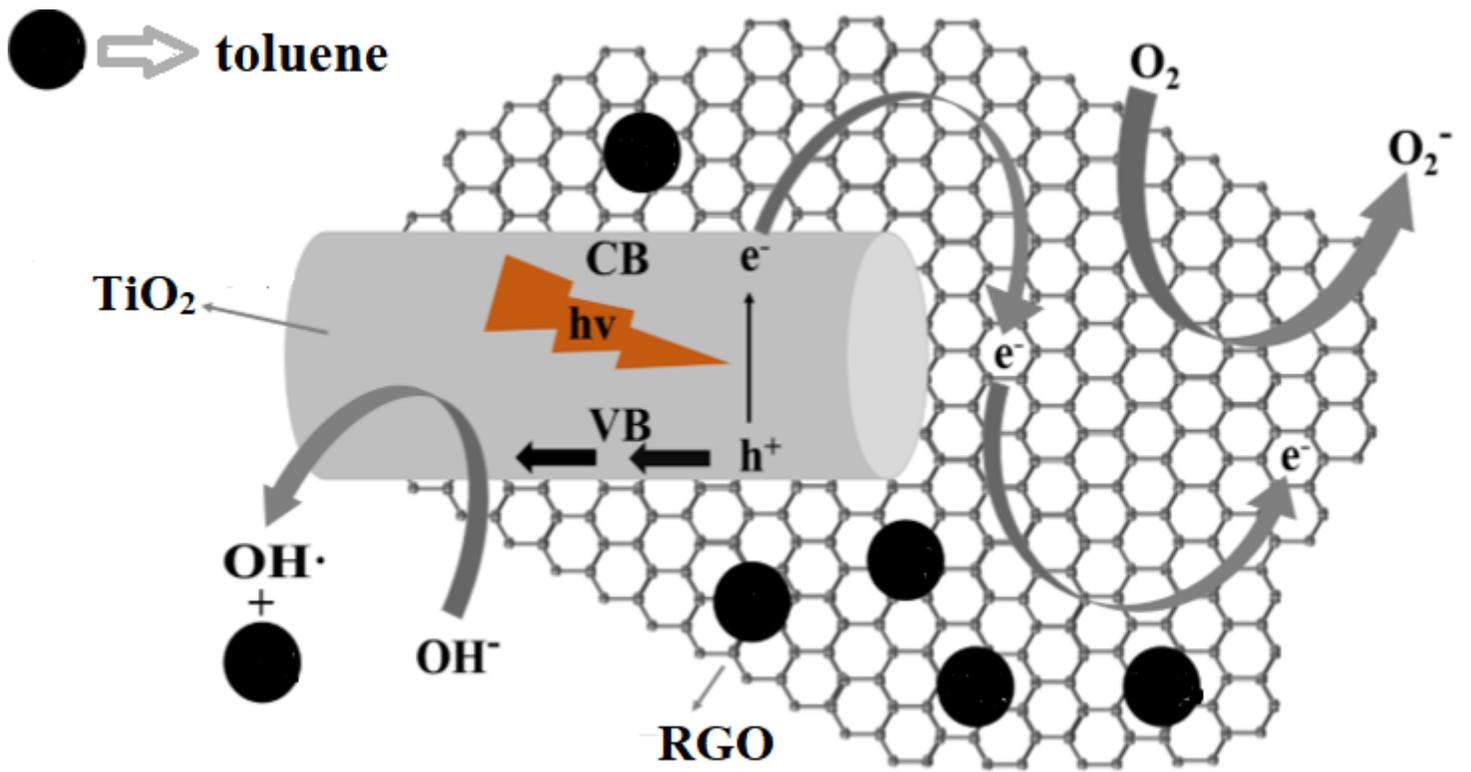


Figure 5

The photocatalytic degradation mechanism of toluene using Co-TiO₂/RGO.