Preparation and characterization of AgNPs@SNC nanocomposites

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Abstract—Starch nanocrystal (SNC) was prepared by 40℃ weak sulfuric acid hydrolysis method. Silver nanoparticles (AgNPs) were simply and quickly reduced in situ on starch nanocrystal by ultrasonic assisted reduction method. UV-vis absorption spectrum verified the existence of AgNPs. The surface modification of AgNPs@SNC was carried out by using 3-aminopropyltriethoxysilane (APTES) with simple structure and low cost to improve its dispersivity in the hydrophobic polymer matrix. Then the success of modification was preliminarily confirmed by the Fourier-transform infrared spectroscopy. Taking Staphylococcus aureus and Escherichia coli bacteria as objects of the study, the antibacterial properties of AgNPs@SNC were also explored, and the test results showed that AgNPs@SNC had certain inhibitory effect on Escherichia coli.

1. Introduction

Starch nanocrystal (SNC) is nowadays receiving more and more attention from the research groups [1]. As a good candidate for nanomaterial, its miscibility is limited by the presence of many hydroxyl groups on its surface. Nevertheless, the large surface area of nanostructure and the presence of active hydroxyl groups result in a good surface chemical modification potential for SNC. A large number of physical or chemical modifications have been carried out to make SNC can be uniformly dispersed in the polymer matrix, such as crosslinking, esterification, acetylation and graft copolymerization [2-5]. Surface modification of silane has been proved to be a good method to improve the surface hydrophobicity of nanocrystals. For the first time, 3-aminopropyltriethoxysilane (APTES) was chosen to achieve surface modification of the waxy potato starch as well as waxy corn starch, thereby improving their hydrophobicity [6].

For the preparation of green antibacterial nanocomposites, it is urgent for its development to combine antibacterial efficiency with low-toxicity or non-toxicity, environmental-friendly, low cost and easy fabrication [7]. Many studies have reported good antibacterial performance of nanocomposites containing AgNPs [7-9]. However, AgNPs obtained by such method usually tend to polymerize, resulting in the disappearance of nanoscale properties and functions. Starch-silver nanoparticles were synthesized in one step by ultrasonic method, which was environmentally friendly and a simple preparation method [9].

The objective of current work is to prepare a kind of nanofiller with good antibacterial properties. In order to achieve this goal, AgNPs@SNC nanohybrid structures were synthetised and characterized at first, then followed by surface-modification using APTES, and finally the success of modification was basically verified.

2. Materials and Methods

2.1 Sample preparation

2.1.1 Synthesis of AgNPs@SNC

SNC was prepared by acid hydrolysis of waxy corn starch, with relatively minor modifications according to different raw materials. 15 g of soluble starch was first dispersed slowly into 3.14 M H_2SO_4 solution (250 mL) , and then the mixture was stirred continuously for 7 days in a 313K water bath at a speed of 180 rpm. After sufficient reaction, a large quantity of deionized water was added into the suspension so as to stop the reaction. The above obtained reactant was further centrifuged for several times (10000 rpm, 10 min) until the final pH of the supernatant turned into neutral, and the final

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prepared SNC water suspension was preserved at low temperature. AgNPs were synthesized in 200 mL SNC dispersion solution through ultrasonic cell crusher, according to our previous study [10]. With the concentration of SNC and $AgNO_3$, ultrasonic power, ultrasonic time as four changing factors, set three levels for each factor. The absorbance at about 410 nm (characteristic peak of silver) when measuring UV-vis absorption spectrum as the test index, orthogonal test was carried out to obtain the optimal group, see Table 1 for details.

Table 1. L9 (34) design of orthogonal array.

#	SNC ($mg \cdot ml^{-1}$)	$AgNO_3$ ($mM \cdot ml^{-1}$)	Time (min)	Power (w)	UV/vis absorbance at 410 nm
T1	0.1	0.05	8	400	410, 0.0382
T2	0.1	0.1	12	600	409, 1.6270
T3	0.1	0.15	16	800	419, 2.4653
T4	0.6	0.05	12	800	408, 0.3645
T5	0.6	0.1	16	400	410, 1.5604
T6	0.6	0.15	8	600	412, 1.3611
T7	1.1	0.05	16	600	400, 0.4772
T8	1.1	0.1	8	800	402, 0.9961
T9	1.1	0.15	12	400	413, 2.4179
R	0.2815	1.7881	0.7025	0.1837	

2.1.2 Surface modification of AgNPs@SNC

Through trial and experiment, the mixed solvent of water and alcohol was finally determined as the hydrolysis solvent of APTES, which ensured that a certain hydrolysis reaction was forward to generate silanol while reducing the self-condensation of silanol, and the stability of the solution was higher. Specifically, the volume ratio of APTES, water and ethanol was 1:3:12, and the ratio of AgNPs@SNC to APTES was 1:10 w/v. Under the action of 300 rpm magnetic stirring, 3 mL water and 12 mL ethanol were mixed evenly. After 1 mL APTES was added, glacial acetic acid was slowly dropped to decrease the PH value of solution to ~4. Subsequently, 0.1 g AgNPs@SNC nanohybrid was weighed and then added into the above solution. The obtained mixture was hydrolyzed for at least 3h at 298K and centrifuged (4000 rpm, 10 min). The precipitation was drained and filtered to remove moisture, and then cured in a vacuum drying oven of 378K for 35 min. After curing, the mixture was ground into powder and labeled AM-AgNPs@SNC. SNC was surface modified in the same way as above, and the prepared powder was labeled AM-SNC. The reaction mechanism is shown in Fig.1.

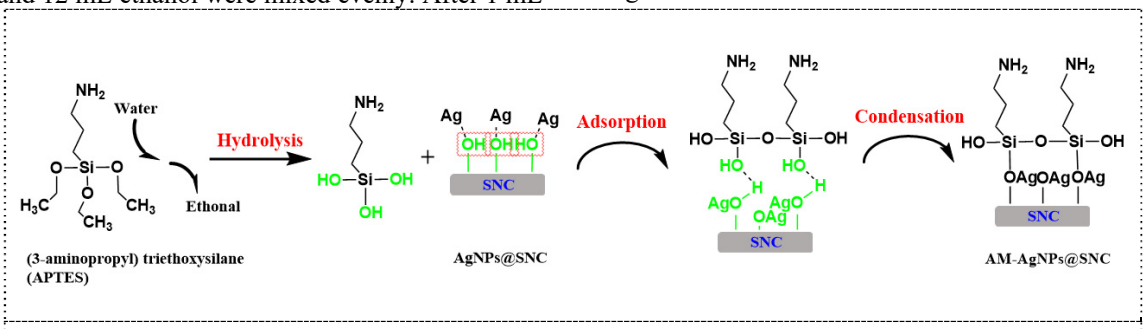

Fig.1 Silane surface modification of AgNPs@SNC.

2.2 Characterization

Particle sizes of SNC and AgNPs@SNC were measured by the 90plus PALS model (Brookhaven, USA) using dynamic light scattering (DLS). All measurements were repeated.

The UV-vis absorption spectrum of AgNPs@SNC suspension were measured by UV-5500 visible spectrophotometer (Shanghai METASH, China), and the wavelength range was 200-800 nm.

The functional groups and chemical structures of the dried AgNPs@SNC, AM-AgNPs@SNC , SNC and AM-SNC powders were primarily analyzed by Fourier-transform infrared spectroscopy (FT-IR,VERTEX 80/80V, Germany) in the range of 200-4000 cm^{-1}.The 1mg freeze-dried sample was first ground with suitable dose of dried potassium bromide (99.5% purity, Merck Co., Ltd.) and then pressed into transparent sheets to form FT-IR test samples

Escherichia coli (E.coli) as well as Staphylococcus aureus (S.aureus) bacteria was selected as gram-positive bacterial model to study the antibacterial activity of AgNPs@SNC. LB solid broth which composed of yeast extract 5 g/L, peptone 10 g/L and NaCl 10 g/L was disinfected with AGAR in a autoclast at 394K for 2 h. The suspensions containning S.aureus or E.coli bacteria were evenly coated on LB solid broth in the petri dish, and the sample was placed in the LB solid broth center.

The petri dish was incubated in 310K incubators for 24 hours.

3. Results and discussion

From the DLS results demonstrated in Fig.2(a), the average particle size of the SNC powder and the AgNPs@SNC nanohybrid was 148.19 nm and 158.81 nm, respectively, indicating that SNC prepared by acid hydrolysis and the in-situ reduced AgNPs were in the nanometer range. From the absorption spectrum in Fig.2(b), some samples had an apparent absorption peak around 410 nm, which usually corresponding to the surface plasmon excitation of Ag atoms. The intensity of absorption peak is not only related to AgNPs@SNC concentration, but also to AgNPs@SNC particle size. And thus as the concentration of Ag^{+} increases, the intensity of the absorption peak at ~410 nm also increases obviously. Based on this, the best test condition for AgNPs synthesis (group T3) was selected. The concentration of SNC and $AgNO_3$ used in AgNPs@SNC suspension was amplified five times in equal proportion, and the ultrasonic time and power remained unchanged, the samples obtained were freeze-dried and sealed for subsequent experiments.

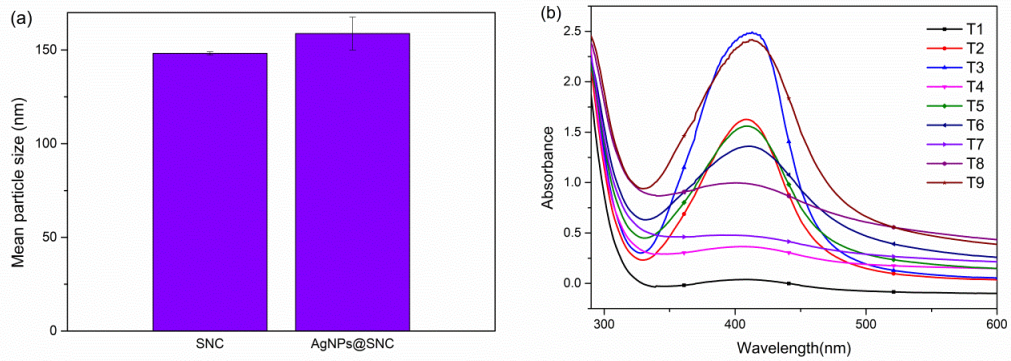

Fig.2 (a) DLS of SNC and AgNPs@SNC and (b) UV absorption spectrum of AgNPs@SNC suspension.

The FT-IR results confirmed that the desired product was obtained (Fig.3). SNC and AM-SNC obviously had similar spectral characteristics. After silane surface modification of AgNPs@SNC, a new IR absorption peak appeared at 1560 cm^{-1} in the silanized SNC, corresponding to the amino-shear bending vibration. Meanwhile, this also indicated that the functional groups had been successfully introduced into the surface of the SNC. In addition, AgNPs@SNC did not form a new IR absorption peak compared to pure SNC. This was probably because AgNPs were only physically adsorbed, and no chemical bond is formed on the surface of the SNC. For the AM-AgNPs@SNC, the absorption peak intensity of hydroxyl (corresponding to the wavenumbers ranging from 3600cm^{-1} to 3000 cm^{-1}) exhibited an obvious decreased trend. Such changes also indicated that polysiloxane was physically adsorbed through hydrogen bonding with hydroxyl group on the surface of SNC, which further confirmed the success of modification.

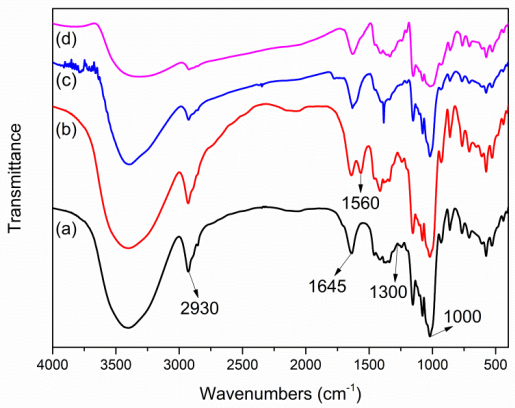

Fig.3 FT-IR spectra of (a)SNC, (b)AM-SNC, (c)AgNPs@SNC, and (d)AM-AgNPs@SNC.

The AgNPs@SNC powder before and after silane modification was dissolved in water and chloroform, respectively, and the initial modification was successfully verified. The relevant verification results are depicted in the Fig.4.

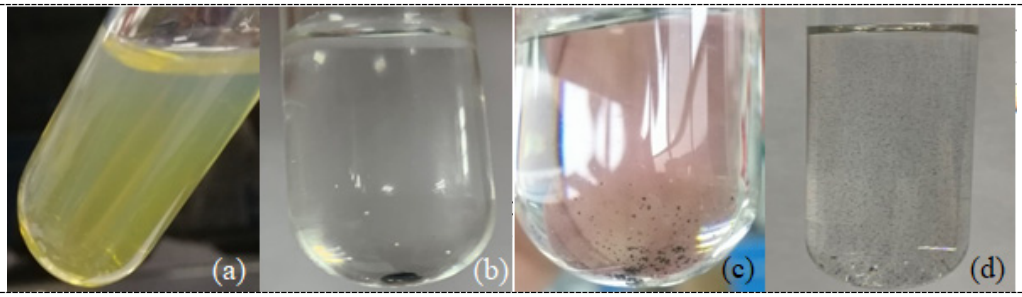

Fig.4 Comparison of before and after silane modification
(The solvent of (a) and (b) is water; The solvent of (c) and (d) is chloroform).

The antibacterial activity of AgNPs@SNC nanohybrid against S.aureus and E.coli bacteria under dark field conditions was finally explored. The corresponding antibacterial activity was evaluated by the bacteriostatic ring, as shown in the Fig.5. The width of E.coli was 2.2 mm, but S.aureus did not work well. The results showed that AgNPs@SNC nanohybrid had certain inhibitory effect on E.coli, but the inhibitory effect on S.aureus bacteria was poor. In this study, to a certain extent, the antibacterial activity of AgNPs@SNC nanohybrid was dependent directly on the existence of the AgNPs, and moreover, the concentration of Ag^+ played a vital role in bacteriostasis on the above bacteria.

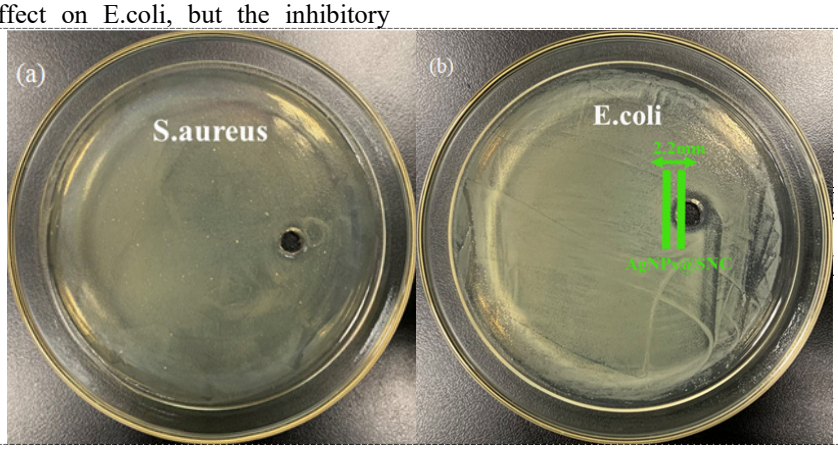

Fig.5 (a) DLS of SNC and AgNPs@SNC and (b) UV absorption spectrum of AgNPs@SNC suspension.

4. Conclusion

In summary, AgNPs@SNC was synthesized in situ assisted by ultrasound. AgNO3 was added to SNC suspension, glucose was used as green reducing agent, sodium hydroxide provided alkaline environment, and silver nanoparticles were generated in situ. The method was green, easy to operate and easy to expand. The nanocomposites were characterized by UV-vis, DLS and FT-IR. UV-visible absorption spectra showed high Ag content in AgNPs@SNC suspension, especially in T3 sample, with a high absorption peak at 420 nm. The particle size analysis confirmed that SNC and AgNPs@SNC were nanomaterials, and the particle size changed little after loading silver nanoparticles. The successful silanization of AgNPs@SNC was preliminarily verified by FT-IR analysis of the structure.

Acknowledgments

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