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Synthesis of small silver nanoparticles under light radiation by fungus *Penicillium oxalicum* and its application for the catalytic reduction of methylene blue

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HIGHLIGHTS

- Extracellular silver nanoparticles were synthesized using *Penicillium oxalicum* assisted by simulated sunlight.
- The pH of the cell filtrate affected the synthesis of silver nanoparticles.
- The silver nanoparticles were more stable in weakly alkaline and alkaline solutions.
- Small silver nanoparticles with good dispersibility and stability were rapidly synthesized at pH 12.0.
- The reduction of methylene blue was instantly completed with silver nanoparticles synthesized at pH 8.0 used as catalyst.

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ABSTRACT

At present, green and efficient synthetic strategies have been gaining great interest for the synthesis of metal nanoparticles. In this study, the synthesis of extracellular silver nanoparticles (AgNPs) under light radiation was described using the cell filtrate of *Penicillium oxalicum* 1–208. The pH effect of the cell filtrate on nanosynthesis was investigated by visual observation, ultraviolet–visible absorption spectroscopy, dynamic light scattering and zeta potential. The results showed that the pH of the cell filtrate affected the time of nanosynthesis, and the size, size distribution and stability of the synthesized nanoparticles. The AgNPs synthesized at pH 8.0 and 12.0 were further characterized by X-ray diffraction, selected area electron diffraction, energy-dispersive X-ray spectroscopy and transmission electron microscopy. The synthesized AgNPs were spherical in shape, crystalline in nature and preferentially oriented in (111) plane. Small AgNPs with an average particle size of about 4 nm were successfully synthesized at pH 12.0 and well dispersed in solution without obvious aggregation. Furthermore, the AgNPs synthesized at pH 8.0 were used as catalyst and exhibited excellent catalytic activity for the reduction of methylene blue in the presence of $NaBH_4$ at ambient temperature.

1. Introduction

The synthesis of metal nanoparticles is rapidly gaining increasing importance in academia, as it is essential for the development and application of nanotechnology. Physicochemical methods are conventionally adopted to synthesize metal nanoparticles, but there are several disadvantages such as cumbersome, high energy consumption and generation of hazardous by-products [1]. Nowadays, biosynthetic methods based on microorganisms are gaining worldwide popularity due to their environmentally benign nature. Among them, filamentous fungi are excellent candidates as nanofactories for the green synthesis of metal nanoparticles with a wide variety of advantages such as high metal tolerance level, secreting large amounts of extracellular proteins and simpler to handle in the laboratory [2,3].

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However, long reaction time has been a major drawback for many biosynthetic procedures compared with the conventional methods used for nanosynthesis [4,5]. Photochemical pathways have been explored to assist the biosynthesis of metal nanoparticles at ambient temperature. It has been reported that light radiation is effective in the synthesis of silver nanoparticles (AgNPs) obtained by cell-free extracts of *Bacillus amyloliquefaciens* [6]. Mokhtari et al. have reported that visible-light emission can significantly prompt the synthesis of AgNPs using the culture supernatant of *Klebsiella pneumonia* [7]. The effective decrease of the reaction time by light radiation is a promising result, which provides the biosynthetic methods with a greater applicability [3].

The study on AgNPs has increased extensively due to their unique properties, which make them attractive in a wide range of applications such as optical, catalysis, biolabeling and antibacterials. However, shape, size, dispersity and stability of the nanoparticles are critical for their applications in diverse areas. As a result, it will be significantly beneficial for their applications if the synthesized nanoparticles have uniform morphology and high stability.

In our earlier study, fungus *Penicillium* sp. 1–208 was successfully used for the rapid extra-/intracellular biosynthesis of gold nanoparticles [8]. To further study this system, we developed the biosynthesis of extracellular AgNPs with the cell filtrate of *Penicillium* sp. 1–208 under light radiation. It was found that the reaction time, particle size, dispersity and stability of the synthesized AgNPs were affected by the pH of the cell filtrate. Moreover, the AgNPs synthesized at pH 8.0 exhibited excellent catalytic activity towards the reduction of methylene blue (MB) in the presence of $NaBH_4$.

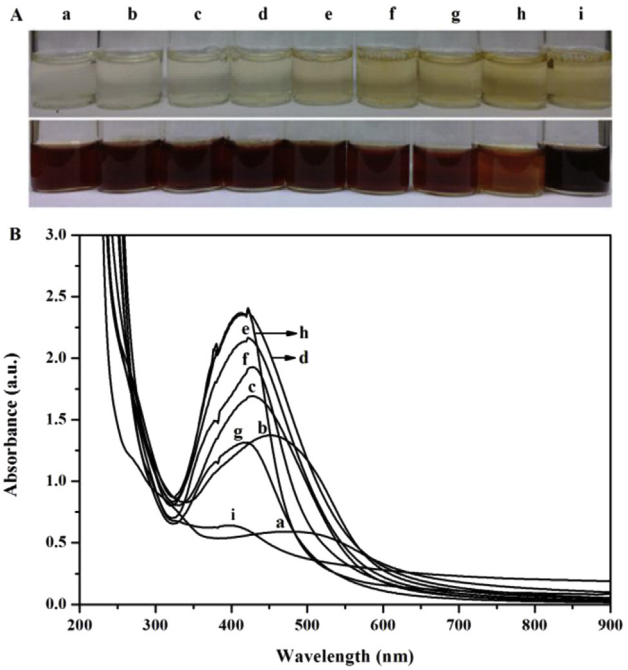

Fig. 1. (A) The color photographs of the cell filtrates of *Penicillium oxalicum* 1–208 (upper) and after reaction with $AgNO_3$ solution for 30 min (lower) under nine different pH conditions from 5.0 to 13.0 at intervals of 1.0 shown from a to i, respectively. (B) The corresponding UV–Vis absorption spectra of the synthesized AgNPs after reaction for 30 min under the same nine different pH conditions as in (A).

2. Materials and methods

2.1. Reagents

Silver nitrate ($AgNO_3$) was obtained from Shanghai Chemical Reagent Co. Ltd., China. MB was purchased from East China Normal University Chemical Factory, China. $NaBH_4$ was procured from KeLong Chemical, China. These reagents were used as received and were all analytically pure. Unless otherwise stated, deionized water was used in all of the experiments.

2.2. Synthesis of AgNPs

The growth conditions of fungal strain *Penicillium* sp. 1–208 and the preparation method of the cell filtrate were the same as described previously [8]. The fungus *Penicillium* sp. 1–208 was identified as *Penicillium oxalicum* (see Supplementary materials). To synthesize the extracellular AgNPs, 100 μL of 0.1 mol/L $AgNO_3$ stock solution was added dropwise to 10 mL of the cell filtrate under stirring. The reaction mixture, placed in a quartz cylindrical tube, was exposed to light radiation generated by a 500 W xenon lamp to simulate the sunlight in a photochemical reaction instrument equipped with a cooling water circulation system to maintain the reaction temperature at 25 °C (Deyangyibang, DY-B, China). Unless otherwise stated, the reaction time to synthesize the AgNPs was 30 min. The same reaction mixture was shielded from light as control sample. The control groups including only the cell filtrate or only $AgNO_3$ solution with the concentration of 1 mmol/L were also carried out in the presence and absence of light.

To study the effect of the pH on nanosynthesis, cell filtrates with nine different pH values adjusted using NaOH or HNO_3 solutions, i.e. pH 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0 and 13.0, were used for the synthesis of AgNPs.

2.3. Apparatus and measurements

All the ultraviolet–visible (UV–Vis) absorption spectra were recorded by a Lambda 35 spectrophotometer (PerkinElmer, USA) measured using a 1.0 cm light-path length cuvette at the resolution of 1 nm. For the analysis of the pH effect, 0.2 mL of the Ag nanoparticle solutions synthesized at different pH values were extracted after the reaction was carried out for 30 min, then diluted by adding 0.4 mL of deionized water, and the resulting diluents were subjected to UV–Vis spectroscopy analysis. To study the reaction kinetics, 0.2 mL of the reaction solutions synthesized at pH 8.0 and 12.0 were withdrawn at different time intervals during the reaction process, then the samples were diluted with 0.4 mL of deionized water and subsequently the UV–Vis spectra of the resulting diluents were measured.

The effect of the pH on nanosynthesis was also analyzed using a Zetasizer Nano ZS90 (Malvern Instruments, UK). The dispersibility and hydrodynamic diameters of the AgNPs were measured by dynamic light scattering (DLS) technique. Zeta potential was determined based on laser Doppler electrophoresis using the same instrument. All the measurements of the nanoparticle solutions synthesized at different pH values were carried out at least three times at the constant temperature of 25 °C.

X-ray diffraction (XRD) measurements of the nanoparticles synthesized at pH 8.0 and 12.0 were performed with an X-ray diffractometer (Rigaku D/MAX 2500 V, Japan). Samples for XRD measurements were prepared by drop coating the solution on Si (111) substrates, followed by drying at room temperature.

Transmission electron microscopy (TEM) and selected area electron diffraction (SADE) analyses of the AgNPs synthesized at pH 8.0 and 12.0 were carried out on a TEM instrument (FEI Tecnai G2 F30, USA). Meanwhile, an energy-dispersive X-ray spectroscopy (EDX) analyzer attached to the TEM instrument was used to confirm the presence of Ag element. Samples were prepared by

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