available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on Environmental and Energy Catalysis for Sustainable Development)

Light-induced ZnO/Ag/rGO bactericidal photocatalyst with synergistic effect of sustained release of silver ions and enhanced reactive oxygen species

Yunyan Wu ^a, Lili Zhang ^a, Yazhou Zhou ^a, Lili Zhang ^b, Yi Li ^a, Qinqin Liu ^{a,*}, Juan Hu ^a, Juan Yang ^{a,#}^a School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, Jiangsu, China^b Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials, School of Chemistry and Chemical Engineering, Huaiyin Normal University, Huaian 223300, Jiangsu, China

ARTICLE INFO

Article history:

Received 13 August 2018

Accepted 13 October 2018

Published 5 May 2019

Keywords:

Zinc oxide

Silver nanoparticle

Reduced graphene oxide

Sustained Ag⁺ ions release

Synergistic antibacterial mechanism

Reactive oxygen species

ABSTRACT

Silver nanoparticles (Ag NPs) can effectively address the issue of antibiotic-resistant bacterial infections to reduce the potential toxicity of Ag NPs. Although challenging, it is, therefore, necessary to achieve the sustainable release of Ag⁺ ions from a finite amount of Ag NPs. This study aims at designing an efficient and benign antimicrobial silver-based ternary composite composed of photocatalysis zinc oxide (ZnO) and reduced graphene oxide (rGO) as a carrier, in which the reactive oxygen species (ROS) excited from ZnO and Ag⁺ ions released from the Ag NPs cooperate to realize an effective antibacterial activity against *E. coli* and *S. aureus*. The constant effective bacterial performance of the ternary photocatalyst with minimum Ag content can be attributed to the increase in the available quantity of ROS, which results from the enhanced separation efficiency of the photogenerated carriers. The proposed system notably realized the long-term sustainable release of Ag⁺ ions with low concentration for 30 days when compared with an equivalent amount of silver nitrate. Moreover, the use of the composite prevents biotoxicity and silver wastage, and imparts enhanced stability to the long-lasting antibacterial efficacy.

© 2019, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Nowadays, antibiotic therapy is widely developed for the treatment of bacterial infections that threaten public health. The misuse of antibiotics leads to the dramatic emergence of super-bacteria with antibiotic resistance, which is considered as one of the three major threats to human health by the World Health Organization [1–3]. Thus, methods that effectively resolve drug-resistance should be evaluated [4]. Bacterial resistance can be addressed by developing novel bacteriostatic

formulations based on nanoparticles, including metal-based nanoparticles (gold, silver, copper) or metal-oxide materials (ZnO, TiO₂, CeO₂) [5,6]. Noble silver nanoparticles (Ag NPs) have been practically utilized in several medical products because of their effective broad-spectrum antibacterial activity [7,8]. The antibacterial mechanism of Ag NPs is mainly attributed to the destruction of the cell membranes of pathogens under ambient conditions because of the Ag⁺ ions released in the oxidization of Ag NPs [9,10]. However, a sudden and large release of Ag⁺ ions induced by the uncontrollable oxidization

^{*} Corresponding author. Tel: +86-511-88780195; E-mail: qqliu@ujs.edu.cn[#] Corresponding author. Tel: +86-511-88780195; E-mail: yangjuan6347@ujs.edu.cn

This work was supported by the National Natural Science Foundation of China (51472101, 51572114, 21773062, 21577036) and the Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials (JSKC17003).

DOI: 10.1016/S1872-2067(18)63193-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 5, May 2019

behavior of Ag NPs may cause cell toxicity and impair their stability and usage in long-term applications, which may result in an environmental hazard and increased health safety risk [11]. To balance their antibacterial efficacy and potential toxicity, the use of Ag NPs should be minimized to achieve an effective antibacterial effect and control and maintain the sustained release of Ag⁺ ions in low concentration [12–14].

The introduction of suitable carriers can effectively improve long-term sustainability of low-concentration Ag NPs. Graphene oxide (GO) having a monolayer structure and exhibiting good biocompatibility is considered as a reliable bio-platform for drug carriers [15]. In addition, GO with abundant oxygen-containing groups can serve as a fixed platform to provide sufficient anchoring sites for the attachment of silver cations and the growth of the Ag NPs. The aggregation of Ag NPs can, therefore, be prevented due to the confinement effect of GO, which promotes the sustainable stability and antimicrobial efficacy of the Ag/GO composites. Furthermore, the release of Ag⁺ ions is the predominant bactericidal mechanism observed in the Ag/GO composites [16,17]. To reduce the potential toxicity of the Ag/GO composites, strategies to minimize the use of Ag NPs in the composite and maintain the effective antimicrobial efficacy are required.

Compared with conventional methods, photocatalysis is more applicable because of its low cost, low toxicity, and high stability under facile conditions. Under solar irradiation, the high efficiency of reactive oxygen species (ROS) could be generated from the photocatalyst to attack the cell wall and membrane of *E. coli*, which leads to the death of the cell [18,19]. As green technology, environment-friendly photocatalytic sterilization does not induce antibiotic resistance and biotoxicity [20–22]. Kong et al. [23] reported that the TiO₂-biocidal polymer nanocomposites synthesized by a surface-initiated photo-polymerization method exhibited excellent photocatalytic antibacterial capabilities. Surendra et al. [24] photosynthesized CeO₂ NPs via the route of the *Moringa oleifera* peel extract, which exhibited good antibacterial properties. Sun et al. [25] achieved good antibacterial activity in a GO/g-C₃N₄ composite through photocatalytic disinfection under visible light. In particular, ZnO NPs, regarded as a recognized safe material by US Food and Drug Administration (21 CFR 182.8991), are attracting increasing attention because of their broad antibacterial activities against microorganisms and good biocompatibility with humans and the environment [26–29]. However, bare ZnO NPs exhibited a low photoenergy conversion efficiency because of the rapid recombination of photogenerated electron-hole pairs [30,31]. The hybridization of Ag NPs with ZnO NPs may have a two-fold advantage. The amount of Ag NPs required for effective bactericidal performance can be significantly reduced by the auxiliary photocatalytic bactericidal effect of ROS. In addition, the surface plasmon resonance (SPR) effect of Ag NPs can increase the separation rate of the photogenerated electron-hole pairs of ZnO, thereby enhancing the ROS activity and improving the antimicrobial efficacy [7,32–35]. Hence, the combination of minimum Ag NPs with ZnO NPs can potentially replace noble Ag for practical applications because of its optimized antibacterial efficiency, low toxicity, and reduction in

noble Ag wastage.

In this study, a benign antimicrobial material, i.e., a ZnO/Ag/rGO ternary composite, was developed in which Ag⁺ ions released from Ag NPs and ROS excited from ZnO photocatalysts cooperate to achieve an effective antibacterial performance against drug-resistant species. Typical bacteria *E. coli* and *S. aureus* were used to study the antibacterial activity in detail, and the photocatalytic disinfection of the composites was carried out under electromagnetic radiation. The ZnO/Ag/rGO ternary composite exhibited a superior antibacterial efficiency as compared to the ZnO/rGO and Ag/rGO composites. Furthermore, the optimized amount of Ag NPs in the ternary composite was determined to clarify the synergistic antiseptic action. Moreover, the use of rGO as a carrier enables the ternary composite to improve the stability for sterilization with the long-term slow release of Ag⁺ ions, implying its potential use as a novel disinfection photocatalyst for practical applications.

2. Experimental

2.1. Materials

Ethanol (99.9%), zinc acetate (Zn(CH₃COO)₂·2H₂O), sodium hydroxide (NaOH), and silver nitrate (AgNO₃) were purchased from Sigma-Aldrich. Graphene oxide was prepared via the modified Hummer method.

2.2. Synthesis of ZnO/Ag/rGO composites

Graphene oxide was dispersed in ethanol and sonicated under ambient conditions to obtain a brown dispersion, and Zn(CH₃COO)₂·2H₂O dissolved in ethanol was then added to the brown dispersion under magnetic stirring. Thereafter, 30 mg of NaOH dissolved in 5 mL of distilled water was added to the mixture. After stirring, the AgNO₃ solution was added. The weight ratios of AgNO₃ and GO were adjusted to 1:1, 1:2, and 1:3. The mixture was reacted at 160 °C for 24 h in a Teflon-lined stainless steel autoclave, thoroughly washed with deionized water, and freeze-dried. The as-obtained composites fabricated with AgNO₃:GO weight ratios of 1:1, 1:2, and 1:3 were denoted as ZRA 1-1, ZRA 1-2, and ZRA 1-3, respectively. For comparison, ZnO/rGO and Ag/rGO composites were prepared using the same method without Zn(CH₃COO)₂·2H₂O and AgNO₃, respectively.

2.3. Materials characterization

The structure phases were characterized by X-ray diffraction (XRD) using a Dutch Philips 1730 X-ray diffractometer with a Cu K α target test source and scanning speed of 8°/min. The morphological structure of the sample was analyzed using a JSM-7001F scanning electron microscope (SEM) and JEOL 2011 transmission electron microscope (TEM) at an acceleration voltage of 200 kV. The interplanar spacing of the nanoparticles was determined using an American FEI company Tecnai G2 high-resolution transmission electron microscope (HRTEM)

by the high-angle ring dark-field scanning transmission electron microscopy spectrometer mapping (HAADF-STEM-EDS mapping) characterization of the selected area element. The measurement of the antimicrobial activity was conducted using the modified Kirby-Bauer method. The surface composition of the sample was characterized by a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer (XPS) using an Al $K\alpha$ target (1486.6 eV), test power of 150 W, and 500 μm beam spot.

2.4. Photocatalytic test

The compound rate of the luminous carrier of the sample was analyzed using a QuantaMaster™ 40 steady transient fluorescence measurement system (PL). The ROS, including $\text{O}_2^{\cdot-}$ (peroxide) and $\cdot\text{OH}$ (hydroxyl radicals) from the solution of the ZnO/rGO and ZnO/Ag/rGO composites, was identified and quantified using a JES FA200 electron-spin resonance (ESR) spectrometer with spin trapping. Using DMPO as a capture agent, the $\cdot\text{OH}$ signal was detected in the aqueous solution and the $\text{O}_2^{\cdot-}$ signal in the methanol solution. The samples were dispersed in solution, and the signal intensity of the ROS in solution was then detected under low-light conditions and exposure to a 300 W Xe lamp after 4, 8, and 12 min.

2.5. Antibacterial test

Gram-negative bacteria *Escherichia coli* (*E. coli*) and gram-positive bacteria *Staphylococcus aureus* (*S. aureus*) were selected as the experimental strains. The bacteria were cultured in a Luria-Bertani (LB) medium and suspended in a phosphate-buffered saline (PBS) solution. The antimicrobial germicidal properties of the composites were determined under low-light conditions and exposure to a 300 W Xe lamp by using the common Agar diffusion method. The release rate of silver ions, which is related to the toxicity, was determined using an inductively coupled plasma optical emission spectrometer (ICP-OES; VISTAMPX, Varian Inc.).

2.5.1. Agar diffusion method

The *E. coli* and *S. aureus* bacteria were removed from the freezer ($-79\text{ }^\circ\text{C}$) and activated overnight. Thereafter, the bacteria were transferred and cultured to a logarithmic stage of growth, and then the concentrations of the bacteria were diluted to 1/1000 using PBS. Moreover, 100 μL of the diluted bacterial solution was applied to the solid LB medium plate. A sterilized Oxford cup was used to perforate the plate, and the bottom of the holes was sealed using a small amount of the unfrozen solid LB medium. Thereafter, a 50 μL solution of ZnO/Ag/rGO composites with different concentrations was added to the hole. In addition, 50 μL of sterilized water was added as contrast. The culture dish was then placed in a $37\text{ }^\circ\text{C}$ incubator under light and cultured for 24 h, to observe the growth of the bacteria.

2.5.2. Minimum inhibitory concentration (MIC) test

The bacteria were cultured to a logarithmic growth phase and then transferred into another LB medium. Different

amounts of composite materials were added to the several groups of mixture, to obtain different concentrations. No composite material was added to the control group. The mixture was then placed in an incubator to promote the culture $37\text{ }^\circ\text{C}$ under a 300 W Xe lamp. To obtain the growth curve of the bacteria, the bacterial solution was recorded every hour, from which the absorbance was measured using a UV-Vis spectrophotometer at 600 nm (OD_{600}).

2.5.3. Minimum bactericidal concentration MBC test

A pre-experiment was conducted prior to the MBC test. The results revealed that the composites prepared using AgNO_3 and GO with a weight ratio of 1:2 killed the *E. coli* and *S. aureus* at concentrations of 100×10^{-6} and $120 \times 10^{-6}\text{ }\mu\text{g/mL}$ within 3 h, respectively. The bacteria were cultured to a logarithmic growth phase in the LB medium, then re-suspended in the PBS and diluted to an OD_{600} value of 0.02. The composites were added to two groups of mixture to obtain the concentrations of 100×10^{-6} and $120 \times 10^{-6}\text{ }\mu\text{g/mL}$, which correspond to *E. coli* and *S. aureus*, respectively. Two groups without material were used as control groups. The mixture was then set in an incubator to promote the culture at $25\text{ }^\circ\text{C}$ under a 300 W Xe lamp. Moreover, 1 μL of the bacterial solution was extracted in 30 min intervals and diluted to 1/1000 using the PBS. After the dilution, a 100 μL solution was applied to the solid LB medium plate, and then cultured in an oven at $37\text{ }^\circ\text{C}$ for 24 h, to observe the colony growth on the plate.

2.6. Ag⁺ release

The Ag⁺ release experiment was conducted to investigate the stability and antibacterial mechanism of ZRA 1–2. Thereafter, 20 mL of 1 mg/mL ZRA 1–2 aqueous solution was exposed to the outdoor environment with slow magnetic stirring. After a given time interval, 1 mL of the solution was extracted, and the ZRA 1–2 was removed by centrifugation. The amount of Ag⁺ released into the solution was measured using ICP-OES, to evaluate the stability of the materials. Moreover, the AgNO_3 was used as the control.

3. Results and discussion

3.1. Formation of ZnO/Ag/rGO composites

The crystal structures of the ZnO/Ag/rGO ternary composites were characterized using XRD, and the XRD patterns of the ZnO/rGO and Ag/rGO composites are presented as references in Fig. 1(a). For the ZnO/rGO composite, the characteristic peaks at $2\theta = 31.8^\circ, 34.4^\circ, 36.3^\circ, 47.5^\circ, 56.6^\circ, 62.9^\circ, 66.4^\circ, 68.0^\circ, 69.1^\circ, 72.6^\circ, 77.0^\circ, 81.4^\circ$, and 89.6° correspond to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202), (104), and (203) crystal planes of hexagonal wurtzite ZnO (JCPDS No. 36-1451), respectively. Moreover, the broad diffraction peak at $2\theta = 24.1^\circ$ can be attributed to the (002) crystal plane of rGO, thus indicating the co-existence of ZnO and rGO. For the Ag/rGO composite, the characteristic diffraction peaks at $2\theta = 38.1^\circ, 44.3^\circ, 64.4^\circ, 77.4^\circ, 81.5^\circ$ and

Fig. 1. X-ray diffraction patterns of as-prepared samples. (a) ZnO/rGO and ZnO/Ag/rGO composites; (b) ZnO/Ag/rGO composites prepared using AgNO_3 and GO with weight ratios of 1:1 (ZRA 1-1), 1:2 (ZRA 1-2), and 1:3 (ZRA 1-3).

68.9° can be attributed to the (111), (200), (220), (311), and (222) planes of face-centered-cubic (FCC) metallic Ag (JCPDS 04-0783) [36,37], respectively. In addition to the (002) peak of rGO, this confirms the successful fabrication of the Ag/rGO composite. For the ZnO/Ag/rGO composite, all the ZnO, Ag, and rGO peaks are present, which further indicates the successful synthesis of the ternary composite. Moreover, the XRD patterns of the ZnO/Ag/rGO composites with different Ag contents are presented in Fig. 1(b). As expected, the intensity of the characteristic Ag peaks increased with an increase in the AgNO_3 content.

For a further study of the ZnO/Ag/rGO ternary composites, the representative ternary composite (ZRA 1-2) was analyzed using XPS. Fig. 2(a) presents the C 1s XPS spectrum of

ZnO/Ag/rGO, and four binding energies related to C–C, C–O, C=O, and O–C=O were observed at 284.8, 285.8, 287.0, and 288.6 eV, respectively. Fig. 2(b) presents the XPS spectrum of O 1s with corresponding binding energies of 531.4, 532.6, 533.9, and 535.5 eV for ZnO–O, C–O/C=O, H_2O , and O–C=O, respectively. The C/O value of the ZnO/Ag/rGO composite was 3.33, which is significantly higher than that of GO (1.38) [38–40]. The decrease in the C/O value suggests the partial reduction of GO to rGO, which maintains the dispersivity and stability of the ZnO/Ag/rGO composite. Moreover, a low reduction of the oxygen content indicates that Ag^+ and Zn^{2+} anchored to the functional groups of the oxygen. The characteristic peaks for Ag $3d_{5/2}$ and Ag $3d_{3/2}$ (at the binding energies of 368.6 and 374.6 eV, respectively) were found in the spectrum of Ag 3d (Fig.

Fig. 2. (a) C 1s, (b) O 1s, (c) Ag 3d, and (d) Zn 2p XPS spectra of ZRA 1-2 ternary composite.

2(c)), which indicates that the formation of metallic silver is in good agreement with the XRD result [41–43]. Fig. 2(d) presents the Zn 2p XPS spectrum. The binding energy of Zn 2p_{1/2} is at 1045.5 eV and the binding energy of Zn 2p_{3/2} is at 1022.5 eV, which is consistent with the standard data of ZnO. The elemental contents obtained from the XPS analysis are presented in Table S1 in Supporting Information. With an increase in the weight ratio of AgNO₃ and GO, the relative content of Ag increased from 2.82% to 6.58%, as shown in Table S1.

The morphologies of the ZnO/rGO composite and the representative ternary composite (ZRA 1–2) were examined using SEM and TEM. As shown in Figs. 3(a) and 3(b), the ZnO particles were micro-sized (diameter = 1–1.5 μm) with hexagonal shapes, which can be seen on the transparent rGO sheet in the ZnO/rGO composite. Moreover, no small particles were observed. As for the ZRA 1–2 ternary composite (Figs. 3(c) and 3(d)), the transparent rGO sheets were loaded with several larger hexagonal particles and smaller circular particles in a uniform distribution. Compared with the SEM images of the ZnO/rGO composite, it was conjectured that the larger hexagonal particles were micron-scale ZnO.

The reaction mechanism of the preparation process is presented in Fig. 4(a). First, the Zn²⁺ cations were electrostatically adsorbed to the oxygen-containing groups on the GO sheets during the sonication. The reduction of the sodium hydroxide solution caused OH⁻ to react with Zn²⁺, and therefore led to the

Fig. 3. SEM images of (a,b) the ZnO/rGO composite and (c,d) ZRA 1–2 ternary composite; (e,f) TEM images of the ZRA 1–2 ternary composite.

formation of ZnO nuclei. With the electrostatic adherence of Ag⁺ ions to GO sheets, ethanol simultaneously reduced Ag⁺ and GO to Ag NPs and rGO, respectively, during the solvothermal process. Meanwhile, the ZnO nuclei grew by Oswald ripening. The simultaneous formation of metal and metal oxide crystals with the reduction of GO was achieved using this one-step process. The smaller particles were further characterized using TEM (Figs. 4(b), 3(e), and 3(f)). There are two different sizes of particles: the first with a diameter of approximately 200 nm, and the second with a diameter below 10 nm. High-resolution transmission electron micrograph (HRTEM) analysis was conducted to distinguish the two types of particles, as shown in

Fig. 4. (a) Schematic for the preparation of ZnO/Ag/rGO ternary composites; (b) TEM image of ZRA 1–2 ternary composite; HRTEM images of (c) large particle and (d) small particle; and (e) STEM image of ZRA 1–2 ternary composite and the corresponding HAADF-STEM-EDS mapping images showing C, O, Zn, and Ag in the selected area.

Figs. 4(c) and 4(d). The nanoparticles with $d = 0.235$ nm and $d = 0.278$ nm for the Ag(111) and ZnO(100) planes were observed, respectively, which indicates that the larger particle is Ag, whereas the smaller particle is ZnO. The elemental distribution mappings (C, O, Zn, and Ag, respectively) revealed that the elements of C, O and Zn were distributed uniformly, whereas larger particles with an inhomogeneous distribution represent the Ag element. From the images of ZnO/rGO, it can be seen that ZnO particles (1–1.5 μm) with hexagonal-shaped structures were uniformly dispersed on the surface of rGO. After adding the Ag precursor, they were partially transformed to the smaller nanoparticles (5–10 nm). Therefore, it is expected that the nanocomposite ZnO/Ag/rGO with small and dispersive ZnO and Ag nanoparticles present in the rGO layers can demonstrate an effective antibacterial activity.

3.2. Antibacterial behavior of the ZnO/Ag/rGO ternary composites

To evaluate the antibacterial properties of the ZnO/Ag/rGO ternary composite, both Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria were used as the target bacteria for the testing of the inhibition zones using the agar diffusion method, as shown in Fig. 5. The bacterial strains could grow on the medium plate for the ZnO/rGO (Figs. 5(a) and 5(b)) and Ag/rGO (Figs. 5(c) and 5(d)) composites with low concentrations; however, *E. coli* bacteria could not grow around the Ag/rGO composite at the concentration of 2 mg/mL, thus forming a sterile ring with a diameter of 14 mm. The ZnO/rGO composite yielded a very small inhibition zone against *S. aureus*, which indicates that the Ag/rGO and ZnO/rGO composites demonstrated certain pertinence to the killing of bacteria.

The presence of the clear zone of inhibition for the ZnO/Ag/rGO composite under all the tested concentration conditions, as shown in Figs. 5(e) and 5(f), indicates that the ternary composite can effectively suppress the growth for both bacteria types. Thus, the ZnO/Ag/rGO composite exhibited a better antibacterial performance than the binary composites, which indicates that the synergistic effect between the ZnO, Ag, and rGO contributed to the improved antibacterial performance [44–46]. The diameters of the inhibition zones against *E. coli* were 17.5, 21, and 23 mm and those against *S. aureus* were 12, 15, and 18.5 mm when the ZnO/Ag/rGO composite concentrations were 0.5, 1, and 2 mg/mL, respectively. The larger inhibition zone of the ZnO/Ag/rGO composite against *E. coli*, when compared with that against *S. aureus*, indicated that the antibacterial activity of the ZnO/Ag/rGO composite was higher against *E. coli* than *S. aureus*.

MIC is an important indicator of the antibacterial performance. Fig. 6 presents the growth curves of *S. aureus* and *E. coli* treated with the as-prepared samples with different concentrations under a 300 W Xe lamp. The ZnO/Ag/rGO, Ag/rGO, and ZnO/rGO composites exhibited antibacterial activities against both bacteria types. For the ZnO/rGO composite, the growths of *E. coli* and *S. aureus* were completely inhibited at the concen-

Fig. 5. Images of antibacterial activities of (a,b) ZnO/rGO, (c,d) Ag/rGO, and (e,f) ZRA 1–2.

trations of 200×10^{-6} and 300×10^{-6} $\mu\text{g/mL}$, respectively (Figs. 6(a) and 6(b)); whereas for the Ag/rGO composite, the MICs against *E. coli* and *S. aureus* were 280×10^{-6} and 360×10^{-6} $\mu\text{g/mL}$, respectively (Figs. 6(c) and 6(d)). The MIC of the ZnO/Ag/rGO composite was significantly lower than that of the binary composites, and the ZRA 1–1 ternary composite exhibited the best antibacterial activity. The MIC against *E. coli* and *S. aureus* was 60×10^{-6} $\mu\text{g/mL}$ when the bacteria were treated with the ZRA 1–1 ternary composite (Figs. 6(e) and 6(f)). Moreover, the growth of the bacteria could not be inhibited at the concentration of 60×10^{-6} $\mu\text{g/mL}$ in low-light conditions. For the ZRA 1–2 ternary composite, the concentrations required for the complete inhibition of the bacterial growth against *E. coli* and *S. aureus* were 100×10^{-6} and 80×10^{-6} $\mu\text{g/mL}$, respectively (Figs. 6(g) and 6(h)). Furthermore, the delays in the growth of *E. coli* and *S. aureus* by 10 h occurred at the concentrations of 260×10^{-6} and 180×10^{-6} $\mu\text{g/mL}$, respectively.

The MIC of the ZRA 1–3 ternary composite against *E. coli* was 280×10^{-6} $\mu\text{g/mL}$, and 240×10^{-6} $\mu\text{g/mL}$ for *S. aureus* (Figs. 6(i) and 6(j)). The inhibitory effect of the Ag NPs against *E. coli* was better than that on *S. aureus*, due to the differences in the membrane between the negative and positive bacteria

Fig. 6. Bacterial growth curves of *E. coli* (a, c, e, g, and i) and *S. aureus* (b, d, f, h, and j) treated using (a,b) ZnO/rGO, (c,d) Ag/rGO, and ZnO/Ag/rGO composites prepared using Ag and GO with weight ratios of (e,f) 1:1, (g,h) 1:2, and (i,j) 1:3 ternary composite in agar-well diffusion.

[47]. However, the ZnO/Ag/rGO composites exhibited a better antibacterial property against *S. aureus* than *E. coli* because the ROS generated by ZnO may be pertinent to the positive bacte-

ria. Moreover, the inhibition of bacterial growth was not realized under low-light conditions for all the ternary samples, which indicates that irradiation is essential for the antibacterial

Table 1MIC and MBC of composites against *E. coli* and *S. aureus*.

Material	MIC (10^{-6} $\mu\text{g/mL}$)		MBC (10^{-6} $\mu\text{g/mL}$)	
	<i>E. coli</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>S. aureus</i>
ZRA 1-1	60	60	20	40
ZRA 1-2	100	80	100	120
ZRA 1-3	160	200	140	160
ZnO/rGO	200	300	320	350
Ag/rGO	300	> 400	350	> 400

performance. For the ZnO/Ag/rGO ternary composite with different silver contents, the silver content positively correlated with the MIC, and the ZnO/Ag/rGO ternary composite with a higher silver content demonstrated a better antibacterial performance, which can be attributed to the excellent antibacterial property of Ag NPs. The results are presented in Table 1. The ZRA 1-2 composite with a lower Ag content can achieve a similar antibacterial performance to that of the ZRA 1-1 composite, and the lower content of Ag NPs can reduce the biotoxicity risk of Ag-based materials for practical applications.

MBC was evaluated to characterize the bactericidal performance by assessing the number of colonies formed on the culture plate. As shown in Figs. 7(a)–7(d), the number of bacterial colonies was partially inhibited by the ZnO/rGO and Ag/rGO composites; whereas several colonies were present on the culture plate, even when the concentrations of the ZnO/rGO and Ag/rGO composites were fixed at 300×10^{-6} $\mu\text{g/mL}$. In contrast, as confirmed by the results of the pre-experiment, the ZRA 1-2 ternary composite killed *E. coli* at a concentration of 100×10^{-6} $\mu\text{g/mL}$ (silver content of 4.3×10^{-6} $\mu\text{g/mL}$), and *S. aureus* at a concentration of 120×10^{-6} $\mu\text{g/mL}$ (silver content of 5.2×10^{-6} $\mu\text{g/mL}$) within 3 h. In this study, the ZRA 1-2 ternary composite demonstrated a superior antibacterial performance to that of the ZnO/rGO and Ag/rGO composites. The changes in the number of colonies over time can be seen in Fig. S1 and Figs. 7(e) and 7(f) when the *E. coli* and *S. aureus* solution was mixed with the ZRA 1-2 ternary composite. The number of colonies gradually decreased over time for both bacteria. The colony forming units of the bacteria were reduced to less than 10. Moreover, no colonies were on the culture plate after 2.5 h,

Fig. 7. Images of antibacterial activities of (a,b) Ag/rGO, (c,d) ZnO/rGO, and (e,f) ZnO/Ag/rGO against *E. coli* (a, c, e) and *S. aureus* (b, d, f) in agar-well diffusion.

which implies that both *E. coli* and *S. aureus* were completely killed.

The changes in the morphologies of *E. coli* and *S. aureus* after treatment with 100×10^{-6} $\mu\text{g/mL}$ of the bio-photocatalyst were investigated using SEM and TEM. As shown in Figs. 8(a), 8(b), 8(e), and 8(f), the untreated cells exhibited the typical ellipsoid morphology with intact cell walls and flagella. However, the bacteria cell structure was destroyed (red arrows) after incubating it with ZRA 1-2 for 3 h (Figs. 8(c), 8(d), 8(g), and 8(h)). The bacteria cells were wrapped with rGO sheets, which demonstrates that rGO can strongly interact with bacteria cells through adsorption to directly affect the cells and accelerate the death of bacteria.

From the results of the abovementioned antibacterial experiment, the silver content was positively correlated with the antibacterial property. Moreover, the ZRA 1-2 ternary composite with half the Ag content can exhibit antibacterial performance similar to ZRA 1-1 given that the generated ROS from ZnO and Ag⁺ from the Ag NPs have an optimal synergistic effect

Fig. 8. SEM and TEM images of *E. coli* and *S. aureus* cells (a, b, e, and f) before and (c, d, g, and h) after the treatment with 100×10^{-6} $\mu\text{g/mL}$ of ZRA 1-2 for 3 h under irradiation.

Fig. 9. ESR spectra of (a) $O_2^{\bullet-}$ and (b) $\bullet OH$ obtained from the ZnO/Ag/rGO composites recorded after different exposure times under simulated sunlight; (c) $O_2^{\bullet-}$ and (d) $\bullet OH$ obtained from ZnO/rGO and ZnO/Ag/rGO ternary composites prepared using $AgNO_3$ and GO with weight ratios of 1:1 and 1:2 recorded after 12 min of exposure to simulated sunlight; (e) PL spectra of ZnO/rGO and ZnO/Ag/rGO composites prepared using $AgNO_3$ and GO with weight ratios of 1:1, 1:2, and 1:3; (f) Release rate of Ag^+ from ZRA 1–2 ternary composite and $AgNO_3$.

under this proportional condition. The ZnO semiconductor can absorb light energy and create electron-hole pairs under electromagnetic radiation. The separated electrons and holes then react with O_2 or H_2O molecules to generate ROS, including $O_2^{\bullet-}$ (peroxide), $\bullet OH$ (hydroxyl radicals), and hydrogen peroxide (H_2O_2) [48,49]. Electron spin trapping (ESR) is a well-established technique used to detect short-lived ROS. Figs. 9(a)–9(d) present the ESR spectra obtained from the ZnO/rGO and ZnO/Ag/rGO ternary composites before and during irradiation using simulated sunlight. No ESR signal was observed for $O_2^{\bullet-}$ (Fig. 9(a)) and $\bullet OH$ (Fig. 9(b)) from ZnO/Ag/rGO without irradiation. With an increase in the exposure time, there was an increase in the amount of ROS produced by the ZnO/Ag/rGO composite. The mechanism by which ZnO produces ROS in water is as follows: $ZnO + h\nu \rightarrow e^- + h^+$, $h^+ + OH^- \rightarrow \bullet OH$, $e^- + O_2 \rightarrow O_2^{\bullet-}$ [50]. The electrons excited from ZnO are first transferred from the conduction band of ZnO to the Ag NPs, and then to the rGO sheets. Thus, the photogenerated carriers are separated effectively, and an increased quantity of ROS is available for antibacterial action. As shown in Fig. 10, both the ROS and Ag^+ released from the ZnO/Ag/rGO composites can lead to bacterial death. The ESR signals of $O_2^{\bullet-}$ (Fig. 9(c)) and $\bullet OH$ (Fig. 9(d)) generated from the ZnO/rGO, ZRA 1–1, and ZRA 1–2 composites were observed after 12 min of radiation, and the ESR signals of the ROS from the ZnO/rGO composite were relatively lower than those of the ZnO/Ag/rGO composites. Based on the results of the MIC experiment, ROS is essential for the antibacterial performance given that the bactericidal properties of the ternary composites are significantly reduced under the low-light condition, whereas the presence or absence of light has little effect on the bactericidal performance of Ag NPs. Moreover, ROS primarily causes the inhibition of cell growth

and death [51]; therefore, higher is the amount of generated ROS, better is the antibacterial property. Thus, the ZRA 1–2 ternary composite exhibited the strongest ESR signal, which may explain its good bactericidal effect with a lower silver content. The ability to produce ROS is consistent with the migration efficiency of the photogenerated carriers, which is presented in the PL spectra. The antibacterial property of the ZnO/Ag/rGO composite is related to the number of free radicals generated under electromagnetic radiation. A higher separation efficiency of photogenerated carriers helps to improve the antibacterial property [52]. Photoluminescence (PL) spectra obtained with the excitation wavelength of 360 nm were used to study the separation efficiency of the photogenerated electrons and holes (Fig. 9(e)). The ZnO/rGO and ZnO/Ag/rGO composites with different silver contents had emission peaks at approximately 469 nm. Compared with the ZnO/rGO composite, the emission peak intensities of the ZnO/Ag/rGO compo-

Fig. 10. Antibacterial mechanism of ZnO/Ag/rGO composite.

sites were significantly weaker than that of the ZnO/rGO composite, and the ZRA 1–2 ternary composite exhibited the weakest peak intensity, which indicates that the ZnO/Ag/rGO composites have a higher separation efficiency of photogenerated electron-hole pairs than that of the ZnO/rGO composite, and that the ZRA 1–2 composite exhibits the best separation efficiency of the photogenerated carriers. Therefore, the best synergistic antibacterial efficacy between ZnO and the Ag NPs was achieved with the ZRA 1–2 ternary composite with the lower amount of silver depletion, as it can produce a significant number of ROS, which enhances the antibacterial performance under electromagnetic radiation. Moreover, this phenomenon is consistent with the results of the antibacterial experiment and ESR [53].

The stability of Ag-based materials is essential for their practical applications. Moreover, the main cause of the instability of Ag NPs is the easy oxidation of Ag, which results in a sudden release of Ag⁺ ions. This leads to inefficient long-term applications and biotoxicity. Slower the release of silver ions, lower is the biotoxicity of the material. Therefore, the stable release of Ag⁺ ions is an important index of the stability of Ag-based antibacterial materials. The ZRA 1–2 ternary composite was dispersed in deionized water, and then a portion of the solution was extracted on day 0, 1, 2, 3, 5, 10, 15, 20, 25, and 30 to detect the release content of the Ag⁺ ions. Fig. 9f presents the release rate of Ag⁺ from the ZnO/Ag/rGO composite. As a common silver-based antimicrobial material, AgNO₃ with the same silver content was chosen for comparison. AgNO₃ releases Ag⁺ ions at a high rate, in particular, over several hours, which confirms the short duration of its ability to sterilize. Hence, AgNO₃ is commonly used as a fast-acting bactericidal agent in emergency situations. Compared with AgNO₃, the release of Ag⁺ ions from the ZRA 1–2 ternary composite was significantly delayed. After the reaction, the ZRA 1–2 ternary composite can be easily recycled, as shown in Fig. S2. Compared with the other state-of-the-art antibacterial materials listed in Tables S2 and S3, the ability of the ZnO/Ag/rGO composite to release Ag⁺ over a long period of time ensures the

durability and safety of the antibacterial activity.

4. Conclusions

In summary, the ZnO/Ag/rGO ternary composite was designed and successfully prepared using a simple one-step hydrothermal method. Compared with the Ag/rGO composite with an equivalent amount of Ag, the ZnO/Ag/rGO composite demonstrated a superior broad-spectrum antibacterial performance against *E. coli* and *S. aureus* because of the synergetic effect of the Ag⁺ ions released from the Ag NPs and the ROS generated by the ZnO NPs. The most significant synergetic effect was achieved with the ZRA 1–2 ternary composite, and its MICs against *E. coli* and *S. aureus* were 100×10^{-6} µg/mL (silver content of 4.3×10^{-6} µg/mL) and 80×10^{-6} µg/mL (silver content of 3.5×10^{-6} µg/mL), respectively. The mechanism of this optimization was confirmed by the PL spectra and ESR characterization. The maximum quantity of ROS, which is positively correlated to the antibacterial performance, is generated because of the enhanced separation efficiency of photogenerated carriers. Moreover, given that significantly low content of Ag⁺ ions can be constantly released in this ternary system in addition to the minimum loading amount of Ag NPs, the consequences of the biotoxicity are mitigated and Ag wastage is prevented. The ZnO/Ag/rGO antibacterial material is, therefore, a potential alternative to the conventional Ag NPs. This study offers a detailed insight into the comprehensive effects of Ag⁺ and ROS on the antibacterial mechanism and the proposed composite achieves the constant release of antibacterial agents with promising practical applications.

References

- [1] C. M. Wilke, B. Wunderlich, J. F. Gaillard, K. A. Gray, *Environ. Sci. Technol.*, **2018**, 52, 3185–3194.
- [2] Z. Zheng, J. Guo, H. Mao, Q. Xu, J. Qin, F. Yan, *ACS Biomater. Sci. Eng.*, **2017**, 3, 922–928.
- [3] Q. Q. Zhang, G. G. Ying, C. G. Pan, Y. S. Liu, J. L. Zhao, *Environ. Sci.*

Graphical Abstract

Chin. J. Catal., 2019, 40: 691–702 doi: 10.1016/S1872-2067(18)63193-6

Light-induced ZnO/Ag/rGO bactericidal photocatalyst with synergistic effect of sustained release of silver ions and enhanced reactive oxygen species

Yunyan Wu, Lili Zhang, Yazhou Zhou, Lili Zhang, Yi Li, Qinqin Liu*, Juan Hu, Juan Yang*

Jiangsu University; Huaiyin Normal University

ZnO/Ag/rGO bactericidal photocatalyst can realize effective antibacterial activity against *E. coli* and *S. aureus* by synergistic effects of Ag⁺ and reactive oxygen species (ROS). The sufficient radicals, together with sustained Ag⁺ can accelerate the death of bacteria through the destruction of biomolecules.

- Technol.*, **2015**, 49, 6772–6782.
- [4] F. Huang, Y. Gao, Y. Zhang, T. Cheng, H. Ou, L. Yang, J. Liu, L. Shi, J. Liu, *ACS Appl. Mater. Interfaces*, **2017**, 9, 16880–16889.
 - [5] J. Tang, Q. Chen, L. Xu, S. Zhang, L. Feng, L. Cheng, H. Xu, Z. Liu, R. Peng, *ACS Appl. Mater. Interfaces*, **2013**, 5, 3867–3874.
 - [6] Z. Huang, Z. Gao, S. Gao, Q. Wang, Z. Wang, B. Huang, Y. Dai, *Chin. J. Catal.*, **2017**, 38, 821–830.
 - [7] T. Sinha, M. Ahmaruzzaman, P. P. Adhikari, R. Bora, *ACS Sustain. Chem. Eng.*, **2017**, 5, 4645–4655.
 - [8] G. A. Kahrilas, W. Haggren, R. L. Read, L. M. Wally, S. J. Fredrick, M. Hiskey, A. L. Prieto, J. E. Owens, *ACS Sustain. Chem. Eng.*, **2014**, 2, 590–598.
 - [9] Q. Tang, J. Liu, L. K. Shrestha, K. Ariga, Q. Ji, *ACS Appl. Mater. Interfaces*, **2016**, 8, 18922–18929.
 - [10] D. Xia, Y. L. G. Huang, C. C. Fong, T. An, G. Li, H. Y. Yip, H. Zhao, A. Lu, P. K. Wong, *Appl. Catal. B*, **2015**, 176–177, 749–756.
 - [11] J. Lu, H. Wang, Y. Dong, F. Wang, S. Dong, *Chin. J. Catal.*, **2014**, 35, 1113–1125.
 - [12] N. Gao, Y. Chen, J. Jiang, *ACS Appl. Mater. Interfaces*, **2013**, 5, 11307–11314.
 - [13] D. Xia, T. An, G. Li, W. Wang, H. Zhao, P. K. Wong, *Water Res.*, **2016**, 99, 149–161.
 - [14] H. Moussa, E. Girot, K. Mozet, H. Alem, G. Medjahdi, R. Schneider, *Appl. Catal. B*, **2016**, 185, 11–21.
 - [15] S. Pramanik, J. Hazarika, A. Kumar, L. Aidew, A. K. Buragohain, N. Karak, *ACS Sustain. Chem. Eng.*, **2014**, 2, 2510–2518.
 - [16] A. Perdikaki, A. Galeou, G. Pilatos, I. Karatasios, N. K. Kanellopoulos, A. Prombona, G. N. Karanikolos, *ACS Appl. Mater. Interfaces*, **2016**, 8, 27498–27510.
 - [17] S. F. Situ, A. C. S. Samia, *ACS Appl. Mater. Interfaces*, **2014**, 6, 20154–20163.
 - [18] D. Xia, Z. Shen, G. Huang, W. Wang, J. C. Yu, P. K. Wong, *Environ. Sci. Technol.*, **2015**, 49, 6264–6273.
 - [19] H. Kim, G. Moon, D. Monllor-Satoca, Y. Park, W. Choi, *J. Phys. Chem. C*, **2012**, 116, 1535–1543.
 - [20] M. Q. Yang, Y. J. Xu, *J. Phys. Chem. C*, **2013**, 117, 21724–21734.
 - [21] J. Xu, T. J. Brenner, Z. Chen, D. Neher, M. Antonietti, M. Shalom, *ACS Appl. Mater. Interfaces*, **2014**, 6, 16481–16486.
 - [22] D. Xia, H. Liu, Z. Jiang, T. W. Ng, W. S. Leng, T. An, W. Wang, P. K. Wong, *Appl. Catal. B*, **2018**, 224, 541–522.
 - [23] H. Kong, J. Song, J. Jang, *Environ. Sci. Technol.*, **2010**, 44, 5672–5676.
 - [24] T. V. Surendra, S. M. Roopan, *J. Photochem. Photobiol. B*, **2016**, 161, 122–128.
 - [25] L. Sun, T. Du, C. Hu, J. Chen, J. Lu, Z. Lu, H. Han, *ACS Sustain. Chem. Eng.*, **2017**, 5, 8693–8701.
 - [26] H. Alinezhad, S. M. Tavakkoli, P. Biparva, *Chin. J. Catal.*, **2014**, 35, 560–564.
 - [27] V. Lakshmi Prasanna, R. Vijayaraghavan, *Langmuir*, **2015**, 31, 9155–9162.
 - [28] P. Patra, S. Mitra, N. Debnath, A. Goswami, *Langmuir*, **2012**, 28, 16966–16978.
 - [29] F. Fu, J. Gu, J. Cao, R. Shen, H. Liu, Y. Zhang, X. Liu, J. Zhou, *ACS Sustain. Chem. Eng.*, **2018**, 6, 738–748.
 - [30] J. Manna, S. Goswami, N. Shilpa, N. Sahu, R. K. Rana, *ACS Appl. Mater. Interfaces*, **2015**, 7, 8076–8082.
 - [31] J. Liu, S. Zou, J. Wu, H. Kobayashi, H. Zhao, J. Fan, *Chin. J. Catal.*, **2018**, 39, 1081–1089.
 - [32] F. Chen, H. Yang, W. Luo, P. Wang, H. Yu, *Chin. J. Catal.*, **2017**, 38, 1990–1998.
 - [33] W. He, H. K. Kim, W. G. Wamer, D. Melka, J. H. Callahan, J. J. Yin, *J. Am. Chem. Soc.*, **2014**, 136, 750–757.
 - [34] J. M. Wu, W. T. Kao, *J. Phys. Chem. C*, **2015**, 119, 1433–1441.
 - [35] H. R. Pant, B. Pant, H. J. Kim, A. Amarjatgal, C. H. Park, L. D. Tijing, E. K. Kim, C. S. Kim, *Ceram. Int.*, **2013**, 39, 5083–5091.
 - [36] Y. Zhou, J. Yang, T. He, H. Shi, X. Cheng, Y. Lu, *Small*, **2013**, 9, 3445–3454.
 - [37] X. Yang, H. Cui, Y. Li, J. Qin, R. Zhang, H. Tang, *ACS Catal.*, **2013**, 3, 363–369.
 - [38] F. Perreault, A. F. de Faria, M. Elimelech, *Chem. Soc. Rev.*, **2015**, 44, 5861–5896.
 - [39] Q. Liu, Y. Liu, Y. Yin, *Natl. Sci. Rev.*, **2018**, 5, 128–130.
 - [40] W. Liu, J. Shen, Q. Liu, X. Yang, H. Tang, *Appl. Surf. Sci.*, **2018**, 462, 822–830.
 - [41] X. H. Li, W. E. I. Sha, W. C. H. Choy, D. D. S. Fung, F. X. Xie, *J. Phys. Chem. C*, **2012**, 116, 7200–7206.
 - [42] X. Yang, J. Qin, Y. Jiang, K. Chen, X. Yan, D. Zhang, R. Li, H. Tang, *Appl. Catal. B*, **2015**, 166–167, 231–240.
 - [43] Y. Fu, Z. Li, Q. Liu, X. Yang, H. Tang, *Chin. J. Catal.*, **2017**, 38, 2160–2170.
 - [44] Y. Wu, Y. Zhou, H. Xu, Q. Liu, Y. Li, L. Zhang, H. Liu, Z. Tu, X. Cheng, J. Yang, *ACS Sustain. Chem. Eng.*, **2018**, Ahead of Print.
 - [45] Q. Liu, J. Shen, X. Yang, T. Zhang, H. Tang, *Appl. Catal. B*, **2018**, 232, 562–573.
 - [46] G. Li, C. Cherqui, N. W. Bigelow, G. Duscher, P. J. Straney, J. E. Millstone, D. J. Masiello, J. P. Camden, *Nano Lett.*, **2015**, 15, 3465–3471.
 - [47] J. Lee, S. Mubeen, X. Ji, G. D. Stucky, M. Moskovits, *Nano Lett.*, **2012**, 12, 5014–5019.
 - [48] Y. W. Wang, A. Cao, Y. Jiang, X. Zhang, J. H. Liu, Y. Liu, H. Wang, *ACS Appl. Mater. Interfaces*, **2014**, 6, 2791–2798.
 - [49] A. Sirelkhatim, S. Mahmud, A. Seenii, N. H. M. Kaus, L. C. Ann, S. K. M. Bakhori, H. Hasan, D. Mohamad, *Nano-Micro Lett.*, **2015**, 7, 219–242.
 - [50] J. Xu, M. Antonietti, M. Shalom, *Chem. Asian J.*, **2016**, 11, 2499–2512.
 - [51] J. Xu, M. Shalom, *ACS Appl. Mater. Interfaces*, **2016**, 8, 13058–13063.
 - [52] K. Shen, M. A. Gondal, R. G. Siddique, S. Shi, S. Wang, J. Sun, Q. Xu, *Chin. J. Catal.*, **2014**, 35, 78–84.
 - [53] D. Xia, Y. Li, G. Huang, R. Yin, T. An, G. Li, H. Zhao, A. Lu, P. K. Wong, *Water Res.*, **2017**, 112, 236–247.

可持续释放银离子和活性氧的ZnO/Ag/rGO三元新型光催化抗菌剂

吴赞炎^a, 张莉莉^a, 周亚洲^a, 张莉莉^b, 李 毅^a, 刘芹芹^{a,*}, 胡 娟^a, 杨 娟^{a,#}

^a江苏大学材料科学与工程学院, 江苏镇江212013

^b淮阴师范学院化学化工学院江苏省低维材料化学重点实验室, 江苏淮安223300

摘要: 由于具有独特的物理与化学性质, 银纳米粒子被广泛应用于传感器、电化学、光催化等多个领域。在生物领域, 银纳米粒子可以通过释放银离子有效地解决细菌感染问题, 但是其本身的毒性不可忽略。为了减小银纳米粒子的潜在毒性, 迫

切需要寻找一种可持续释放银离子(Ag^+)的新型复合光催化抗菌剂。已有研究报道可将银纳米粒子负载在氧化铝、凝胶和二氧化硅上形成银基抗菌材料,但是大多数材料中银纳米颗粒尺寸较大,分布不均匀,且仅靠快速释放的银离子进行抗菌。

本文通过一步溶剂热法制备了 $\text{ZnO}/\text{Ag}/\text{rGO}$ 三元光催化抗菌剂,其中分别由银纳米粒子和氧化锌(ZnO)形成的银离子和活性氧(ROS)可对大肠杆菌和金黄色葡萄球菌产生协同抗菌作用。负载在还原氧化石墨烯(rGO)上的银纳米粒子持续释放出微量的银离子,后者通过库仑引力牢固地吸附在带负电荷的细菌细胞膜上,从而干扰细菌DNA合成,进而使细菌丧失分裂繁殖能力;与还原氧化石墨烯和银纳米粒子复合的氧化锌可以产生更多的 $\text{O}_2^{\cdot-}$ 和 $\cdot\text{OH}$ 等自由基,具有氧化能力的自由基可分解细菌细胞膜使细菌破裂死亡。银纳米粒子的表面等离子体共振效应不仅可以拓宽氧化锌半导体材料的光吸收范围,而且可以作为电子捕获阱捕获电子,加速光生电子与空穴的分离,有效抑制光生载流子的复合。与其他银基抗菌材料相比,该材料可以实现了30天低浓度银离子持续释放,并利用产生的活性氧和银离子稳定高效地进行抗菌。

采用XRD, XPS, SEM, TEM, HRTEM, PL和ESR等表征方法分析了材料的结构、形貌、化学组成、元素价态及光学性质,并通过抑菌圈、最低抑菌浓度(MIC)和最低杀菌浓度(MBC)等性能测试比较了材料的抗菌性能。XRD和XPS结果证明银和氧化锌纳米粒子成功地负载在还原氧化石墨烯上。SEM, TEM和HRTEM分析发现还原氧化石墨烯上的银和氧化锌纳米粒子分布均匀,尺寸较小(5–10 nm)。PL和ESR表征表明 $\text{ZnO}/\text{Ag}/\text{rGO}$ 相比于 ZnO/rGO 和 Ag/rGO 有更好的载流子分离和自由基产生能力。因此, $\text{ZnO}/\text{Ag}/\text{rGO}$ 材料对大肠杆菌和金黄色葡萄球菌具有更低的最低抑菌浓度($\text{MIC}_{E. coli} = 100 \times 10^{-6} \mu\text{g/mL}$, $\text{MIC}_{S. aureus} = 80 \times 10^{-6} \mu\text{g/mL}$)和最低杀菌浓度,该材料在抗菌领域具有潜在的应用前景。

关键词: 氧化锌; 银纳米粒子; 还原氧化石墨烯; 银离子持续释放; 协同抗菌机制; 活性氧

收稿日期: 2018-08-13. 接受日期: 2018-10-13. 出版日期: 2019-05-05.

*通讯联系人. 电话: (0511)88780195; 电子信箱: qqliu@ujcs.edu.cn

#通讯联系人. 电话: (0511)88780195; 电子信箱: yangjuan6347@ujcs.edu.cn

基金来源: 国家自然科学基金(51472101, 51572114, 21773062, 21577036); 江苏省低维材料化学重点实验室(JSKC17003).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).