Silver-loaded delaminated hectorite nanoparticles for antibacterial materials

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Silver nanoparticles are excellent antibacterial materials with wide application. However, it is extremely unstable associated with easy aggregation and colour changes. Although a great number of carriers have been developed for stable silver nanoparticles, it is never ending to broaden silver carrier to meet varying applications. Herein, delaminated hectorite was developed as an alternative silver carrier. The structure of silver-loaded delaminated hectorite was confirmed by X-ray diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy/energy-dispersive X-ray studies. Silver (8.69 wt%) was loaded onto the hectorite nanoparticles by cationic ionic repulsion and electrostatic repulsion are conventionally used to enhance the stability of silver particles [4]. A large number of silver carriers, such as polymers [5], surfactants [6, 7], carbon [8], zeolite [9] etc. are developed to achieve these goals [10, 11]. However, it is never ending to develop novel materials for silver stability to fit varying situations.

Herein, we present a silver-loaded delaminated hectorite (Ag@HEC) material for the antimicrobial application. The delaminated hectorite was prepared by the hydrothermal method. Dodecyl trimethyl ammonium chloride solution and subject to hydrothermal treatment at 180°C for 2 h, and then calcined at 620°C for 75 min to obtain delaminated hectorite. Silver was incorporated into hectorite by a pyrolysis process according to Huang et al. [10]. Sodium hydroxide solution (2 wt%) was added drop wise to a silver nitrate solution (20 ml, 5 wt%) until pH=9, and then mixed with the as-prepared hectorite (1 g in 5 ml water). The mixture was heated in a furnace at 400°C for 5 min to obtain Ag@HEC.

The sample crystalline structure was studied using a D8 advance X-ray diffractometer (Bruker, Germany) with a Cu target and Kα radiation (λ = 0.15418 nm). Intercalation of silver in hectorite was studied using XPS using an Axis Ultra DLD XPS spectrometer (Kratos Analytical, UK) with a monochromated Al Kα source. The surface morphology was analysed by SEM/EDX. The cell cultures were studied using a Hitachi H-7650 (Tokyo, Japan) transmission electron microscope. The antibacterial activities against Escherichia coli ATCC 8739 and Staphylococcus aureus ATCC 6538 were performed according to ASTM F859-11. Inhibition zone studies against E. coli ATCC 8739 and S. aureus ATCC 6538 were performed according to ASTM F859-11.

1. Introduction: Silver has been used as broad-spectrum antimicrobial since ancient times and has found wide application in package, cosmetics, textile, and electronic equipment industries [1–3]. As the outbreak of world wide antibiotic resistance has given rise to great health threat to the human being, silver-based antibacterial material gains increasing interest because of no bacterial resistance [1].

Silver particles are extremely unstable. It suffers from easy particle aggregation and colour changes associated with environmentally induced reductions [1]. Steric repulsion and electrostatic repulsion are conventionally used to enhance the stability of silver particles [4]. A large number of silver carriers, such as polymers [5], surfactants [6, 7], carbon [8], zeolite [9] etc. are developed to achieve these goals [10, 11]. However, it is never ending to develop novel materials for silver stability to fit varying situations.

Hectorite clay is well-known silicate nanoparticles with one central octahedral magnesia sheet sandwiched between two layers of tetrahedral silica sheets [12]. Its special structure and morphology make hectorite an advanced material with high cation exchange capacity and interesting surface, thickening and stabilising properties [13]. Also, it can be used as an excellent carrier for drugs and metallic nanoparticles [14, 15]. For example, mafenide-loaded synthetic hectorite wound dressing gel and film were prepared for burn wound treatment [15]. Copper catalyst-loaded delaminated hectorite was prepared by impregnation, solids blending, and ion-exchange for hydrogenolysis of glycerol [14].

Herein, we present a silver-loaded delaminated hectorite (Ag@HEC) material for the antimicrobial application. The delaminated hectorite was prepared by the hydrothermal method, and then silver was incorporated by a pyrolysis process. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy/energy-dispersive X-ray (SEM/EDX) studies were performed to confirm the structure of the as-synthesised Ag@HEC. The antibacterial activity of Ag@HEC was assayed under dynamic contact conditions. Transmission electron microscopy (TEM) study was performed to understand the antibacterial mechanism of Ag@HEC.

2. Experimental: Delaminated hectorite was synthesised according to Sánchez et al. [14]. Magnesium chloride and lithium fluoride were mixed with acidified silicate solution with a molar ratio Si:Mg:Li = 8.5:2:0.8. The mixture pH was adjusted to 12 with LiOH solution and then set in an ultrasound bath for 15 min. The mixture was then filtered, and solid was collected and dried after washing with deionised water. This solid was dispersed in dodecyl trimethyl ammonium chloride solution and subjected to hydrothermal treatment at 180°C for 2 h, and then calcined at 620°C for 75 min to obtain delaminated hectorite.

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Ag\(^{0}\) are observed because no deoxidiser was applied. XPS studies were performed to further confirm the existence state of silver. The results showed that there was 8.69 wt% Ag element in the composite. As shown in Fig. 1b, two peaks at 366.0 and 372.0 eV related to Ag 3d\(_{5/2}\) and Ag 3d\(_{3/2}\) [17] were observed in the Ag 3d XPS spectrum. The binding energy of Ag 3d\(_{5/2}\) for the as-prepared Ag@HEC shifts remarkably to a lower value compared with that of synthesised pure metallic Ag ionic (about 367.2 eV). The result suggests the decrease of Ag\(^{+}\) electron density, due to electron transfer to hectorite [17], indicating hectorite serves as a good carrier for Ag. SEM studies were performed to further understanding the silver loading on hectorite. As shown in Fig. 2, hectorite was a porous material. As the loading of silver, Ag@HEC showed bigger particle size than hectorite, suggesting silver coat on the surface of hectorite. EDX analysis showed that there were as high as 49 wt% Ag element on the surface of the as-prepared Ag@HEC materials. This result is higher than that of XPS studies, further illustrating that silver was loaded to hectorite by surface coating in majority. The high amount of surface silver element makes it a good antibacterial material candidate, which would easily release silver to kill bacteria [1, 2].

The antibacterial activities of the Ag@HEC composite against *E. coli* and *S. aureus* were determined by the zone of inhibition, and dynamic contact conditions according to ASTM E2149-2013a. As is shown in Fig. 3, no inhibition zone was observed for hectorite, regardless of the applied bacteria, the same as the saline solution. Inhibition rings with a diameter of 0.6 and 0.7 cm to *E. coli* and *S. aureus*, respectively, were observed for the as-prepared Ag@HEC sample. Antimicrobial assay by dynamic contact condition showed that hectorite could kill 27% *E. coli* at 50 ppm within 1 h, but non-toxic to *S. aureus*. The as-prepared Ag@HEC was able to kill >94% *E. coli* and 83% *S. aureus* at 50 ppm within 1 h. The result was close to previous reports [10]. However, the previous reports performed the antibacterial assay at very high material concentration, 200 ppm for Ag@graphene oxide, 250 ppm for Ag@cellulose, and 500 ppm for Ag@polystyrene, and for long contact time, namely 24 h [10]. Considering the fast bacterial killing ability of Ag@HEC at a low concentration, it may be used for surface coating in varied materials, such as package.

TEM studies were performed to understand the antibacterial mechanism of the Ag@HEC (Fig. 4). The results showed that...
hectorite could be well dispersed in the water as nanoparticles, which is of help in preventing silver particle aggregation and promoting its diffusion. As the addition of hectorite into bacterial solutions, the material gathered onto the surface of the bacterial cell wall, and the bacterial cell wall was clearly observed as a thick layer. With the addition of Ag@HEC into bacterial solutions, a small amount of Ag@HEC on bacterial surface was observed. Most of the bacterial cell wall was lost. The results suggest that hectorite serves as a carrier that brings silver onto the bacterial surface. Then, silver is released to damage the bacterial cell wall, leading to its dissolution, and subsequently, kill the bacteria [18].

4. Conclusion: Delaminated hectorite was synthesised by a hydrothermal process using quaternary ammonium salt as an exfoliating reagent. It was subsequently used as a carrier for silver by a pyrolysis process. Silver was loaded at delaminated hectorite through cationic ionic change and surface coating. The Ag@HEC showed fast bacterial killing ability because hectorite can easily gather on the bacterial cell wall, and then release silver, damaging the bacterial cell wall.

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