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**Figure 1.** TEM images of (a and b) 10% CeO$_2$-g-C$_3$N$_4$, (c) HRTEM image of the CeO$_2$ cubes.

**Figure 2.** XRD pattern of g-C$_3$N$_4$ and the CeO$_2$/g-C$_3$N$_4$ composites.

**Figure 3.** C 1s (a), N 1s (b) and (c) O 1s XPS spectra, (d) High-resolution Ce 3d spectra.

**Figure 4.** (a) FT-IR spectra and (b) UV-visible absorption spectra of the g-C$_3$N$_4$ and CeO$_2$/g-C$_3$N$_4$, (c) estimated band gaps of the g-C$_3$N$_4$ and CeO$_2$/g-C$_3$N$_4$, (d) photocurrent-time dependence of the g-C$_3$N$_4$ and 2.5%, 5%, 10% CeO$_2$/g-C$_3$N$_4$ electrodes in NaNO$_3$ (0.1 M) aqueous solution under visible light irradiation.

**Figure 5.** (a) The photocatalytic degradation of MB dye by the photocatalysts, (b) the kinetics of MB degradation using various photocatalysts under visible-light irradiation, (c) cycling runs for the photocatalytic degradation of MB in the presence of 5% CeO$_2$/g-C$_3$N$_4$ under visible light irradiation.

**Figure 6.** (a) XRD patterns and (b) FT-IR spectra of 5% CeO$_2$/g-C$_3$N$_4$ before and after the cycling photocatalytic experiments.

**Figure 7.** (a), (b), (c) and (d) changes in UV-visible absorption spectra of MB by g-C$_3$N$_4$ and CeO$_2$/g-C$_3$N$_4$ composites.

**Figure 8.** (a) Photocurrent intensity of ITO/5% CeO$_2$/g-C$_3$N$_4$ in the presence of different Cu$^{2+}$ concentrations, (b) plot of photocurrent I of ITO/5% CeO$_2$/g-C$_3$N$_4$ versus Cu$^{2+}$ concentration, (c) photocurrent intensity of ITO/5% CeO$_2$/g-C$_3$N$_4$ in the presence of 4.0 μM solutions of various metal ions.

**Figure 9.** Schematic illustration of exciton trapping mechanism and photoelectrochemistry for sensing of trace amounts of Cu$^{2+}$. 
Figure 1
Figure 2
Figure 3
Figure 4

(c) 

\[(\Delta E_{\text{photon}})^2\] vs. \(E_{\text{photon}}\) (eV)

- \(g\text{-C}_3\text{N}_4\)
- 10% CeO\(_2\)/g-C\(_3\)N\(_4\)
- 5% CeO\(_2\)/g-C\(_3\)N\(_4\)
- 2.5% CeO\(_2\)/g-C\(_3\)N\(_4\)

2.65, 2.79, 2.81, 2.83 eV

(d) 

Photocurrent (µA) vs. Time (s)

- 5% CeO\(_2\)/g-C\(_3\)N\(_4\)
- 10% CeO\(_2\)/g-C\(_3\)N\(_4\)
- 2.5% CeO\(_2\)/g-C\(_3\)N\(_4\)
- g-C\(_3\)N\(_4\)
Figure 5
Figure 6
Figure (a) shows the absorbance spectra of g-C$_3$N$_4$ with different irradiation times. Figure (b) displays the absorbance spectra of 2.5% CeO$_2$/g-C$_3$N$_4$ with varying irradiation times.
Figure 7
Figure 8
Figure 9
Table 1. Kinetic Constants and Regression Coefficients of MB Degradation under Visible Light Irradiation.
Table 1.

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<th>Photocatalysts</th>
<th>Kinetic constant ($k$, h$^{-1}$)</th>
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<td>g-C$_3$N$_4$</td>
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Controllable synthesis of CeO$_2$/g-C$_3$N$_4$ composites and their applications in environment

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Through the hydrothermal method, the ultrafine CeO$_2$ cubes and g-C$_3$N$_4$ formed the heterojunction structure. And the homogeneous dispersedness of CeO$_2$ cubes on g-C$_3$N$_4$, effective combination of ultrafine CeO$_2$ cubes on g-C$_3$N$_4$ and high crystallinity of CeO$_2$ improved the photocatalytic activity of CeO$_2$/g-C$_3$N$_4$ nanocomposites. Meanwhile, 5% CeO$_2$/g-C$_3$N$_4$ gave other birth to new promising properties: highly selective and sensitive sensor for the detection of trace amount of Cu$^{2+}$. And the exploited novel photocatalytic reactor insured the efficiency of photocatalytic reaction.
Controllable synthesis of CeO$_2$/g-C$_3$N$_4$ composites and their applications in environment

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ABSTRACT:

The experiment developed a photocatalytic reactor which includes circulating water, light, and temperature control system. CeO$_2$/g-C$_3$N$_4$ composites with high photocatalytic activity and stability were synthesized by a simple and facile hydrothermal method. The obtained photocatalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). It is found that in CeO$_2$/g-C$_3$N$_4$ composites, CeO$_2$ presented homogeneous shape of the cube (from 3 to 10 nm) and it was equably dispersed on the surface of g-C$_3$N$_4$. At constant temperature (30°C), 5% CeO$_2$/g-C$_3$N$_4$ photocatalyst showed the best photocatalytic activity for degrading organic dye methylene blue (MB) under visible light irradiation. And the photocatalytic reaction for MB followed first-order kinetics and 5% CeO$_2$/g-C$_3$N$_4$ exhibited a higher apparent rate of 1.2686 min$^{-1}$, which was 7.8 times as high as that of the pure g-C$_3$N$_4$ (0.1621 min$^{-1}$). What’s more, it was found that 5% CeO$_2$/g-C$_3$N$_4$ had a new property that it could be used as the sensor for tracing amounts of Cu$^{2+}$ determination. Such unique design and one-step synthesis with an exposed high-activity surface are important for both technical applications and theoretical investigations. Moreover, the excellent photocatalytic reactors were exploited, so it could promote further development of photocatalysis technology.
1 Introduction

In order to further solve the energy dilemma, the problems of environmental pollution and enhance the application of solar energy, photocatalysis has become one of the most promising technology, both in field of research and in industrial applications. The ideal photocatalyst should be activated as well as stable for decreasing the economic and environmental costs of potential metallic or toxic elements’ secondary pollution. However, both high-powered photocatalyst and excellent photocatalytic reactors limited the development of the photocatalysis technology. Typically, due to large bandgap, the excellent and stable metal oxide photocatalyst TiO$_2$ has no or limited visible light absorption, which does not meet the requirements for the industry. So, in order to solve these problems, the researchers has taken many measures as changing the morphology of TiO$_2$, loading of nonmetal, constructing a heterojunction composite with another semiconductor and dye sensitization. Although, these approaches have resulted in some improvements of their photocatalytic performance, it still has not meet the requirements of industrial application. For the composites of TiO$_2$, the size of TiO$_2$ was unhomogeneous and quite large, the morphology of TiO$_2$ could not be controlled well and TiO$_2$ could not bond with another semiconductor. The composites were very unstable and showed low photocatalytic activity as a result. What’s more, very few photocatalytic reactors can provide stable dynamic response environments. General photocatalytic reactors have some general problems. For example, light source is not stable because the bulb providing high intensity of visible light was usually broken, temperature control system was not satisfying because of some design defects, water circulation systems consumed energy, circuit security system could not ensure absolute safety and so on. For those reasons, the development of an efficient photocatalyst under visible-light and excellent reactors (or equipments) are still desired.

The graphitic carbon nitride (g-C$_3$N$_4$) that is the organic polymeric semiconductor material and is like the graphite owning layer structure, has attracted more and more attention from researchers, relying on its visible light response, high thermal and chemical stability, and abundant yet low-cost nitrogen-rich precursor materials. As a
metal-free, nontoxic and organic semiconductor, g-C₃N₄ is made up of carbon and nitrogen. It shows great advantages in photocatalytic water splitting, photodegradation of environmental organic pollutants, electrochemical sensors and bioimaging, so it becomes one of the most prospective photocatalyst. However, as photocatalyst, g-C₃N₄ also has some inevitable shortcomings, such as: high recombination rate of photoexcited charge carriers, low quantum efficiency, lower specific surface area, lack of absorption above 460 nm, the lesser active sites, etc, which leads to low photocatalytic activity. With those disadvantages, the development of g-C₃N₄ is hampered badly. In order to solve these defects, many methods have been taken to improve the photocatalytic activity of g-C₃N₄ under visible light irradiation, such as chemical doping with foreign elements, preparing novel nanostructures, constructing a heterojunction composite with another semiconductor, etc. (Ag/g-C₃N₄, AgX/g-C₃N₄, ZnO/g-C₃N₄, g-C₃N₄-WO₃, C-60/g-C₃N₄, and Cu₂O/g-C₃N₄)

Specially, the metal or metallic oxide-containing g-C₃N₄ composites (Fe/g-C₃N₄, Co₃O₄/g-C₃N₄, Fe₃O₄/g-C₃N₄, TiO₂/g-C₃N₄) have been proved to be an effective photochemical oxidation catalysts under visible light irradiation. Obviously, the modification of g-C₃N₄ is very efficient as improving the optical absorption and photocatalytic performance under visible light irradiation. However, in the modification of g-C₃N₄ system, the light harvesting ability and quantum efficiency of the materials are still unsatisfying. Thus, it is still necessary to find an appropriate composites to further enhance the photocatalytic performance of g-C₃N₄ so that g-C₃N₄ can be exploited and applied in environment and industrial manufacture better.

CeO₂ has been reported as an efficient photocatalyst with a band gap (Eg = 2.92 eV), it absorbs light near UV and slightly in the visible light region. CeO₂ is also one of the most important rare earth materials and it has been extensively studied for many technological applications including fuel cells, catalytic, luminescent and solar cells due to its chemical stability and high oxygen storage capacity. What’s more, many composites of CeO₂ have been prepared. Therefore, if CeO₂/g-C₃N₄ composite material could be obtained, it might be an excellent photocatalyst with visible-light
response. However, how to obtain high-powered, stable and homogeneous CeO$_2$ in composite material remains to be an intractable problem. Although, the various microstructures of CeO$_2$ and composites of CeO$_2$ (including CeO$_2$/Graphene$^{24}$ and ultrathin mesoporous single-crystal-like CeO$_2$$^{28}$) have been prepared, in the synthesis of composite materials of CeO$_2$, getting a uniform, homogeneous size and a good morphology of CeO$_2$ with excellent performance was still very challenging. Because, firstly, the size of CeO$_2$ was very difficult to control; secondly, in many composites, whether CeO$_2$ could bond with other materials well and dispersed well were still the inevitable questions; thirdly, the ideal CeO$_2$’s crystallinity was difficult to be obtained; fourthly, the dispersibility of CeO$_2$ in composite materials still perplexed the researchers, which leads to the result that the prepared composite materials of CeO$_2$ were not stable, even CeO$_2$ could drop from the composite material, when composite material was sonicated. Not to mention, the poor photocatalytic activity was also followed. Thus, how to control the size, morphology, binding force and dispersibility of CeO$_2$ in composite materials, is considered to be very significant. If CeO$_2$ in composite materials could be controlled and synthesized well, it is likely that the composite materials might have some exciting performances or applied further for environment or industrial manufacture. Extravagant hopes could also be possessed: if CeO$_2$/g-C$_3$N$_4$ composites were successfully prepared, and the homogeneous CeO$_2$ nanocubes could be dispersed well onto g-C$_3$N$_4$, and formed a heterojunction structure, it was hopeful that CeO$_2$/g-C$_3$N$_4$ composites may become a multi-function photocatalyst.

Within this work, we demonstrated the preparation of g-C$_3$N$_4$ and CeO$_2$/g-C$_3$N$_4$ composites, and investigated the effect of different mass ratios of CeO$_2$/g-C$_3$N$_4$ and the pure g-C$_3$N$_4$ on photocatalytic performance. Photocatalytic experiments for improving the accuracy of the experimental data, exploiting stable, controllable and high-efficiency photocatalytic reactor has also been performed. The model of the photocatalytic reactor and all parameters were revealed. Moreover, a novel feature was found that 5% CeO$_2$/g-C$_3$N$_4$ could be used for highly efficient photoelectrochemical selective sensing of trace amounts of Cu$^{2+}$, because of its higher
photocurrent intensity, compared with g-C\textsubscript{3}N\textsubscript{4}. In conclusion, CeO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} composite is a novel and promising candidate for heavy metal ions (Cu\textsuperscript{2+}) determination in water environment, which will promote the further development of photocatalytic materials in practical applications of the environment. The developed photocatalytic reactor could also support the light-catalyzed reaction well, which also may be the photocatalytic reactors for further development.

2. Experimental section

2.1 Preparation of the g-C\textsubscript{3}N\textsubscript{4}

As shown in Figure S1, the preparation of g-C\textsubscript{3}N\textsubscript{4} was by heating dicyandiamide in the pipe furnace directly, 2g dicyandiamide was put into a crucible with a cover. Hit the temperature to 350\textdegree C within 90 min and kept 350\textdegree C for 2 h, and then made it rise to 600\textdegree C within another 90 min and kept 600\textdegree C for another 2 h. For consideration, the whole process of the reaction was taken under flowing-nitrogen atmosphere (200 ml/min). And the nubbly g-C\textsubscript{3}N\textsubscript{4} was grinded into the powder before further characterizations, as shown in Figure S1.

2.2 Preparation of the CeO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}

The g-C\textsubscript{3}N\textsubscript{4} (0.1 g) and a certain quantity of Ce(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O were added into 19 mL of H\textsubscript{2}O, and the suspension was stirred magnetically for 30 min, and then was sonicated for 30 min. Subsequently, 0.5 mL of NH\textsubscript{3}·H\textsubscript{2}O was injected into the mixture under magnetic stirring. Then, the mixture was transferred into a Teflon-lined stainless steel autoclave with 20 mL of capacity and the sealed tank was put into an oven and heated at 160\textdegree C for 12 h. The resulting product was separated by centrifuging and washed several times with distilled water and ethanol, respectively. Finally, the obtained composites were dried in air at 60\textdegree C for 8 h. According to this method, different molar ratios of the CeO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} samples were obtained and denoted as 2.5% CeO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}, 5% CeO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} and 10% CeO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}.

2.3 Photoelectrochemical measurements

The photocurrents were measured with an electrochemical analyzer (CHI660B, Chen Hua Instruments, Shanghai, China) in a standard three-electrode system, which
employed a platinum wire as the counter electrode, indium-tin oxide glass (ITO) as the working electrode, and Ag/AgCl (saturated KCl solution) as the reference electrode. 5 mg sample powder was dispersed ultrasonically in 1 mL of ethanol, and 20 µL of the resulting colloidal dispersion (5 mg/mL) was drop-cast onto a piece of ITO slice with a fixed area of 0.5 cm$^2$ and dried under the infrared lamp to form the sample modified ITO electrode. All the photocurrent measurements were performed at a constant potential of -0.2 V (vs. SCE). Sodium nitrate solution (NaNO$_3$, 0.1 M) was used as the supporting electrolyte for photocurrent measurements. A 500-W Xe arc lamp was utilized as the light source.

2.4 Photocatalytic reactor and photocatalytic activity

The organic dye methylene blue (MB) was used as a model pollutant. It could be known that MB had high photostability and water solubility, making this chemical difficult to be degraded using conventional wastewater treatment methods under visible light. The photocatalytic reaction was performed under a 300W Xe lamp with a 400 nm cutoff filter, and the model of photocatalytic apparatus was shown in Figure S2a, and schematic illustration of experimental setup was shown in Figure S2b. The photo-catalytic reactor was divided into two parts: one was the water cycle system and the other was the light source system, as shown in Figure S2b. The water cycle system controlled the temperature, which avoided interference of thermocatalytic to the light-catalyzed reaction. And the light source system insured the energy of light-catalyzed reaction. Moreover, to ensure that the light source system continued working normally, the water pressure controller was used to protect the light source system.

Typically, 0.025 g of sample was added into 50 mL MB (10 mg/L) in a Pyrex photocatalytic reactor. The air velocity was 2 L/min, and the temperature of reaction was 30°C under constant stirring. Prior to irradiation, the suspensions were magnetically stirred for 30 min in the dark to ensure that the MB could reach the absorption-desorption equilibrium on the photocatalyst surface. At certain time intervals, 3 mL aliquots were sampled and centrifuged to remove the photocatalyst particles. Then the filtrates were analyzed by recording variations of the absorption
band maximum (664 nm) in the UV-vis spectra of MB by using an UV-vis spectrophotometer (UV-2450 Shimadzu).

2.5 Characterization

The obtained CeO$_2$/g-C$_3$N$_4$ composites were characterized by X-ray diffraction (XRD) using Bruker D8 diffractometer with Cu Kα radiation ($\lambda=1.5418$ Å) in the range of 2θ=10-80°. The transmission electron microscopy (TEM) images were carried out on a JEOL-JEM-2010 (JEOL, Japan) operated at 200 kV. The Fourier transform infrared spectra (FT-IR) of the samples were recorded using Nicolet Nexus 470 spectrometer. Ultraviolet visible (UV-vis) diffuse reflection spectra were measured using a UV-vis spectrophotometer (Shimadzu UV-2450, Japan) in the range of 200 to 800 nm. BaSO$_4$ was used as reflectance standard material. X-Ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALab MKII X-ray photo-electron spectrometer using Mg Ka radiation.

3. Results and discussion

3.1 TEM and HRTEM analyses

To survey the morphology and microstructure of the CeO$_2$/g-C$_3$N$_4$, it was researched via transmission electron microscopy (TEM) (Figure 1). In Figure 1a and b, it was obvious that ultrafine CeO$_2$ presented cube structure, and the ultrafine CeO$_2$ nanocubes with size of 3-10 nm were anchored onto the g-C$_3$N$_4$. Moreover, the high-resolution TEM (HRTEM) image in Figure 1c displayed clear (111) lattice fringe with the interplanar spacing of 0.31 nm, implying that the ultrafine CeO$_2$ nanocubes are enclosed by the (111) planes (JCPDF no. 34-0394), which could be very important for the photocatalytic activity, because an exposed high-activity surface with high crystallinity was very significant to light-catalyzed reaction. From the Figure 1, it could be known that CeO$_2$ nanocubes and g-C$_3$N$_4$ closely bonded together and they did not separate after a long ultrasonication treatment at room temperature, and formed a heterojunction structure, which was very important to transfer inter-particle electron between component semiconductors. Such cube shapes had rarely been observed for CeO$_2$ in previous studies.
3.2 XRD and XPS analyses

The crystal structure of CeO$_2$/g-C$_3$N$_4$ composites was further studied by X-ray diffraction (XRD), as shown in Figure 2. The diffraction peak of the g-C$_3$N$_4$ at $\sim$13.1° correspond to the (100) planes and strong XRD peak of the g-C$_3$N$_4$ at $\sim$27.3° are (002) plane, which were interlayer stacking reflections. With increase of the content of CeO$_2$, the diffraction peaks at $\sim$33.1°, $\sim$47.5° and $\sim$56.3° gradually appeared and intensity increased gradually, and the peaks were assigned to the (200), (220), and (311) planes of CeO$_2$ crystal (JCPDS no: 34-0394), respectively. However, the diffraction peaks of CeO$_2$ at $\sim$28.5° assigned to the (111) planes of CeO$_2$ crystal were not observed from the patterns, which might be because of the relatively low percentage of CeO$_2$ in the composites, while the diffraction peaks of CeO$_2$ at $\sim$28.5° might be covered by the strong peak of g-C$_3$N$_4$ at 27.3°. Moreover, compared with the g-C$_3$N$_4$, in CeO$_2$/g-C$_3$N$_4$ composites, the characteristic interlayer stacking peak of aromatic systems of g-C$_3$N$_4$ has changed from $\sim$27.3° to $\sim$27.7°, and this smaller value of diffraction angle might be the attachment of the CeO$_2$.

To further confirm the composition and the chemical states of the samples, X-ray photoelectron spectroscopy (XPS) measurements were performed and the XPS spectra of C 1s, N 1s for the g-C$_3$N$_4$ and C 1s, N 1s, Ce 3d, O 1s for 5% CeO$_2$/g-C$_3$N$_4$ were provided, as shown in Figure 3. From Figure 3a and b, it was found that there was no obvious binding energy shift of C 1s and N 1s for 5% CeO$_2$/g-C$_3$N$_4$ and the g-C$_3$N$_4$, suggesting that the chemical states of both carbon and nitrogen in the 5% CeO$_2$/g-C$_3$N$_4$ were the same as in the g-C$_3$N$_4$. In Figure 3a, the peak located at $\sim$284.6 eV was related to carbon contamination, and was observed in the bulk g-C$_3$N$_4$ and 5% CeO$_2$/g-C$_3$N$_4$. The binding energy at $\sim$288.2 eV was assigned to sp$^2$-bonded carbon (C=N-C) of the g-C$_3$N$_4$ in the aromatic ring. In Figure 3b, it could be observed that 5% CeO$_2$/g-C$_3$N$_4$ had the same N 1s binding energy of g-C$_3$N$_4$ at $\sim$398.7 eV, which could be attributed to sp$^2$-hybridized nitrogen (C=N-C). Record all above confirmed the presence of sp$^2$-bonded graphitic carbon nitride in 5% CeO$_2$/g-C$_3$N$_4$. The XPS spectra of O 1s were shown in Figure 3c. From Figure 3c, two strong peaks at $\sim$529.4 eV and $\sim$531.6 eV for O 1s were obviously observed,
indicating that there were two forms of O species in the sample. The peak at ~529.4 eV was due to the lattice oxygen (O$^{2-}$ in the CeO$_2$).$^{33}$ Whereas the peak at ~531.6 eV was due to the chemisorbed oxygen.\textsuperscript{33} Ce 3d XPS spectra of 5% CeO$_2$/g-C$_3$N$_4$ could be assigned to be 3d$_{3/2}$ spin-orbit states (labeled u) and 3d$_{5/2}$ states (labeled v), as presented in Figure 3d. The bands v, v2, v3, u, u2 and u3 were attributed to Ce$^{3+}$, whereas v1 and u1 are due to Ce$^{4+}$.\textsuperscript{33-35} From Figure 3d, it could be found that the coexistence of Ce$^{3+}$/Ce$^{4+}$ oxidation states existed on the surface of the catalysts, which indicated that the catalyst surfaces might be not fully oxidized. According to the previous reports,\textsuperscript{22,35} these might lead to the conclusion that some oxygen vacancies might be produced.\textsuperscript{22,35} Records above might be very important to the performance of the photocatalyst, and the further research is still needed.

3.3 FT-IR, DRS and Photocurrent-time analyses

To make the structure of CeO$_2$/g-C$_3$N$_4$ clearly, the samples were analyzed by FT-IR spectra, as shown in Figure 4a. The FT-IR spectrum of various CeO$_2$/g-C$_3$N$_4$ was similar to g-C$_3$N$_4$, indicating that g-C$_3$N$_4$ in CeO$_2$/g-C$_3$N$_4$ kept the same chemical structure as g-C$_3$N$_4$. The broad peaks between 3600 and 3000 cm$^{-1}$ were caused by the N-H stretches, indicating that there could be dangling hydrogens in the C-N layers of the g-C$_3$N$_4$. The peaks at ~1242, 1322, 1412, 1563, and 1634 cm$^{-1}$ were typical stretching vibration modes of C=N and C-N heterocycles.\textsuperscript{9,32,36} The peak at 807 cm$^{-1}$ was the characteristic breathing mode of s-triazine ring system.\textsuperscript{32,36} And all characteristic vibrational peaks related to g-C$_3$N$_4$ could also be found in various CeO$_2$/g-C$_3$N$_4$, indicating that the structural integrity of g-C$_3$N$_4$ remained intact after the hydrothermal reaction.

To identify the photoelectric property and electronic structure of various CeO$_2$/g-C$_3$N$_4$, UV-vis diffuse reflectance spectroscopy (DRS) was used, as shown in Figure 4b. And it could be known that the UV-visible absorption spectrum of various CeO$_2$/g-C$_3$N$_4$ displayed a slight blue shift in comparison with the g-C$_3$N$_4$. The blue shift could be caused by the famous quantum confinement effect with the conduction and valence bands shifing in opposite directions.\textsuperscript{37-39} From Figure 4c, it could be known that the bandgaps of the g-C$_3$N$_4$, 2.5% CeO$_2$/g-C$_3$N$_4$, 5% CeO$_2$/g-C$_3$N$_4$ and
10% CeO$_2$/g-C$_3$N$_4$ were about 2.65, 2.83, 2.81 and 2.79 eV, respectively.

To make sure 5% CeO$_2$/g-C$_3$N$_4$ was an excellent photocatalyst, its electronic structure, photogenerated charge separation and electron transfer performance were investigated by the photocurrent-time analysis, as shown in Figure 4d. Under visible light irradiation, compared with g-C$_3$N$_4$ and the other mass samples, 5% CeO$_2$/g-C$_3$N$_4$ showed the best photocurrent responses, which was about twice higher than g-C$_3$N$_4$. What’s more, the photocurrents of 2.5% and 10% CeO$_2$/g-C$_3$N$_4$ were less than 5% CeO$_2$/g-C$_3$N$_4$ and they were close. Obviously, an appropriate CeO$_2$ ratio was very significant for increasing the photocurrent responses. The increased photocurrents of 2.5%, 5% and 10% CeO$_2$/g-C$_3$N$_4$ were due to the improved photoabsorption and photoresponsivity. Obviously, 5% CeO$_2$/g-C$_3$N$_4$ had less recombination and a more efficient separation of photogenerated electron and hole pairs, compared with g-C$_3$N$_4$ and the other mass content. Thus, 5% CeO$_2$/g-C$_3$N$_4$ could have the fascinating photocatalytic performance.

3.4 Nitrogen adsorption analysis

The Brunauer-Emmett-Teller (BET) specific surface area of all samples were carried out. From Figure S3, it could be known that the specific surface area of g-C$_3$N$_4$, 2.5%, 5% and 10% CeO$_2$/g-C$_3$N$_4$ were ~3.3, 68.4, 78.8 and 96.3 m$^2$/g, respectively. The surface area improved a lot, as the introduction of CeO$_2$ to g-C$_3$N$_4$. And BET of the composites were increased with the contents of CeO$_2$ increased from 2.5% to 10%, which could be caused by the interaction of CeO$_2$ and g-C$_3$N$_4$. It could be known that the large surface area was beneficial to the photocatalytic activity increase, due to more adsorption sites and photocatalytic reaction centers. Thus, CeO$_2$/g-C$_3$N$_4$ composites could have excellent photocatalytic performance.

3.5 Photocatalytic activity test and kinetics

The photocatalytic activity of the samples for the degradation of MB was evaluated under visible light irradiation, as shown in Figure 5a. The photocatalytic activity of the pure g-C$_3$N$_4$ was the lowest and the photocatalytic degradation efficiency was only ~56% after 3.5 h of visible light irradiation. Meanwhile, ~86.07%, ~89.16% and ~98.59% of MB were degraded using 10%
CeO$_2$/g-C$_3$N$_4$, 2.5% CeO$_2$/g-C$_3$N$_4$ and 5% CeO$_2$/g-C$_3$N$_4$, respectively. Obviously, 5% CeO$_2$/g-C$_3$N$_4$ had the optimal photocatalytic activity for MB decomposition, and an appropriate CeO$_2$ ratio in CeO$_2$/g-C$_3$N$_4$ nanocomposites could significantly improve the resulting photocatalytic activity. Moreover, from data above, it could be known that the photocatalytic degradation efficiency of the CeO$_2$/g-C$_3$N$_4$ composites was obviously and extensively improved, compared with the g-C$_3$N$_4$, and the optimal percentage of CeO$_2$/g-C$_3$N$_4$ was 5%. Moreover, the result in Figure 5c indicated that after 4 cycles, the photocatalytic activity of the 5% CeO$_2$/g-C$_3$N$_4$ only reduced a little, which could due to the loss of the photocatalyst during the experiments. Therefore, for industrial application, 5% CeO$_2$/g-C$_3$N$_4$ should be considered. In addition, XRD (Figure 6a) and FT-IR (Figure 6b) analyses of 5% CeO$_2$/g-C$_3$N$_4$ before and after the photocatalytic reactions was carried out. Obviously, both XRD and FT-IR spectra of 5% CeO$_2$/g-C$_3$N$_4$ before and after the photocatalytic reactions were similar. That is to say, the crystal structures and chemical structures of 5% CeO$_2$/g-C$_3$N$_4$ didn’t change after photocatalytic cycle, which obviously suggested that 5% CeO$_2$/g-C$_3$N$_4$ were stable during the photodegradation process.

The large BET could offer more adsorption sites and photocatalytic reaction centers. But the specific surface area was not a crucial factor for improving photocatalytic activity in CeO$_2$/g-C$_3$N$_4$ system. When the weight content of CeO$_2$ was increasing to 10%, the degradation rate of MB decreased, and the reason should be explained as follows: firstly, when the contents of CeO$_2$ increased to 10%, although the sample’s BET was the largest, a large amount of CeO$_2$ wrapped on the surface of g-C$_3$N$_4$, which hindered that g-C$_3$N$_4$ absorbed light. Secondly, a dense mass of CeO$_2$ cubes on the surface of g-C$_3$N$_4$ were not conducive to form heterojunction structure, yet could lead to the self-destruction of heterojunction structure. Thirdly, a large amount of CeO$_2$ cubes wrapping on the surface of g-C$_3$N$_4$ were harmful to the separation of electrons and holes, which leads to the reduction of the active sites in the CeO$_2$/g-C$_3$N$_4$ composites. All in all, the degradation rate of MB decreased when the weight content of CeO$_2$ was increasing to 10%. The optimal percentage of CeO$_2$/g-C$_3$N$_4$ was 5%.
The variations of UV-vis absorption spectra of MB degradation using g-C₃N₄ and CeO₂/g-C₃N₄ composites were shown in Figure 7a-d. It was obvious that after visible light illumination, with 5% CeO₂/g-C₃N₄ composites, the color of MB solution changed from blue to colourless during the reaction, as shown in Figure 7c and in the inset of Figure 7c. The peak intensity of the UV-vis absorption related to MB decreased sharply, and the main absorption band at 664 nm almost completely disappeared after 3.5 h, which indicated the chromophoric structure of the MB dye was decomposed. Improved photocatalytic activity could be ascribed to the synergistic effects of the effective combination of ultrafine CeO₂ cubes on g-C₃N₄, high crystallinity of the sample and the facile optical properties.

To understand the process of the light-catalyzed reaction, kinetics was used to analyze. It could be known that the kinetics of heterogeneous catalysis of a liquid-solid system has frequently been described using Langmuir-Hinshelwood (L-H) model, which was Equation 1.

\[ r = - \frac{dC}{dt} = \frac{k_r KC}{1 + KC + K_s C_s} \quad (1) \]

In Equation 1, \( k_r \) is the reaction rate constant, \( C \) is the concentration of the reactant, \( t \) is the reaction time, \( K_s \) is the adsorption coefficient of the solvent, \( K \) is the adsorption coefficient of the reactant and \( C_s \) is the concentration of the solvent. When the reactant is more strongly adsorbed than solvent, Equation 1 could be simplified to Equation 2. When the initial concentration of reactant is very low (\( KC \ll 1 \)), Equation 2 can be further simplified to Equation 3, where \( k_{app} \) represents the apparent reaction rate constant.

\[ r = - \frac{dC}{dt} = \frac{k_r KC}{1 + KC} = k_{app} \quad (2) \]

\[ r = \frac{dC}{dt} = k_r KC = k_{app} C \quad (3) \]

According to the previous work, it can be known that the photocatalytic reaction of MB can be described by the simplified L-H model. And Equation 3 can be written Equation 4:

\[ r = k_r K_{MB} = k_{app} C_{MB} \quad (4) \]
Moreover, the linear relationship of \( \ln(C_0/C) \) versus time is shown in Figure 5b and the kinetic constant \( (k) \) and regression coefficient \( (R^2) \) were calculated and given in Table 1. The results indicated that for all investigated photocatalysts, the photocatalytic degradation of MB followed first-order reaction dynamics under the experimental conditions. From Figure 5b, 5% \( \text{CeO}_2/\text{g-C}_3\text{N}_4 \) exhibited high apparent rate of 1.2686 h\(^{-1}\), which was 7.8 times as high as than that of \( \text{g-C}_3\text{N}_4 \) (0.1621 h\(^{-1}\)), and the \( k \) for MB degradation with the 2.5% and 10% \( \text{CeO}_2/\text{g-C}_3\text{N}_4 \) composites were estimated to be 0.5687 and 0.6226 h\(^{-1}\), respectively.

### 3.6 Photoelectrochemical selective sensing of \( \text{Cu}^{2+} \)

On account of increasing photocurrent intensity of 5% \( \text{CeO}_2/\text{g-C}_3\text{N}_4 \), excellent charge-carrier-transfer behavior and charge separation, 5% \( \text{CeO}_2/\text{g-C}_3\text{N}_4 \) was an ideal candidate material for photoelectrochemical application. On the other hand, owing to the fact that the photocurrent intensity of the \( \text{g-C}_3\text{N}_4 \) was low-grade, as shown in Figure 4d, from the comparison of 5% \( \text{CeO}_2/\text{g-C}_3\text{N}_4 \) composites and \( \text{g-C}_3\text{N}_4 \) for the detection of trace amounts of \( \text{Cu}^{2+} \), the photocurrent intensity of \( \text{g-C}_3\text{N}_4 \) was not sensitive enough, which was discussed in our previous work.\(^{32,42,43} \)

Therefore, in \( \text{g-C}_3\text{N}_4 \)-supported \( \text{CeO}_2 \) cubes, because of the more sensitive photoelectrochemical performance of 5% \( \text{CeO}_2/\text{g-C}_3\text{N}_4 \), it had been evaluated by the sensing of trace amounts of \( \text{Cu}^{2+} \) which was an essential element for living organisms but toxic at high concentrations.\(^{32,44} \) The rule of \( \text{Cu}^{2+} \) concentration on the photocurrent at the ITO/5% \( \text{CeO}_2/\text{g-C}_3\text{N}_4 \) electrode was found to be concentration-dependent in Figure 8a. The photocurrent of 5% \( \text{CeO}_2/\text{g-C}_3\text{N}_4 \) gradually increased when the concentration of \( \text{Cu}^{2+} \) increased. What’s more, a good linear relationship \( (R^2 = 0.9956) \) could be seen between the value of the photocurrent increasing. And the linear equation was \( y = 0.3056x + 5.8184 \), as shown in Figure 8b. The photocurrent intensities of ITO/5% \( \text{CeO}_2/\text{g-C}_3\text{N}_4 \) electrode in the presence and absence of \( \text{Cu}^{2+} \) and the concentration of \( \text{Cu}^{2+} \) over the range from 0 to 10 µM are very significant for the detection of trace amounts of \( \text{Cu}^{2+} \).

The mechanism of photoelectrochemical selective sensing of trace amounts of \( \text{Cu}^{2+} \) was discussed in detail, as shown in Figure 9. When 5% \( \text{CeO}_2/\text{g-C}_3\text{N}_4 \) was
irradiated with visible light, it absorbed photons, meanwhile it excited electron and hole pairs. Based on the band gap theory, the band gap of CeO$_2$ was 2.92 eV, which was higher than that of g-C$_3$N$_4$ (2.65 eV). The excited electrons in the conduction band of g-C$_3$N$_4$ could be easily transferred to surface of the CeO$_2$, and then transferred to the ITO electrode and generated the photocurrent because the energy level of the conduction band of ITO was low. And the generated holes could move to the surface of g-C$_3$N$_4$, which promoted the effective separation of photoexcited electron-hole pairs and decreased the probability of electron and hole recombination. Then photoexcited electrons moved to the ITO and then to the Pt electrode, so it could formed a closed circuit. In the presence of Cu$^{2+}$, Cu$^{2+}$ could be seen as the electron acceptor. The excited and transferred electrons could be accepted by Cu$^{2+}$ to form metal Cu, and then metal Cu deposited on the Pt electrode. This phenomenon can be observed when the duration of light was extended. There were tiny yellow metal Cu particles on the surface of Pt electrode as Cu$^{2+}$ could capture the electrons and continuously form metal Cu, and the details were in previous work. According to previous reports, it could be known that the selection determination of Cu$^{2+}$ could mainly come from g-C$_3$N$_4$ in the CeO$_2$/g-C$_3$N$_4$ composite. Although g-C$_3$N$_4$ had detection signal for selection determination for Cu$^{2+}$, g-C$_3$N$_4$’s photocurrent intensity was not high enough. Thus, the sensitivity of Cu$^{2+}$ is weak. Nevertheless, 5% CeO$_2$/g-C$_3$N$_4$ had the better photocurrent, which overcame g-C$_3$N$_4$’s defects of the weak photocurrent well. The function of the appropriate CeO$_2$ in the composite could be to transfer electrons, which resulted in the less recombination and a more efficient separation of photogenerated electron and hole pairs. Thus, the selection determination of Cu$^{2+}$ could mainly come from g-C$_3$N$_4$, the introduction of CeO$_2$ improved the sensitivity of the determination for Cu$^{2+}$. Finally, the synergistic effect of CeO$_2$ and g-C$_3$N$_4$ led to the selective and sensitive detection of trace amounts Cu$^{2+}$.

Compared with traditional methods of the detection of trace amounts of Cu$^{2+}$, such as flame atomic absorption method, the photoelectrochemical method is especially suited to selectively sense of the trace concentration of Cu$^{2+}$, as well as
sensitive, simple, timesaving and economic which due to this method avoids the preconcentration process and relatively expensive apparatus required for the fluorescence method, flame atomic absorption method.

To assess the selectivity of the 5% CeO$_2$/g-C$_3$N$_4$ as well as to trace amounts of Cu$^{2+}$, the effect of different metal ions (Ag$^+$, Co$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, Cu$^{2+}$, Hg$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$) with the concentration of 4.0 $\mu$M on the photocurrent intensities were investigated, as shown in Figure 8c. It could be effectively observed that the ITO/5% CeO$_2$/g-C$_3$N$_4$ electrode was much more sensitive to Cu$^{2+}$ than to the other metal ions. Owing to the highly sensitive and selective increased effect of Cu$^{2+}$ on the photocurrent intensity of ITO/5% CeO$_2$/g-C$_3$N$_4$ electrode, a highly selective and sensitive sensor for the detection of Cu$^{2+}$ was further developed in metal oxide composites.

4. Conclusions

Finally, the CeO$_2$/g-C$_3$N$_4$ composites were prepared successfully by a simple and facile hydrothermal method. Thereinto, CeO$_2$ with 111 planes was in the shape of the cube (from ~3 to 10 nm). After the introduction of CeO$_2$, the photocatalytic activities of g-C$_3$N$_4$ on MB degradation under visible light irradiation increased dramatically. The results indicated that 5% CeO$_2$/g-C$_3$N$_4$ exhibited the optimal photocatalytic performance. The further studies confirmed that 5% CeO$_2$/g-C$_3$N$_4$ could be used as for the detection of trace amounts Cu$^{2+}$ in water environment. In addition, the excellent photocatalytic reactor had also been exploited successfully, which could promote the further development of photocatalysis technology. In conclusion, this report could be useful for preparation of particles, especially with a view to filtrating photocatalyst, promoting the material properties and expanding the practical application of the photocatalysis technology.
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Notes and References