

Research Article

Synthesis of Luminescent Ag Nanoclusters with Antibacterial Activity

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This paper focuses on the synthesis of novel Ag nanoclusters (NCs) using DHLA as capping reagents in aqueous solution by a photoreduction method. Luminescence studies indicated that the DHLA-Ag NCs exhibited strong blue emission with maximum peak at 480 nm. The maximum emission of the NCs can be greatly improved with irradiating time by around 15-fold from 3 h to 67 h. By means of mycelium growth rate, the results showed that the Ag NCs with smaller sizes had a good antimicrobial effect.

1. Introduction

Luminescent nanomaterials are currently attracting enthusiastic interest due to their applications in biomedical field such as cell imaging or photodynamic therapy [1–3], solar cells [4], lasers [5], lighting, and display technologies [6]. For bioimaging applications, luminescent semiconductor nanocrystals (quantum dots) have several advantages over the conventional organic fluorophores [7–10]. One issue with the use of small molecule fluorophores is a lack of photostability under prolonged excitation. Quantum dots also have excellent photostability, but there are potential cytotoxicity issues due to containing highly toxic metals such as cadmium [11, 12]. Therefore, there always is a challenge to explore alternate luminescent materials.

Silver nanodots are a new class of fluorophores with photophysical properties approaching those of semiconductor quantum dots. Silver nanodots also were named as silver nanoclusters, silver clusters, or silver quantum dots, consisting of several to roughly hundred atoms, possess sizes comparable to the Fermi wavelength of electrons, and

exhibit molecule-like properties, including discrete electronic transitions and strong fluorescence. Extensive efforts have been devoted to the facile preparation of highly fluorescent, water-soluble metallic nanoclusters [13–16]. Zhang et al. utilized photoreduction to synthesize Ag clusters. A mixture of silver ions and poly(N-isopropylacrylamide-acrylic acid-2-hydroxy acrylate) microgel was irradiated with 365 nm light. As the irradiation continued, the solution became light pink, then purple, and dark red in the end [17]. Similar approach was reported with multiarm polymer [18]. Instead of UV light, visible light was applied to photoactivate a mixture of silver ions and poly(methacrylic acid) (PMAA) [19]. An increase in the silver/methacrylic acid (Ag/MAA) molar ratio resulted in red shifts of the absorption peaks and the corresponding emission peaks. A typical example is Ag clusters which exhibited a photoluminescence emission peak at 610 nm with excitation peaks at 400 nm and 450 nm. Such stabilization might be ascribed to the strong interaction between carboxylic acid and silver ions. DNA or RNA exhibit strong affinity for silver ions; therefore, DNA or RNA molecules have been widely utilized to template

the formation of Ag nanoparticles [20–24]. Thiol is one of the common chelating groups for synthesizing silver clusters. However, weakly luminescent Ag species were reported using ether 2,3-dimercaptosuccinic acid and mercaptosuccinic acid [25, 26] ordihydrolipoic acid (DHHLA) [27–29]. In these data, the nanoparticles were usually synthesized by sodium borohydride reduction reaction. There is an urgent need to design luminescent materials with high PL QY, good stability, and low cytotoxicity. DHHLA as the capping reagents has been used to synthesize the CdTe, HgTe, and Ag₂S QDs due to the fact that the bidentate DHHLA can simultaneously attach to two surface sites on the QDs resulting in more stable interaction of stabilizer reagents and NCs [30–32]. Recently, Zhang et al. reported a stepwise method to prepare stable green-emitting Ag NCs. For their method, parent Ag NPs were firstly prepared using a chemical reduction method in the presence of gelatin; then, dihydrolipoic acid (DHHLA) was chosen as the etching ligand [33].

Here, we present a new strong UV photochemical reduction synthesis of water-soluble luminescent Ag NCs using DHHLA as the capping reagents to stabilize the Ag NCs in the solution. In the present work, we found that luminescence of DHHLA-capped Ag NCs could be greatly improved by around 15-fold from 3 to 67 h. Also, by means of mycelium growth rate [34], antibacterial ability of the Ag NCs was tested.

2. Experimental Section

2.1. Chemicals. Lipoic acid (TA, 99%) and NaBH₄ (96%) were obtained from Sigma, Inc. AgNO₃ was obtained from Shanghai Chemical Reagents Company. High purity deionized water (>18.3 MΩ/cm) was produced by Millipore A10 Milli-Q.

2.2. Preparation of Dihydrolipoic Acid (DHHLA). DHHLA was prepared by treating TA with NaBH₄ using a method described in a previous report [27]. TA (5.225 g, 25 mmol) was dissolved in deionized water (200 mL) and then NaBH₄ (1.91 g, 50 mmol) was slowly added to the stirred solution as a reductant. The solution was stirred at room temperature for 2 h and then heated to 100°C until no more gas (H₂) was generated. The final concentration of the DHHLA aqueous solution was 0.125 M.

2.3. Synthesis of Ag Nanoclusters. Water-soluble fluorescent Ag nanoclusters were prepared as follows: a solution of AgNO₃ in water (85 mg, 0.5 mmol) was added to the DHHLA solution (0.125 M, 200 mL) under room-temperature conditions with stirring. Silver was reduced to the zero-valent state by strong UV irradiation at $\lambda = 365$ nm (UV intensity of 400 W). Aliquots of the reaction solution were removed at regular intervals for UV absorption and luminescence experiments. Samples were precipitated by acetone and dried in a vacuum oven for XPS characterization. Finally, the DHHLA-Ag precipitate was dried and collected as a brown yellow powder. TEM sample was prepared by dropping the aqueous Ag nanoclusters solution onto carbon-coated copper grids and the excessive solvent was evaporated.

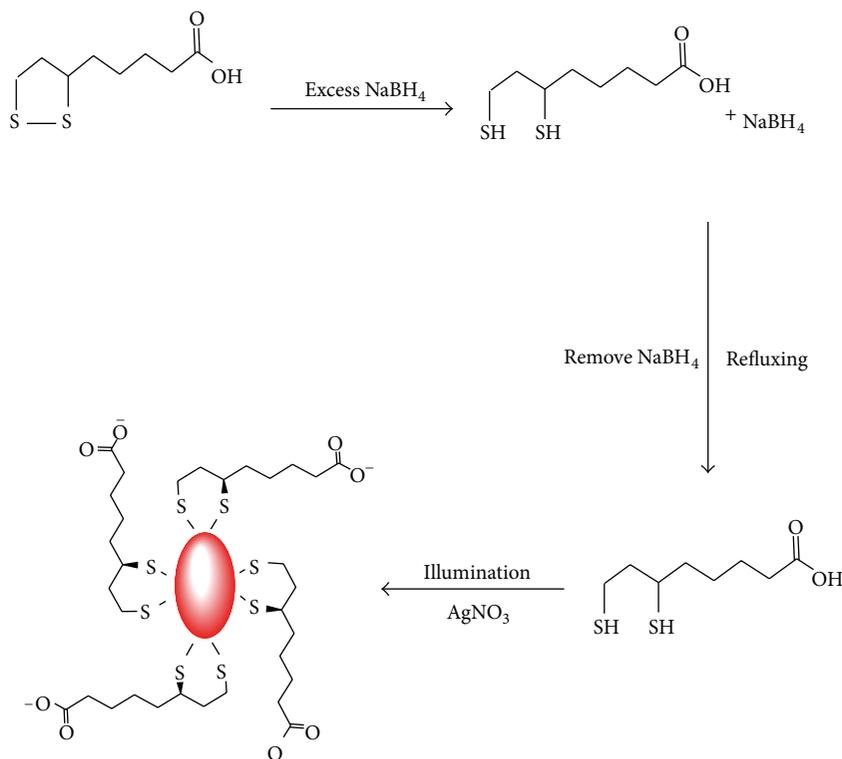
2.4. Assay for Antimicrobial Activity of Ag NCs against Wheat Phytoalexin. The antimicrobial activity of Ag-DHHLA complex, Ag (200 nm), and Ag (2 nm) NCs was investigated against wheat phytoalexin. The concentration of Ag-DHHLA complex, Ag (200 nm), and Ag (2 nm) NCs was the same as 62.5 μ M. As a positive control of growth, microorganisms containing only water were used. Bacteria colony with a disk shape and diameter of 40 mm was reverse placed on the center of the agar plates, added into antimicrobial reagents, respectively, and then cultured in the incubator at 20°C. The antibacterial inhibition rate of the Ag NCs was calculated from the diameter of bacterial colony when its growth diameter was 2/3 of the diameter of diffusion disk. The inhibition rate = $(D_1 - D_2)/(D_1 - 0.4)$, D_1 being the diameter of control bacteria colony and D_2 being the diameter of test bacteria colony.

2.5. Characterization. UV-vis absorption and luminescence spectra were measured at room temperature with a Shimadzu UV-3100 spectrophotometer and a Hitachi 7000 fluorescence spectrometer, respectively. Luminescence spectra were taken at the excitation wavelength $\lambda_{\text{ex}} = 390$ nm. Time-resolved luminescence measurements were carried out on a Fluorolog-3 spectrofluorometer with 390 nm LED lamp. Ludox was applied for PL lifetime measurement in order to eliminate the influence of light scattering (i.e., excitation and emission). Powder XRD measurements were taken on a Philips X'Pert PRO X-ray diffractometer. Transmission electron microscopy (TEM) was performed on a Philips FEI Tecnai G2 F20 S-Twin.

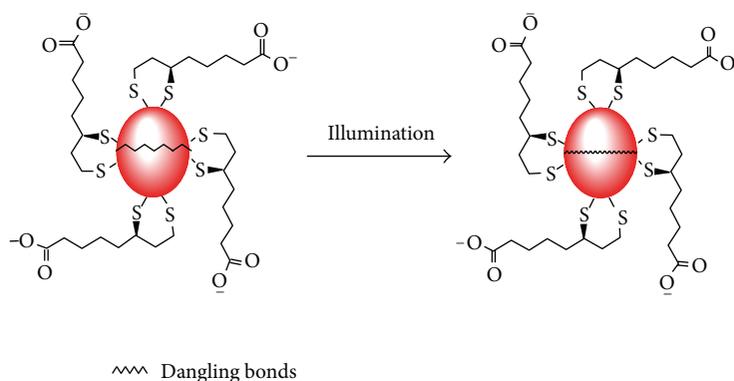
3. Results and Discussion

3.1. The Synthesis and Optical Properties of Ag NCs. Our previous research shows that luminescent pen-stabilized Ag NCs can be prepared by photoreduction method [35], but the luminescence intensity of the system is gradually decreased after irradiating for several ten min. In this study, we selected DHHLA molecules as capping reagents to synthesize Ag NCs in the aqueous phase. Scheme 1 gives the synthetic route of DHHLA and Ag NCs.

To produce Ag NCs, a freshly prepared aqueous solution of 2 mM silver nitrate was added to the solution of DHHLA in a molar ratio $[\text{Ag}^+]/[\text{DHHLA}]$ of 50 : 1. The system was mixed and subjected to strong UV irradiation at $\lambda = 365$ nm (UV intensity of 400 W) for various time intervals. The system was mixed for half an hour. Subsequently, photoreduction was carried out under UV irradiation at $\lambda = 365$ nm for various time intervals. During a total irradiation time of 67 h, the color of the solution gradually changed from colorless to yellow. Figure 1(a) shows absorption spectra of the solution of DHHLA with Ag⁺ ions after UV irradiation for different periods of time. When the irradiation time was increased from 3 to 67 h, the absorption band-edge slightly red shifted and the intensity of the absorbance was gradually increased, which indicated that size of the Ag NCs became correspondingly bigger and the concentration of Ag NCs was gradually increased upon prolonged UV irradiation. We noticed that, after an irradiation time of 3 h, the reaction mixture of



SCHEME 1: Synthesis of DHLA and Ag NCs.



SCHEME 2: Illustration of the change of surface dangling bonds on the Ag NCs.

the DHLA and Ag⁺ ions became luminescence (Figure 1(b)). Irradiation between 3 and 67 h led to an emission peak centered at about 480 nm and spanning the wavelength range 408–630 nm. For irradiating times of 3, 12, 25, 33, 42, 63, and 67 h, Ag NCs are obtained with maximum blue luminescent emission at 470, 472, 476, 477, 479, 482, and 485 nm, respectively. A strong increase in intensity was observed with increasing irradiating time, eventually resulting in a 15-fold increase compared to the original emission. When irradiated for 67 h, the intensity reaches a plateau. By further irradiation, the system started to precipitate. The lifetime of the Ag NCs was also measured. Figure S1 (see Supplementary Material available online at <http://dx.doi.org/10.1155/2015/792095>)

shows the time-resolved luminescence decay curves of the Ag NCs, which can be satisfactorily fitted into triexponential function. The decay lifetime of the NCs with blue emission is $\tau_1 = 3.65$ ns (52%), $\tau_2 = 0.56$ ns (31%), and $\tau_3 = 12.9$ ns (17%) and has a 9.4 ns average excited state lifetime. The blue emitter Ex₃₅₀/Em₄₄₀ usually exhibits a very short lifetime (0.01 ns) [36, 37], whereas 9.4 ns (Ex₃₉₀/Em₄₈₀) is the longest reported lifetime of such thiol-stabilized Ag NCs.

As shown in Figure 1(b), the intensity is simply enhanced as illumination is prolonged. The fact that illumination can result in increase of the luminescence of Ag nanocrystals has little been reported. Scheme 2 gives illustration of the change of surface dangling bonds on the Ag NCs. Due

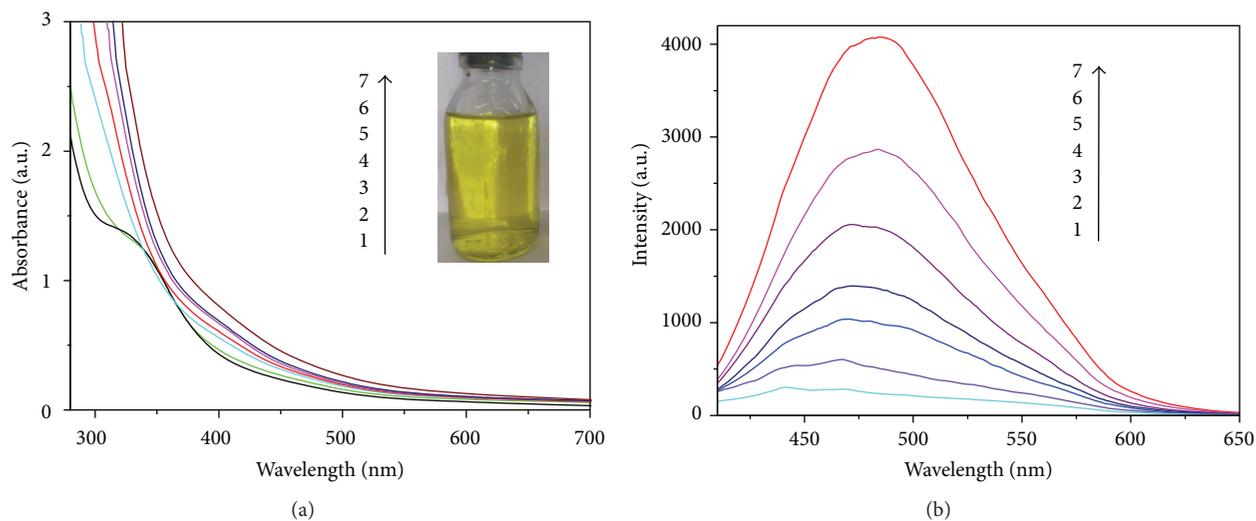


FIGURE 1: UV-vis (a) and luminescence spectra (b) of the Ag NCs after different periods of UV irradiation: (1) 3, (2) 12, (3) 25, (4) 33, (5) 42, (6) 63, and (8) 67 h. The inset shows the images of Ag NCs illuminated under room natural light. The excitation wavelength was set as 390 nm.

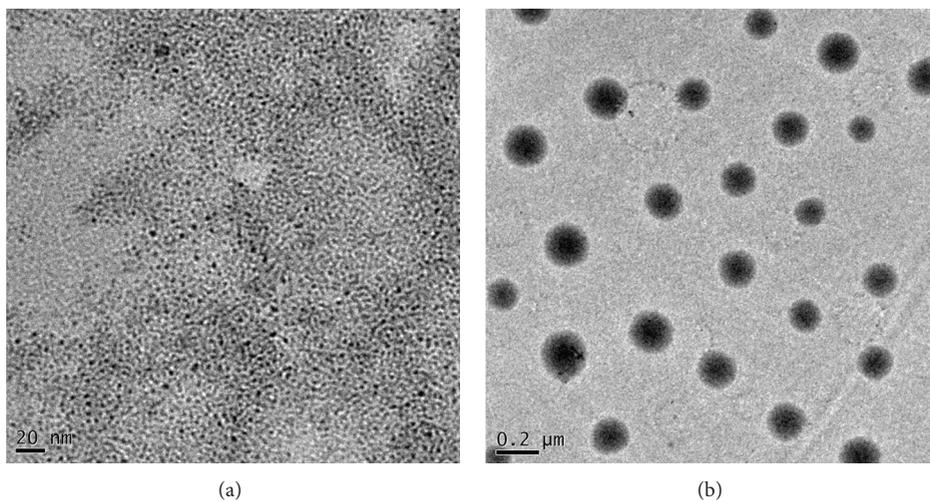


FIGURE 2: Typical TEM images of DHLA-capped Ag NCs obtained after irradiating for 12 h (a) and 63 h (b).

to the large surface/volume ratio, nanoclusters have lots of surface dangling bonds which become reactive upon illumination. Therefore, illumination-assisting enhancement effects were probably explained by the rearrangement of NC surface atoms and thus the decrease of dangling bonds.

It was interesting that the photoluminescence (480 nm) of DHLA-stabilized Ag NCs could also be obtained at the excitation wavelength $\lambda_{ex} = 780$ nm, which seemed to be “upconversion” phenomenon and agreed with the relevant document [38]. However, when a long pass filter, for example, 520 nm, in the excitation part of fluorimeter was put, the photoluminescence of the NCs could not be observed. Therefore, the “upconversion” is actually due to 390 nm light that passes through fluorimeter (half of 780 nm).

3.2. TEM, XRD, XPS, and EDX Characterization. Typical TEM images for Ag NCs are shown in Figure 2. These

images show that the Ag NCs possess a good dispersed crystalline structure and have the average diameters of about 2 nm after irradiating for 12 h. Further irradiating for 63 h, larger sized NCs formed and the average diameter of the NCs is about 200 nm. Although the diameter of the NCs increased 100-fold, the NCs still possess a good dispersed crystalline structure and the luminescence of these NCs is greatly improved.

Powder X-ray diffractions (XRD) were carried out on the as-formed product. The XRD of the Ag NCs powder sample (Figure 3) exhibits a broad and intense (121) peak of silver at $2\theta = \sim 35^\circ$, which agreed with previous result [35]. X-ray photoelectron spectroscopy was measured for the surface analysis of the washed DHLA-capped Ag NCs. A full survey scan and Ag and S photoelectron spectra of the Ag NCs are displayed in Figure 4. Besides the Ag levels, these spectra are dominated by the Cls and Ols signals stemming from

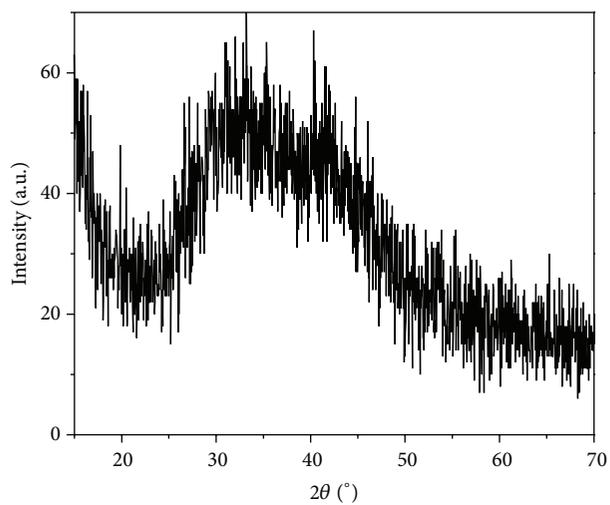


FIGURE 3: XRD pattern of Ag NCs.

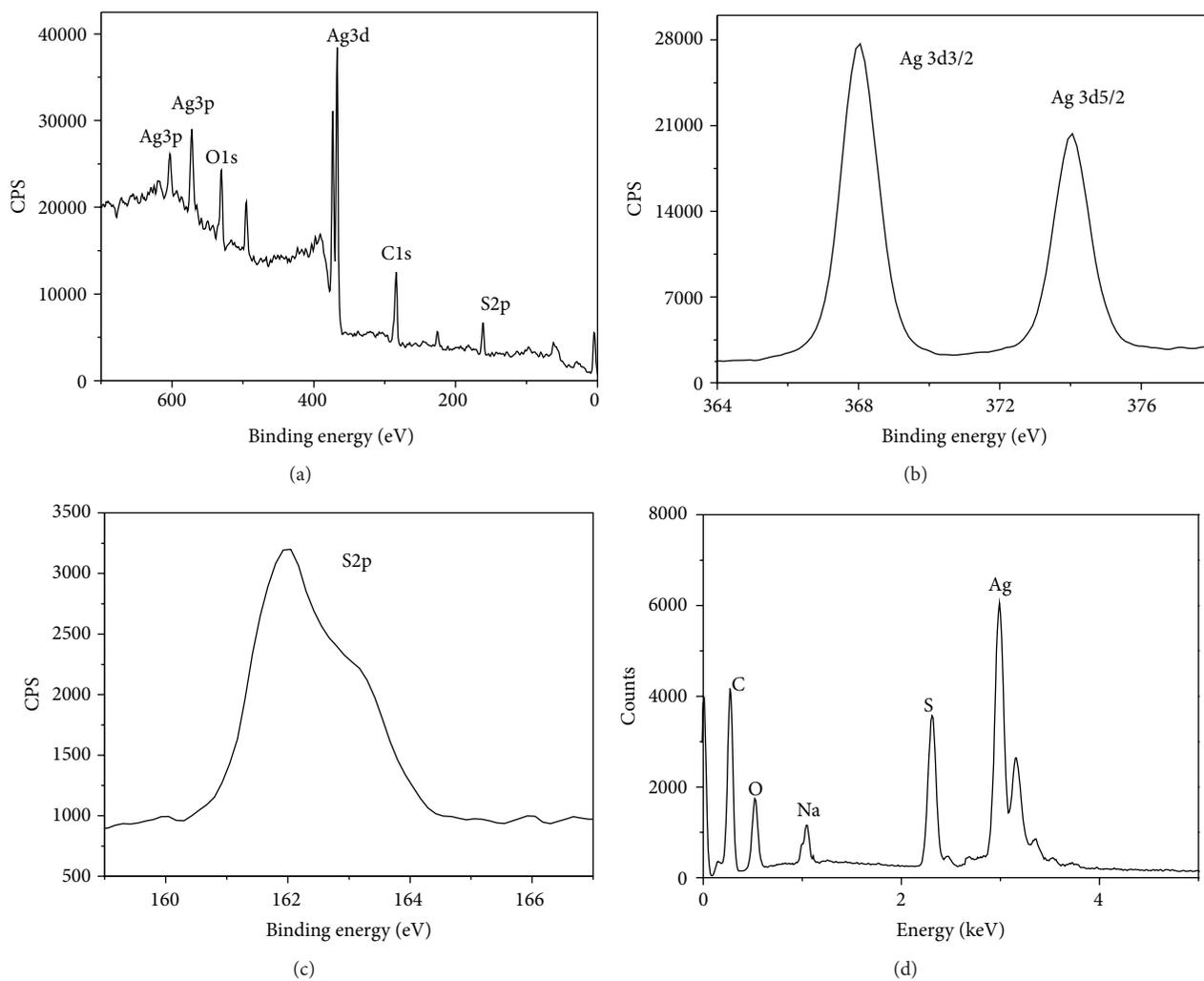


FIGURE 4: The XPS spectra of (a) the whole survey, (b) Ag 3d, and (c) S 2p of the as-prepared Ag NCs. (d) Typical EDX spectra of DHLA-capped Ag NCs.

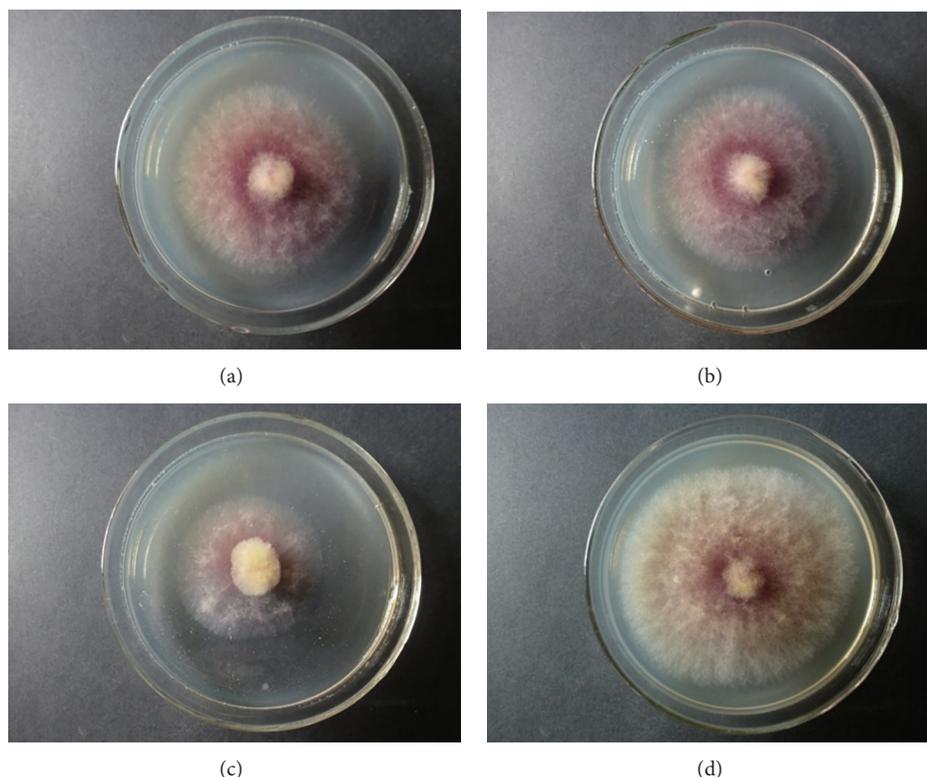


FIGURE 5: Antibacterial ability of Ag NCs. Photographs were taken after incubation for 5d at 20°C. (a), (b), and (c) represent Ag-DHLA complex, 2 nm Ag NCs, and 200 nm Ag NCs, respectively; (d) represents water (control). The inhibition rates of (a), (b), and (c) against wheat phytoalexin were 15.47%, 25.46%, and 49.64%, respectively. The concentration of Ag-DHLA complex was 62.5 μM .

the capping agent. XPS spectra in Figure 4 show that there exist Ag3d and S2p. The two peaks in Figure 4(b) of 368 eV and 374 eV can be assigned to the binding energy of Ag 3d_{5/2} and Ag 3d_{3/2}, respectively, which is characteristic of Ag product [39]. The peak at 161.9 eV belongs to S2p_{1/2} in a stabilizer DHLA. X-ray photoelectron spectroscopy (XPS) provides evidence for the formation of Ag NCs.

Further, we carried out energy dispersive X-ray spectroscopy (EDX) measurements for DHLA-capped Ag NCs. The EDX spectrum shows the existence of Ag and S in the Ag samples (Figure 4(d)). The silver sulfur and peak peaks are at 2.99 keV and 2.3 keV, respectively, the latter mainly from the stabilizer DHLA.

3.3. Assay for Antimicrobial Activity of Ag NCs. Recently silver nanoparticles became a fresh member of antimicrobial Ag family due to their higher specific surface area and high fraction of surface atoms compared to bulk Ag [40, 41]. By means of mycelium growth rate, the results showed that, at the same conditions, the inhibition rates of Ag⁺, Ag (200 nm), and Ag (2 nm) against wheat phytoalexin were 15.47%, 25.46%, and 49.64%, respectively (Figure 5). Therefore, the Ag NCs with smaller sizes had a good antimicrobial effect, which might be caused by their larger surface area and higher surface energy. Ag NCs break permeability of outer membrane, inhibit respiration and growth of cells, and destroy the structure of membrane, resulting in cell decomposition and death eventually.

4. Summary

In summary, to the best of our knowledge, this is the first report of a synthesis of DHLA-capped Ag NCs by photoreduction method. The prepared DHLA-stabilized Ag NCs exhibited strong PL emission with maximum peak at 480 nm. Because luminescence of these NCs can be greatly improved, they may be found in vast applications, not only in chemistry and biology such as biolabeling and imaging but also in forensic science. The test of antimicrobial activity showed that the Ag NCs with smaller sizes had a good antimicrobial effect.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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