Research Article

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Synthesis, characterization, and photocatalysis of a rare-earth cerium/silver/zinc oxide inorganic nanocomposite

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Abstract: A cerium/silver/zinc oxide (Ce/Ag/ZnO) inorganic nanocomposite was synthesized through a homogeneous precipitation method. The characterization and photocatalysis procedures were carried out by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photo-electron spectroscopy (XPS), UV-Vis diffuse reflection spectroscopy, and photocatalytic performance. The characteristic absorption peak of ZnO was near 432 cm⁻¹, no absorption was observed peak near 1,083 cm⁻¹ for CeO₂ and ZnO, the absorption peak near 721 cm⁻¹ was generated by the vibration of CeO₂, and the absorption peak had an obvious blue shift. The XRD results showed a strong interfacial interaction among Ag, CeO₂ and ZnO to form a core–shell structure. The SEM image showed that the Ce/Ag/ZnO samples are approximately 25 nm. The XPS spectra showed that the Ce/Ag/ZnO nanocomposite powders were successfully prepared. The UV-Vis diffuse reflection spectra showed that the Ce/Ag/ZnO nanocomposites reduced the band gap and increased the ability of visible light response. The addition of rare earth Ce could inhibit the recombination of ZnO photoelectron pairs and improve the photocatalytic effect. Therefore, Ce/Ag/ZnO exhibited good characteristics of nanocomposite materials and good photocatalytic ability.

Keywords: cerium/silver/zinc oxide, nanocomposite, characterization, band gap, photocatalysis ability

1 Introduction

Currently, nanoinorganic antibacterial agents, which have advantages such as small size effects, macroscopic quantum tunneling, and surface effects, exhibit properties including a broad antibacterial spectrum, effective antibacterial activity, good stability, and no antibiotic resistance mechanism [1–4]. Rare earth elements have active coordination properties due to their unique electron configuration and have attracted much attention in biomedical fields such as antibacterial, antitumor, and biocompatibility [5,6]. In the early stage, our research group carried out the synthesis and characterization of the nanocomposite Sm/Ag/TiO₂ and examined its antibacterial properties [7]. Cerium (Ce) is the most abundant rare earth metal in lanthanides [8], and it possesses two oxidation states, Ce³⁺ and Ce⁴⁺. Cerium oxide (CeO₂) has a large number of surface defects, high oxygen storage capacity, excellent chemical and structural stability, and a wide range of applications in alloys, phosphors, catalysis, magnetism, medicine, and other fields [9,10]. Silver nanoparticles, titanium dioxide nanoparticles, and zinc oxide nanoparticles are common inorganic antibacterial agents that are used in stomatology. Among them, zinc oxide nanoparticles are antibacterial agents that are multifunctional and environmentally friendly. Zinc oxide nanoparticles exhibit chemical stability, biocompatibility, photocatalytic bactericidal activity, broad-spectrum antibacterial ability, and low bacterial resistance [11]. Nanoparticles, and low toxicity to mammalian tissues. The composite of the three components can produce a synergistic effect to improve its biocompatibility, reduce the toxicity of materials, and obtain a better antibacterial effect.

Therefore, nanocomposite Ce/Ag/ZnO was synthesized by the homogeneous precipitation method. The main objective of this experiment was to study the characterization
and photocatalysis of the inorganic nanomaterial Ce/Ag/ZnO. This study provided necessary data to support this antibacterial material in medical applications.

2 Materials and methods

2.1 Preparation of the inorganic Ce/Ag/ZnO nanomaterials

The solution was prepared by dissolving 12 g of Zn(NO$_3$)$_2$·6(H$_2$O) in 200 mL of deionized water, dissolving 0.12 g of silver nitrate and 0.12 g of cerium nitrate tetrahydrate in the above zinc nitrate solution, and fully mixing the solution. Then, 300 mL of 0.25 mol·L$^{-1}$ NaOH solution was slowly added to the mixture at a rate of 3 drops·min$^{-1}$ with constant stirring, and a white precipitate was obtained. The precipitate was washed with deionized water and anhydrous ethanol three times and then dried at 70°C for 4 h to obtain the precursor. Then, the precursor was annealed at 300°C, 400°C, and 500°C for 4 h in a tube resistance furnace. Finally, the sample powder Ce/Ag/ZnO was obtained.

2.2 Characteristic analysis

The ZnO, Ag/ZnO, and Ce/Ag/ZnO powders were characterized by Fourier transform infrared (FT-IR) spectroscopy (BRUKER VERTEX70). The Ce/Ag/ZnO powders were characterized by X-ray diffraction (BRUKER D8 ADVANCE) with a Cu target X-ray tube at 40 kV and 30 mA and a scanning range of 20–80°. The particulate morphology of Ce/Ag/ZnO was observed by scanning electron microscopy (HITACHI S-4800). The Ag/ZnO and Ce/Ag/ZnO spectra were analyzed by X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha Nexsa) with Al Kα X-ray, and the binding energy standard was C1s = 284.80 eV. The Ag/ZnO and Ce/Ag/ZnO spectra were analyzed by UV-Vis diffuse reflection spectroscopy (UV-3600).

2.3 Photocatalytic performance

A 300 mL methyl orange solution with a certain concentration was prepared under a normal temperature, and then, a certain concentration of sample reserve solution and a certain amount of buffer solution were added. After stirring in a dark room for 30 min, ultrasonic dispersion was performed for 3 min, a UV lamp was applied to irritate the solution 15 cm away from the liquid level, and 5 mL of solution was removed every 20 min. The absorbance $A$ was measured at 464 nm. The standard curve equation of methyl orange concentration and absorbance was obtained as follows:

$$A = 0.0715 C + 0.013 \quad (1)$$

According to the curve equation, the degradation rate was

$$X = (C_0 - C_t)/C_0 \quad (2)$$

where $C_0$ and $C_t$ are the initial concentration of methyl orange and the concentration at time $t$, respectively. The degradation rate of methyl orange was proportional to photocatalysis.

3 Results and discussion

3.1 Fourier transform infrared spectroscopy analysis

Figure 1 shows that in the infrared spectra of the ZnO, Ag/ZnO, and Ce/Ag/ZnO nanocomposites, there was a wide absorption peak of –OH near 3,440 cm$^{-1}$. This result showed that there was a large amount of hydroxide in the samples. The absorption peak near 1,647 cm$^{-1}$ was the H–O–H bending vibration peak in free water.

![Figure 1: FT-IR of ZnO, Ag-ZnO, and Ce/Ag/ZnO spectra.](image-url)
The absorption peak near 721 cm$^{-1}$ was generated by the vibration of CeO$_2$, and the absorption peak had an obvious blue shift. The characteristic absorption peak of ZnO was near 432 cm$^{-1}$. CeO$_2$ and ZnO had no absorption peak near 1,083 cm$^{-1}$, and the Ce–O–Zn bond absorption peak was possibly formed due to bond cooperation between CeO$_2$ and ZnO. These results showed that the Ce–O–Zn bond might be formed during the synthesis of Ce/Ag/ZnO composite powder, which was beneficial in improving the properties of the composite powder.

### 3.2 XRD analysis

Figure 2 shows the XRD patterns of the ZnO, Ag/ZnO, and Ce/Ag/ZnO nanocomposites. Compared with the XRD peaks of the ZnO and Ag nanoparticles, the Ag nuclei were completely covered by Ce and ZnO shells, so the diffraction peaks of Ag nuclei were lower than those of the pure Ag nanoparticles. In the Ce/Ag/ZnO nanostructures, no obvious shift was observed in the Ag and ZnO diffraction peaks, which indicated that there was a strong interfacial interaction among Ag, CeO$_2$, and ZnO to form a core–shell structure.

The diffraction peaks at $2\theta = 28.58, 33.12, 47.54,$ and $56.42^\circ$ were consistent with the characteristic peaks of the JCHS CeO$_2$ standard card. The diffraction peaks at $2\theta = 31.76, 34.42, 36.25, 47.53,$ and $56.6^\circ$ were consistent with the characteristic peaks of the JCHS ZnO standard cards. The $2\theta = 28.40, 33.34, 69.58,$ and $76.66^\circ$ diffraction peaks were consistent with the characteristic peaks of the JCHS Ag/ZnO standard cards. The samples were a mixture of CeO$_2$, ZnO, and Ag/ZnO. The prepared Ce/Ag/ZnO nanocomposite powders were not only mixed at the atomic level of CeO$_2$, ZnO, and Ag/ZnO but also had Ce–O–Zn bonds. The results showed that the Ce/Ag/ZnO nanocomposites were successfully prepared.

### 3.3 SEM measurements

The particle sizes of the two samples are relatively uniform, and there is a small amount of agglomeration (Figure 3). The average particle size of the Ag/ZnO samples is approximately 30 nm, and that of the Ce/Ag/ZnO samples is approximately 25 nm, which is in good agreement with the predicted value of Scherrer's formula.

The structure of the Ce/Ag/ZnO nanocomposites was magnified 10,000 times under SEM, with a thickness of approximately 0.1–0.3 $\mu$m and a diameter of approximately 1 $\mu$m (Figure 4). After ion modification, the original

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**Figure 2:** Powder XRD analysis of ZnO, Ag/ZnO, and Ce/Ag/ZnO.

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**Figure 3:** SEM patterns of Ag/ZnO and Ce/Ag/ZnO: (a) Ag/ZnO, (b) Ce/Ag/ZnO.
The structure of the Ce/Ag/ZnO nanocomposites magnified 10,000 times under SEM.

physical structure was not changed, which was consistent with the characterization results.

### 3.4 XPS spectra

Figures 5 and 6 show that the C–C/C–H binding energy of C1s adsorbed carbon was 284.8 eV to calibrate all spectral peaks, and Avantage software was used to perform peak fitting for the XPS data. The XPS spectra showed that the C1s, O1s, N1s, Zn2p, Ag3d, and Ce3d were observed. The XPS spectra of Ag/ZnO and Ce/Ag/ZnO showed that the binding energy deviation was ±0.2 eV, and the Ce/Ag/ZnO nanocomposites were successfully prepared.

### 3.5 UV-Vis diffuse reflection spectroscopy

When the formation rate of the crystal nucleus is greater than its growth rate, the UV absorption of the product is related to the particle size; the smaller the particle size, the higher the UV absorption value. Figures 7 and 8 show that the UV shielding performance of ternary composite powder was better than that of binary powder. The band gap width corresponding to the Ag/ZnO and Ce/Ag/ZnO composite samples was calculated by the formula. The figure shows that the absorption band of the Ag/ZnO composite samples was approximately 410 nm, $E_g = 4.68$ eV. The absorption band of the Ce/Ag/ZnO composite samples was about 415 nm, $E_g = 4.62$ eV. The results showed that the preparation of Ce/Ag/ZnO composite samples greatly reduced the band gap width, increased the ability of composite samples to have a visible light response, and improved the photocatalytic efficiency [13].

### 3.6 Photocatalytic analysis

The anionic surfactants used in the experiment were sodium dodecylbenzene sulfonate (SDBS) and sodium polyacrylate (PAAS). The experimental conditions included a pH of 7.0, the methyl orange solution in the concentration range of $0 − 2.0 \times 10^{-2}$ g·L$^{-1}$, and the sample solution at a concentration of 8 mg·L$^{-1}$. Figure 9 shows that the degradation rate of the Ce/Ag/ZnO samples to methyl orange was greater than that of the Ag/ZnO samples, and the degradation rate of methyl orange in the surfactant group was almost zero. Figure 10 shows that the degradation rate of methyl orange by adding surfactant PAAS to the sample was significantly higher than that by adding surfactant SDBS, and the maximum degradation rate reached approximately 90%. Therefore, the above results showed that the addition of rare earth Ce could inhibit the recombination of ZnO photoelectron pairs and improve the photocatalytic effect [14]. At the same time, the results showed that the performance of the surfactant PAAS is better than that of SDBS, and it could improve the dispersion of nanoparticles, reduce the surface energy, and improve the photocatalysis of Ce/Ag/ZnO.

In the study of the nanocomposite Sm/Ag/TiO$_2$, we found that the photocatalytic activity was proportional to the antibacterial activity [7]. When the energy of incoming radiation from the outside exceeds the band gap of the nanoparticle, the electron-stimulated transition produces a highly active photogenic hole ($h^+$) and photogenic electron ($e^-$). $e^-$ and $h^+$ react with oxygen, hydroxyl, and water adsorbed on the surface of the material to produce ROS such as hydroxide, oxygen anions, and hydrogen peroxide, thus inducing optical toxicity [15]. Reactive oxygen species with strong oxidation damage the integrity of cells, affect the metabolism of cellular energy, interfere with DNA replication, destroy protein expression, and eventually lead to cell apoptosis [16,17]. In addition, we found in the antibacterial test that the MIC and MBC of Ce/Ag/ZnO were 0.156 and 0.313 mg·mL$^{-1}$, respectively [18]. According to “The chemical industry standards of the People’s Republic of China: inorganic antibacterial performance and evaluation,” a material that exhibits a bacteriostatic effect is considered to be a bacteriostatic agent when used with a concentration of less than 800 μg·mL$^{-1}$.

Therefore, the photocatalytic properties of nano-materials can induce optical toxicity and thus exert antibacterial activity [19], which can also indirectly indicate that the Ce/Ag/ZnO composite has good antibacterial activity.
Figure 5: Full spectrum XPS analysis diagram of Ag/ZnO.
Figure 6: Full spectrum XPS analysis diagram of Ce/Ag/ZnO.
4 Conclusion

This study showed that Ce/Ag/ZnO exhibited good nano-composite material characteristics and photocatalysis ability. This study also found that the surfactant sodium polyacrylate (PAAS) could improve the photocatalytic activity of Ce/Ag/ZnO nanocomposites. Therefore, the feasibility of the combined application of Ce/Ag/ZnO nanocomposites with surfactant sodium polyacrylate (PAAS) and oral therapy materials should be explored.
in the future. This study provided the necessary data to support this kind of antibacterial material in antibacterial mechanisms and medical applications.

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