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A Facile Approach to Incorporate Silver Nanoparticles into Dextran-Based Hydrogels for Antibacterial and Catalytical Application

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Dextran hydrogel was prepared by the crosslinking reaction of dextran and *N,N*-methylenebisacrylamide in aqueous sodium hydroxide aqueous solution. Highly stable and uniformly distributed silver nanoparticles have been prepared using these hydrogel networks as a carrier via *in situ* reduction of silver nitrate without the addition of any reducing agent. The spherical silver nanoparticles with diameters of 20–30 nm were found to adopt a face centered cubic structure. The hydrogel hybrid with silver nanoparticles can be effectively employed as antibacterial and catalytic materials.

Keywords: Silver nanocomposite, antibacterial, catalyst

1 Introduction

Nanoparticles and nanostructured materials (1) are important materials that have generated considerable interests in biomedical (2), catalytical (3,4), optical (5), and electronic (6), as well as quantum-size domain (7) applications. A number of methods have been developed (1,8,9) for the synthesis of non-agglomerated nanoparticles. These include polymers (10,11), biological macromolecules (12,13), latex particles (14), mesoporous inorganic materials (15), dendrimers (16,17), microgels or hydrogels (18–22), colloidal systems (23,24), and others. Most of the above-mentioned methods produce highly stable nanoparticles. Microgel or hydrogel network template/carrier systems can act in a similar way. In addition, these systems provide a convenient approach for producing smaller size nanoparticles since the hydrogel network can immobilize the nanoparticles in a certain place and prevent them from aggregation. Recent research efforts focus on the *in situ* synthesis of metal nanoparticles within polymeric network

architectures (25,26), and the synthesized products lead to the development of new hybrids or composite systems in chemistry and engineering science. Zhang et al. (27) produced Au nanoparticles by reducing H₂AuCl₄ within a hydrogel system under UV irradiation and obtained Au nanoparticles with different geometrical shapes and sizes by controlling the microenvironment of the gel matrix and the initial concentration of H₂AuCl₄. Saravanan et al. (28) synthesized Ag nanoparticles in polyacrylamide (PAm) hydrogel by hydrolyzation of Ag⁺ ion-functionalized PAm hydrogel matrix in 5 wt% of aqueous NaOH solution. Murthy et al. (29) successfully designed antibacterial materials of semi-interpenetrating polymer network hydrogel-Ag nanocomposites. It is noted that most of the gel networks in these materials are non-biocompatible.

Silver nanoparticles are non-toxic, environmentally friendly and antibacterial. Dextran is hydrophilic and water-soluble; it is inert in biological systems and does not affect cell viability. Thus, in this research, we explored the feasibility of precisely producing silver nanoparticles in natural dextran hydrogel networks without the use of reduction agents, and demonstrated their excellent antibacterial activity and catalytic performance. In view of the good biocompatibility and biodegradability of dextran hydrogel, as well as the good binding affinity of Ag-dextran gel nanocomposites with surface, the Ag-dextran gel nanocomposites can be used as an effective antimicrobial material and catalyst.

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2 Experimental

2.1 Materials

Dextran (M_w 40,000) was purchased from Sinopharm Chemical Reagent Co., Ltd, China. *N,N*-methylenebisacrylamide (MBA) was purchased from Merck-Schuchardt, Germany. Silver nitrate (AgNO_3), methylene blue (MB), sodium hydroxide (NaOH), sodium chloride (NaCl), sodium borohydride (NaBH_4), and sodium bicarbonate (NaHCO_3) were purchased from Guangzhou Chemical Reagent Factory, China. Tryptone, beef extract and agar were supplied by Guangzhou Huankai Microorganism Technology Co., Ltd. All chemicals were used without further purification. Deionized water was used for the preparation of all solutions in this study.

2.2 Preparation of Dextran Hydrogels

Dextran hydrogels were synthesized (30) by crosslinking reactions of dextran and MBA in 2.8 mol.L^{-1} aqueous NaOH solution. Firstly, 2.236 g dextran and 10 mL 2.8 mol.L^{-1} aqueous NaOH solution were mixed in a 50 mL beaker, and stirred continuously until dextran dissolved absolutely. Under continuous stirring, different amounts of MBA (0.40, 0.35, 0.30 g) were added (the corresponding DexCG-Ag nanocomposites are labeled MBA400, MBA350 and MBA300, respectively). After stirring slowly for about 3 h under room temperature, the solution gradually became viscous. Ten minutes after the stirring was stopped, hydrogel was formed. Finally the beaker was kept under 30°C for 6 h to achieve complete network formation for the hydrogels. The gels obtained were cut into small pieces and they were washed thoroughly with deionized water for one week to leach out NaOH and unreacted compounds.

2.3 Preparation of Dextran Hydrogel-Silver Nanocomposites

Swollen dextran hydrogel pieces were placed into 20 mL of AgNO_3 aqueous solution (5 mmol.L^{-1}) with the temperature kept under 30°C . Deep-yellow hydrogel-silver nanocomposites were obtained after 2 days.

2.4 Characterization

UV-Vis spectra of dexCG-Ag nanocomposites (5 mg/mL) were acquired using a UV-3150 (Japan) spectrophotometer over the range 300 to 700 nm with a 0.5 nm resolution. X-ray diffraction patterns were recorded using a Rigaku Diffractometer (Cu radiation, $\lambda = 0.1546$) running at 40 kV and 40 mA and the XRD patterns were recorded at a scanning rate of 2° min^{-1} in the 2θ range of $30\text{--}80^\circ$. TEM measurements of Ag nanoparticles stabilized by hydrogels were performed using a JEM-2010HR transmission

electron microscope. The samples were dispersed in deionized water and a copper mesh covered with a carbon film was used as the carrier.

2.5 Swelling Ratio

Accurately weighed fully swollen hydrogel disc and hydrogel with Ag nanoparticles disc were vacuum dried at 50°C for one day. The equilibrium swelling ratio (Q) of the hydrogels was calculated using $Q = (W_e - W_d)/W_d$, where W_e is the weight of swollen hydrogel and W_d is the dry weight of the hydrogels.

2.6 Antibacterial Experiment

Gram positive *Bacillus cereus* was used to test the antibacterial activity of dexCG-Ag nanocomposites. Firstly, tryptone 1.5 g, beef extract 0.75 g, NaCl 0.75 g agar 3.0 g, and deionized water 150 mL were put into a beaker, and heated under continuous stirring until all the substances dissolved. The pH of the solution was adjusted to 7.2 with 1.0 mol.L^{-1} NaOH solution. The solution was sterilized using high pressure steam at 120° for 20 min. The culture medium was cooled to about 50°C . A proper amount of bacterial suspension was then added, and shaken in order to disperse bacteria well in the culture medium. 10–15 mL of bacteria-containing culture medium was placed in a Petri dish until the content solidified. DexCG-Ag nanocomposite disks were placed on the surface of solid culture medium and incubated for 20 h at 37°C .

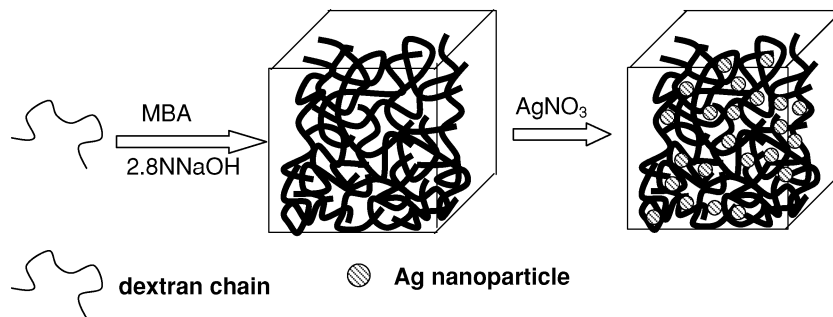
2.7 Catalysis Experiment

The methylene blue (MB) reduction reaction using DexCG-Ag nanocomposites as catalyst was studied by dispersing dexCG-Ag nanocomposites in a buffer solution in the presence of MB. In a typical experiment, 5 mg dexCG-Ag was mixed with 10 mL of 0.02 mol.L^{-1} NaHCO_3 buffer solution and stirred to allow dexCG-Ag to be dispersed well in the solution. After that, 0.05 mL (0.01 mol.L^{-1}) of MB solution was added. Finally, 0.3 mL (0.1 mol.L^{-1}) of freshly prepared NaBH_4 solution was added to the mixture. The progress of the reaction was followed using a spectrophotometer by monitoring the absorbance of MB at 657 nm.

3 Results and Discussion

3.1 *In situ* Formation of Silver Nanoparticles in Dextran Hydrogel

In this study, we report a method to obtain silver nanoparticles in dextran hydrogels through *in situ* reduction without adding a reducing agent. The hydrogels used in this research had a number of hydrophilic hydroxides which could absorb Ag^+ ions in the solution, and some aldehydes which



Sch. 1. Scheme showing the *in situ* preparation of Ag nanoparticles in dextran hydrogels.

acted as both a reducing agent and adsorbent groups. The hydrogel network acted as the carriers in the reaction process. Scheme 1 shows the formation of Ag nanoparticles in the hydrogels. Once fully swollen, dextran hydrogels were put in AgNO_3 solution, and the absorption and reduction of Ag^+ happened slowly at the same time. The colorless, transparent hydrogels gradually changed into deep yellow in about two days at 30°C . Figure 1 clearly demonstrates the different appearance of hydrogel and hydrogel with Ag nanoparticles.

3.2 Characterization of Ag Nanoparticles Formed in Dextran Hydrogel Network

The *in situ* reduced Ag nanoparticles in the hydrogel networks have an obvious influence on the bulk properties of the hydrogels because they can change the microenvironment of the networks. Precursor hydrogels with different amounts of MBA crosslinker were prepared and it was noted that, as the crosslinker concentration increased in the hydrogels, their swelling ratio decreased to a greater extent,

as shown in Figure 2. This phenomenon is quite common and is widely attributed to the smaller mesh size of the networks. Compared with the precursor hydrogels, the hydrogels with Ag nanoparticles show a larger decrease in the swelling ratio, showing that the formation of Ag nanoparticles in hydrogel network can enhance the flexibility of the hydrogels. That can be explained as follows: When Ag nanoparticles were formed in hydrogel network, the interactions between Ag and $-\text{OH}$ of the dextran chains reduced the hydrophilicity of the hydrogels, and hence decreased the swelling ratio of hydrogels.

To confirm the formation of silver nanoparticles in the networks, UV-visible spectra were acquired and the results are presented in Figures 3 and 4. Figure 3 shows the influence of AgNO_3 concentration on the size and size distribution of Ag nanoparticles. A characteristic absorption peak around 420 nm is noted for the silver nanoparticles in each hydrogel sample due to the surface plasmon resonance effect. There are no peaks around 335 and 560 nm, indicating the complete absence of Ag nanoparticle aggregation or Ag clusters (31,32). With increasing the AgNO_3 concentration,



Fig. 1. Photographs of (a) dextran hydrogel, and (b) dextran hydrogel-silver nanocomposites.

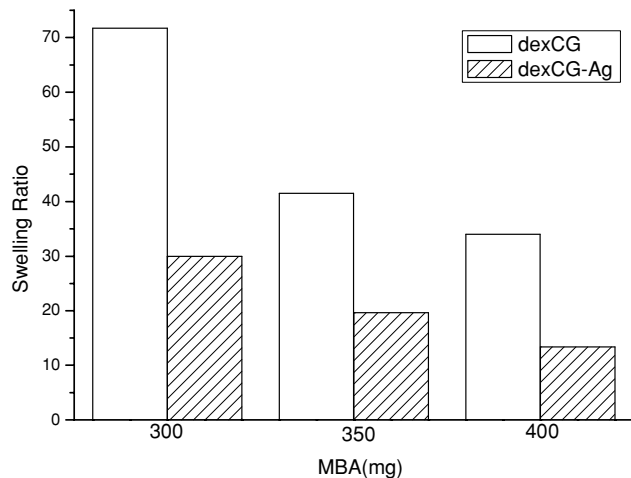


Fig. 2. Swelling ratios of dextran hydrogels and silver-dextran hydrogel nanocomposites with different amounts of crosslinking agent.

the half width of the peak became narrower, and the peak became more intense. In other words, the distribution of Ag nanoparticles was narrow in a relatively concentrated AgNO_3 solution and the number of Ag nanoparticles in hydrogel was much higher in a certain concentration range (1.0–5.0 mM). Beyond a certain concentration, the size and size distribution remained unchanged. These phenomena can be explained by the formation of Ag^+ concentration differences between the solution and hydrogel network and the amount of aldehyde reducing groups. At a low AgNO_3 concentration, there were enough reducing groups to completely reduce the Ag^+ diffused into the hydrogel, and the distribution and number of Ag nanoparticles in hydrogels only depended on the concentration gradient. With

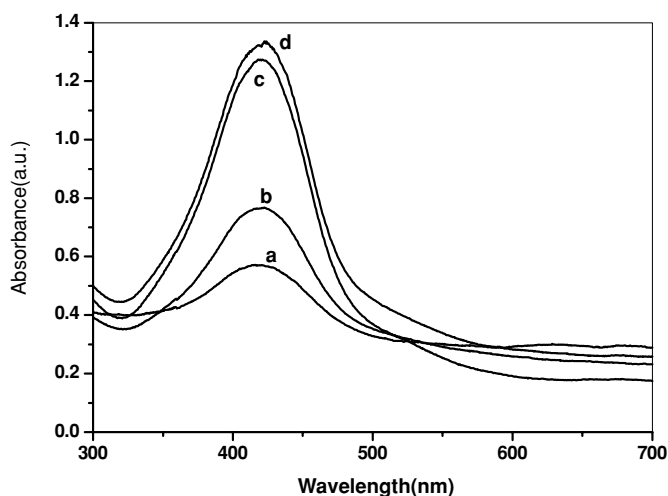


Fig. 3. UV-Vis spectra of Ag-dextran hydrogel nanocomposites prepared from different AgNO_3 concentrations: (a) 1.0 mM, (b) 2.5 mM, (c) 5 mM, (d) 10 mM.

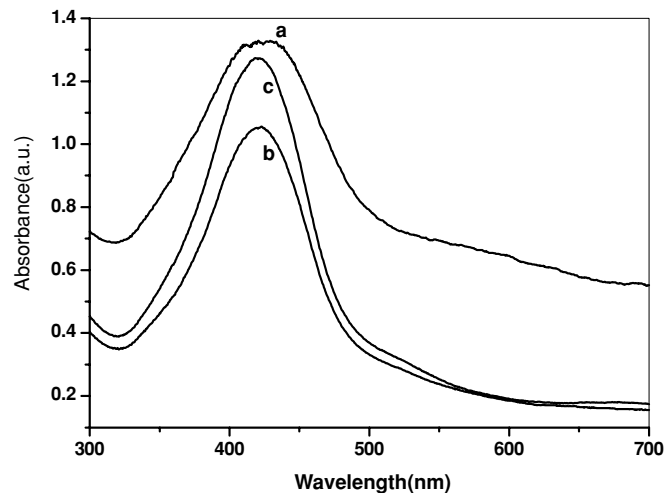


Fig. 4. UV-Vis spectra of Ag-dextran hydrogel nanocomposites using different amounts of crosslinking agent: (a) MBA300, (b) MBA350, (c) MBA400.

increasing AgNO_3 concentration, there were a great number of Ag^+ ions diffused into hydrogels that all the reducing groups were exhausted, and a further increase in Ag^+ concentration would have no influence on Ag nanoparticles formed in the hydrogel. Therefore, the UV-Vis spectra of Ag nanoparticles did not change with increasing the AgNO_3 concentration.

Figure 4 shows the influence of hydrogels with different amounts of crosslinking agent on the size and size distribution of Ag nanoparticles. The characteristic absorption peak shifts from 429.0 nm in the case of MBA300 to 418.5 nm in the case of MBA400, indicating that the sizes of Ag nanoparticles decrease with increasing crosslinking density. It is proved by TEM studies as discussed in the next section.

The TEM images of silver nanoparticles in the hydrogel networks crosslinked with different amounts of MBA are shown in Figure 5. It is obvious that the silver nanoparticles formed in different crosslinked networks showed a similar spherical shape and uniform distribution in all the samples. The average size of Ag nanoparticle for MBA400 and MBA350 is around 20 nm and 30 nm, respectively, indicating that the MBA concentration strongly influenced the Ag nanoparticle size. Highly dense hydrogel networks (using a high MBA concentration) favor smaller silver nanoparticles, since they allow the establishment of inter- and intramolecular attractions between the hydrogel networks due to less free space in the hydrogel networks (33). This would help stabilize as well as control the size of the nanoparticles.

Figure 6 shows the XRD patterns of the hydrogel and MBA400 nanocomposite. The diffraction peaks for MBA400 nanocomposite are found at 38.28, 44.38, 64.6 and 77.54 degree and assigned to the (111), (200), (220) and (311) planes of face centered cubic (fcc) silver, respectively. On the other hand, the pure hydrogels without Ag

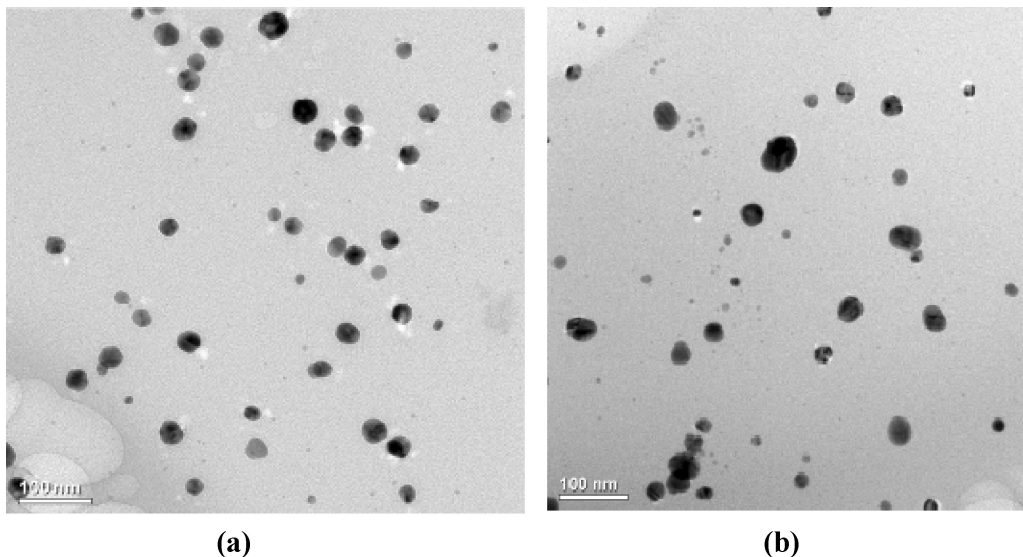


Fig. 5. TEM images of Ag nanoparticles in hydrogels using different amounts of crosslinking agent: (a)MBA400; (b)MBA350.

nanoparticles did not possess such peaks in their X-ray diffraction patterns, indicating the absence of crystallinity.

Figure 7 illustrates the antibacterial effect of pure hydrogels and hydrogel–silver nanocomposites on *Bacillus cereus*. As expected, the number of colonies grown surrounding the hydrogel–Ag nanocomposite was found to be almost nil, whereas the pure hydrogel did not show any effect on *Bacillus cereus*. Therefore, we conclude that the hydrogel–silver nanocomposites are excellent antibacterial materials.

Figure 8 illustrates the catalytic roles of hydrogel–Ag nanocomposite in the selective catalytic reduction of MB and NaBH₄. For the investigation of reaction kinetics, the UV–visible spectra of MB in NaHCO₃ buffer were recorded. A certain amount of MB and NaBH₄ solutions

in NaHCO₃ buffer were mixed, and the blue color of MB in reaction remained at room condition. The addition of 0.0050 g of the nanocomposite catalyst into the reaction mixture caused a gradual fading of the characteristic blue color, and finally a complete bleaching of the blue color of the MB solution was observed after about 15 min. However, the addition of 0.0050 g hydrogel into the reaction mixture did not produce fading and bleaching of the blue color,

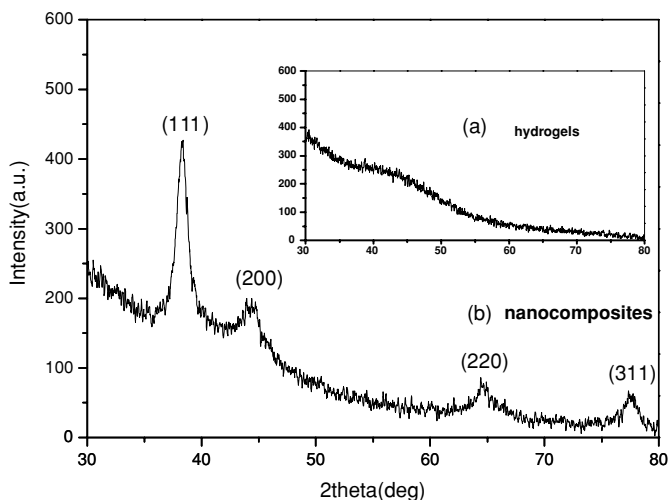


Fig. 6. X-ray diffraction patterns of (a) dextran hydrogels and (b) DexCG-Ag nanocomposites.

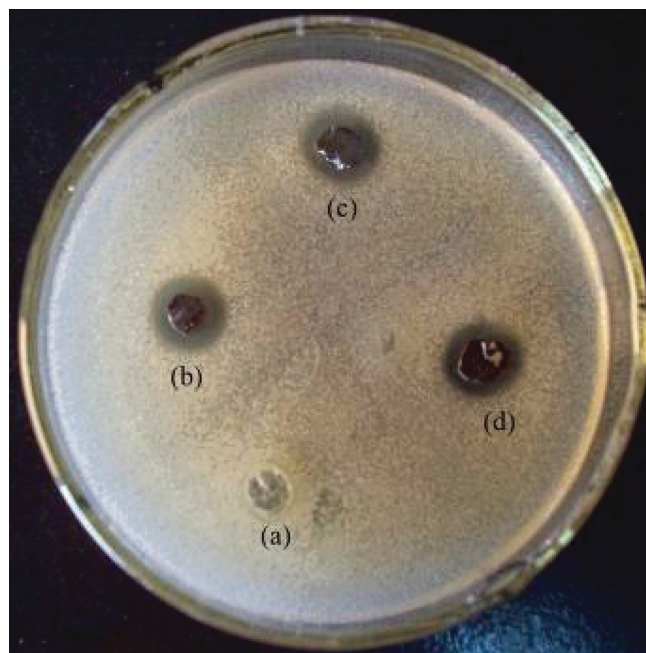


Fig. 7. photographs of hydrogel and nanocomposites on *Bacillus cereus* after 20 h incubation (a) dexCG; (b) dexCG-Ag (MBA300); (c) dexCG-Ag (MBA350); (d) dexCG-Ag (MBA400).

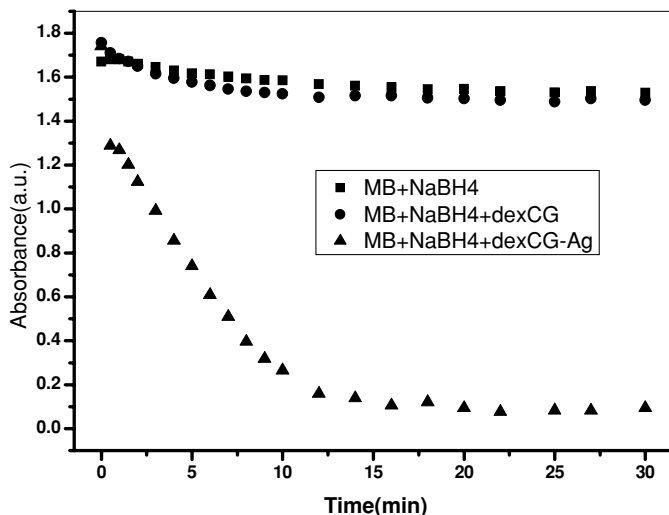


Fig. 8. Catalytic effects of hydrogel-Ag nanocomposites on the reduction of MB and NaBH₄. Conditions: [MB] = 5×10^{-5} mol.L⁻¹; [NaBH₄] = 3×10^{-3} mol.L⁻¹; amount of catalyst = 0.0050 g.

indicating that pure hydrogel without Ag nanoparticles has no catalytic effect on the redox system.

As a biodegradable catalyst, hydrogel-Ag nanocomposite remained stable for a long time. It is a type of promising environment friendly catalyst.

4 Conclusions

In conclusion, Ag nanoparticles were *in situ* synthesized in dextran hydrogel network. The antibacterial activity against *Bacillus cereus* was found to be excellent and the catalytic effect on MB reduction was apparent. In view of the good biocompatibility and biodegradability of dextran hydrogel, the Ag nanoparticles in hydrogel can be used as an effective antimicrobial material and catalyst.

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