Mechanism Research on Photocatalytic Degradation of Organic Waste-water by Ce-Ti- graphene Composite

J Wen1,2, G Hu2 and J Yang2

1Chongqing Real Estate College, Chongqing, 401331, P.R.China
2College of Material Science and Engineering, Chongqing University, Chongqing 400044, P.R. China

The corresponding author’s e-mail: huguang@cqu.edu.cn

Abstract. Introducing a third kind of materials in the binary system of TiO2/ graphene to synthesize ternary system of dopant /TiO2/ graphene is another main measure to improve the photocatalytic properties of the composites, and we can use the properties of dopants to enhance the synergistic effect of these three components. In this paper, the influence of micro mechanism of a series of self-made ternary system of CeO2/TiO2/ graphene photocatalysts on their activity was studied by the instruments such as SEM, FT-IR, Raman spectroscopy, XPS, UV-Vis DRS, and PL. The results show that the optical absorption properties of TiO2 are modified by loading CeO2 or graphene, and by loading the same mass, the effect of graphene on the increase of optical response range of the composites is better than that of CeO2. Furthermore, the optical response range of the ternary system of CeO2-TiO2-RGO composite photocatalysts was the maximum. And the addition of CeO2 or graphene affects the recombination of the photoelectron-hole to a certain extent, but it is weaker than the synergistic effect of graphene and CeO2 on preventing the recombination of photoelectron-hole pairs. And in the ternary system, with the content of CeO2 in the range from 0%-10%, the more the content of CeO2 is, the more obvious the synergistic effect is, and the lower the electron hole recombination probability is. The micromechanism detective results confirmed the photocatalysis experiments results that, the photocatalytic performance of the ternary system of CeO2-TiO2-RGO composite photocatalysts is better than that of the binary system of either CeO2-TiO2 or TiO2-RGO composite photocatalysts, and its photocatalytic performance is improved with the increase of the CeO2 content in the ternary system.

1. Introduction
Graphene based composites have attracted the attention of researchers for their distinguished performance in the fields of photocatalysis, solar cells and hydrogen production by photocatalysis. Many scientists in the fields of chemistry and chemical engineering, material, physical, environmental and energy have gained great achievements in designing and preparing new graphene based composites and their applications. Significant progress has been made in the fields of the preparation methods of graphene with titanium [1-3], bismuth [4-5], zinc [6-7], iron [8] and other compounds, and their applications in the field of photocatalytic degradation of organic pollutants.

In view of the graphene with TiO2 photocatalysts, the domestic and foreign scholars mainly focus on the design and preparation of new photocatalysts with different components and structures. The photocatalytic activity and selectivity of the photocatalyst are improved by the adjustment of components, precursors and structure. For example, Lanruijia [9] and Li Xuandong [10] prepared the
TiO$_2$/graphene composite by hydro-thermal method, using the precursor of four n-butyl titanate, and the photocatalytic activity of the composite was studied. The results showed that the catalytic activity of TiO$_2$/graphene composite was significantly higher than that of TiO$_2$ under the same condition. The results of Zhang’s study$^{[11]}$ show that the optical absorption range of the TiO$_2$/ graphene composite is extended to the visible light region, but that TiO$_2$ can not be dispersed evenly on the surface of graphene is the main problem of the photocatalyst of TiO$_2$/ graphene composite. Xu Yi-Jun’s team$^{[12]}$ found that the preparation method had an important influence on the photocatalytic properties of the TiO$_2$/ graphene composite. Compared with the TiO$_2$/ graphene composite synthesized with the solid TiO$_2$ powder as the titanium source, the photocatalytic properties of the TiO$_2$/ graphene composite synthesized by the titanium liquid as the titanium source have been greatly improved. It is because that synthesized by the titanium liquid as a titanium source, the TiO$_2$ can be loaded on the surface of graphene more uniformly, and thus enhance the interaction between TiO$_2$ and graphene. In order to strengthen this interaction between graphene and TiO$_2$ particles in the composite, Lee,at el$^{[13]}$ used 3-amino propyl triethoxy silane to modify the surface of TiO$_2$ particles, and so that graphene and TiO$_2$ are tightly combined. And it is proved that the TiO$_2$/ graphene composite prepared by this method has a higher photocatalytic activity and a narrower forbidden band than normal methods. And the photocatalytic activity of the TiO$_2$/ graphene composites with different morphologies will also be quite different. Zhou$^{[14]}$ found that compared with TiO$_2$ nanoparticles, the TiO$_2$ nanotubes had better contact properties to graphene, and could more effectively promote the transfer of photoelectrons to the surface of graphene and better inhibited the recombination of photoelectron-hole pairs, thus showed a stronger photocatalytic activity.

While introducing a third kind of materials in the binary system of TiO$_2$/ graphene to synthesize ternary system of dopant TiO$_2$/ graphene is another main measure to improve the photocatalytic properties of the composites, and we can use the properties of dopants to enhance the synergistic effect of these three components. Khalid$^{[15]}$ prepared Fe /TiO$_2$/ graphene composite and found that the doping of Fe not only narrowed the forbidden band of the catalyst, but also promoted the separation of the photoelectron-hole pairs more effectively. And the material showed a higher photocatalytic degradation efficiency than that of TiO$_2$/ graphene or pure TiO$_2$. The addition of other dopants$^{[16-19]}$, such as Cu$_2$O, Ag, SiO$_2$, CeO$_2$ to the binary system of TiO$_2$/ graphene, can also improve the separation of the photoelectron-hole pairs and the response to the visible light.

Although the ternary system of TiO$_2$/ graphene with different dopants has been synthesized, the specific reasons for the enhancement of their catalytic efficiency are not clear and lack of in-depth study. The synergistic effect among these components and the mechanism for their photocatalytic efficiency, which can provide a theoretical basis for the design of a new type of photocatalyst and broaden the practical application of TiO$_2$/ graphene composite in the degradation of organic contaminants, however ,these are studied very little. In this paper, the mechanism of the photocatalytic degradation of organic waste-water by a series of ternary system of dopant CeO$_2$/TiO$_2$/graphene photocatalysts was studied by means of analyzing these catalysts’ micromechanism.

2. Methods

The means of characterization of the composites include scanning electron microscopy (SEM), Fourier transformation infrared spectrometer (FT-IR), Raman spectroscopy (Raman), X- ray photoelectron spectroscopy (XPS), ultraviolet visible diffuse reflectance spectroscopy (UV-Vis DRS), photoluminescence (PL) and so on. A series of ternary system of CeO$_2$/TiO$_2$/ graphene photocatalysts were prepared and in this paper the influence of micromechanism on the activity of them was studied by these instruments shown in Table 1.
Table 1. Micromechanism analysis instrument and equipment for graphene based composite catalysts.

| Name                          | Model             | Resource                                |
|-------------------------------|-------------------|-----------------------------------------|
| Ultraviolet spectrophotometer | T6 series         | Beijing Purkinje General Instrument Co., Ltd. |
| XPS                           | ESCALAB250Xi      | Thermo Fisher Scientific (China)        |
| Microconfocal Raman           | LabRAM HR Evolution | HORIBA Jobin Yvon S.A.S (France)   |
| spectrometer                  |                   |                                         |
| Fluorescence / phosphor       | Cary eclipse      | Agilent Technologies (America)         |
| spectrophotometer             |                   |                                         |
| Field Emission Scanning       | JEOL JSM-7800F    | JEOL                                    |
| Electron Microscopy           |                   |                                         |
| Ultraviolet visible          | UV-2100           | Shimadzu                                |
| spectrophotometer             |                   |                                         |
| Fourier transformation        | Nicolet iS50      | Thermo Fisher Scientific (China)        |
| infrared spectrometer         |                   |                                         |

3. Results and Discussion

3.1. Phase analysis

Microconfocal Raman spectrometer was used for phase analysis of different TiO$_2$/graphene composite photocatalysts. Figure 1 is the Raman spectra of different samples. It can be observed from the diagram that the $E_{1g}$, $B_{1g}$, $A_{1g}$ and $E_g$ bands of anatase phase appeared near 153, 395, 514 and 624 cm$^{-1}$, respectively, which indicates that anatase is present in the self-prepared catalysts.

![Figure 1: The Raman spectra of different TiO$_2$/graphene composite photocatalysts](image)

In highly ordered graphite, Raman spectrum will show two peaks, commonly known as D band and G band. The D band represents the peaks of edges, other defects and irregular carbon in the graphite materials, which is sp$^3$ dominated and indicates the disorder of the graphite materials. While the G band represents the hexagonal arrangement of carbon atoms, which is sp$^2$ dominated and is the main characteristic peak of graphene$^{[20-21]}$. After graphene was added to TiO$_2$ photocatalysts, the G
band and D band of graphite materials were found in the samples, which were located at 1335 and 1588 cm$^{-1}$, respectively, and the anatase crystal of TiO$_2$ did not change.

The G band and D band of graphite materials represent the graphitization degree of graphene. In order to further study the micromechanism characteristics of graphite materials, the part of Figure 1 ranging from the abscissa 1000 cm$^{-1}$ to 1800 cm$^{-1}$ are intercepted and zoomed up as shown in Figure 2. It is clear from the diagram that, compared with GO (Graphene Oxide), the D band and the G band of the TiO$_2$/graphene composite photocatalysts offset slightly to the right on the abscissa, and especially, the D band and the G band of the TiO$_2$/10% RGO composite photocatalyst offset to 1338 and 1594 cm$^{-1}$, respectively. This is probably due to the decrease in the number of graphene sheets during hydro-thermal synthesis.

![Figure 2: The D band and G band of different TiO$_2$/graphene composite photocatalysts.](image)

The value of $I_D/I_G$ is often used to measure the degree of irregular and the order of matter. The smaller the value of $I_D/I_G$ is, the less defective in samples and the better the ordering degree is[22]. The values of $I_D/I_G$ corresponding to the Raman spectra of different graphene composites are shown in Table 2.

| Samples | 10%CeO$_2$-TiO$_2$/10% RGO | 5% CeO$_2$-TiO$_2$/10% RGO | 1% CeO$_2$-TiO$_2$/10% RGO | TiO$_2$/10% RGO | GO |
|---------|-----------------------------|-----------------------------|-----------------------------|-----------------|----|
| $I_D/I_G$ | 1.1507 | 1.0765 | 1.0713 | 1.0844 | 0.9607 |

As shown in Table 2, the value of $I_D/I_G$ of GO is less than 1, while the value of $I_D/I_G$ of other samples is larger than 1. The value of $I_D/I_G$ of the graphene composite catalyst is larger than that of the pure GO, which is attributed to the fracture of the sp$^2$ domain during the hydro-thermal synthesis. Paredes[23] and Stankvoich[24] think this is due to the fact that although the reduction process has repaired the communal areas, in generally it has added more small areas and eventually led to an increase in the $I_D/I_G$ values. As the total amount of CeO$_2$ and TiO$_2$ in the graphene composite catalyst increases, the value of $I_D/I_G$ increases, indicating that the role of CeO$_2$ and TiO$_2$ with graphene makes sp$^3$ defects increase. It is worth noting that the value of $I_D/I_G$ of the TiO$_2$/10% RGO sample is a little higher than that of the TiO$_2$/graphene photocatalysts with doping low dose CeO$_2$, indicating that the addition of a small amount of CeO$_2$ can show a better defect repair mechanism.
3.2. Morphology analysis
Field Emission Scanning Electron Microscopy was used for morphology analysis of different photocatalysts. The (a) diagram of Figure 3 is the SEM micrograph of TiO$_2$. From the (a) diagram, it can be clearly seen that the particles of TiO$_2$ are more plump, and dispersed evenly, and the particle size is about 20nm. The (b) diagram of Figure 3 is the SEM micrograph of 10%CeO$_2$-TiO$_2$, and in which it can be seen that the particle size is not uniform. The (c) diagram of Figure 3 is the SEM micrograph of 10%CeO$_2$-TiO$_2$/10% RGO. By contrast these three diagrams, it can be indicated that after a hydro-thermal reaction, a transparent and wrinkled graphene sheet has successfully loaded homogeneous TiO$_2$ particles evenly.

![Figure 3. The SEM micrograph of different photocatalysts.](image)

3.3. Surface functional group analysis
Fourier transformation infrared spectrometer was used for surface functional group analysis of different TiO$_2$/ graphene composite photocatalysts. Figure 4 is the infrared spectrum analysis of GO. It can be seen that there are several obvious absorption peaks. The absorption peak near 3438 cm$^{-1}$ represents the stretching vibration of -OH hydroxyl in water, and the absorption peak near 1735 cm$^{-1}$ represents the stretching vibration of C=O in carboxylic acid group, which mainly exists at the edge position of the graphite layer, and the absorption peak near 1633 cm$^{-1}$ represents the stretching vibration of C=C carbon-carbon double bond, and the absorption peak near the 1397 cm$^{-1}$ represents the stretching vibration of C-OH, and the absorption peak near 1059 cm$^{-1}$ represents the stretching vibration of C-O. This shows that after the oxidation by different strong oxidants, abundant oxygen-containing functional groups were introduced on the surface of graphite.

While using the hydro-thermal method, GO was synthetized with other materials, and the changes of oxygen containing functional groups in different photocatalysts are shown in Figure 5. It is obvious from the diagram that compared with pure GO, absorption peaks of the graphene based composite photocatalysts near 1059 and 1735 cm$^{-1}$ are basically disappearing, which infers that the C-O groups on the surface and the C=O groups in carboxylic acid groups are reduced during the hydro-thermal process. The absorption peak intensity of the ternary system of CeO$_2$-TiO$_2$/10% RGO is obviously enhanced near 1397 cm$^{-1}$, while that of the binary system of TiO$_2$/10% RGO is basically unchanged there. And the new broad absorption peaks near the 726 cm$^{-1}$ and 559 cm$^{-1}$ of the graphene based photocatalysts may be due to the stretching vibration of Ti-O bonds and Ce-O bonds. The above results show that GO is reduced during hydro-thermal synthesis, and there is a coupling effect between TiO$_2$-CeO$_2$ and graphene.
3.4. Atomic analysis

XPS was used to analyze the elements on the surface of different TiO$_2$/graphene composite photocatalysts. Figure 6 is the XPS full spectra of five different catalysts: 10%CeO$_2$-TiO$_2$, 10%CeO$_2$-TiO$_2$/10% RGO, 5% CeO$_2$-TiO$_2$/10% RGO, 1% CeO$_2$-TiO$_2$/10% RGO, and TiO$_2$/10% RGO. It can be seen from the diagram that compared with TiO$_2$/10% RGO, a new peak has been found at 889 eV in other composites containing CeO$_2$, which is caused by Ce$^{3d}$ orbitals. Moreover, the peak intensity of CeO$_2$ varies with the content of CeO$_2$ in composites, and will increase when the amount of CeO$_2$ added in the composites increase.
Figure 6. The XPS spectra analysis of different photocatalysts: (a) 10%CeO2-TiO2; (b) 1%CeO2-TiO2/10%RGO; (c) 5%CeO2-TiO2/10%RGO; (d) 10%CeO2-TiO2/10%RGO; (e) TiO2/10%RGO. Figure 7 is the Ti2p spectra of these five composite photocatalysts. It can be obtained from the diagram that, the peaks at 465.0eV and 459.3eV, respectively, are corresponding to Ti2p1/2 and Ti2p3/2.

Figure 7. The Ti2p spectra of different photocatalysts.

While Figure 8 is the Ce3d spectra of 10%CeO2-TiO2 and 10%CeO2-TiO2/10% RGO samples. The image shows that the Ce3d binding energy of the two samples in the spectra presents a multiple state (peak position), which is due to the different occupying of the electrons of CeO2 in the Ce4f energy level. In the spectrogram, u and v represent the spin orbit components of 3d3/2 and 3d5/2 respectively. After fitting, there are eight binding energies, of which u' and v' belong to Ce3+, and the others belong to Ce4+. And the fitting calculation results show that the ratio of Ce3+ in 10%CeO2-TiO2 catalyst (Ce3+/Ce) is 37.36%, while the ratio of Ce3+ in 10% CeO2-TiO2/10% RGO is 33.62%. The addition of graphene reduces the proportion of Ce3+ content. It can be deduced that graphene can play a reduction in the recombination of photoelectron-hole pairs, which reduces the electrons that Ce4+ can capture.
and prevent Ce$^{4+}$ from converting into Ce$^{3+}$, thus proves that there is a synergistic effect between CeO$_2$ and graphene.

![Ce$^{3d}$ spectra](image_url)

Figure 8. The Ce$^{3d}$ spectra of (a)10%CeO$_2$-TiO$_2$ and (b)10%CeO$_2$-TiO$_2$/10% RGO photocatalysts.

3.5. Analysis of optical absorption properties

The optical absorption properties of different photocatalysts were investigated by using ultraviolet visible spectrophotometer, and the results were shown in Figure 9. From this image, we can see that the light response range of sample TiO$_2$ is about 250-402 nm. Compared with pure TiO$_2$, the light response range of photocatalyst sample 10%CeO$_2$-TiO$_2$ is broadened and the absorption edge red shifted about 22 nm. The red shift of optical absorption may be related to the spectral characteristics of CeO$_2$, that the charge transfer transition from O$_{2p}$ to Ce$_{4f}$ may occur to a certain extent, and the intensity of this transition is weak, resulting a small range of absorption edge redshift. And the absorption edge of photocatalyst sample TiO$_2$/10% RGO red shifted 23 nm more than that of sample 10%CeO$_2$-TiO$_2$. It can be deduced that the optical absorption properties of TiO$_2$ are modified by loading CeO$_2$ or graphene, and by loading the same mass, the effect of graphene on the increase of optical response range of the composites is better than that of CeO$_2$. The optical response range of the ternary system of CeO$_2$-TiO$_2$-RGO composite photocatalysts was the maximum, with the maximum absorption wavelengths of 484 nm, 462 nm and 450 nm respectively. And it is found that the absorption edge of the ternary system of CeO$_2$-TiO$_2$-RGO composite photocatalysts red shift more than that of the binary system of either CeO$_2$- TiO$_2$ or TiO$_2$-RGO composite photocatalysts, indicating that the two materials of CeO$_2$ and graphene play a role by synergism. And with the increase of CeO$_2$ content, the larger the light response range is, which shows that the doping amount of CeO$_2$ will affect the light response range. And with the range of CeO$_2$ doping amount from 0%-10%, the light response range has a positive correlation with the content of CeO$_2$. 
Figure 9. The UV-Vis diffuse reflectance spectra of different photocatalysts: (a) 10%CeO$_2$-TiO$_2$; (b) 1%CeO$_2$-TiO$_2$/10%RGO; (c) 5%CeO$_2$-TiO$_2$/10%RGO; (d) 10%CeO$_2$-TiO$_2$/10%RGO; (e) TiO$_2$/10%RGO; (f) TiO$_2$.

By Tauc plot method, the band gap of different photocatalysts was obtained from their UV-Vis DRS, shown as Figure 10, a diagram of the relationship between $h\nu$ and $(Ah\nu)^2$. The linear part of the curve in the graph is extrapolated to the abscissa axis, and the intersection point is the band gap of different photocatalysts.

As can be seen from Figure 10, the band gap of 10%CeO$_2$-TiO$_2$, 10%CeO$_2$-TiO$_2$/10%RGO, 5% CeO$_2$-TiO$_2$/10%RGO, 1% CeO$_2$-TiO$_2$/10% RGO, TiO$_2$/10% RGO and TiO$_2$ are 3.01, 2.43, 2.68, 2.95, 2.94 and 3.27 eV, respectively. The wider the light response range is, the narrower the band gap is. In addition, the introduction of graphene and CeO$_2$ leads to the narrowing of the band gap of the photocatalyst. Especially, when the addition of CeO$_2$ increases up to 10%, the band gap of the photocatalyst decreases from 3.27 eV to 2.43 eV, which indicates that the synergistic effect of graphene and CeO$_2$ narrowed the band gap of the photocatalyst and expanded the light response range.
3.6. Analysis of fluorescence properties

The fluorescence properties of five different photocatalysts, 10%CeO$_2$-TiO$_2$, 10%CeO$_2$-TiO$_2$/10% RGO, 5% CeO$_2$-TiO$_2$/10% RGO, 1% CeO$_2$-TiO$_2$/10% RGO and TiO$_2$/10% RGO, were investigated by using the Fluorescence / phosphor spectrophotometer, and the results were shown in Figure 11.

![Figure 11. The PL spectra of different photocatalysts.](image)

From Figure 11, it can be seen that the trend of the photoluminescence curves of all samples is approximately the same, and the PL luminescence signals are strong and wide in the range of 425 nm-475 nm. Generally, the stronger the luminescence peak, the stronger the energy loss and the lower the composite photocatalytic activity. The intensity of the luminescence peak can reflect the recombination probability of the photoelectron-hole pairs [25]. Therefore, it can be found from Figure 11. that the intensity of the luminescence peak of different photocatalysts is in the order that TiO$_2$/10%RGO >10%CeO$_2$-TiO$_2$ >1% CeO$_2$-TiO$_2$/10% RGO >5% CeO$_2$-TiO$_2$/10% RGO >10%CeO$_2$-TiO$_2$/10% RGO, indicating that the recombination probability of the photoelectron-hole pairs is getting smaller and smaller. The intensity of the luminescence peak of the TiO$_2$/10% RGO samples is the highest, while the others’ is reduced because of the addition of CeO$_2$. Compared to the 10%CeO$_2$-TiO$_2$ samples, the intensity of the luminescence peaks of the other ternary system of CeO$_2$-TiO$_2$-RGO composite photocatalysts reduced more obviously, and the intensity of the luminescence peak was also decreasing with the increase of the content of CeO$_2$ in the ternary system of CeO$_2$-TiO$_2$-RGO composite photocatalysts. The results show that the addition of CeO$_2$ affects the recombination of the photoelectron-hole to a certain extent, but it is weaker than the synergistic effect of graphene and CeO$_2$ on preventing the recombination of photoelectron-hole pairs. With the content of CeO$_2$ in the range from 0%-10%, the more the content of CeO$_2$ is, the more obvious the synergistic effect is, and the lower the electron hole recombination probability is.

3.7. Analysis of photocatalytic performance

UV spectrophotometer was used to test the photocatalytic performance of the different composite catalysts made on the self-made experimental platform. Figure 12 shows the photocatalytic degradation curves of Rhodamine B organic solution in the photocatalysis experiments with the addition of different composite catalyst samples.
After 30 minutes dark adsorption, the concentration of Rhodamine B organic solution at this time is set to $C_0$, and the relationship between $C/C_0$ and time is shown in Figure 12. It can be seen that the photocatalytic performance of the composite is much better than that of pure TiO$_2$. After 30 minutes light adsorption, the photocatalytic degradation rate of Rhodamine B solution in the photocatalytic experiment with the addition of 10% CeO$_2$-TiO$_2$ whose photocatalytic performance is the worst in these composites, is 4.36 times as much as that with the addition of pure TiO$_2$ sample, while that with the addition of 10% CeO$_2$-TiO$_2$/10% RGO whose photocatalytic performance is the best, is 6.71 times that with the addition of pure TiO$_2$. In the binary system of either CeO$_2$-TiO$_2$ or TiO$_2$-RGO composite photocatalysts, by loading the same mass, the effect of graphene on the increase of photocatalytic degradation of Rhodamine B organic solution is better than that of CeO$_2$. And the effect of the ternary system of CeO$_2$-TiO$_2$-RGO composite photocatalysts on the increase of photocatalytic degradation of Rhodamine B organic solution is better than that of the binary system of CeO$_2$-TiO$_2$ or TiO$_2$-RGO composite photocatalysts. By loading the same mass of RGO, the photocatalytic performance of the ternary system of CeO$_2$-TiO$_2$-RGO composite photocatalysts increased with the increase of the CeO$_2$ concentration. These photocatalysis experiments results are coordinate to the results of UV-Vis DRS and PL analysis.

4. Conclusion
The influence of micro mechanism of a series of self-made ternary system of CeO$_2$/TiO$_2$/graphene photocatalysts on their activity was studied by the instruments such as SEM, FT-IR, Raman spectroscopy, XPS, UV-Vis DRS, PL et al. The main conclusion are as follows.

The XPS fitting calculation results show that the ratio of Ce$^{3+}$ in 10% CeO$_2$-TiO$_2$ catalyst (Ce$^{3+}$/Ce) is 37.36%, while the ratio of Ce$^{3+}$ in 10% CeO$_2$-TiO$_2$/10% RGO is 33.62%. The addition of graphene reduces the proportion of Ce$^{3+}$ content. It can be deduced that graphene can play a reduction in the recombination of photoelectron-hole pairs, which reduces the electrons that Ce$^{4+}$ can capture, and prevent Ce$^{4+}$ from converting into Ce$^{3+}$, thus proves that there is a synergistic effect between CeO$_2$ and graphene.

Though the addition of CeO$_2$ affects the recombination of the photoelectron-hole to a certain extent, but it is weaker than the synergistic effect of graphene and CeO$_2$ on preventing the recombination of photoelectron-hole pairs. With the content of CeO$_2$ in the range from 0% to 10%, the more the content of CeO$_2$ is, the more obvious the synergistic effect is, and the lower the electron hole recombination probability is.
And the introduction of graphene and CeO$_2$ leads to the narrowing of the band gap of the photocatalyst. Especially, when the addition of CeO$_2$ increases up to 10%, the band gap of the photocatalyst decreases from 3.27 eV to 2.43 eV, which indicates that the synergistic effect of graphene and CeO$_2$ narrowed the band gap of the photocatalyst and expanded the light response range.

Both the micromechanism detection results and photocatalysis experiments results show that, the photocatalytic performance of the ternary system of CeO$_2$- TiO$_2$-RGO composite photocatalysts is better than that of the binary system of either CeO$_2$-TiO$_2$ or TiO$_2$-RGO composite photocatalysts, and its photocatalytic performance is improved with the increase of the CeO$_2$ content in the ternary system.

**Acknowledgments**

This research was financially supported by the project “Photocatalytic decomposition of organic wastewater by graphene complex” of the third batch of funding scheme for young backbone teachers in Chongqing colleges and universities.

**References**

[1] Williams G, Seger B, and Kamat P V. 2008 J. *ACS Nano*. 2 1487-1491
[2] Jo W K and Kang H J 2013 *Powder technology* 250 115-121
[3] Han Z Z, Wei L Y, Pan H B, Li C Y and Chen J H 2015 *Journal of Molecular Catalysis A-Chemical* 398 399-406
[4] Sun S, Wang W and Zhang L 2013 *The Journal of Physical Chemistry C* 117 9113-9120
[5] Liu H, Cao W R, Su Y, Chen Z and Wang Y 2013 *Journal of colloid and interface science* 398 161-167
[6] Geng Y L, GUO W B and Kuang S P. 2014 *Journal of Qingdao University Science and Technology(Natural Science Edition)* 35 119-124
[7] Fu Y and Wang X 2011 *Industrial & Engineering Chemistry Research* 50 7210-7218
[8] He L M, Jing L Q, Lan Y B, Wang L, and Fu H G 2014 *ACS Catalysis* 4 990-998
[9] Lan R J, Li J T, Zhou Q X and Qiu M D 2013 *Journal of Hebei University(Natural Science Edition)* 33 608-613
[10] Li X D, Liu X H, Han X J, Wang J Y, Wen A H and Lv Z S 2011 *Journal of Harbin Institute of Technology* 29 267-271
[11] Zhang H, Lv X J, Li Y M, Wang Y and Li J H 2009 *ACS nano* 4 380-386
[12] Zhang Y, Tang Z R, Fu X and Xu Y J 2011 *ACS nano* 5 7426-7435
[13] Lee J S, You K H and Park C B 2012 *Advanced Materials* 24 1084-1088
[14] Zhou X, Shi T, Wu J and Zhou H 2013 *Applied Surface Science* 287 359-368
[15] Khalid N R, Hong Z, Ahmed E, Zhang Y W, Chan H and Ahmad M 2012 *Applied Surface Science* 258 5827-5834
[16] Ghasemi S, Setayesh S R, Habibi-Yangjeh A, Hormozi-Nezhad MR and Gholami MR 2012 *Journal of hazardous materials* 199 170-178
[17] Khalid N R, Ahmed E, Hong Z, Ahmad M, Zhang Y W and Khalid S 2013 *Ceramics International*, 39 7107-7113
[18] Bo Z T, Dong R L, Wang X H, Zhang H P, Cheng Z D and Jin C C 2018 *New Chemical Materials* 46 91-94
[19] Jiang L X, Li K X, Yan L S, Dai Y H and Huang Z M 2012 *Chinese Journal of Catalysis* 33 1974-1981
[20] Thomsen C and Reich S 2000 *Physical review letters* 85 5214-5217
[21] Saito R, Hofmann M, Dresselhaus G, Jorio A and Dresselhaus M S 2011 *Advances in Physics* 60 413-550
[22] Kudin K N, Ozbas B, Schniepp H C, Prudhomme R K, Aksay I A and Car R 2008 *Nano Letters* 8 36-37
[23] Paredes J I, Villarrodil S, Solísfernandez P, Martínezalonso A and Tascon J M 2009 *Langmuir the Acs Journal of Surface &Colloids* 25 5957-5986
[24] Stankovich S, Piner R D, Chen X Q, Wu N, Nguyen S B T and Ruoff R S 2006 *Journal of Materials Chemistry* **16** 155-158

[25] Hao Y Y, Zhang Y and Zhao L 2017 *Journal of Synthetic Crystal* **46** 1379-1346