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Rice husk based porous carbon loaded with silver nanoparticles by a simple and cost-effective approach and their antibacterial activity

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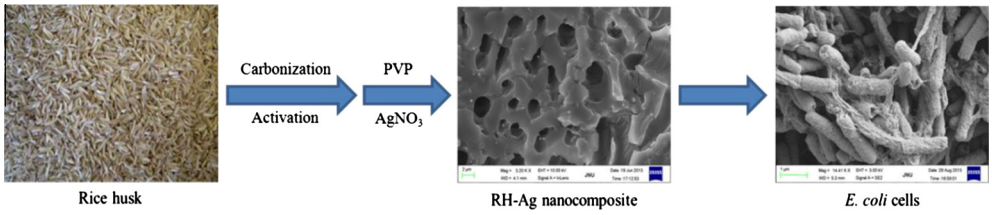
GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, we chose rice husk as raw material and synthesized successfully porous carbon loaded with silver nanoparticles (RH-Ag) composites by simple and cost-effective method. The as-prepared RH-Ag composites have a BET-specific surface area of 1996 $m^2 g^{-1}$ and result in strong capacity of bacteria adsorption. The result of antibacterial study indicated that the RH-Ag system displayed antibacterial activity that was two times better than pure Ag NPs. Our study demonstrates that the antibacterial activity of RH-Ag composites may be attributed to their strong adsorption ability with bacteria and result in the disorganization of the bacterial membrane ultrastructure. In addition, RH-Ag system was found to be durative slow-releasing of silver ions and biocompatible for human skin keratinocytes cells. In terms of these advantages, the RH-Ag composites have potential application in antibacterial infections and therapy.

1. Introduction

In recent years, nanostructured materials have attracted a great attention because of their novel physical, chemical, and biological properties and potential use in antibacterial application, especially those of metallic nanoparticles and their corresponding metal oxides, such as copper [1,2], silver [3–7], titanium oxide [8,9], and zinc oxide [10,11]. Among them, silver nanoparticles (Ag NPs) are extensively used in a variety of medical materials and devices to prevent infection, for instance, wound dressing [12], catheters [13] and bone fixation devices [14]. However, the self-aggregation or precipitation of Ag NPs, due to minimizing their surface energy, will lead to a loss of surface area and decrease antibacterial activity [6,15,16]. Therefore, how to develop a stable, dispersed Ag NPs substrates and control the release of Ag^+ are worth of considering.

To deal with these problems, many different silver nanocomposites have been prepared. For example, Gao et al. reported that the synthesis of titanium nanotubes embedded with Ag NPs and their long lasting antibacterial ability was observed [17]. It has also been reported that Ag/alginate nanocomposite hydrogel have antibacterial activity and could be used for wound dressings [18]. In particular, carbon materials, such as graphene oxide [19–21], and carbon nanotubes [22–24] have been used as support

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materials to load Ag NPs, integrating excellent antibacterial effects and the other optical and magnetic properties. We have previously incorporated Ag NPs into carbonaceous nanospheres by hydrothermal method and their antibacterial ability has been observed. However, these materials require complex, tedious and high cost preparation method with. Therefore, it is very necessary to design cost-effective Ag-based composites by simple method. The Food and Agriculture Organization (FAO) reported that the world's annual rice production is about 650 million tons, in which the rice husk (RH) available for using is 145 million tons and the annual yield of China is about 40 millinon tons [25]. In some countries, RH has been disposed and even leading to pollution issues. Harvesting carbon from RH can not only take full advantage of the highest value, but also minimize the related environmental issues from the current disposals of RH [26]. It was reported that high-quality graphene sheets have been synthesized by using natural and industrial carbonaceous wastes as the main starting material [27].

Here, we prepared porous carbon using RH as a candidate for supporting biomaterial by carbonization and activation. With the aim of improving the antibacterial activity of Ag NPs, poly(N-vinyl-2-pyrrolidone) (PVP) could reduce silver ions to form Ag NPs onto the surface of rice husk based porous carbon (RHPC). The antibacterial activity of as-synthesized porous carbon loaded with silver nanoparticles (RH-Ag) composites was investigated. The results showed that the antibacterial activity of RH-Ag composites was almost two times greater than free Ag NPs system under the same experimental conditions. In addition, RH-Ag system was found to be biocompatible for human skin keratinocytes cells.

2. Materials and methods

2.1. Preparation of rice hull based porous carbon

The chemical reagents used in our experiments were of analytical grade. The rice husks used as raw materials were getting from a local village of Huaihua in Hunan province. Firstly, it was directly carbonized at 400 °C in the presence of nitrogen for 2 h at the rising rate of 5 °C/min. Then, the carbonized rice husk was mixed with sodium hydroxide, the ratio of sodium hydroxide/carbon was 3, then the carbon sample was heated to 800 °C at the rising rate of 5 °C/min and kept for 1 h. The sample was washed with distilled water until the pH came near to neutral and dried in 60 °C oven for 12 h.

2.2. Preparation of rice hull based porous carbon loaded silver nanoparticles

100 mg RHPC powder in 100 mL H_2O was sonicated for 30 min to form a homogeneous suspension before 3 g PVP was dissolved in the solution. Then 20 mL $AgNO_3$ (1 mM) aqueous solution was rapidly added into above solution at 65 °C under vigorous stirring. The reaction was allowed for 6 h in the dark. Finally, the sample was collected by centrifugation with deionized water for several times, and then dried at 60 °C in vacuum for 3 h.

2.3. Characterization

The surface morphologies of the samples were performed by field emission scanning electron microscopy (FESEM, Hitachi, S-4700). Morphological features of samples were performed by Philips TECNAI 10 high-resolution transmission electron microscopy (HRTEM). Energy-dispersive X-ray spectroscopy (EDS) analysis was obtained with an Oxford INCA Energy TEM 200 EDS system. The obtained samples were performed by X-ray diffraction (XRD) on a MSAL-XD2 with a Cu target in the 2θ range from 10° to 80° (40 kV, 30 mA, λ = 1.54051 Å). Raman spectroscopy was conducted with a Renishaw inVia Raman microspectrometer at room temperature. FTIR spectra of RHPC and RH-Ag were recorded on a Nicolet 6700 FT-IR spectrometer. The samples were carried out over the 400–4000 cm^{-1} range at room temperature. N_2 adsorption/desorption isotherms were measured at liquid nitrogen temperature (77 K) using a surface area and porosimetry analyzer (Micromeritics Tristar 3000). Samples were dissolved in deionized water and measured with quartz cuvettes by absorption of UV–vis spectra with a Varian Cary 5000 spectrophotometer. The particle size distribution of Ag NPs in water was analyzed by dynamic light scattering using a Malvern Zetasizer Nano ZS Nicomp 380. Prior to the measurements, the samples were pretreated heating at 150 °C for 3 h under a vacuum to remove moisture. X-ray photoelectron spectroscopy (XPS) measurement was obtained from an ESCALAB-MKII spectrometer with an Axis Ultra photoelectron spectrometer using monochromatic Mg Kα X-ray (1253.6 eV) and binding energies were referred to C1s (284.8 eV). The concentration of silver was estimated using an inductively-coupled plasma atomic emission spectrometry (ICP-AES).

2.4. Release property

The amounts of Ag^+ released from the samples were monitored by ICP-AES. The RH-Ag and the same equivalent $AgNO_3$ solution were immersed into 5 mL distilled water in a shaking incubator at 37 °C for 1 day, and transfer the solutions into dialysis tubes and immersed in 100 mL of distilled water for another day, and the process was repeated for a total of 5 days to generate a serial of solutions containing released Ag^+ at different times. Afterwards, the solutions containing released silver were analyzed by ICP-AES.

2.5. Antibacterial activity

To evaluate the antibacterial activity of against *Escherichia coli*, the effect of RH-Ag material on the bacterial growth kinetics in liquid media was quantitatively studied. All materials were autoclaved to ensure sterility before experiment, *E. coli* K12 cells were grown in 50 mL liquid medium supplemented with 12.5, 25, 50, 100 μg mL^{-1} of Ag NPs, RHPC and RH-Ag. The growth rate of bacteria was evaluated by measuring the optical density at 600 nm (OD_{600}) based on the turbidity of the suspension each 2 h. Each experiment was performed in triplicate. In order to study further antibacterial effect, *E. coli* cells were spread onto agar plates with suspensions of samples by the disk-diffusion test [28]. The paper disks containing RHPC or RH-Ag (50 μg/mL) were placed on the Petri dish respectively. After incubating at 37 °C for 48 h, the zone of inhibition was measured and imaged.

2.6. Cell morphological change

To study the morphology of the test bacterial in detail after treatment with the synthesized RH-Ag material, we selected 25 μg mL^{-1} of the synthesized RH-Ag material as the final concentration to treat the *E. coli* K12 cells in a microtiter plates with a silicon chip in the bottom. Silicon chip with K12 cells grown in materials-free medium was used as control. After incubated for 24 h, the silicon chip was harvested and processed for FESEM. According to the following the techniques, the silicon chip was removed from the microtiter plates, and washed three times with buffer to remove nonadherent *E. coli* K12 cells and medium. Subsequently, the chip was fixed in 2.5% glutaraldehyde for 2 h. After fixation the silicon chip was rinsed with buffer twice. And