Constructing supported Ag antibacterial nano-agent with high activity and stability for broad-spectrum antibiosis

Haibin Xue 1, Xuewei Gao 1, Xiangnan Feng 1, Shan He 2,*, Feifei Zhao 1, Guiju Zhang 2,*, Xinrui Wang 3, Xiaobo Luo 1,∗ and Shanyue Guan 1

1 The 8th Medical Center, General Hospital of Chinese People’s Liberation Army, People’s Republic of China
2 School of Light Industry, Beijing Technology and Business University, 11 Fucheng Road, Haidian District, Beijing, 100048, People’s Republic of China
3 Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China

* Authors to whom any correspondence should be addressed.

E-mail: vh30@163.com, zhangguiju@th.btbu.edu.cn and luoxiaobo_309@163.com

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Abstract

The developing a green and facile synthetic approach of Ag-based antibacterial nanomaterials with controlled composition, size, and shape, to acquire high antibacterial activity and long-term durability, is of vital importance and remains a challenging goal. Herein, a novel LDHs-supported Ag antibacterial nanomaterial (Ag/CoAl-LDHs) are fabricated via an in situ deposition of the Ag nanoparticles onto the CoAl-LDHs surface. X-ray diffraction pattern (XRD) and High-resolution TEM (HRTEM) measurements confirm that the uniform Ag nanoparticles (the average particle size of 16.5 nm) are highly dispersed and firmly anchored onto CoAl-LDHs surface. As revealed by x-ray photoelectron spectroscopy (XPS), the CoAl-LDHs nanoplates play the roles of both a support and a reductant without any external, and there was a redox reaction between Co2+ in LDHs layers and Ag+ in AgNO3 solution, giving rise to in situ loading of Ag nanoparticles onto LDHs. Moreover, antibacterial experiments verify that Ag/CoAl-LDHs not only have efficient antibacterial activity against both Escherichia coli and Staphylococcus aureus, but also exhibit very stable antibacterial properties for both bacteria. Therefore, this research demonstrates a successful paradigm for the rational design and preparation of new antibacterial nanomaterials with high antibacterial activity and long-term durability.

1. Introduction

In the decade, fatal infectious diseases and serious complications arising from bacterial infection have become an urgent health problem for human all over the world [1–3]. Thus, it is realized that the development of efficient bactericidal agents with broad-spectrum antibacterial ability is of great significance for improving the quality of health and enhancing our ability to fight against diseases [4–6]. In recent years, with the development of the nanotechnology, inorganic nanomaterials as antibacterial agents, which have advantages of long durability, strong heat resistant, high activity, low drug resistant and high selectivity compared to organic antibacterial materials, have attracted considerable attention in the realm of bactericidal application [7–10]. Various antibacterial nanomaterials, such as Ag nanoparticles (NPs), ZnO NPs, Au NPs, TiO2 NPs and Cu NPs, have been synthetized as well as studied in depth [11–15]. Among numerous antibacterial nanomaterials, Ag-based antibacterial nanomaterials have received special attention owing to outstanding antibacterial activity and low microbial drug resistance [16–18]. It is well known that the antibacterial capacity of Ag-based nanomaterials is significantly affected by their particle size, dispersion and stability in the process of practical application [19–22]. For the preparation of Ag-based antibacterial nanomaterials with uniform size and stable dispersion, many synthetic methods, such as microemulsion technique, high temperature calcination of the oxide precursors and
solvothermal reaction, have been reported [19–22]. However, these methods not only require noxious organic reagents (e.g., toxic reducing agents or dispersing or capping agents) and rigorous conditions, but also suffer from serious aggregation of Ag NPs in the preparation process, which results in remarkable reduction of antibacterial properties and poor stability [4,6,23–25]. Therefore, developing a green and facile synthetic approach of Ag-based antibacterial nanomaterials with controlled composition, size and shape, so as to acquire high antibacterial activity and long-term durability, is of vital importance and remains a challenging goal.

Layered double hydroxides (LDHs) as a class of anion-intercalated materials have aroused wide attention from both industry and academia due to their potential applications in areas such as catalysis, electrochemistry, photochemistry, and biochemistry [26–29]. LDHs is composed of positively charged host layers and exchangeable interlayer anions, which can be expressed by the formula $[\text{M}^{2+} \text{M}^{3+} (\text{OH})_2]^{x+} \text{An}^{-x/n} \cdot n\text{H}_2\text{O}$. M$^{2+}$ and M$^{3+}$ metal cations are distributed at atomic levels in the hydroxide layers, and An$^{-}$ is an anion located in the interlayer region [30,31]. Recently, extensive studies have been focused on LDHs as precursors or templates for the formation of supported metal nanoparticles, owing to their adjustable variability in physicochemical properties and architecture [32–35]. This preparation strategy for supported metal nanoparticles is not only simple, efficient and green, but also provides a controlled morphology of metal nanoparticles with a uniform size as well as high dispersion and stability [36–38]. This unique property of LDHs materials, therefore, inspires us to explore LDHs-supported Ag nanoparticles toward antibacterial application.

In this work, we reported a supported Ag nanomaterial with high antibacterial performance via a facile fabrication procedure: the in situ immobilization of the Ag nanoparticles onto the CoAl-LDHs. XRD and HRTEM measurements demonstrated that LDHs-supported Ag antibacterial nanomaterials (denoted as Ag/CoAl-LDHs) showed a uniform size (16.5 nm) and high dispersion of Ag nanoparticles. As revealed by XPS, the CoAl-LDHs nanoplates played the roles of both a support and a reductant without any external, and there was an oxidation-reduction process between the CoAl-LDHs nanoplate and the AgNO$_3$ solution, giving rise to Ag/CoAl-LDHs. Moreover, antibacterial experiments verified that Ag/CoAl-LDHs not only had efficient antibacterial activity against both Escherichia coli and Staphylococcus aureus, but also exhibited very stable antibacterial properties for both bacteria. This work provided a green and facile synthetic approach of Ag-based nanomaterials with high antibacterial performance, which had potential application value in the field of health and hygiene.

2. Experimental section

2.1. Materials

Analytical grade chemicals including Co(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, AgNO$_3$, NaOH, and Na$_2$CO$_3$ were supplied by Aladdin reagent Co, Ltd and used without further purification. Deionized water was used in the all experiments.

2.2. Synthesis of CoAl-LDHs

The Co$_2$Al-CO$_3$$_2$·6H$_2$O nanolayers were prepared by the hydrothermal method reported previously [39]. A solution of Co(NO$_3$)$_2$·6H$_2$O (0.008 mol) and Al(NO$_3$)$_3$·9H$_2$O (0.004 mol) in 40 ml of water was quickly added to 40 ml of NaOH (0.025 mol) and Na$_2$CO$_3$ (0.1 g) solution with vigorous agitation at room temperature. The mixture was transferred into an autoclave, followed by hydrothermal treatment at 80 °C for 5 h. The precipitate was separated by centrifugation and washed thoroughly with water.

2.3. Synthesis of LDHs-supported Ag nanoparticles (Ag/CoAl-LDHs)

LDHs-supported Ag nanoparticles (Ag/CoAl-LDHs) were prepared by a facile in situ oxidation-reduction process between the CoAl-LDHs nanoplate and the AgNO$_3$ solution. In a typical procedure, the suspension of CoAl-LDHs nanolayers (about 4 mg ml$^{-1}$) was firstly obtained by fresh LDHs precipitate ultrasonically dispersed in the deionized water. Afterwards, AgNO$_3$ solution (12 ml, 5 mg ml$^{-1}$) was added into LDHs suspensions (50 ml, 4 mg ml$^{-1}$) at 50 °C for 6 h under stirring. The redox reaction process resulted in the in situ deposition of Ag nanoparticles onto the surface of CoAl-LDHs nanoplate. Finally, the resulting product was separated by centrifugation, washed thoroughly with water and dried under vacuum for 24 h.

2.4. Sample characterization

The zeta potential and dynamic lighting scattering (DLS) diameter were measured by photon correlation spectroscopy (PCS, Nanosizer Nano ZS, MALVERN Instruments). TEM images were obtained by a JEM-2100F high resolution transmission electron microscope with an accelerating voltage of 200 kV. Powder x-ray diffraction (XRD) patterns were collected on a Bruker x-ray diffractometer (D8 focus, Cu Kα, $\lambda = 0.15178$ nm) operated at a scan rate of 0.1° s$^{-1}$. Fourier transform infrared spectra (FT-IR) were acquired on a Varian
3.1. Structural and morphological characterizations

3. Results and discussion

Excalibur 3100 FTIR spectrophotometer using the KBr pellet technique in the range 4000–500 cm⁻¹. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) data were obtained on a Varian 710–OES. XPS measurements used an ESCALAB 250Xi (Thermo Scientific), equipped with a non-monochromatized Al-Kα x-ray source (hν = 1486.7 eV).

2.5. Antibacterial test of Ag/CoAl-LDHs

To evaluate antimicrobial activity, the antimicrobial tests of Ag/CoAl-LDHs with varied concentrations (50, 100, 500, and 1000 μg ml⁻¹) were performed by using Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli) as a microorganism, respectively. The microbial population was analyzed by counting colony-forming units (CFUs) using the pour-plate technique. S. aureus or E. coli was first incubated with varied concentrations of Ag/CoAl-LDHs at 37 °C for 30 min in PBS. A 100 ml portion of the S. aureus or E. coli suspension was spread on a solid LB (Luria Bertani medium) nutrient agar plate. The colonies formed after 16 h incubation at 37 °C for S. aureus or E. coli were counted. The diameter of the solid agar plates was 90 mm. In addition, the antimicrobial activity of CoAl-LDHs (1000 μg ml⁻¹) and only PBS as two control samples were evaluated under same method, respectively. All tests were performed in triplicate.

To study the antibacterial efficiency and stability, the antibacterial growth curves of S. aureus and E. coli treated with Ag/CoAl-LDHs (1000 μg ml⁻¹) was investigated using Bioscreen C. The two strains in the logarithmic growth phase were suspended in nutrient broth medium at 10⁻⁶ CFU/ml. Bacterial suspension (30 μl) was mixed with 180 μl nutrient broth medium and 30 μl of Ag/CoAl-LDHs, such that the final concentrations of Ag/CoAl-LDHs were 1000 μg ml⁻¹. The same volume of physiological saline was added instead of the Ag/CoAl-LDHs solution in the negative control. The medium was incubated at 37 °C for 33 h in the Bioscreen C system (Oy Growth Curves, Helsinki, Finland). All tests were performed in triplicate.

3. Results and discussion

3.1. Structural and morphological characterizations

LDHs-supported Ag antibacterial nanomaterials (Ag/CoAl-LDHs) were synthetized by the in situ immobilization of the Ag NPs onto the CoAl-LDHs surface (see the Experimental section for details). The CoAl-LDHs precursors with Co/Al ratio of ~2 was firstly synthetized on the basis of the hydrothermal method reported previously by our group. The XRD patterns of the CoAl-LDHs precursors (figure 1 (A-a)) showed a series of diffraction peaks at 11.7°, 23.5°, 34.6°, 60.4°, and 61.7°, which can be assigned to (003), (006), (009), (110), and (113) characteristic reflections of the LDH structure [39]. The basal spacing (d003) for CoAl-LDHs precursors was 0.769 nm, which was in agreement with the value reported for CoAl-CO3⁶⁻/LDHs phase [39]. In addition, (110) and (113) reflections can be observed, indicating the formation of a well crystallized CoAl-LDHs phase [39]. Figure 1(B) showed that the CoAl-LDHs precursors had a mean lateral size of ~165 nm, as determined by Dynamic Lighting Scattering (DLS). As shown in TEM image (figure 1(C)), the CoAl-LDHs precursors had a typical morphology of two-dimensional nanoplate, and the nanoplates thickness of ~6 nm can be observed from the cross section of CoAl-LDHs (in inset).

After an in situ deposition process, LDHs-supported Ag antibacterial nanomaterials were obtained (see the Experimental section for details). Compared with the CoAl-LDHs precursors, the obtained Ag/CoAl-LDHs (figure 1 (A-b)) showed a similar characteristic reflection of LDHs phase, and a series of extra diffraction peaks at 38.1°, 44.4°, and 64.9° were observed, which can be assigned to metallic Ag phase (JCPDS 04-0783). This implied the formation of Ag/CoAl-LDHs antibacterial nanomaterials. TEM and HRTEM were further applied to confirm the morphology and fine structure of Ag/CoAl-LDHs (figures 1(D)-(F)). Figure 1(D) showed that Ag/CoAl-LDHs inherited the nanoplate morphology of CoAl-LDHs precursors, and with close average size of LDHs nanoplate. Notably, it can be observed that high contrast black dots (figures 1(D) and (E)) with a uniform size distribution (16.5 nm) were well-dispersed on the surface of CoAl-LDHs nanoplates, suggesting the deposition of Ag nanoparticles owing to the higher bright-field image contrast compared with CoAl-LDHs nanoplates. To study the crystalline structure of LDHs-supported Ag nanoparticles, the HRTEM image for one single Ag nanoparticle was shown in figure 1(F). The lattice fringe of 0.235 nm corresponded to the (111) plane of the face centered cubic (fcc) Ag phase [40]. These results revealed that Ag nanoparticles were successfully in situ loaded onto the surface of CoAl-LDHs surface, forming Ag/CoAl-LDHs antibacterial nanomaterials. To perform a X-ray photoelectron spectroscopy (XPS) was performed to investigate the surface electronic structure of Ag/CoAl-LDHs (figures 2(A) and (B)). Previous investigations of XPS spectra for Ag 3d₅/₂ reported that binding energy values of 367.4 and 367.8 eV corresponded to AgO and Ag₂O, respectively, while that of metallic Ag are usually located around 368.2 eV [41, 42]. In this work, as shown in the figure 2(A), the Ag 3d₅/₂ XPS peak for Ag/CoAl-LDHs at ~368.2 eV was observed, which can be assigned the Ag⁰ state. Moreover, one O1s peak around 531.9 eV, corresponding to surface adsorption oxygen species (e.g., adsorbed hydroxyl, adsorbed carbonate) can
Figure 1. (A) XRD patterns of (a) CoAl-LDHs and (b) Ag/CoAl-LDHs. (B) The size distribution of the as-prepared Ag/CoAl-LDHs. (C) TEM image of the CoAl-LDHs precursor (inset: the cross section of CoAl-LDHs nanoplate). TEM images of the as-prepared Ag/CoAl-LDHs at (D) low magnification and (E) high magnification (inset: the size distribution of Ag nanoparticles). (F) HRTEM images of Ag/CoAl-LDHs.

Figure 2. (A) XPS Ag 3d of Ag/CoAl-LDHs. (B) XPS O 1s of Ag/CoAl-LDHs. (C) XPS Co 2P of Ag/CoAl-LDHs and CoAl-LDHs. (D) XPS Al 2P of Ag/CoAl-LDHs and CoAl-LDHs.
be observed in Ag/CoAl-LDHs, while the characteristic peaks of silver oxidized species (around 529.5 eV) were not found (figure 2(B)) [42–44]. Therefore, these indicated that the surface electronic states of supported Ag nanoparticles in Ag/CoAl-LDHs belonged to the zero-valence state of metallic Ag. In addition, the loading amount of Ag nanoparticles in CoAl-LDHs was observed to be ~15 wt% by ICP–AES spectroscopy.

The in situ loading of Ag nanoparticles onto the surface of CoAl-LDHs nanoplate can be understood from the viewpoint of oxidation-reduction process: there was a redox reaction between Co\(^{2+}\) in LDHs layers and Ag\(^+\) from AgNO\(_3\) solution, inducing the in situ reducing and dispersing of the Ag nanoparticles onto the LDHs surface. As shown in XPS of Co 2P (figure 2(C)), the peaks for CoAl-LDHs at ∼797.5, ∼781.3, ∼803.5, and ∼787.1 eV were assigned to the Co\(^{2+}\) state and their two satellite peaks [42, 44]. Notably, after an in situ deposition process, the two Co 2P peaks for Ag/CoAl-LDHs shifted to low binding energy (796.8 and 780.6 eV, respectively) compared with that of CoAl-LDHs, indicating the occurrence of a partial valence change from Co\(^{2+}\) to Co\(^{3+}\). Meanwhile, after an in situ reduction process, Al 2P peak (around 74.3 eV) in Ag/CoAl-LDHs did not shift compared with that of CoAl-LDHs [42, 44]. These revealed that the driving force for the immobilization of the Ag nanoparticles originated from the redox reaction between Ag\(^+\) from AgNO\(_3\) solution and Co\(^{2+}\) in LDH layers. Thus, it was reasonable to propose that CoAl-LDHs nanoplates played the roles of both a support and a reductant without any external agent, and subsequently the redox reaction between Ag\(^+\) and Co\(^{2+}\) led to the in situ spontaneous deposition of Ag nanoparticles onto the LDH surface. In addition, the specific ordered arrangement of the Co\(^{2+}\) and Al\(^{3+}\) cations in the LDH layers provided well-dispersive and uniform Co\(^{2+}\) active sites for the reduction of Ag\(^+\) from AgNO\(_3\) solution, imparting a good microenvironment for the nucleation and stabilization of the Ag nanoparticles onto the LDHs surface. Therefore, this work provides a green and facile synthetic approach for supported Ag antibacterial nanomaterials with a uniform size and high dispersion of Ag nanoparticles.

### 3.2. Antibacterial performance of Ag/CoAl-LDHs

To evaluate antimicrobial activity, the antimicrobial tests for Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli) was performed by Ag/CoAl-LDHs with varied concentrations (50, 100, 500, and 1000 \(\mu\text{g ml}^{-1}\)), respectively, based on counting colony-forming units (CFUs) method. In the case of S. aureus (figure 3(A)), many bacterial colonies flourished in the control plate. However, when co-incubated with Ag/CoAl-LDHs antibacterial nanomaterials, the bacterial cells of S. aureus decreased gradually with the treatment concentration increasing from 50 to 1000 \(\mu\text{g ml}^{-1}\). Correspondingly, antibacterial rate for S. aureus (calculated by CFUs method) increased from 24% to 73% with the treatment concentration (figure 3(B)). These results indicated that the antibacterial ability of Ag/CoAl-LDHs for S. aureus enhanced with the treatment concentration. Moreover, under the same treatment concentration (1000 \(\mu\text{g ml}^{-1}\)), Ag/CoAl-LDHs showed a stronger bacteriostatic effect compared with that of CoAl-LDHs (73% versus 57%). For E. coli (figure 3(A)), no obvious antibacterial effect was observed for the control group, and Ag/CoAl-LDHs at concentration of 50 \(\mu\text{g ml}^{-1}\) (figure 3(C)) showed a high colony counts but low antibacterial rate (14%). In contrast, when the treatment concentration was higher than 100 \(\mu\text{g ml}^{-1}\) (figures 3(A) and (C)), the colony counts decreased significantly, and the antibacterial rate remained at a high level (about 74% to 78%), suggesting a strong antibacterial ability for E. coli. Additionally, Ag/CoAl-LDHs showed much better bacteriostatic effect than CoAl-LDHs (74% versus 20%), under the same treatment concentration (1000 \(\mu\text{g ml}^{-1}\)). To study the antibacterial efficiency and stability, the antibacterial growth curves of S. aureus and E. coli treated with Ag/CoAl-LDHs (1000 \(\mu\text{g ml}^{-1}\)) was further investigated using Bioscreen C (figures 3(D) and (E)). It was worth noting that the growth of S. aureus and E. coli in the groups treated with Ag/CoAl-LDHs were essentially suppressed within 5 h, respectively, and no regained growth was found at all subsequent investigated time points. Moreover, antibacterial rate for S. aureus and E. coli, calculated by the antibacterial growth curves, were close to those based on CFUs method. Therefore, antibacterial experiments verified that Ag/CoAl-LDHs as antibacterial nanomaterials not only had an efficient antibacterial activity against both S. aureus and E. coli, but also exhibited a very stable antibacterial properties for both bacteria.

### 4. Conclusion

In summary, the Ag/CoAl-LDHs sample have been successfully fabricated via a facile fabrication procedure: the in situ immobilization of the Ag nanoparticles onto the CoAl-LDHs. This Ag/CoAl-LDHs sample showed a uniform size (16.5 nm) and high dispersion of Ag nanoparticles. Moreover, antibacterial experiments verified that Ag/CoAl-LDHs not only had efficient antibacterial activity against both Escherichia coli and Staphylococcus aureus, but also exhibited very stable antibacterial properties for both bacteria. This work provided a green and facile synthetic approach of Ag-based nanomaterials with high antibacterial performance, offering great potential for the development of health and hygiene.
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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
Notes

The authors declare no competing financial interest.

Associated content

ORCID iDs

Shanyue Guan  https://orcid.org/0000-0001-9842-7982

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